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Sang Yeob Kim

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DISSERTATION

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To my parents

and

sisters

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Thesis summary

The performance of aerobic biological wastewater treatment process using activated sludge process (ASP) is dependent on dissolved oxygen (DO) concentration in aerobic basins supplied through aeration systems. Supplying DO into conventional activated sludge (CAS) wastewater treatment plants (WWTP) is an inefficient and costly process. The aeration costs of aerobic WWTP account for more than half of the total energy requirements of WWTPs. Oxygen transfer in CAS processes is a complicated phenomenon due to heterogeneous mixture of microorganisms and its brownian motion. Among various activated sludge-related parameters, the concentration of mixed liquor suspended solids (MLSS) in wastewater has been regarded as the primary factor affecting oxygen transfer in CAS systems. Particularly, the detrimental effect has been clearly observed and reported when supplying air into CAS systems using conventional diffused aeration systems. So far, conventional diffused aeration (e.g., fine and coarse bubble diffusers) systems have been widely adopted for supplying DO into mixed liquor in spite of its low oxygen transfer efficiency (OTE).

Compared to CAS processes, membrane bioreactors (MBRs) integrate micro-ultra membrane filtration with ASP have become a promising wastewater treatment technology thanks to its several benefits. In addition, among the commercially available activated sludge wastewater treatment technologies, MBRs are arguably the most appropriate technology to be operated at high MLSS concentrations. However, one of the major impediments to the widespread application of MBR technology could be the operating costs imposed by aeration requirements characterized by high energy consumption. In general, as MLSS increases the OTE decreases. The decrease in the alpha factor (mass transfer ratio of process water to clean water) is more noticeable at an MLSS higher than 15 g L^{-1}, even reaching a limit at an MLSS of approximately 20 g L^{-1}. That is, operating MBRs technologies in such conditions bring about not only requires higher aeration costs but also influences the maximum achievable MLSS in the MBR with a direct impact on the footprint requirements of the system. In this context, there is a need for innovation on more efficient oxygen transfer systems to reduce the energy for aeration, as well as to allow the design of more compact and movable MBRs, for operating MBRs at high MLSS beyond conventional MLSS concentrations (i.e., above 15 g L^{-1}).

Oxygen transfer performance at high MLSS concentrations (Chapters 3 and 4)

Among the non-conventional aeration systems, the supersaturated oxygen aeration systems working with high purity oxygen and at high-pressure conditions have been developed for achieving higher oxygen transfer rates (OTRs). Specifically, the supersaturated dissolved oxygen (SDOX) system was employed in this PhD research. To conduct this PhD study, understanding how SDOX affects the performance of biological wastewater treatment, as well as oxygen transfer performance in mixed liquor environments, was critical in optimizing and

improving the performance of bioreactors in wastewater treatment plants. This study using SDOX technology was performed in two major steps. The first stage focused on the evaluation of SDOX on the oxygen transfer performance. The second stage was an application of SDOX to the wastewater treatment processes (i.e., MBRs) to investigate how the SDOX technology would affect the biological wastewater treatment process.

Chapter 3 describes the oxygen transfer limitations imposed by conventional diffused aeration systems in the context of a high loaded MBR (HL-MBR). A biological reactor with a working volume of approximately 20 L was inoculated with activated sludge, aerated by a fine bubble diffuser. The Fresh activated sludge was collected from a full-scale WWTP treating municipal wastewater operated as a CAS process at a solid retention time (SRT) of approximately 5 days. The results demonstrated that fine bubble diffusers limit the maximum MLSS concentration for a HL-MBR at 30 g L^{-1}; beyond that point is either not technically or not economically feasible to operate. An optimum MLSS concentration of 20 g L^{-1} is suggested to maximize the treatment capacity while minimizing the system's footprint.

In **Chapter 4**, as a solution for overcoming the oxygen transfer limitations caused by conventional diffused aeration systems, the oxygen transfer performance of SDOX system was assessed in the context of HL-MBR (that is, particularly at high MLSS concentration above 20 g L^{-1}). Similar experimental conditions as described in Chapter 3 were provided except for an aeration system type. Chapter 4 gives convincing answers to various doubts concerning oxygen transfer performance of SDOX in mixed liquor environment. The SDOX exhibited oxygen mass transfer rate coefficient (K_La) values (2.6 h^{-1}) in clean water lower than for fine bubble diffusers (11 h^{-1}). However, higher OTR values and alpha factors as a function of the MLSS concentration were reported compared to fine bubble diffusers. Furthermore, the SDOX exhibited approximately 100% of standard oxygen transfer efficiency (SOTE) in clean water. Compared to conventional diffused aeration systems, considering the relatively low energy requirements of the SDOX at high MLSS concentration, the SDOX technology can be presented as a prospective alternative for supplying DO into mixed liquor solutions. In particular, SDOX seems to be applicable to biological wastewater systems such as HL-MBRs and aerobic digesters operated at high MLSS concentrations.

On the application of the SDOX to biological wastewater treatment and impact of SDOX on membrane filtration performance (Chapters 5 and 6)

As a part of applying the SDOX system to wastewater treatment processes, Chapters 5 and 6 present the long-term impact of the high-pressure aeration system (SDOX) on the biological wastewater treatment performance, the shift in microbial population dynamics, and membrane fouling propensity in an MBR. A lab-scale MBR treating synthetic wastewater was sequentially operated under two aeration systems (conventional diffused aeration system followed by SDOX)

at MLSS of 15 g L^{-1} in four phases as follows: (P1) with fine bubble diffusers, (P2) with the SDOX unit, (P3) with the fine bubble diffusers, and (P4) with the SDOX unit.

In **Chapter 5**, the performance of the MBR was evaluated by monitoring the sludge concentration, as well as changes in the particle size distribution, sludge activity, organic matter removal and nitrification performance, and changes in the microbial community within the MBR. The operational conditions exerted by the SDOX technology did not affect the concentration of active biomass during the study period. The biological performance of the MBR was not affected by the introduction of the SDOX technology. Specifically, the chemical oxygen demand removal efficiency was 95% on average for both aeration systems throughout the MBR operation. In terms of nitrification, the ammonia was almost completely removed corresponding to the average ammonia removal efficiency of 99% during the entire evaluated period. Accordingly, the MBR achieved full nitrification, which was also confirmed by the effluent concentration of ammonia (<0.1 mgNH_4-N L^{-1}). Finally, the microbial community was relatively stable although some variations at the family and genus level were evident during each of the study phases. Therefore, the SDOX system can be proposed as an alternative technology for DO supply in WWTPs increasing the overall treatment capacity.

As described in **Chapter 6**, the results clearly confirmed that the high-pressure aeration system (SDOX) fairly contributed to severe membrane fouling compared to conventional fine bubble aeration system, by reporting much higher values of transmembrane pressure in time (referred as dTMP dt^{-1}). Among the monitored factors affecting membrane fouling, the loss in permeability, extracellular polymeric substances, scanning electron microscope images along with the energy dispersive X-ray analysis were insufficient to elucidate the intensive membrane fouling imposed by high-pressure aeration system. Biofouling seemed the principal contributor to the cake layer when using fine bubble diffusers, whereas organic fouling seemed to be the primary contributor to the cake layer when using concentrated oxygen supply system (i.e., SDOX). It is plausible that the small-sized particle size in MBRs aerated with the SDOX would be a main parameter affecting the intensive membrane fouling (e.g., formation of a dense and thin cake layer). However, notwithstanding several possibilities, particle size distribution itself alone cannot unquestionably explain the deteriorated membrane fouling propensity. Therefore, presumably, a combination of several factors (certainly including particle size distribution) resulted in the serious membrane fouling imposed by the high-pressure and shear effect.

Advantages of using NIR spectroscopy on predicting wastewater constituents (Chapter 7)

In **Chapter 7**, as an alternative way to monitor wastewater constituents, near infrared (NIR) spectroscopy was applied and evaluated. Analyzed parameters through the NIR spectroscopy were applied both to partial least squares regression (PLSR) models and artificial neural

networks (ANN) to evaluate how many of analysed parameters could be monitored with NIRs. Excellent results were obtained with both PLSR and ANN models. The combination of NIR technology and chemometric modelling would be useful for estimating wastewater constituents. As an alternative to conventional analytical methods, the NIR spectroscopy could be applied to wastewater treatment monitoring to overcome the issues that are now being faced by current analytical methods such as time consuming and complex sample preparation.

Samenvatting

De prestaties van aërobe biologisch afvalwaterzuiveringsprocessen met actief slib (ASP) zijn afhankelijk van de concentratie opgeloste zuurstof (DO) in de aërobe bassins, die toegevoerd wordt met behulp van beluchtingssystemen. Het leveren van DO aan conventionele afvalwaterzuiveringsinstallaties met actief slib (CAS) is een inefficiënt en kostbaar proces. De beluchtingskosten van aërobe afvalwaterzuiveringsinstallaties (AWZI's) vertegenwoordigen meer dan de helft van de totale energiebehoefte van RWZI's. Zuurstofoverdracht in CAS-processen is een gecompliceerd fenomeen vanwege het heterogene mengsel van micro-organismen en de brownse beweging ervan. Van verschillende parameters die verband houden met actief slib, wordt de concentratie van gesuspendeerde vaste stoffen (MLSS) in afvalwater beschouwd, als de belangrijkste factor die de zuurstofoverdracht in CAS-systemen beïnvloedt. In het bijzonder is het negatieve effect van MLSS duidelijk waargenomen en gerapporteerd bij het toevoeren van lucht aan CAS-systemen met conventionele diffuse beluchtingssystemen. Tot nu toe zijn conventionele diffuse beluchtingssystemen (bijv. fijne en grove bellendiffusors) op grote schaal toegepast voor het toevoeren van DO aan gemengde vloeistof, ondanks de lage zuurstofoverdracht efficiëntie (OTE).

In vergelijking met CAS-processen zijn membraanbioreactoren (MBR's), die micro-ultramembraanfiltratie integreren met ASP, een veelbelovende technologie voor afvalwaterzuivering geworden, dankzij de verschillende voordelen ervan. Bovendien zijn MBR's, van de commercieel beschikbare actief slib technologieën voor de behandeling van afvalwater, waarschijnlijk de meest geschikte technologie om te worden gebruikt bij hoge MLSS-concentraties. Een van de belangrijkste belemmeringen, voor de wijdverbreide toepassing van MBR-technologie, zijn de hoge kosten, die veroorzaakt worden door de hoge beluchtingsvereisten en gepaard gaan met een hoog energieverbruik. In het algemeen, als MLSS toeneemt, neemt de OTE af. De afname van de alfafactor (verhouding tussen massaoverdracht van zuurstof in proceswater en schoon water) is meer merkbaar bij een MLSS hoger dan 15 g L^{-1} is, en bereikt zelfs een limiet bij een MLSS van ongeveer 20 g L^{-1}. Dat wil zeggen dat het gebruik van MBR-technologieën in dergelijke omstandigheden niet alleen hogere beluchtingskosten met zich meebrengt, maar ook de maximaal haalbare MLSS in de MBR beïnvloedt met een directe impact op de voetafdruk vereisten van het systeem. In deze context is er behoefte aan innovatie op het gebied van efficiëntere zuurstofoverdracht systemen om de energie voor beluchting te verminderen, en om het ontwerp van compactere en verplaatsbare MBR's mogelijk te maken, voor het werken met MBR's bij hoge MLSS, boven conventionele MLSS-concentraties (d.w.z. meer dan 15 g L^{-1}).

Zuurstofoverdracht prestaties bij hoge MLSS-concentraties (hoofdstukken 3 en 4)

Van de niet-conventionele beluchtingssystemen, zijn de oververzadigde zuurstofbeluchtingssystemen, die werken met zuivere zuurstof en onder hoge druk omstandigheden, ontwikkeld om hogere zuurstofoverdrachtssnelheden (OTR's) te bereiken. In dit promotieonderzoek werd specifiek het oververzadigde opgeloste zuurstof (SDOX) systeem gebruikt. Om dit doctoraatsonderzoek uit te voeren, was het van cruciaal belang om te begrijpen hoe SDOX de prestaties van biologische afvalwaterbehandeling beïnvloedt, evenals de prestaties van zuurstofoverdracht in omgevingen met gemengd actief slib, voor het optimaliseren en verbeteren van de prestaties van bioreactoren in afvalwaterzuiveringsinstallaties. Dit onderzoek met behulp van SDOX-technologie is uitgevoerd in twee fasen. De eerste fase was gericht op de evaluatie van de zuurstofoverdracht prestaties van SDOX. De tweede fase was gericht op de toepassing van SDOX op de afvalwaterzuiveringsprocessen (d.w.z. MBR's) om te onderzoeken hoe de SDOX-technologie het biologische afvalwaterzuiveringsproces zou beïnvloeden.

Hoofdstuk 3 beschrijft de zuurstofoverdracht beperkingen van conventionele diffuse beluchtingssystemen in de context van een hoogbelaste MBR (HL-MBR). Een biologische reactor met een werkvolume van ongeveer 20 L werd geënt met actief slib en belucht met een fijnbellige diffusor. Vers actief slib was verzameld in een volle schaal AWZI die gemeentelijk afvalwater behandelt en werkte als een CAS-proces met een vaste retentietijd (SRT) van ongeveer 5 dagen. De resultaten toonden aan dat fijne bellendiffusors de maximale MLSS-concentratie voor een HL-MBR beperken tot 30 g L-1; bij hogere concentraties is het technisch of economisch niet haalbaar om het proces te opereren. Een optimale MLSS-concentratie van 20 g L-1 wordt aanbevolen om de behandelingscapaciteit te maximaliseren en tegelijkertijd de voetafdruk van het systeem te minimaliseren.

In **Hoofdstuk 4**, als een oplossing voor de zuurstofoverdracht beperkingen, die worden veroorzaakt door conventionele diffuse beluchtingssystemen, werd de zuurstofoverdracht prestatie van het SDOX-systeem beoordeeld in de context van HL-MBR (dat wil zeggen, met name bij hoge MLSS-concentraties boven 20 g L^{-1}). Vergelijkbare experimentele omstandigheden, zoals beschreven in Hoofdstuk 3, werden toegepast, met uitzondering van het type beluchtingssysteem. Hoofdstuk 4 geeft overtuigende antwoorden op verschillende twijfels over de zuurstofoverdracht prestaties van SDOX in actief slib mengsels. Met de SDOX werden zuurstofoverdrachtscoëfficiënten (K_La) (2.6 h^{-1}) in schoon water behaald die lager waren dan voor diffusors met fijne bellen (11 h^{-1}). Er werden echter hogere OTR-waarden en alfafactoren als functie van de MLSS-concentratie gerapporteerd in vergelijking met diffusors met fijne bellen. Bovendien werd er met de SDOX ongeveer 100% van de standaard zuurstofoverdrachtsefficiëntie (SOTE) in schoon water behaald. Vergeleken met conventionele diffuse beluchtingssystemen kan de SDOX-technologie, gezien de relatief lage energievereisten van de SDOX bij een hoge MLSS-concentratie, worden gezien als een toekomstig alternatief

voor het leveren van DO aan actief slib mengsels. SDOX lijkt met name toepasbaar op biologische afvalwatersystemen zoals HL-MBR's en aerobe vergisters die bij hoge MLSS-concentraties bedreven worden.

Over de toepassing van SDOX op biologische afvalwaterzuivering en de impact van SDOX op membraanfiltratieprestaties (hoofdstukken 5 en 6)

Als onderdeel van de toepassing van het SDOX-systeem op afvalwaterzuiveringsprocessen, presenteren de hoofdstukken 5 en 6 de lange termijn effecten van het hogedruk beluchtingssysteem (SDOX) op de prestaties van de biologische afvalwaterwaterzuivering, de verschuiving in de microbiële populatie dynamiek en membraanvervuiling in een MBR. Een laboratoriumschaal MBR, gevoed met synthetisch afvalwater, werd achtereenvolgens bedreven met twee beluchtingssystemen (conventioneel diffuus beluchtingssysteem, gevolgd door SDOX) bij MLSS concentraties van 15 g L^{-1} in vier fasen: (P1) met de fijne bellen diffusors, (P2) met de SDOX, (P3) met de fijne bellen diffusors, en (P4) met de SDOX.

In **Hoofdstuk 5** werden de prestaties van de MBR geëvalueerd door de slibconcentratie te volgen, evenals veranderingen in de deeltjesgrootteverdeling, slibactiviteit, organische stof (chemisch zuurstof verbruik) verwijdering en nitrificatie prestaties, en veranderingen in de microbiële populatie in de MBR. De operationele omstandigheden van de SDOX-technologie hadden geen invloed op de concentratie van actieve biomassa tijdens de onderzoeksperiode. De biologische prestaties van de MBR werden niet beïnvloed door de introductie van de SDOX-technologie. In het bijzonder was de efficiëntie van de verwijdering van organische stof (chemisch zuurstofverbruik) gemiddeld 95% voor beide beluchtingssystemen tijdens de MBR-operatie. Wat betreft het nitrificatie proces, werd ammoniak bijna volledig verwijderd, wat overeenkomt met een gemiddeld ammoniakverwijderingsrendement van 99% gedurende de gehele geëvalueerde periode. Hiermee bereikte de MBR volledige nitrificatie, wat ook werd bevestigd door de effluentconcentratie van ammoniak (<0.1 mgNH_4-N L^{-1}). Alhoewel er tijdens elk van de studiefasen enkele variaties op familie- en genus niveau waar te nemen waren, was de microbiële gemeenschap relatief stabiel. Daarom kan het SDOX-systeem gezien worden als een alternatieve technologie voor de toevoer van DO in AWZI’s, waardoor de totale behandelingscapaciteit wordt vergroot.

Zoals beschreven in **Hoofdstuk 6**, bevestigden de resultaten duidelijk dat het hogedrukbeluchtingssysteem (SDOX) behoorlijk bijdroeg aan ernstige membraanvervuiling in vergelijking met het conventionele beluchtingssysteem met fijne bellen. Dit was te zien aan veel hogere waarden van transmembraandruk in de tijd (aangeduid als dTMP dt^{-1}). Onder de gemonitorde factoren die membraanvervuiling beïnvloeden, waren het verlies aan permeabiliteit, extracellulaire polymere stoffen, scanning elektronenmicroscoopbeelden samen met de energiedispersieve röntgenanalyse, onvoldoende om op te helderen wat de intensieve

membraanvervuiling bij een hogedrukbeluchtingssysteem veroorzaakt. Biofouling leek de belangrijkste bijdrage aan de cakelaag te leveren bij het gebruik van diffusors met fijne bellen, terwijl organische vervuiling de belangrijkste bijdrage leek te leveren aan de cakelaag bij gebruik van een geconcentreerd zuurstoftoevoersysteem (d.w.z. SDOX). Het is aannemelijk dat de kleine deeltjesgrootte in MBR's belucht met de SDOX een hoofdparameter zou zijn die de intensieve membraanvervuiling beïnvloedt (bijv. de vorming van een dichte en dunne cakelaag). Ondanks verschillende mogelijkheden kan de deeltjesgrootteverdeling op zichzelf, echter niet zonder twijfel, de verslechterde membraanvervuiling verklaren. Daarom heeft vermoedelijk een combinatie van verschillende factoren (waaronder zeker ook de deeltjesgrootteverdeling) geleid tot de ernstige membraanvervuiling die wordt veroorzaakt door het hogedruk- en shear effect.

Voordelen van het gebruik van NIR-spectroscopie bij het voorspellen van afvalwaterbestanddelen (hoofdstuk 7)

In **Hoofdstuk 7** werd, als een alternatieve manier om afvalwaterbestanddelen te monitoren, nabij-infrarood (NIR) spectroscopie toegepast en geëvalueerd. De parameters geanalyseerde met de NIR-spectroscopie werden onderzocht met zowel partiële kleinste-kwadratenregressie (PLSR) -modellen als kunstmatige neurale netwerken (ANN) om te evalueren hoeveel van de geanalyseerde parameters konden worden gemonitord met NIRs. Uitstekende resultaten werden verkregen met zowel de PLSR- als ANN-modellen. De combinatie van NIR-technologie en chemometrische modellering zou nuttig zijn voor het schatten van afvalwaterbestanddelen. Als alternatief voor conventionele analytische methoden zou de NIR-spectroscopie kunnen worden toegepast op het monitoren van afvalwaterzuivering om de problemen op te lossen van de huidige analytische methoden, zoals tijdrovende en complexe monstervoorbereiding.

요약

활성슬러지 공정(ASP)을 이용하는 호기성 생물학적 하수처리 공정의 성능은 폭기 시스템을 통해 공급되는 호기성 유역의 용존 산소(DO) 농도에 따라 좌우된다. 전통활성슬러지(CAS) 하수 처리장(WWTP)에 용존 산소를 공급하는 것은 비효율적이고 비용이 많이 요구되는 공정이다. 호기성 하수처리장의 폭기 비용은 하수처리장의 총 에너지 요구량의 절반 이상을 차지한다. 전통활성슬러지 공정에서의 산소 전달은 미생물의 불균질한 혼합과 브라운 운동으로 인해 복잡한 현상이다. 다양한 활성슬러지 관련 매개변수 중 폐수 내 혼합액부유고형물(MLSS) 농도는 전통활성슬러지 시스템의 산소 전달에 영향을 미치는 주요 인자로 간주되어 왔다. 특히, 기존의 확산 폭기 시스템을 사용하여 전통활성슬러지 시스템에 공기를 공급할 때 유해한 영향이 명확하게 관찰 및 보고되다. 산소 전달 효율(OTE)이 낮음에도 불구하고 혼합액에 용존 산소를 공급하기 위해 현재까지 기존의 확산 폭기(예: 미세 및 조대 기포 확산기) 시스템이 널리 이용되었다.

전통활성슬러지 공정과 비교하여 막생물반응기(MBR)는 활성슬러지 공정과 정밀–한외여과를 결합한 방식으로 몇 가지 이점으로 인해 유망한 폐수 처리 기술로 자리잡았다. 또한, 상업적으로 이용 가능한 활성슬러지 폐수처리 기술 중 막생물반응기는 높은 혼합액부유고형물 농도에서 운영하기에 가장 적합한 기술임에 틀림없다. 그러나 막생물반응기 기술의 광범위한 적용에 대한 주요 장애물 중 하나는 높은 에너지 소비를 특징으로 하는 폭기 요구량으로 인해 부과되는 운영 비용일 수 있다. 일반적으로 혼합액부유고형물이 증가함에 따라 산소전달효율은 감소한다. Alpha factor (깨끗한물에 대한 공정수(폐수)의 물질 전달 비율)의 감소는 15 g L^{-1}보다 높은 혼합액부유고형물에서 더 두드러지며 약 20g L^{-1}의 혼합액부유고형물에서 한계에 도달한다. 즉, 이러한 조건에서 막생물반응기 기술을 적용하면 더 높은 폭기 비용이 필요할 뿐만 아니라 시스템의 설치 공간 요구 사항에 직접적인 영향을 주어 막생물반응기에서 달성 가능한 최대 혼합액부유고형물에 영향을 준다. 이러한 맥락에서, 기존의 혼합액부유고형물 농도(즉, 15g L^{-1} 이상)를 넘어 높은 혼합액부유고형물에서 생물막반응기를 운전하기 위해 더 컴팩트하고 이동 가능한 생물막반응기의 설계를 허용할 뿐만 아니라 폭기 에너지를 줄이기 위해 더 효율적인 산소 전달 시스템에 대한 혁신이 필요하다.

높은 MLSS 농도에서의 산소 전달 성능(3 장 및 4 장)

비전통적인 폭기 시스템 중 고순도 산소와 고압 조건에서 작동하는 과포화 산소 폭기 시스템은 더 높은 산소 전달률 (OTR)을 달성하기 위해 개발되었다. 특히, 본 박사학위 연구에서는 과포화용존산소(SDOX) 시스템을 사용했다. 본 연구를 수행하기 위해 SDOX가 생물학적 폐수처리 성능과 혼합액 환경에서 산소 전달 성능에 미치는 영향을 이해하는 것이 폐수처리 공정에서 생물 반응기의 성능을 최적화하고 개선하는 데 중요했다. SDOX 기술을 사용한 이 연구는 두 가지 주요 단계로 수행되었다. 첫 번째 단계는 SDOX의 산소 전달 성능에 대한 평가에 중점을 두었다. 두 번째 단계는 SDOX 기술이 생물학적 폐수처리 공정에 어떤 영향을 미치는지 조사하기 위해 폐수처리 공정 (즉, 생물막반응기)에 SDOX를 적용하는 것이었다.

3장에서는 고부하 생물막반응기 (HL-MBR)의 맥락에서 기존의 확산 폭기 시스템에 의해 제공되는 산소 전달 제한에 대해 설명하였다. 부피가 약 20L인 생물반응기에 활성 슬러지를 접종하였고 이를 미세 기포 확산기로 폭기시켰다. 활성슬러지는 약 5일의 고형물체류시간 (SRT)에서 전통활성슬러지 공정으로 운영되는 도시 하수를 처리하는 하수처리장에서 수집되었다. 본 연구 결과는 미세 기포 확산기가 30g L^{-1}에서 고부하 생물막반응기에 대한 최대 혼합액부유고형물 농도를 제한한다는 것을 보여주었다. 그 지점을 넘어서는 것은 기술적으로 작동하지 않거나 경제적으로 실행 가능하지 않았다. 시스템의 공간을 최소화하면서 처리 용량을 최대화하기 위해 20g L^{-1}의 최적 MLSS 농도가 본 장에서 제안되었다.

4장에서는 기존의 확산 폭기 시스템으로 인한 산소 전달 한계를 극복하기 위한 대안으로 SDOX 시스템의 산소 전달 성능을 고부하 생물막반응기의 맥락에서 평가했다 (즉, 특히 20g L^{-1}이상의 높은 혼합액부유고형물 농도에서). 폭기 시스템 유형을 제외하고 3장에서 설명한 것과 유사한 실험 조건이 제공되었다. 4장은 혼합액 환경에서 SDOX의 산소 전달 성능에 관한 다양한 의문에 대한 설득력 있는 답변을 제공한다. SDOX는 깨끗한 물에서 미세 기포 확산기(11 h^{-1})보다 낮은 산소 질량 전달 계수(K_La) 값(2.6 h^{-1})을 나타냈다. 그러나 미세 기포 확산기에 비해 혼합액부유고형물 농도의 함수로서 더 높은 산소 전달률 값과 Alpha factor가 보고되었다. 또한 SDOX는 깨끗한 물에서 약 100%의 표준 산소 전달 효율(SOTE)을 보여주었다. 기존의 확산 폭기 시스템과 비교할 때, 높은 혼합액부유고형물 농도에서 SDOX의 상대적으로 낮은 에너지 요구량을 고려할 때, SDOX 기술은 용존 산소를 혼합액 용액에 공급하기 위한 전향적 대안으로 제시될 수 있다. 특히, SDOX는 높은 혼합액부유고형물 농도에서 운전되는 고부하 생물막반응기 및 호기성 소화조와 같은 생물학적 폐수 시스템에 적용할 수 있을 것으로 보인다.

생물학적 폐수 처리에 대한 SDOX의 적용 및 막 여과 성능에 대한 SDOX의 영향(5장 및 6장)

SDOX 시스템을 폐수처리 공정에 적용하는 것의 일환으로 5장과 6장에서는 생물막반응기에서의 생물학적 폐수처리 성능, 미생물 군집 역학의 변화 및 막 오염 경향에 대한 SDOX의 장기적인 영향을 제시한다. 합성 폐수를 처리하는 실험실 규모의 생물막반응기는 15g L^{-1}의 혼합액부유고형물 농도에서 2개의 폭기 시스템(전통적인 확산 폭기 시스템에 이어 SDOX) 하에서 다음과 같이 4단계로 연속적으로 작동되었다: (P1) 미세 기포 디퓨저, (P2) SDOX, (P3) 미세 기포 디퓨저, (P4) SDOX.

5장에서는 슬러지 농도와 입경 분포 변화, 슬러지 활성도, 유기물 제거 및 질산화 성능 변화, 생물막반응기 내 미생물 군집 변화를 모니터링하여 생물막반응기의 성능을 평가하였다. SDOX가 결합되어 운전되는 생물막반응기의 경우, 실험 기간 동안 활성 미생물의 농도에 영향을 미치지 않았다. 생물막반응기의 생물학적 성능은 SDOX 도입에 의해 영향을 받지 않았다. 특히, 화학적산소요구량 제거 효율은 생물막반응기 운전 전반에 걸쳐 두 폭기 시스템 모두에서 평균 95%로 나타났다. 질산화의 경우 전체 실험 평가 기간 동안 평균 암모니아 제거 효율이 99%에로 암모니아가 거의 완전히 제거되었다. 따라서 생물막반응기는 완전한 질산화를 달성했으며 이는 암모니아의 유출 농도(<0.1 $mgNH_4-N\ L^{-1}$)로도 확인되었다. 마지막으로, 미생물 군집은 각 실험 단계 동안 과 및 속 수준에서 약간의 변이가 분명했지만 상대적으로 안정적이었다. 따라서 SDOX 시스템은 전체 처리 용량을 증가시키는 하수처리장에서 용존 산소 공급을 위한 대체 기술로 제안될 수 있다.

6장에 기술된 바와 같이, 연구 결과는 SDOX가 시간에 따라 훨씬 더 높은 막횡단 압력 값(dTMP dt^{-1}로 지칭됨)을 나타냄으로써 기존의 미세 기포 폭기 시스템에 비해 심각한 막 오염에 상당히 기여한다는 것을 분명히 확인했다. 막 오염에 영향을 미치는 모니터링 요소 중 투과성 손실, 세포 외 고분자 물질, 에너지 분산 X-선 분석과 함께 주사 전자 현미경 이미지는 고압 폭기 시스템에 의해 부과되는 집중적 막 오염을 설명하기에는 불충분했다. 미세 기포 디퓨저를 사용할 때 생물 오손이 케이크 층 형성의 주요 원인인 것으로 보인 반면, 유기 오염은 SDOX를 사용할 때 케이크 층 형성의 주요 원인인 것으로 보인다. SDOX로 폭기된 생물막반응기의 작은 입자 크기는 강력한 막 오염(예: 조밀하고 얇은 케이크 층의 형성)에 영향을 미치는 주요 매개변수가 될 것이다. 그러나 여러 가능성에도 불구하고 입자 크기 분포 자체만으로는 악화된 막 오염 경향을 충분히 설명할 수 없다. 따라서 아마도 여러 요인(확실히, 입자 크기 분포 포함)의 조합으로 인해 고압 및 전단 효과에 의해

부과되는 심각한 막 오염이 발생했을 것이다.

폐수 성분 예측에 NIR 분광법을 사용할 때의 이점(7 장)

7장에서는 폐수 성분을 모니터링하는 대안으로 근적외선(NIR) 분광법을 적용하여 평가했다. 근적외선 분광기를 통해 분석된 매개변수를 PLSR(부분 최소 자승 회귀) 모델과 인공 신경망(ANN)에 모두 적용하여 NIR로 모니터링할 수 있는 분석 매개변수의 수를 평가했다. PLSR 및 ANN 모델 모두에서 우수한 결과를 얻었다. NIR 기술과 화학 측정 모델링의 조합은 폐수 성분을 추정하는 데 유용할 것이다. 기존 분석 방법의 대안으로 NIR 분광법을 폐수 처리 모니터링에 적용하여 시간이 많이 걸리고 복잡한 샘플 준비와 같은 현재 분석 방법이 직면한 문제를 극복할 수 있을것으로 보인다.

Chapter 1

General introduction

1.1 Background and motivation

Sanitation remains a challenge to overcome, and it is one of the most important foundations of health, dignity, and development of society. Sanitation refers to services for the safe disposal of human urine and faeces and the provision of facilities in a broad sense. Improved sanitation positively affects health both in households and across communities; inappropriate sanitation results in a primary cause of disease world-wide. Sanitation can be also defined as the maintenance of hygienic conditions by providing services such as garbage collection and wastewater disposal (http://www.who.int/topics/sanitation/en, accessed on 11 November 2019). According to Hannah and Max (2019), 2.4 billion people in the world remained without access to improved sanitation facilities, mostly in sub-Saharan Africa and Southern Asia (Figure 1.1).

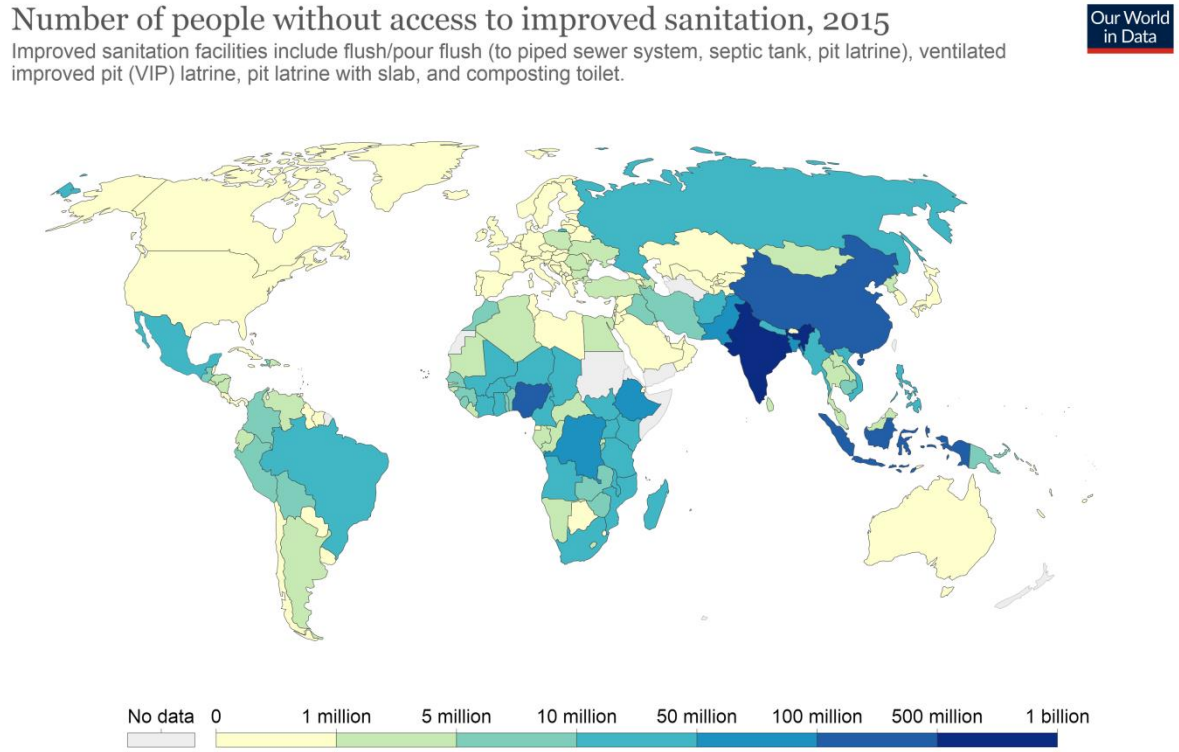

Figure 1.1 The number of people without access to improved sanitation in 2015 (adapted from Hannah and Max (2019))

Sanitation is directly connected to wastewater treatment and water scarcity. People consume water every day; the used water becomes sewage, and should be discharged into a water body after being properly treated. The main reason for the generation of large amount of wastewater with high pollutants is due to the increased allocations of water for domestic and industrial uses. In accordance, both the deterioration of the water quality, and the increment of water scarcity result from human activity due to urbanization. In addition, frequent droughts and water pollution episodes derived from climate change has reduced the amount of clean water available exacerbating water shortages. According to United Nations, as much as 40% of the global

population may suffer water scarcity by the year 2030 (https://www.un.org, accessed on 27 December 2019). Therefore, the availability of water encapsulates a world-wide concern. Untreated or insufficiently treated water have a negative effect on human health and the environment. Consequently, there is a need to protect the finite water resources; thus to keep innovating on robust wastewater treatment technologies that can effectively and efficiently treat large quantities of wastewater. Among all the available technological alternatives for wastewater treatment, conventional activated sludge (CAS) processes have been introduced and being used with the objective of preserving public health and population safety.

As shown in Figure 1.2, the CAS process introduced by Ardern and Lockett (1914) in general includes a primary settling (as a primary treatment), an aerobic biological reactor, and a secondary clarifier (as a secondary treatment) for dealing with the liquid line for wastewater treatment. The sludge that is produced mostly in the clarifiers is treated in a solid/sludge treatment line including the following processes: thickening, sludge stabilization (digestion), and sludge dewatering. The CAS process became commercially available in the 1930s as a standard process for sewage treatment (Rittmann 1987). Still nowadays, the CAS process has been extensively used for biological treatment of municipal and industrial wastewater world-wide. The main disadvantages of CAS systems include: high capital costs (approximately 20 years are required to recover the invested expenditure), and large footprint requirements due to the needs mostly for accommodating the secondary clarifiers to achieve a proper solid-liquid separation (Van Loosdrecht and Brdjanovic 2014). In addition, CAS systems exhibit operational issues. For instance, both bulking sludge (Guo et al. 2014) and sludge rising due to denitrification in the secondary clarifier (Henze et al. 1993) may cause poor settleability of the activated sludge. Solids can escape together with the treated/clarified effluent negatively affecting the effluent quality (Benefield and Randall 1980; Kõrgmaa et al. 2019; Rossetti et al. 2017); in this regard, CAS process may exhibit some difficulties reaching the most recently strengthened effluent discharge standards. However, the CAS process is a well-established and reliable technology with many installations working world-wide. The mixed liquor suspended solid (MLSS) concentration in the aerobic bioreactor of CAS systems should be maintained between 1500 to 5000 mg L^{-1} range to avoid settling issues in the secondary clarifier.

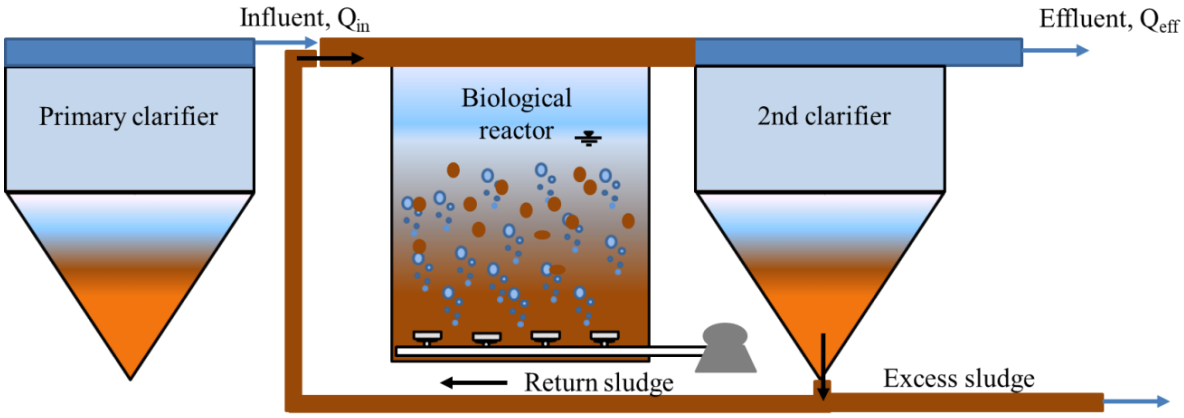

Figure 1.2 Schematic diagram of an activated sludge process (ASP)

In the face of such limitations Dorr-Oliver Inc. back in 1969 coupled a biological reactor based on the activated sludge process with a cross-flow membrane-filtration loop (Smith et al. 1969) introducing the concept of a membrane bioreactor (MBR) system. The MBR can be defined as a system combining a biological process based on the activated sludge process (ASP) with a membrane filtration process (shown in Figure 1.3) to carry out the solid-liquid separation; thus, substituting the secondary clarifier in CAS system (Fortunato et al. 2018). Since then, MBRs have become a very effective and well-known wastewater treatment technology; nowadays, MBRs can be seen as an effective alternative to the CAS wastewater treatment process (Khouni et al. 2020).

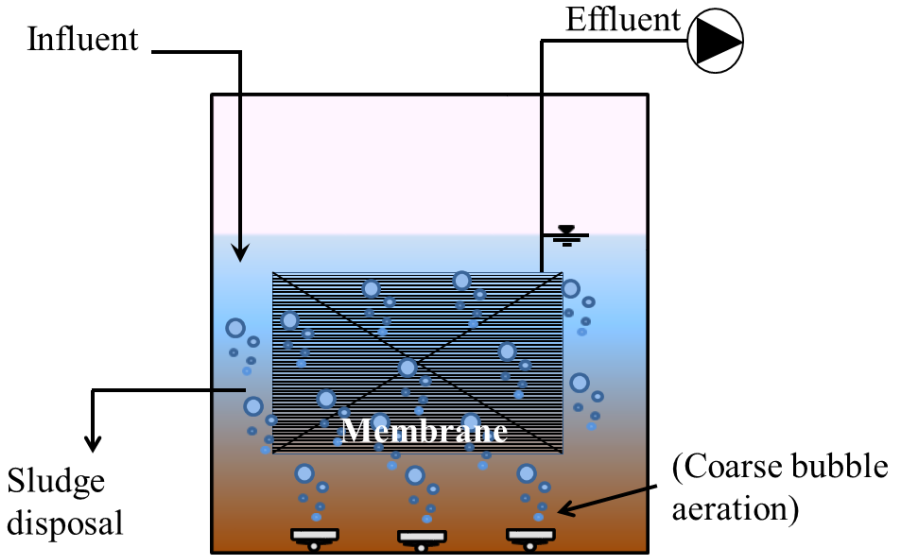

Figure 1.3 Schematic diagram of a membrane bioreactor

MBRs are provided with low pressure filtration membranes (microfiltration (MF) or ultrafiltration (UF)) for performing the solid/liquid separation retaining the suspended solids and biomass in the MBR (Pathak et al. 2020). The operation of MBRs do not depend on the settleability of the sludge; thus, MBRs can be operated at much higher MLSS concentrations and sludge retention times (SRTs) compared to CAS systems. Advantages of MBRs compared to CAS systems include: (i) the production of a consistent and reliable high-quality treated effluent (i.e., low biochemical oxygen demand concentrations, low turbidity, and a mostly disinfected treated effluent); (ii) low footprint (MBRs can operate at higher MLSS concentrations than CAS systems without the needs for settlers); (iii) the production of small amounts of sludge (mostly digested); (iv) excellent control conditions for the effective removal of nutrients; (v) the possibility of handling shock loads; and (vi) the compliance with the most strengthen discharge standards; among others (El-Fadel et al. 2018; Henze et al. 2008; Judd and Judd 2011; Kim et al. 2019; Mannina and Cosenza 2013). In addition, MBRs has gained increasing importance to water reclamation with the recent global concerns of the scarcity of water resources (Ma et al. 2018). Notwithstanding the benefits offered by the MBR technology, MBRs may be more complex to operate and more expensive in terms of capital and operational costs compared to CAS systems (Drews 2010; Hai et al. 2019).

1.2 Problem Statement

MBRs provide a consistent high quality effluent requiring a smaller footprint that any other wastewater treatment system; nevertheless, MBRs can still be much more improved in terms of: (i) reducing even further the footprint requirements; and (ii) decreasing the operational cost by reducing the energy needs introduced by the high aeration demands of such systems. Reducing the footprint requirement of MBRs may allow the design of more compact containerized systems capable of treating high loads of either municipal or industrial wastewater in a very small footprint. The reduction in the footprint requirements has a strong impact on the mobility of the MBRs systems. Currently, movable MBR systems (i.e., those that can be accommodated in standard cargo containers) have a maximum treatment capacity of approximately 200 $m^3 d^{-1}$ fed municipal wastewater (OVIVO microBLOX^{TM}, Econity CF-MBR, among others). Therefore, by reducing the footprint requirements, the treatment capacity (for the same total occupied volume) of these movable systems can be considerably increased. Significantly, the aeration in an MBR system is the most energy-consuming component representing up to 70% of the total energy costs of the treatment system (Hawari et al. 2019; Krzeminski et al. 2012). Therefore, the total energy requirement of an MBR system can be dramatically reduced by increasing the oxygen transfer performance of commonly used aeration systems in MBRs. The oxygen transfer performance of aeration technologies is closely related to the footprint requirements as follows.

The higher the MLSS concentrations at which an MBR can be operated, the lower the footprint requirements. However, as the MLSS increases, the oxygen transfer performance when using conventional diffused aeration (fine and coarse bubble diffusers) get negatively affected (Germain et al. 2007). The negative effects observed in the oxygen transfer performance are more noticeable at MLSS concentrations higher than 15 g L^{-1}, even reaching a limit at MLSS concentrations of approximately 20 g L^{-1} where oxygen cannot longer be transferred into the mixed liquor solution when using conventional diffused aeration systems. Thus, conventional oxygen transfer technologies introduce not only higher aeration costs, but also influence the maximum achievable MLSS concentrations in MBRs (with a direct impact on the footprints requirements of the system). Therefore, there is a need for innovation on more effective and efficient oxygen transfer systems both to reduce the aeration cost, as well as to allow the design of more compact and movable MBRs.

The ratio of the oxygen transfer efficiency (OTE) between process mixed liquor and clean water is often expressed as the alpha factor (α) (Henze et al. 2008), which can be also described as the ratio of oxygen mass transfer in process and clean water (Kim et al. 2019). The alpha factor declines exponentially with the increase of the MLSS concentration as reported by various authors (Capodici et al. 2019; Cornel et al. 2003; Germain et al. 2007; Henkel et al. 2009; Krampe and Krauth 2003; Rodriguez et al. 2012; Xu et al. 2017). Particularly, a research conducted by Germain et al. (2007), demonstrated that the decrease on the OTE (as the MLSS

increases) not only limits the operation of MBR systems at MLSS concentrations higher than approximately 20 g L^{-1}, but also introduces considerable energy losses at MLSS concentrations lower than 20 g L^{-1}. So far, conventional diffused aeration has been widely used for supplying dissolved oxygen (DO) to treat municipal/industrial wastewater. However, a high percentage of the oxygen introduced into an MBR escape to the atmosphere without being dissolved into the mixed liquor solution. That is, the OTE of this type of aeration system is very low, accounting for 1 to 5% per meter of submergence in clean water (Mueller et al. 2002).
Therefore, maximizing the oxygen transfer performance is very significant to optimize the design and performance of MBRs. Recent developments on conventional diffused aeration systems have improved considerably the standard oxygen transfer efficiency (SOTE) and standard oxygen transfer rates (OTRs) in clean water. Some examples include the AEROSTRIP® fine pore diffusers by OVIVO (SOTE of 8-10% m^{-1}), the PRK300 fine-bubble by SULZ ER (SOTE of 8.25% m^{-1}), the FlexDISC™ Fine bubble membrane diffuser by EVOQUA (SOTE of 7.2% m^{-1}), the SSI12" Disc Diffuser Systems by SSI Aeration (SOTE of 10% m^{-1}), and the FlexAir™ Threaded disc diffusers by EDI (SOTE of 10% m^{-1}). However, there is no information in the literature on the performance of such systems in mixed liquor in wastewater treatment plants; particularly, when working at high MLSS concentration of 20 g L^{-1} and even higher. Therefore, it can be speculated that such fine bubble diffusers would be still highly impacted by the mixed liquor matrix yielding low alpha factors; particularly, at high MLSS concentrations.

Concentrated oxygen delivery systems, such as the supersaturated dissolved oxygen (SDOX) system operate at high-pressure conditions fed high purity oxygen rather than air. The SDOX system was evaluated in this PhD research as a promising technology to overcome the oxygen transfer limitations introduced by diffused aeration in biological wastewater treatment systems; particularly in MBRs operated at higher than usual MLSS concentrations. Up to the PhD candidate knowledge there are no studies in the literature exploring the oxygen transfer performance of concentrated oxygenation systems such as the SDOX system in the context of biological wastewater treatment processes operated at high MLSS concentrations. There is a gap in the literature when using the concentrated oxygenation system such as the SDOX aeration technology in the followings issues: (i) the DO delivery capabilities of the concentrated oxygenation system, SDOX, at different MLSS conditions, (ii) the impacts of the SDOX system on the biological performance of the biological wastewater treatment system, (iii) the effects of the SDOX system on the microbial communities , and (iv) the impact of the SDOX technology on the membrane filtration performance (membrane fouling).

1.3 Main Objectives

Based on the previous research needs, this PhD dissertation aims at addressing such needs; particularly, the oxygen transfer in wastewater treatment systems. The main objective of this research was to assess the impacts of the SDOX technology on the oxygen transfer performance

at a wide range of MLSS concentrations; however, focusing on high MLSS concentrations. Simultaneously, the OTE of the SDOX system was evaluated and compared to the OTE of conventional aeration systems (fine bubble diffusers). Also, the influence of SDOX on the performance of the biological wastewater treatment processes was investigated. In addition, this study also evaluated both the effects of the SDOX system on the shifts in microbial communities, as well as the potential impacts of the SDOX on solid/liquid separation processes and membrane filtration performance. This study contributed to providing guidelines for designing the next generation of MBRs for its application in the biological wastewater treatment sector.

1.4 Key research questions

This PhD study aimed at answering the following questions.

- How does the overall oxygen mass transfer rate coefficient (K_La) and alpha factor behave at different MLSS and mixed liquor volatile suspended solids (MLVSS) concentrations when using different aeration systems (conventional diffused aeration vs. SDOX) in activated sludge from a WWTP operated at a short SRT of approximately 5 days?
- How the solid-liquid separation processes (sedimentation (settleability) and membrane filtration) are affected by the use of the SDOX aeration system?
- What are the short-term (hours) and long-term (several weeks or months) effects of the conditions created by the SDOX aeration system on the changes in microbial communities' composition and on the performance of the biological wastewater treatment processes for COD removal and nitrification?
- Which aeration system (diffused aeration vs. SDOX) is the most suitable for operating MBRs operated at high MLSS concentrations (above 20 g L^{-1}) when considering an energy requirement for each of the aeration system?
- Would it possible to operate an MBR aerated by fine bubble diffuser at MLSSs higher than 20 g L^{-1}?
- Can near infrared (NIR) spectroscopy predict wastewater effluent, soluble microbial products (SMP) and extracellular polymeric substances (EPS)?

Based on the key research questions, the specific research objectives are as follows:

1.5 Specific objectives

- To evaluate the limitations of oxygen transfer imposed by conventional fine bubble diffusers at high MLSS concentration.

- To evaluate the oxygen delivery capability of the SDOX aeration system at different MLSS concentrations compared to the oxygen delivery capability of conventional aeration systems (bubble diffusers): alpha factor comparison between two aeration systems.
- To assess the short-term exposure (hours) and long-terms (days or weeks) effects of the SDOX aeration systems on the biological processes for COD removal and nitrification, and its impact on the physiology and microbial population dynamics.
- To evaluate the impacts of the SDOX aeration system on the sludge solid-liquid separation processes such as membrane filtration (membrane fouling).
- To simulate the measured data of treated wastewater, SMP, and EPS with NIR spectroscopy

The specific hypotheses are defined as follows:

1.6 Hypotheses

- The oxygen transfer capability of the SDOX aeration system will be better than the oxygen transfer capabilities of conventional bubble aeration systems.
- High-pressure influence may impede the normal microbial activity
- Microbial structure and population will change at a long-term exposure to the high-pressure imposed by SDOX.
- An MBR oxygenated with a conventional bubble aeration system cannot be operated at an MLSS higher than 20 g L^{-1}. However, an MBR aerated with the SDOX aeration system could be operated at MLSS higher than 20 g L^{-1}.
- Settleability of activated sludge is reduced when using SDOX due to a reduced particle size.

1.7 Outline of thesis

This dissertation is structured in 8 chapters. The present chapter provides the general introduction of the research. The next chapter aims at providing a comprehensive state-of-the-art review on the oxygen transfer phenomena in the wastewater treatment field. The next five chapters are based on the experimental results produced from each research topic. Particularly, the five chapters can be organized in three different clusters: (i) the problem description of conventional diffused aeration system; (ii) a proposed solution to enhance the oxygen transfer capacities; and (iii) an application of the proposed solution (SDOX technology) in the biological wastewater treatment field. That is, while the conventional diffused aeration systems face oxygen delivery limitations at high MLSS (above 20 g L^{-1}) as described in chapter 3, the SDOX

aeration system can be able to cope with the current limitations imposed by conventional aeration system as described in chapter 4. Chapters 5 and 6 aim at evaluating the influence of the innovative oxygen system (SDOX) on the biological performance along with microbial population dynamics and membrane filtration performance in MBRs, respectively. The chapter 7 describes the results of NIR experiments interpreted with the help of chemometric techniques predict the effluent, SMP and EPS concentration of a wastewater treatment process, without going through the conventional analytical determination of such parameters. The final chapter concludes and summarizes the entire findings of this dissertation. Figure 1.4 displays the flow of this dissertation work.

- **Chapter 1** introduces the topic of this dissertation and provides the background, problem statement, and rationale of this study.
- **Chapter 2** describes the state-of-the-art of the oxygen transfer phenomena in ASP, various aeration systems on oxygen transfer in wastewater treatment, and membrane fouling in MBR systems.
- **Chapter 3** presents the limitations of oxygen transfer at high MLSS concentrations when supplying DO through conventional fine bubble diffusers on the design of a high-loaded MBR (HL-MBR).
- **Chapter 4** introduces the SDOX aeration technology as a possible candidate for uncapping the limitations of oxygen transfer imposed by conventional aeration systems, and evaluate the oxygen transfer capability of the SDOX system at high MLSS concentrations.
- **Chapter 5** demonstrates the feasibility of an MBR coupled with SDOX in terms of biological performance and microbial population dynamics.
- **Chapter 6** investigates membrane fouling propensity imposed by high-pressure aeration system (SDOX), in comparison with a membrane fouling imposed by fine bubble diffusers in a submerged MBR.
- **Chapter 7** shows the applicability of NIR spectroscopy with chemometric techniques on the prediction of wastewater constituents.
- **Chapter 8** discusses the main findings of the study and describes reflection and outlook of this research.

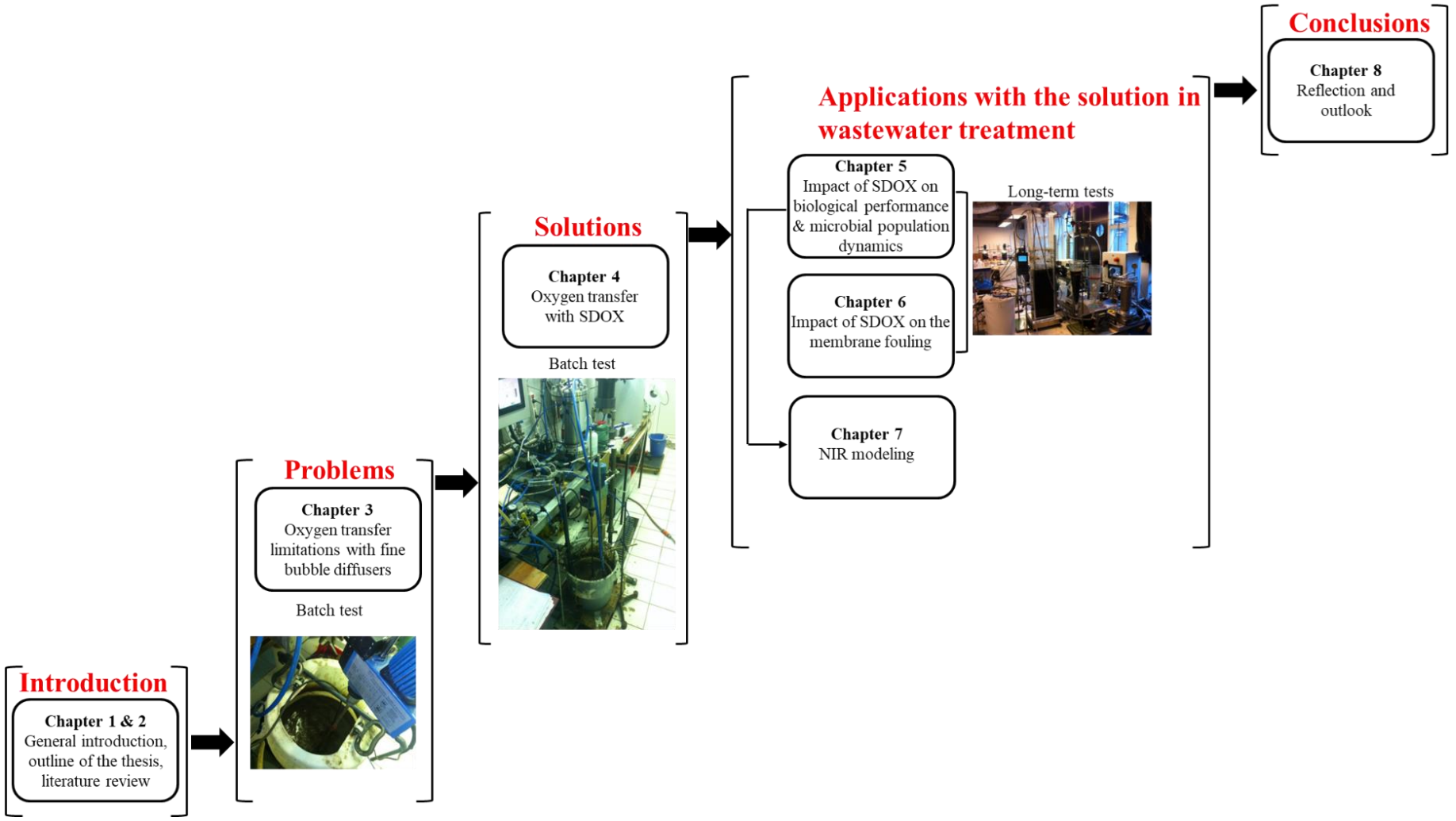

Figure 1.4 Schematic structure of this PhD dissertation research and connection among each chapter

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Chapter 2

Factors affecting oxygen transfer in biological wastewater treatment processes with special emphasis on MBRs: A review

2.1 The principle of aeration

Aeration is the contact of air and liquid solutions so that gas transfer of some gas molecules occurs at the interface between the gas and the liquid film. In aerobic biological wastewater treatment, the most fundamental purpose of aeration is to treat wastewater under microbial biodegradation by supplying dissolved oxygen (DO). Oxygen must be delivered to the liquid solutions (i.e., either to mixed liquor or microorganisms) at a constant rate so that aeration is not a limiting factor influencing the overall performance of a biological treatment system. Specifically, aeration is intended to maintain a constant DO concentration, which is necessary to promote certain reactions (e.g., organic matter removal and nitrification) in mixed liquor environment in aeration basins (i.e., biological tanks) in wastewater treatment plants (WWTPs).

The two-film theory proposed by Lewis and Whitman (1924) is the most widely used to describe the gas transfer process in aeration tanks. The two-film theory is characterized by a physical model in which two films (i.e., gas film and liquid film) simultaneously co-exist at the gas-liquid interface. Figure 2.1 shows the two-film theory with an example of absorption (gas being absorbed into liquid). The two films are defined as liquid on one side and gas on the other side. There are boundary films on both sides of the interface between liquid and gas, which creates a resistance when gas molecules pass through the between bulk-liquid and bulk-gaseous phases. When applying the two-film theory, it is necessary to assume that the concentration and partial pressure in each bulk-liquid and bulk-gaseous phase are uniform. That is, two phases are completely mixed (Metcalf and Eddy 2014).

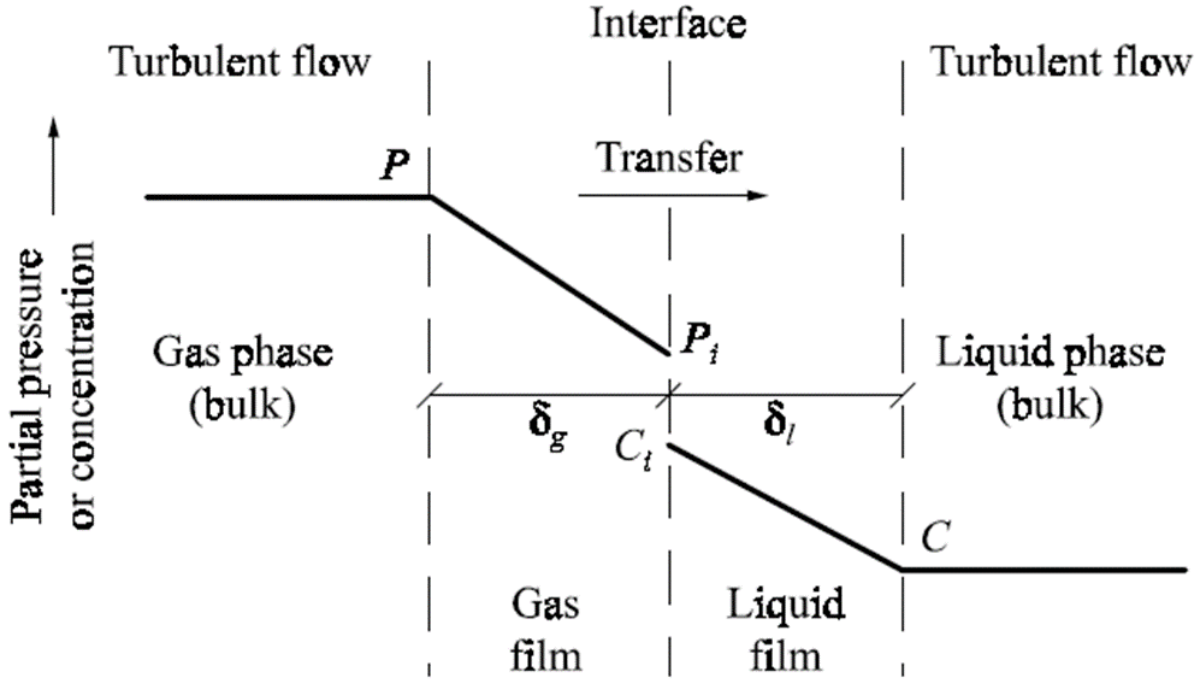

Figure 2.1 A conceptual diagram of the two-film theory of gas transfer (adapted from Metcalf and Eddy 2014)

2.2 Oxygen transfer parameters

Aeration is performed through aeration systems. Each aeration system has different performance or efficiency. Therefore, the following relations (adapted from Henze et al. 2008) are used to compare each specific aeration systems. Oxygen transfer rate (OTR) as exhibited in Equation 2-1 is an indicator of how much oxygen an aeration device can supply, regardless of its efficiency. Equation 2-2 is an index indicating an energy efficiency of a specific aeration system. Among aeration systems, oxygen transfer efficiency (OTE) of diffused aeration (e.g., fine and coarse bubble diffusers) can be calculated through Equation 2-3, providing an absolute efficiency of each of aeration system.

The comparison on the performance of each aeration system is always made under standard conditions (zero DO, zero salinity, 20 °C, 1 atmospheric pressure). Thus, results are reported in the form of standard oxygen transfer efficiency (SOTE, %), standard oxygen transfer rate (SOTR, $kgO_2\ h^{-1}$), and standard aeration efficiency (SAE, $kgO_2\ kWh^{-1}$) (Henze et al. 2008). When designing an aeration tank, the selection of aeration system type is significant. In general, an aeration system is selected by its SOTE, where the efficiency of the aeration system is closely associated with overall oxygen mass transfer rate coefficient (K_La). The alpha factor (Equation 2-4) signifies a degree to which a performance of particular aeration system is disturbed by characteristics of process water (either wastewater or mixed liquor).

$$\mathrm{OTR} = \mathrm{K_L{}^a}(\mathrm{DO} - \mathrm{DO_{sat}})\mathrm{V}\ (\mathrm{kgO_2}h^{-1}) \qquad \text{Eq. (2-1)}$$

Where,

K_La : liquid-side mass transfer coefficient (h^{-1})

DO : dissolved oxygen in water ($kgO_2\ m^{-3}$)

DO_{sat}: dissolved oxygen in water at saturation ($kgO_2\ m^{-3}$)

V : water volume (m^3)

$$\mathrm{AE} = \frac{\mathrm{OTR}}{\mathrm{P}}\left(\frac{\mathrm{kgO_2}}{\mathrm{kWh}}\right) \qquad \text{Eq. (2-2)}$$

Where,

P : power drawn by the aeration system (kW)

$$\mathrm{OTE} = \frac{\mathrm{O_{2,in}} - \mathrm{O_{2,out}}}{\mathrm{O_{2,in}}} \qquad \text{Eq. (2-3)}$$

Where,

$O_{2,in}$: mass fluxes of oxygen in of the clean water volume

$O_{2,out}$: mass fluxes of oxygen out of the clean water volume

$$\alpha = \frac{\mathrm{K_L a_{process\ water}}}{\mathrm{K_L a_{clean\ water}}} \qquad \text{Eq. (2-4)}$$

2.3 Factors affecting the oxygen transfer in biological wastewater treatment processes with special emphasis on membrane bioreactors

Stable oxygen transfer is essential because the performance of the overall process of WWTPs may vary depending on the oxygen transfer characteristics. For instance, supplying oxygen (i.e., aeration) is crucial since a performance of organic matter biodegradation and nitrification depends on DO concentration in mixed liquor matrices. Oxygen transfer is influenced by various parameters; each of them interacts and affects each other. In membrane bioreactors (MBRs) the effects of these parameters are evident than in conventional wastewater treatment processes. General factors affecting oxygen transfer in biological wastewater treatment processes can be summarized as follows.

1. Biomass characteristics
    - Impact of mixed liquor suspended solids (MLSS) concentration (Casey and Karmo 1974; Cornel et al. 2003; Durán et al. 2016; Germain et al. 2007; Gunder 2000; Henkel et al. 2009b; Kim et al. 2019; Krampe and Krauth 2003; Meng et al. 2007; Muller et al. 1995; Rodríguez et al. 2012; Rosenberger 2003)
    - Impact of mixed liquor volatile suspended solids MLVSS concentration (Henkel et al. 2009b; Kim et al. 2019)
    - Soluble microbial products (SMP) and extracellular polymeric substances (EPS) (Germain et al. 2007)
    - Viscosity (Germain Stephenson 2005; Manem and Sanderson 1996; Ozbek and Gayik 2001; Sato and Ishii 1991)
    - Particle size distribution (PSD) (Germain Stephenson 2005; Wisniewski and Grasmick 1998)
    - Influent impurities (effect of salt (Lazarova et al. 1997); effect of surfactants (Chern et al. 2001; Dignac et al. 2000; Henkel et al. 2009b; Quemeneur and Marty 1994; Struijs et al. 1991)
2. Operational conditions
    - Hydrodynamics (e.g. air flow rates (AFRs), mixing intensity) (Germain et al. 2007; Meng et al. 2007; Ozbek and Gayik 2001)
    - Solid retention time (SRT) (Rosso and Stenstrom 2006)
    - Hydraulic retention time (HRT) (Rodríguez et al. 2012)

- Aeration systems cleaning (e.g. physical/chemical cleaning) (Rosso and Stenstrom 2005)
- Effect of selectors (targeting for surfactants removal) (Rosso et al. 2006a, 2006b)
- Use of pure oxygen (Kim et al. 2019; Lee and Kim 2013; Rodríguez et al. 2010, 2011)
- Temperature (Bewtra et al. 1970; Vogelaar et al. 2000)

3. Aeration types
- Bubble size (DeMoyer et al. 2003)
- Diffused aeration (fine and coarse bubble diffuser) (Ashley et al. 1992)
- High purity oxygen systems (Benefield et al. 1977; Wilcox and Mcwhirter 1971)
- Pressured aeration systems (Barreto et al. 2017, 2018; Kim et al. 2020)

Since it is not within the scope of this dissertation research to outline all the factors summarized above, this dissertation details the impact of (i) aeration system type, (ii) MLSS concentration, (iii) SRTs, and (iv) air flow rates, on the oxygen transfer.

2.4 Limitations of oxygen transfer in wastewater treatment when using conventional diffused aeration systems

2.4.1 Impact of aeration system type

Diffused aeration systems transfer DO into liquid solutions under a certain pressure (Mueller et al. 2002) by either dissolving oxygen gas through a semi-permeable membrane or by dispersing oxygen gas through a gas-liquid interface (Rosso et al. 2006b). Conventional bubble diffusers are generally classified into fine and coarse bubble diffusers. Fine bubble diffusers can be described as fine pore diffusers (made by either ceramics, plastics, or perforated membranes) widely employed in aerobic activated sludge process; they typically generate bubbles with a size ranging from 2 to 5 mm (Mueller et al. 2002). Coarse bubble diffusers typically have a pore size greater than 6 mm, and the sizes of the produced bubbles range from 6 to 10 mm (Yoon 2016). Coarse bubble diffusers have relatively higher AFRs and OTRs compared to fine bubble diffusers, since as many diffusers as needed can be accommodated in a given surface area; in addition, they are less affected by clogging and scaling compared to fine bubble diffusers due to the high turbulence nearby to the pores/orifices. However, coarse diffusers exhibit lower OTEs than fine bubble diffusers due to the shorter retention time of the large bubbles in the aerobic basins, and thereby showing low SAEs in the range of 0.6 to 1.5 kgO_2 kWh^{-1} (Henze et al. 2008).

Fine bubble diffusers produce bubbles smaller than 5 mm (Yoon 2016); they are the most employed aeration system in activated sludge process because of their high OTEs compared to

coarse bubble diffusers with SAEs in the range of 3.6 to 4.8 kgO_2 kWh^{-1} (Henze et al. 2008). However, fine bubble diffusers are more vulnerable to get affected by pollutants from wastewater compared to coarse bubble diffusers, and thereby having a detrimental impact on the OTEs; in addition, a regular cleaning and maintenance of the diffusers is required as a shortcoming (Rosso and Stenstrom 2005). Despite the widespread use of conventional bubble diffusers, the oxygen transfer process is still quite inefficient exhibiting fairly low OTEs.

As an example, a single coarse bubble diffuser (static tube type) can provide a maximum AFR of approximately 68.3 m^3 h^{-1} per diffuser surface area (m^2) at an SOTE of approximately 2.88% per meter of submergence in clean water. Similarly, a single fine bubble diffuser (rigid porous plastic tube type) can provide a maximum AFR of 18.8 m^3 h^{-1} per diffuser surface area (m^2) at an SOTE of 5.4% m^{-1} in clean water (Mueller et al. 2002). That is, coarse bubble diffusers provide larger OTRs but lower SOTEs compared to fine bubble diffusers. TRANSMAX™ coarse bubble diffuser (https://www.ovivowater.com, accessed on October 2017) reported SOTEs of 1.64% m^{-1} in clean water; Sanitaire fine bubble diffuser Silver Series II (https://www.xylem.com, accessed on October 2017) reported an SOTE ranging from 6.5 to 10% m^{-1} in clean water. The SOTEs of these aeration systems decrease when operating in process water (either wastewater or mixed liquor solutions). SOTEs from 1.22 to 3.42% m^{-1} and from 1.2 to 5.5% m^{-1} were reported for coarse bubble diffusers in process water (at conventional activated sludge (CAS) relevant MLSS concentrations) and in clean water, respectively; similarly, SOTEs values ranging from 1.2 to 2.3% m^{-1} and from 5.89 to 8.57% m^{-1} were reported for fine bubble diffusers in process water (at conventional CAS MLSS concentrations) and in clean water, respectively (Mueller et al. 2002). The OTEs in fine bubble diffusers are more affected by the wastewater matrix compared to coarse bubble diffusers. Additionally, Mueller et al. (2002) reported a maximum AFR in process water per diffuser surface area (m^2) of 26.8 m^3 h^{-1} at an SOTE of 1.2% m^{-1} for a single coarse bubble diffuser. Similarly, the authors reported a maximum AFR in process water per diffuser surface area of 12.3 m^3 h^{-1} m^{-2} at an SOTE of 2.3% m^{-1}, and of 11.3 m^3 h^{-1} m^{-2} at an SOTE of 2.9% m^{-1} for fine bubble diffusers porous tube type and plastic domes and discs type, respectively.

It should be noted that it is difficult to accurately compare the performance of coarse and fine bubble diffusers based on the SOTEs in process water when considering the differences in the types of diffuser, the placement of the diffusers, and the AFRs at which the evaluations are carried out (Kim et al. 2019). However, it can be concluded that the alpha factors (mass transfer ratio of process-water to clean-water mass transfer) for coarse bubble diffusers are higher than for fine bubble diffusers, and that higher AFRs can be achieved by coarse bubble diffusers compared to fine bubble diffusers. The higher the AFRs, the higher the turbulence at the orifice discharge; therefore, coarse diffusers are less affected by fouling or scaling yielding higher alpha factors (Henze et al. 2008). Groves et al. (1992) reported alpha factors range from 0.55 to 0.94 for coarse bubble diffusers and from 0.32 to 0.55, 0.24 to 0.57, and 0.43 to 0.58 for perforated membrane discs, ceramic domes, and ceramic tubes fine bubble diffusers,

respectively; however, no information was provided regarding the MLSS concentrations at which these experiments were performed.

The two types of conventional bubble diffusers (fine and coarse) exhibit some advantages and disadvantages regarding OTRs, SOTEs, and alpha factors; however, it can be concluded that overall conventional bubble diffusers are quite inefficient introducing dissolved air into mixed liquor solutions. The transfer efficiency is even lower when introducing either air or oxygen in process water (wastewater). Consequently, aeration cost can represent up to 75% of the total operational cost in a conventional wastewater treatment system (Capodici et al. 2019; Reardon 1995; Rosso et al. 2008).

2.4.2 Impact of biomass (mixed liquor suspended solids) concentration on the oxygen transfer

So far, the performance of conventional diffusers was described in the context of conventional CAS systems working at MLSS concentrations in the range of approximately 3 to 5 g L^{-1}. Operating an MBR system at higher than usual CAS-relevant MLSS concentrations would introduce many technical advantages such as lower footprint requirements, lower sludge production, among others. However, the oxygen transfer performance at such high MLSS concentrations can be even further negatively affected. Several authors have evaluated the oxygen transfer performance of conventional bubble diffuser systems when wastewater treatment systems are operated at a high MLSS concentration range.

Muller et al. (1995) operated a pilot-scale MBR treating domestic wastewater at infinite SRT conditions maintaining a constant organic load during the entire evaluation; that is, the MLSS concentration was increased by increasing the SRT. Air was supplied to the aerobic basin of the MBR at a volumetric AFR ranging from approximately 3.3 to 10 $m^3\ m^{-3}\ h^{-1}$ through a diffused aeration system. Alpha factors of 0.98, 0.5, 0.3, and 0.2 were reported at MLSS concentrations of 3, 16, 26, and 39 g L^{-1}, respectively. That is, the alpha factor exponentially decreased with the MLSS concentration.

Gunder (2000) determined the alpha factors on two pilot-scale MBRs fed pre-settled municipal wastewater operated at infinite SRTs. Compressed air was supplied to the aerobic basin of the first and second MBRs through fine bubble diffusers at volumetric AFRs from 6 to 9 $m^3\ m^{-3}\ h^{-1}$ and 8.5 $m^3\ m^{-3}\ h^{-1}$, respectively. In addition, air was supplied to the second MBR through a coarse bubble diffuser for membrane scouring at a volumetric AFR of 13.4 $m^3\ m^{-3}\ h^{-1}$. Alpha factors of 0.5 and 0.12 were reported when supplying air through a combination of fine bubble and coarse bubble diffusers at MLSS concentrations of 8 and 25 g L^{-1}, respectively. The alpha factors decreased exponentially with the MLSS concentration.

Cornel et al. (2003) evaluated two full-scale MBRs treating municipal wastewater operated at SRTs ranging from 30 to 40 days. Air was simultaneously supplied by both fine and coarse bubble diffusers. The volumetric AFR through the fine and coarse bubble diffusers ranged from

1.5 to 3 $m^3 m^{-3} h^{-1}$, and 3 to 7 $m^3 m^{-3} h^{-.1}$, respectively. As expected higher AFRs were possible to apply when using coarse bubble diffusers compared to fine bubble diffusers. Average alpha factors of 0.7 and 0.4 were reported when supplying air through a combination of fine bubble and coarse bubble diffusers at MLSS concentrations of 7 and 17 g L^{-1}, respectively. The alpha factor decreased exponentially in that range of MLSS concentration.

Krampe and Krauth (2003) evaluated the oxygen transfer performance of activated sludge samples taken from different full-scale and pilot WWTPs. No detailed information was provided on the type of wastewater being treated at each WWTP. Moreover, no information was reported regarding the SRTs at which the WWTPs were operating. A volumetric AFR of approximately 7 $m^3 m^{-3} h^{-1}$ was provided through either an injector aerator or a fine bubble diffuser. Alpha factors ranging from approximately 0.5 to 0.1 for the injector aerator and from 0.6 to 0.1 for the fine bubble aeration were reported at an MLSS concentration range from approximately 8 to 28 g L^{-1}. The alpha factor exponentially decreased with the MLSS concentration.

Germain et al. (2007) evaluated the oxygen transfer performance on several sludge samples. The samples were taken from pilot-scale and full-scale MBR plants treating municipal wastewater at MLSS concentrations from 7.2 to 30.2 g L^{-1}. No information on the SRTs at which each treatment plant was operated was given by the authors. Volumetric AFRs ranging from approximately 0.7 to 6 $m^3 m^{-3} h^{-1}$ were supplied to carry out the experiments and to evaluate the effects of the AFR on the oxygen transfer performance; air was supplied through a fine bubble diffuser (Sanitaire ceramic disc). Alpha factors from approximately 0.65 to non-detectable were reported at MLSS concentrations from 7.2 to 30.2 g L^{-1}. The alpha factor exponentially decreased with the MLSS concentration.

Henkel et al. (2009a), evaluated the oxygen transfer performance at two pilot-scale MBRs operated in parallel and fed greywater. The MBRs were provided with both fine and coarse bubble diffusers working simultaneously. The air was supplied at volumetric AFRs from approximately 5.8 to 26.1 $m^3 m^{-3} h^{-1}$ and 1.1 to 6.3 $m^3 m^{-3} h^{-1}$ for the first and second MBR, respectively. The alpha factors were determined at an MLSS concentration range from 4.7 and 19.5 g L^{-1}. The MLSS concentration range was obtained by setting the SRT between 24 and 110 days. Alpha factors from approximately 0.9 to 0.6 were reported at MLSS concentrations from 4.7 to 19.5 g L^{-1}. The alpha factor exponentially decreased with the MLSS concentration. However, higher alpha factors were obtained compared to other authors. This is because the greywater sludge contained a considerable lower concentration of MLVSS. Therefore, when comparing the decrease on the alpha factor as a function of the MLVSS rather than as a function of the MLSS, the results are comparable to the alpha factors reported by other authors such as Muller et al. (1995), Krampe and Krauth (2003), and Rosenberger (2003).

The main findings described above are reported in Table 2.1. The reported alpha factors at each

specific MLSS concentration differ significantly among the different authors. Germain et al. (2007) reported these discrepancies among several authors. At the CAS MLSS range (i.e., MLSS concentrations from 3 to 5 g L^{-1}) at an MLSS concentration of 5 g L^{-1}, Krampe and Krauth (2003) reported an alpha factor of 0.6, while Muller et al. (1995) reported an alpha factor of 0.9. Recently, Kim et al. (2019) reported an alpha factor of 0.9, while Capodici et al. (2019) reported an alpha factor of 0.1. At the conventional MBR MLSS range (i.e., MLSS concentrations from 8 to 12 g L^{-1}) at an MLSS of 12 g L^{-1}, Germain et al. (2007) reported an alpha factor of 0.3, while Muller et al. (1995) reported an alpha factor of 0.6. Recently, Kim et al. (2019) and Xu et al. (2017) reported an alpha factor of 0.75 and 0.7, respectively. At the high MLSS MBR range (i.e., MLSS concentrations from 12 to 40 g L^{-1}) at an MLSS of 30 g L^{-1}, Germain et al. (2007) reported a negligible alpha factor, while Muller et al. (1995) reported an alpha factor of 0.3. Recently, Kim et al. (2019) reported an alpha factor of 0.3.

Table 2.1 Alpha factors for conventional diffusers evaluated at different MLSS concentrations

Author	Alpha factor (MLSS concentration (g L^{-1}))	SRT (days)	Type of wastewater/sludge
Muller et al. (1995)	0.98 (3.0), 0.50 (16.0), 0.30 (26.0), 0.20 (39.0)	Infinite	Domestic wastewater
Gunder (2000)	0.50 (8.0), 0.12 (25.0)	Infinite	Pre-settled municipal wastewater
Cornel et al. (2003)	0.70 (7.0), 0.40 (17.0)	30 to 40	Municipal wastewater
Krampe and Krauth (2003)	0.60 (8.0), 0.10 (28.0)	Not reported	Sludge from full-scale and pilot CAS plants – municipal wastewater
Germain et al. (2007)	0.65 (7.2), non-detectable (30.2)	Not reported	Sludge from pilot-scale and full-scale MBR plants – municipal wastewater
Henkel et al. (2009a)	0.9 (4.7), 0.6 (19.5)	24 to 110	Greywater
Xu et al. (2017)	0.85 (6.0), 0.7 (12.0),0.4 (18.0)	17 to 30	Sludge from full-scale MBR plants– municipal wastewater
Kim et al. (2019)	0.9 (4.0), 0.8 (11.0), 0.45 (20.0), 0.25 (32.0)	5	Sludge from full-scale CAS plants– municipal wastewater

The differences on the reported alpha factors at the same MLSS concentration can be probably attributed to differences on the operational conditions (such as SRTs) and characteristics of the sludge and influent wastewater. Even though there is some discrepancy between authors, most of them agreed that the alpha factor exponentially decreased with the MLSS concentration.

2.4.3 Impact of solid retention times on the oxygen transfer

Increasing the treatment capacity at a given footprint is one of the most relevant drivers for operating a biological system at higher than usual MLSS concentration. For instance, this concept of an MBR system operated at higher than usual MLSS concentrations was introduced by Kim et al (2020) as the high-loaded MBR (HL-MBR). The achievement of a higher treatment capacity at the same footprint requires to increase the MLSS concentration in MBR system up to approximately 40 g L^{-1} or higher by increasing the amount of active biomass in the system, but not by increasing the amount of non-active suspended solids. In this regard, the MBR system should be operated at a high organic load and at a low SRT. Most of the previously reported alpha factors were determined on wastewater treatment systems working at extremely high, even infinite SRTs (Cornel et al. 2003; Germain et al. 2007; Henkel et al. 2009a; Krampe and Krauth 2003); that is, the opposite conditions of what is needed for designing a HL-MBR. As described by Rosso et al. (2008), the OTE is directly proportional to the SRT, signifying the higher the SRT, the higher the OTE and the alpha factors. Therefore, most of the research previously conducted at high MLSS concentrations could underestimate the effect of alpha factors; that is, they are not realistic for determining the alpha factor for designing a HL-MBR aimed at increasing the treatment capacity while minimizing the system footprint.

The impact of the SRT on the OTE and alpha factors has been evaluated by several authors, and the main findings are presented in Table 2.2. However, most of these evaluations were carried out at a relatively low MLSS concentration range (i.e., at a CAS MLSS concentration range from approximately 3 to 6 g L^{-1}). As described by Rosso et al. (2007), the higher the SRT, the higher the chances for biodegrading organic compounds which are not biodegradable at short SRTs; that is, substances that have a negative impact on the oxygen transfer process at short SRTs may be eventually removed by increasing the SRT. Rosso et al. (2008) reported that alpha factors (and consequently, aeration efficiencies) are higher when working at elevated SRTs. The higher the SRTs, the better the removal of the faster acting surfactants which have the most dramatic impact in reducing the oxygen transfer. Surfactants, because of their amphiphilic nature, accumulate at the air-water interface of rising bubbles negatively affecting the oxygen transfer process. Readily biodegradable COD, partially composed of surface active agents or surfactants discharged as oils, soaps, and detergents, has more chances to be removed when working at elevated SRTs. As an example, the authors reported alpha factors of 0.37 and 0.48 obtained at SRTs of 5 and 15 days, respectively.

Groves et al. (1992) evaluated the oxygen transfer performance on two aeration basins of a CAS WWTP. One basin was operated at 14 days of SRT, while the other was operated at 1 day of

SRT. Both basins were provided with fine bubble ceramic dome diffusers. SOTEs of 2.5 and 1.4% m^{-1} and alpha factors of 0.39 and 0.26 were reported at SRTs of 14 and 1 days, respectively. That is, the alpha factor decreased with the reduced SRT. No information on the MLSS concentration at the aeration basins was reported.

Rieth et al. (1995) evaluated the oxygen transfer performance on a CAS wastewater treatment pilot plant equipped with a single ceramic fine bubble dome diffuser operated at an SRT range from 2.0 to 10.2 days. MLSS concentrations ranged from approximately 1.0 to 4.7 g L^{-1}. When working at an MLSS concentration of 4.7 g L^{-1} (at an SRT of 10.1 days) and 1.0 g L^{-1} (at an SRT of 2.0 days), alpha factors of 0.42 (SOTE of 3.3% m^{-1}) and 0.35 (SOTE of 2.1% m^{-1}) were reported, respectively. That is, the lower the SRT, the lower the alpha factor even at lower MLSS concentrations.

Gillot and Héduit (2008) summarized the research performed by Groves et al. (1992), Rieth et al. (1995), Rosso et al. (2001), and Wagner (1999). Alpha factors below 0.3 and above 0.9 were reported by these authors at SRTs of approximately 1 day and 30 days, respectively. Moreover, Gillot and Héduit (2008) investigated the effect of the SRTs on the alpha factors in CAS full-scale WWTP aerobic basins provided with fine bubble diffusers. Fourteen CAS WWTPs treating mainly municipal wastewater and operated as extended aeration systems were evaluated; the average MLSS concentrations ranged from 2.2 to 6.5 g L^{-1} operated at SRTs from 15 to 25 days. The authors reported alpha factors from 0.73 to 0.98 and from 0.44 to 0.78 at SRTs of 25 and 15 days, respectively. Therefore, the lower the SRT the lower the alpha factors.

Rodriguez et al. (2012) investigated the effect of the SRT on the alpha factor on a bench-scale MBR operated at MLSS concentrations of approximately 4.5 g L^{-1} and 11 g L^{-1}. The MBR was fed with municipal wastewater from a primary clarifier from a full-scale WWTP. When working at the lowest MLSS concentration of 4.5 g L^{-1}, alpha factors of 0.9 and 0.6 were reported at SRTs of 149 and 18.8 days, respectively. Moreover, when working at the highest MLSS concentration of approximately 11 g L^{-1}, alpha factors of 0.12 and 0.02 were reported at SRTs of 84.5 and 44.7 days, respectively. Therefore, the authors demonstrated the negative impact of short SRTs on the alpha factor at both representative CAS relevant and MBR relevant MLSS concentrations.

Good agreements with the previous observations were reported by many other authors (Henkel et al. 2009b; Henkel et al. 2011; Rosso and Stenstrom 2005; US EPA 1989); they all concluded a decrease on the OTE at lower SRTs. Several studies were conducted evaluating the impact of the SRT on the OTEs. However, most of them were conducted at CAS relevant MLSS concentration ranges (i.e., from approximately 3 to 6 g L^{-1}).

Table 2.2 Alpha factors for conventional diffusers evaluated at different SRTs

Author	Alpha factor (SRT (days))	MLSS ($g\ L^{-1}$)	Type of wastewater/sludge
Groves et al. (1992)	0.39 (14.0), 0.26 (1.0)	Not reported	Municipal wastewater
Rieth et al. (1995)	0.53 (10.0), 0.35 (2.0)	1.0 to 4.7	Municipal wastewater
Rosso and Stenstrom. (2005)	0.37 (5.0), 0.48 (15.0)	Not reported	22 full-scale WWTP - Not reported
Gillot and Héduit (2008)	0.73 to 0.98 (25.0), 0.44 to 0.48 (15.0)	2.2 to 6.5	14 CAS WWTP - municipal wastewater
Rodriguez et al. (2012)	0.90 (149.0), 0.60 (18.8)	4.5	Wastewater from a primary settling from a real WWTP
	0.12 (84.5), 0.02 (44.7)	11.0	

2.4.4 Impact of air flow rates and oxygen source on the oxygen transfer

The evaluations of the effects of the MLSS concentrations on the alpha factor were carried out at a very diverse range of volumetric gas flow rates. For instance, Muller et al. (1995) worked at volumetric AFRs from 3.3 to 9.8 $m^3\,m^{-3}\,h^{-1}$, and from 24.5 to 57.1 $m^3\,m^{-3}\,h^{-1}$ for CAS and MBR MLSS sludge concentrations, respectively. Gunder (2000) evaluated the alpha factors on two MBR systems at a volumetric AFR from 6.0 to 9.0 $m^3\,m^{-3}\,h^{-1}$; however, a higher volumetric AFR of 13.4 $m^3\,m^{-3}\,h^{-1}$ was used for membrane scouring. Cornel et al. (2003) evaluated alpha factors on MBRs at a volumetric AFR of approximately 3.0 $m^3\,m^{-3}\,h^{-1}$ and from 7 $m^3\,m^{-3}\,h^{-1}$ to 60.0 $m^3\,m^{-3}\,h^{-1}$ for microbial metabolism and membrane scouring, respectively. Krampe and Krauth (2003) worked a volumetric AFR of 7.4 $m^3\,m^{-3}\,h^{-1}$. Henkel et al. (2009a) evaluated the alpha factor in two MBR systems at volumetric AFRs from 5.8 to 26.1 $m^3\,m^{-3}\,h^{-1}$ and from 1.1 to 6.3 $m^3\,m^{-3}\,h^{-1}$, respectively. The volumetric AFR at which the alpha factors were evaluated differed considerable between authors and it might probably indicate some of the differences on the reported alpha factor values at similar MLSS concentrations. However, Germain et al. (2007) evaluated the effects of the volumetric AFRs from 0.7 to 6 $m^3\,m^{-3}\,h^{-1}$ on the alpha factor at an MLSS range from approximately 7 to 30 $g\ L^{-1}$ and concluded that there is not any particular relationship between the volumetric AFR and the alpha factor range. The specific AFR (i.e., standard AFR) ranges from 1 to 10 $m^3\,m^{-3}\,h^{-1}$ when conducting oxygen transfer tests (Henkel 2010).

All previous work reporting alpha factors in CAS and MBR systems were carried out using air

as the main source of oxygen. To our knowledge, Rodriguez et al. (2011) was the only work reporting alpha factor in the context of MBR systems aerated with pure oxygen rather than air. The reactor was fed with wastewater from a primary settler from a local WWTP, and it was operated at an SRT of approximately 40 days. Alpha factors of 0.462 and 0.029 were reported at MLSS concentrations of 3.42 to 12.6 g L^{-1}, respectively. That is, similar findings were reported as when working with compressed air.

2.4.5 Limitations of oxygen transfer in the context of high-loaded MBR

As described in previous sections, several authors have evaluated the effects of the MLSS concentration on the alpha factor. These studies were conducted at MLSS concentrations from approximately 3 to 40 g L^{-1}. However, significant differences were reported on the alpha factors at similar MLSS concentration ranges that could be probably assigned to the different evaluated operational conditions. Most of the research was conducted at high MLSS concentrations, but at extremely high (even infinite) SRTs which could underestimate the effect of the MLSS concentration on the oxygen transfer, and thereby alpha factor. Several studies have indicated a beneficial effect of the SRT on the alpha factor; however, these evaluations were carried out at low MLSS (CAS relevant) concentrations from 3 to 6 g L^{-1}. The concept of a HL-MBR for maximizing the treatment capacity while minimizing the system footprint requires to operate the system at the highest possible oxygen uptake rates; that is, the highest biologically active MLSS concentration is obtained by operating the system at high organic loads and relatively low SRTs (standard SRTs of approximately 10 days). Therefore, the effects of the high MLSS concentration on the alpha factor at low SRTs when using conventional bubble diffusers (i.e., in the context of the HL-MBR) need to be better understood. However, the oxygen transfer is severely inhibited by the presence of MLSS, particularly at high MLSS matrices when using conventional aeration systems. In this context, there is a need for more efficient oxygen supply systems both to reduce the aeration costs, as well as to uncap such design limitations for HL-MBR. The same constrains previously indicated apply to any other aerobic biological wastewater treatment systems designed to be operated at high sludge (MLSS) concentrations such as aerobic digesters.

2.5 Efforts on improving oxygen transfer

Innovative and non-conventional aeration technologies have been recently proposed to enhance the oxygen transfer performance in wastewater treatment process. Aeration processes such as the deep-shaft (U-Tube contactor or vertical shaft), high purity oxygen (HPO) aeration system, and pressurized oxygenation systems (supersaturated oxygen aeration systems) have been developed to improve the OTR and OTE (Xu et al. 2016). Most of these systems rely on increasing the amount of DO in the liquid phase by increasing the partial pressure of oxygen in the gas phase (Barber et al. 2015; Gray 2004).

2.5.1 Deep-shaft reactor

Figure 2.2 shows an example of a deep-shaft reactor. The deep-shaft reactor is characterized by the high depth and relatively the narrow width. The deep-shaft reactors utilize hydrostatic pressure built up in such reactors since they can reach a deepness of between 30 to 220 meters (Metcalf and Eddy 2003); hydrostatic pressures of 5 to 15 bars were reported at the bottom of the reactors, providing much higher partial pressures of oxygen compared to CAS systems (Ellis et al. 1992; Gray 2004). OTEs of approximately 90% were reported in mixed liquor matrices for these systems (Wang et al. 2009). The high OTE is attributed to the much higher contact time (i.e., residence time) of 5 min between air bubbles and the mixed liquor compared to CAS process in a relatively shallow surface basin reporting 15 s of the contact time (Gray 2004). The OTR of the deep-shaft has been reported to be 0.9-2.7 kgO_2 kWh^{-1} (Wang et al. 2009). In general, the system is operated at an MLSS concentration of 5 g L^{-1} at hydraulic residence times (HRT) of 1.5 to 1.75 h, and at an SRT of 4 to 5 d (Gray 2004). The relatively short HRT is vulnerable to hydraulic peak flows (Wang et al. 2009). The deep-shaft system can be operated both in the mesophilic temperature range (25 to 38 ℃) and in the thermophilic range (46 to 60 ℃). It was reported that an OTE is not affected by temperature (Wang et al. 2009).

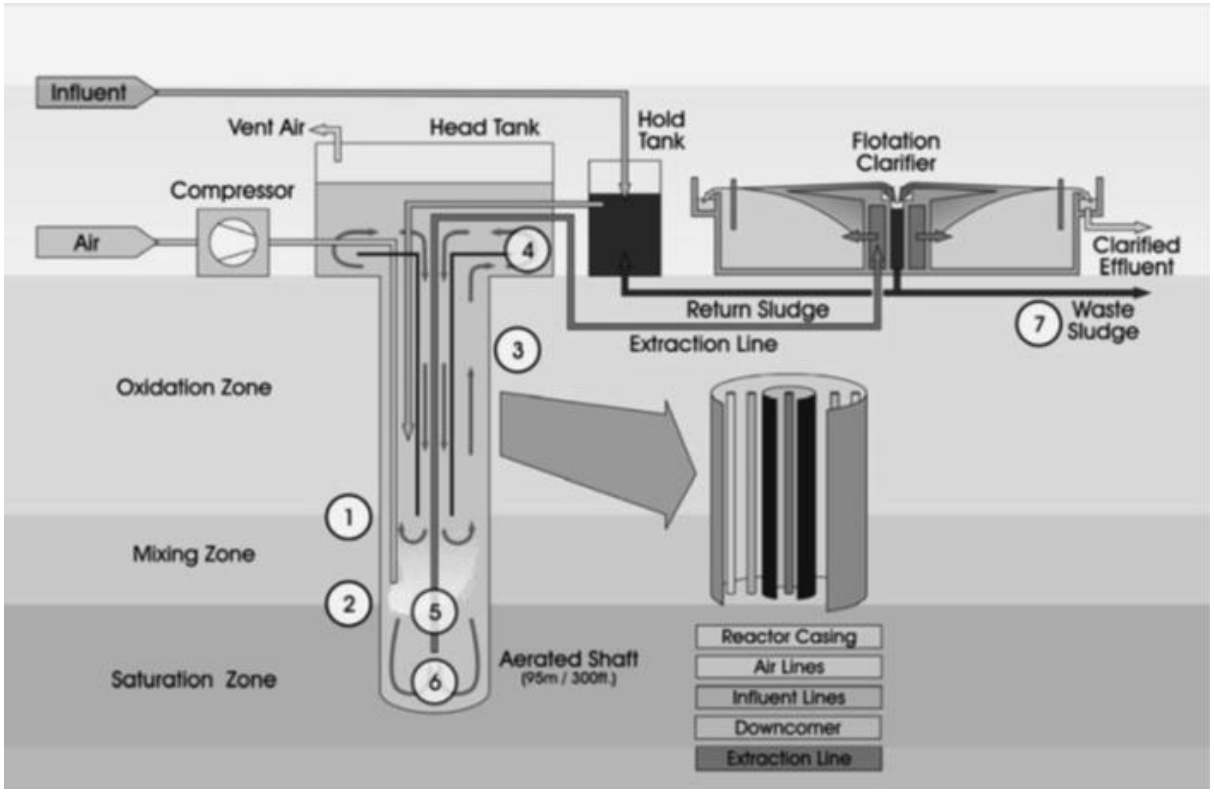

Figure 2.2 The VERTREATTM process (adapted from Wang et al. 2009)

Compared with the CAS process, this technology requires small land occupation since it has no use for primary clarifier. Specifically, a considerable fraction of the total volume of the aeration tank is placed underground, so it uses about 50% less space than CAS systems (Gray 2004). In addition, Wang et al. (2009) reported that the deep-shaft system as a high-rate activated sludge process, has a capacity of operating at food to microorganism ratios (F/M) of between 0.5 and 2.0 $kgBOD_5^*$ $kgMLVSS^{-1}$ d^{-1} (*biochemical oxygen demand (BOD). The high organic loadings

can be managed since the system can maintain MLVSS concentrations ranging from 5 to 10 g L^{-1}, and thereby a much lower reactor volume than CAS processes. Moreover, the benefits of the technology include low operation cost (approximately 0.85 kWh $kgBOD^{-1}$ removed, which includes costs for both aeration and recirculation of sludge) and low costs for sludge disposal (Gray 2004).

The operation of deep-shaft biological technology has already been widely implemented for municipal wastewater treatment, pretreatment of landfill leachate, food processing waste, brewery waste, pulp and paper mill effluent (Niu et al. 2013). It was reported that the performance of pilot-scale and full-scale of deep-shaft plants on the organic matter removal is more than 85%, suggesting that the biomass activity was not affected by moderate pressure (Gray 2004). However, nitrification is usually inhibited due to limited aeration periods (Ellis et al. 1992). As drawbacks, such systems need to be constructed approximately 100 meters underground, and maintenance activities can be challenging (i.e., adding to the capital and operational costs). Moreover, they have not been tested on MLSS concentrations higher than 10 g L^{-1} (Gray 2004; Wang et al. 2009).

2.5.2 High purity oxygen aeration system

Using pure oxygen in place of air has been suggested in biological wastewater treatment because of its higher oxygen dissolution capacity (Wang et al. 2009). The utilization of pure oxygen was proposed by Pirnie in 1948 and became commercially available in the 1970s by developing both covered and opened aeration tanks (Mueller et al. 2002). Air is mainly comprised of 78% of nitrogen and 21% of oxygen, while pure oxygen containing larger than 80% of oxygen has a much higher partial pressure of oxygen, increasing the saturated DO concentration by factor of five; that is, the higher DO saturation concentrations augment the gas-liquid interface, which ultimately improves mass transfer of gaseous oxygen molecules to the liquid phase indicating the enhancement of OTEs and OTRs (Barber et al. 2015; Gray 2004). Pure oxygen gas comprised of micron-size bubbles rather than millimeter sizes normally produced in diffused aeration systems (Wang et al. 2009). Thus, HPO aeration provides higher gas phase oxygen concentration than air, which contributes to promoting the oxygen mass transfer driving force for aeration (Rodriguez et al. 2012) and thereby a decrease in energy consumption required for dissolving oxygen (Mueller et al. 2002). The production of HPO is accomplished by either on-site pressure swing adsorption (PSA) generators for smaller and more common plant scales (less than 150,000 m^3 d^{-1}) or cryogenic air-separation process for large applications. Also, the HPO is purchased as liquid oxygen manufactured off-site and transported and deposited at the treatment plant; the type of wastewater and treatment plant scale would determine the oxygen source (Metcalf and Eddy 2014). In addition, biological processes using pure oxygen are capable of operating at smaller aeration basins with high MLSS concentrations thanks to its higher OTE (Mueller et al. 2002). The following HPO systems have been evaluated in the context of biological wastewater treatment: (i) the Praxair system I-SO system; (ii) the UNOX system; and (iii) the Oxygen-Activated Sludge Process (OASES® from

Veolia). HPO systems exhibit a much higher partial pressure of oxygen, increasing the saturation DO concentration in the liquid phase by a factor of approximately five resulting in higher OTRs (Barber et al. 2015; Gray 2004).

2.5.2.1 I-SO™ system

The I-SO™ system developed by Praxair, Inc., consists of a transportable in-situ floating mechanical aeration system fed with HPO as shown in Figure 2.3. The mixed liquor is introduced into a draft tube through an upper conical baffle where it gets in contact with the HPO. The HPO is supplied under the hood to keep the required DO level. The level of the wastewater in the hood is automatically adjusted according to the pressure in the hood. That is, the lower the pressure of the HPO, the higher the wastewater level in the hood; thus wastewater with less HPO is introduced into the system. On the other hand, the higher the HPO pressure, the higher the wastewater level in the hood; therefore, larger amount of HPO are introduced. The amount of oxygen to be injected is almost equal to the amount of oxygen to be used in the aerobic basin. Vertical vessels submerged in the mixed liquor within the baffle create vortices, resulting in oxygen in the headspace above the water level. Afterwards, a gas-liquid mixture is produced which travels downward the draft tube by means of a rotating impeller. Constant mixing for mixed liquor is guaranteed by an impeller attached in the middle of the vessel. The gas-liquid mixture is continually discharged into the aerobic basin through another set of baffles located at the bottom of the impeller. The system is designed in such a way that the bubbles released at the discharge point are captured back into the systems before it could escape to the atmosphere. The amount of oxygen injected is almost equal to the amount of oxygen consumed; therefore, the I-SO™ system achieves high OTEs of up to approximately 90% (Mueller et al. 2002). The disadvantages of this technology may include the high capital cost and a relatively high maintenance cost associated with such type of floating surface aeration systems compared to conventional aeration system such as bubble diffusers.

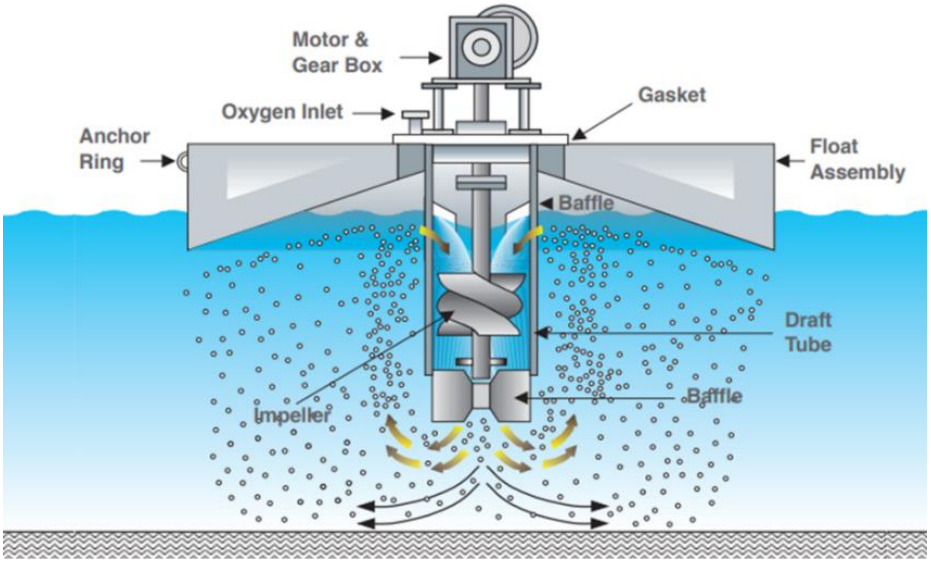

Figure 2.3 Praxair – In-Situ Oxygenation (I-SO™) System (adapted from https://www.praxair.com, accessed on September 2018)

The total power required to operate the system in wastewater treatment is low because of its high OTE of 82%; in addition, the system shows an SAE of 5.7 kg kWh^{-1} (https://www.praxair.com, accessed on September 2018) which is much higher than the SAEs observed in fine bubble diffusers in the range of 3.6 to 4.8 kgO_2 kWh^{-1} and coarse bubble diffusers in the range of 0.6 to 1.5 kgO_2 kWh^{-1} (Henze et al. 2008). In this regard, Fabiyi (2008) reported that the I-SO technology can be used to lower the power cost of MBRs by comparing the operating costs between the I-SO technology using HPO and a conventional aeration device. The I-SO system exhibited a high OTR (corresponding to the higher alpha factor of 1), high SAEs and much lower power costs despite its high costs for HPO generation; all things considered, the total operational costs were about 20% lower than that of the conventional aeration system such as bubble diffusers. So far, I-SO^{TM} technology has been mainly applied to industrial sectors, and is applicable to aeration tanks where those are designed as fully open tanks or fully closed aeration tanks (Mueller et al. 2002). This technology is easy to install and operate as a movable/portable aeration system, and is favorable to the elimination of severe foaming problems where covered aeration tanks are encountered (Mueller et al. 2002).

2.5.2.2 UNOX system

The UNOX activated sludge process was initiated by Union Carbide Corporation with the aim of improving upon the CAS process by using enriched pure oxygen (Wilcox and McWhirter 1971). As exhibited in Figure 2.4, the UNOX activated sludge process consists of a series of covered biological aeration tanks separated by baffles (Wilcox and McWhirter 1971). Each aerobic basin is an independent biological tank due to the baffle, but a portion of the baffle at the top and bottom of each reactor is slightly opened to have an integrated reactor (Wilcox and McWhirter 1971). The number of aerobic basins used for municipal wastewater treatment depends on the characteristics of the wastewater and the level of treatment required, but the compartment number of 4 to 6 would be ideal (Gray 2004). HPO which is either generated on-site or delivered to the plant in the form of liquid oxygen, is introduced into the headspace of the first stage of the biological aerobic basin. In each aerobic basin, there is headspace above mixed liquor where the gases produced by the microbial metabolism accumulate; surface aerators with an impeller situated at its bottom for a mixing purpose are provided to reintroduce the remaining pure oxygen from the headspace into the mixed liquor (Mueller et al. 2002). The excess of the HPO not dissolved in the first tank moves from one reactor into the next one until being finally released to the atmosphere from the last aerobic reactor (Mueller et al. 2002).

UNOX system has been applied to industrial wastewater sectors mainly for treating pulp and paper wastewater (Ueda 2004; Wilcox and McWhirter 1971). The use of pure oxygen allows the operation of UNOX system at an MLSS concentration ranging from 6 to 10 g L^{-1} at a short HRT ranging from 1 to 2 h, indicating the system has a capacity of treating high loads of wastewater in less time with the same land requirements compared to CAS processes; in addition, a DO concentration ranging from 8 to 10 mg O_2 L^{-1} is maintained in the system (Wilcox and McWhirter 1971). For treating municipal wastewater, the MLSS and DO

concentration are maintained at 5 to 6 g L^{-1} and 4 to 8 mg L^{-1}, respectively (Gray 2004). Since UNOX system produces lower sludge yield compared to CAS system, the sludge produced was characterized by highly flocculated and compacted with excellent settling and dewatering properties (Wilcox and McWhirter 1971). As HPO activated sludge process is operated with covered aeration tanks at short HRTs of 1 to 3 h, it can reduce volatile organic compounds (Metcalf and Eddy 2003) and odours (Gray 2004). The system showed a good BOD removal in excess of 90%, and the mean OTE of this technology represented 90-95% (Mueller et al. 2002; Wilcox and McWhirter 1971). The main disadvantage of this technology may include: (i) the high construction cost due to the needs of covering the aerobic basin; (ii) the high maintenance requirement for surface aerators; (iii) no information on the performance of this technology operated at MLSS concentrations higher than the CAS standard range (Ball and Humenick 1972; Bernat et al. 2017; Singh 2017).

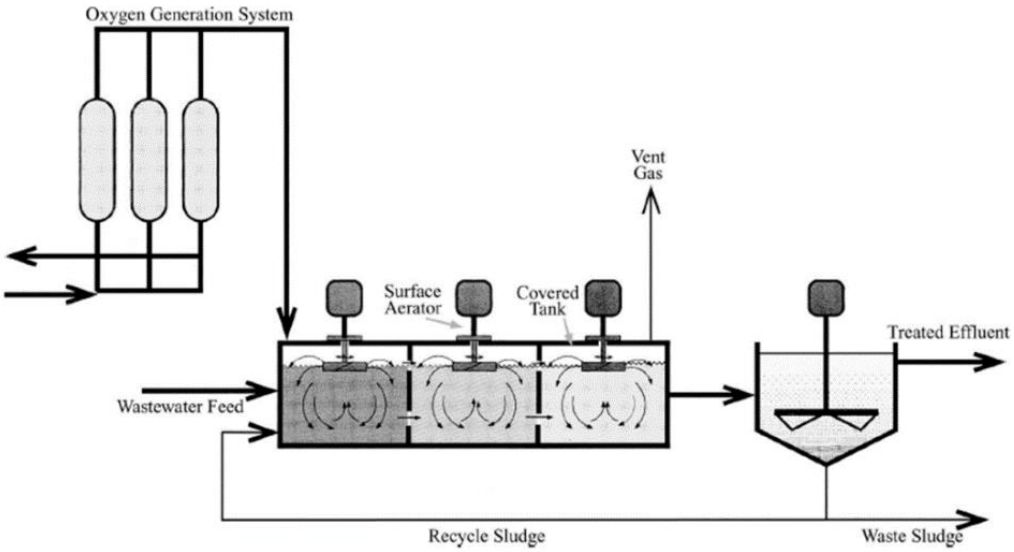

Figure 2.4 UNOX HPO system (adapted from Mueller et al. 2002)

2.5.2.3 OASES® technology

The OASES® technology developed by Air Products and Chemicals Inc., USA, is an automated wastewater treatment system employing pure oxygen for secondary wastewater treatment. The OASES® technology is very similar to the UNOX (Singh 2017). The system consists of parallel covered aerobic basins and each tank is separated as an individual stage. Influent wastewater, return activated sludge, and HPO are simultaneously introduced to the first stage of the aerobic tank, and the HPO together with mixed liquor flow concurrently through following stages (http://www.veoliawatertech.com, accessed on November 2018). In each aerobic basin, surface aerators and turbines situated at the bottom of the reactor provide complete mixing. The biological consumption through the HPO lowers the pressure in the headspace allowing the pressure control valves to introduce more HPO into the system resulting in extremely high OTEs (Singh 2017). OASES® system can be operated at high MLSS and DO concentrations, and thereby requiring short HRTs compared to CAS systems. The process has a capacity of dealing with high organic loads (that is, high F/M ratios), and produces sludge with good

settling characteristics. Since the process is characterized by compact facilities, small footprints are required (http://www.veoliawatertech.com, accessed on November 2018). To our knowledge, scientific research using this technology on wastewater treatment has not been conducted to date, accounting for no data on the alpha factor and OTE of this system. Disadvantages of this technology may include the high capital cost, together with the high maintenance cost of the surface aerators. Notwithstanding the benefits offered by HPO systems, the major impediments for the expansion of these technologies in the wastewater treatment field have been the high capital costs and the cost related to the generation of the HPO source (Ball and Humenick 1972).

2.5.3 Pressurized oxygenation systems

Supersaturated (concentrated) oxygen aeration systems have also been developed as an alternative for DO delivery into biological wastewater treatment systems. These systems take the advantage of both working with HPO, and at high-pressure conditions, and thereby providing higher OTRs (Berktay and Ellis 1997; Jin et al. 2010). Among the supersaturated oxygen aeration systems, the two most relevant technologies include the Speece cone technology and the supersaturated dissolved oxygen (SDOX) system as indicated in Figure 2.5.

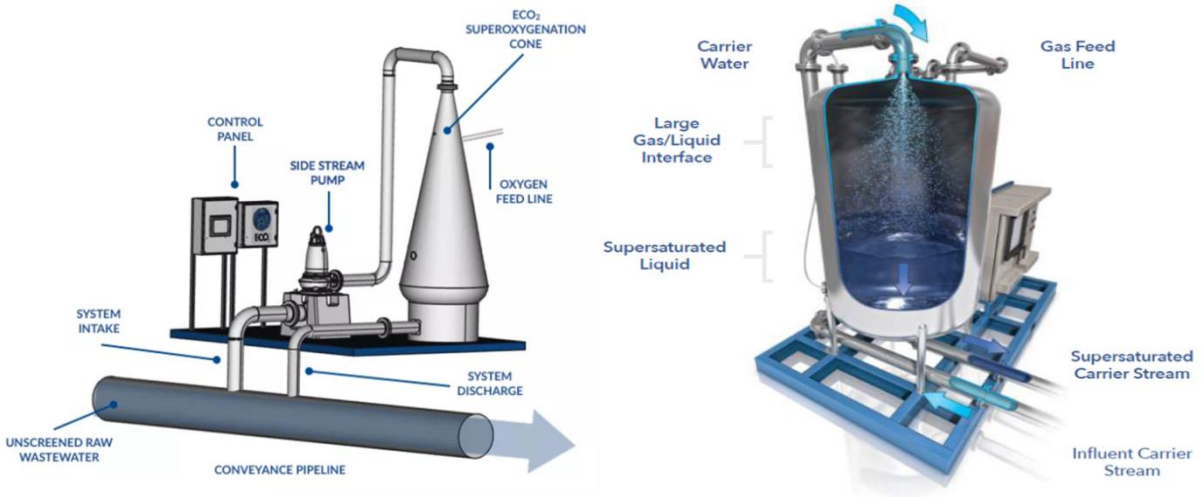

Figure 2.5 Speece cone (adapted from http://www.eco2tech.com, accessed on September 2018, the left) and SDOX (adapted from https://www.blueingreen.com, accessed on September 2018, the right)

2.5.3.1 Speece Cone technology

The Speece cone technology was developed by Dr. Richard Speece in 1971 (McGinnis and Little 1998). The technology consists of a down flow conical bubble contact chamber connected to an HPO source. A stream of the solution to be oxygenated is introduced into the top of the Speece cone chamber at a given flow rate and at high-pressure; an HPO source is simultaneously introduced at the top of the Speece cone. The oxygen-rich supersaturated solution is then returned back into the receiving basin through submerged diffusers. The downward water velocity in the conical contact chamber should be high enough (higher than

the gas buoyance buoyancy of the gas) to push the oxygen bubbles down in the cone, but not too high to avoid the oxygen bubbles to escape the system undissolved (McGinnis and Little 1998).

The Speece cone technology has been mostly applied for lake and river restoration (Ashley et al. 2008). The Speece cone was also applied to industrial wastewater treatment (paper mills, food and beverage, power, caustic management, landfill leachate). The technology represented good organic matter removal efficiency and it was favorable for sulfide oxidation as well as wastewater odour control (http://www.eco2tech.com, accessed on September 2018). Recently, Barreto et al. (2017) have evaluated the Speece cone as an alternative technology for supplying DO in biological wastewater treatment applications. Particularly, the authors evaluated the performance of an MBR provided with a Speece cone system fed municipal wastewater on the organic matter removal and membrane filtration performance. The authors reported that high-pressure affected neither the organic matter removal nor membrane filtration. The OTE of Speece cone has been reported to be above 95% (Ashley et al. 2014; Barreto et al. 2018). Moreover, Barreto et al. (2018) evaluated the oxygen transfer performance of the Speece cone at several operational conditions in clean water and in sludge at an MLSS concentration of 5 g L^{-1}; the authors reported alpha factors at such CAS relevant MLSS concentration ranging from 0.6 to 1.0. The Speece cone system appears as a promising technology for supplying DO at high MLSS concentrations in biological wastewater treatment systems. However, the oxygen transfer performance of such technology needs to be further evaluated at a high MLSS concentration range.

2.5.3.2 SDOX technology

The SDOX system is presented as a novel alternative for supplying DO into biological wastewater treatment systems. The technology was developed by BlueInGreen, LLC in USA (Jones 2010), and it consists of a pressurized chamber maintained at a much higher pressure than the Speece cone (> 8 bars) connected to an HPO source. A stream of the mixed liquor to be oxygenated is recirculated through the pressurized chamber where it gets in contact with the HPO at the high-pressure conditions in the chamber (CDM Smith 2012). A spray nozzle is placed at the top of the pressurized chamber where the influent stream reaches the system. The spray nozzle atomizes the influent stream into tiny droplets maximizing the gas-liquid mass transfer surface area. The oxygen-supersaturated stream is returned back to the receiving basin through specially designed distribution pipes. The high-pressure conditions exerted in the pressurized chamber allows reaching DO concentrations of up to 350 mg L^{-1} in clean water (Jones 2010), higher than other technologies. This leads to OTEs higher than 95% (https://www.blueingreen.com accessed on September 2018). Unlike other dissolved oxygen delivery techniques such as conventional bubble diffusers, the introduced oxygen is completely pre-dissolved inside of the pressurized vessel when employing the SDOX system; that is, the oxygen transfer process occurs in the pressurized vessel built in a side-stream configuration (Jones 2010).

However, as shortcomings, the SDOX technology has been mostly evaluated in the context of lake and river restoration. Thus, no information has been reported in the literature regarding the performance of the SDOX system in activated sludge mixed liquors, despite the potential benefits that this technology can offer in terms of reaching such high-supersaturated DO concentrations. Figure 2.6 shows a lab-scale of SDOX unit used for the current dissertation research. The SDOX unit mainly consists of a pressurized chamber equipped with pressure gauges and a peristaltic pump.

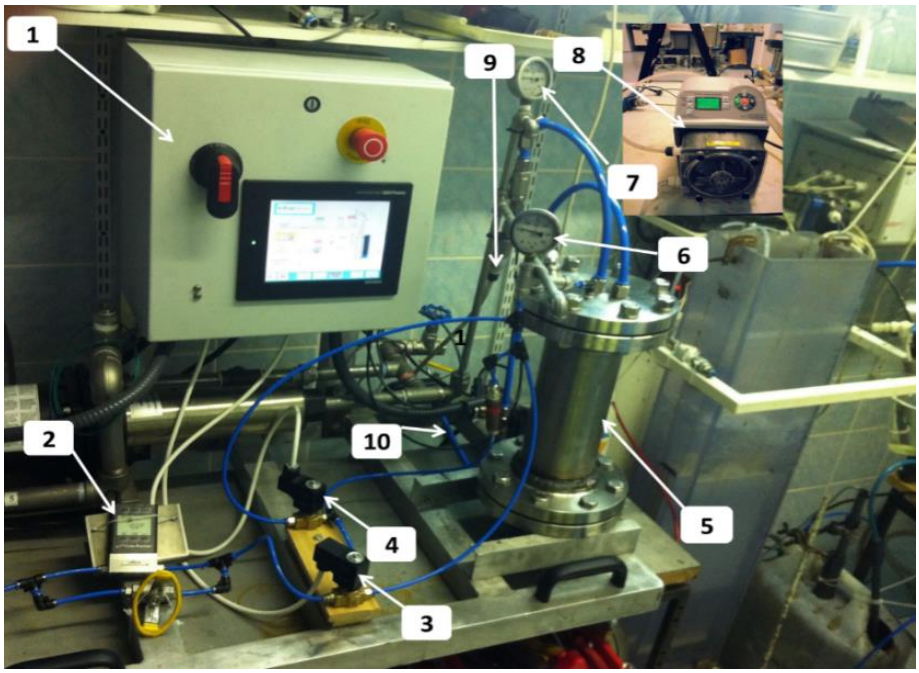

Figure 2.6 The SDOX unit's components (Photo by Sang Yeob Kim): 1. SDOX system's program logic control (PLC); 2. Mass flow controller for the measurement of oxygen flow into the pressurized chamber; 3. Oxygen inlet control valve; 4. Gas pressure valve with sensor; 5. Pressurized saturation chamber; 6. Pressure gauge for the pressurized saturation chamber; 7. Pressure gauge for pump; 8. Peristaltic pump (pump influent process water into the SDOX pressurized chamber; 9. Process water inlet; 10.Supersaturated process water outlet from the SDOX unit to the bioreactor

Supersaturated oxygen aeration systems show several advantages among all the previously presented oxygenation technologies. They show a lower operational cost compared to diffused aeration systems considering both their simple operation and maintenance needs, as well as their excellent reported OTEs of above 95% (Ashley et al. 2014). Moreover, unlike the other oxygen supply technologies, the supersaturated oxygen aeration systems are not affected by the submergence of the system (Jones 2010). That is, the oxygen transfer performance of these systems is completely independent of the water depth at which the system is located (Jones 2010). Besides, the systems are fully movable/portable ideally for coupling this oxygenation technology to movable/portable wastewater treatment systems. In addition, they are very simple and easy to up-scale, so which presents a big advantage for retrofitting wastewater treatment

systems. On the contrary, the primary disadvantage of this technology may represent the high capital costs compared to other technologies (Jones and Stokes 2004). Moreover, little is known on the impact of the mixed liquor matrices on the oxygen transfer performances of such systems in the context of applying this technology into wastewater treatment field.

Conventional diffused aeration systems are very inefficient when supplying DO into biological wastewater treatment systems; particularly, this situation is exacerbated when the systems are operated at higher than usual MLSS concentrations (MBR and HL-MBR MLSS range). Therefore, conventional diffused aeration introduces technical and economical limitations on both the operation of such systems, as well as on uncapping the limitation for designing biological aerobic wastewater treatment systems able to operate at much higher than usual MLSS concentration (i.e., above 15-20 g L^{-1}). Several innovative oxygenation technologies were previously introduced. Among such technologies, the concentrated supersaturated oxygen aeration technologies show substantial potential advantages for being proposed as a feasible technology for supplying DO at such high MLSS concentrations; such advantages include their high reported OTEs, easiness to be installed, and relatively low maintenance and operational needs. The concept of coupling supersaturated oxygenation aeration systems with biological wastewater treatment systems was already presented by Barreto et al. (2017, 2018) for the Speece cone system; however, these tests were carried out at a maximum MLSS concentration of approximately 28 g L^{-1} without enough knowledge of the effects of the system at higher MLSS concentrations. Regarding the SDOX technology, very limited information was reported in the literature. Therefore, there is a need to evaluate the performance of the SDOX on the oxygen transfer performance and biological performance at higher MLSS concentrations (> 20 g L^{-1}) in biological wastewater treatment systems.

2.6 Possible engineering application of SDOX in wastewater treatment

As previously indicated, conventional fine bubble diffusers are highly affected by the presence of MLSS, as exhibited by very low alpha factors at MLSS concentrations higher than 20 g L^{-1} (Cornel et al. 2003; Germain et al. 2007; Henkel et al. 2009b; Kim et al. 2019; Krampe and Krauth 2003; Muller et al. 1995; Xu et al. 2017). To cope with this, considering one of the hypothesis of this PhD study that the oxygen transfer capabilities of the supersaturated aeration technologies will be better than that of conventional bubble aeration systems, supersaturated aeration technologies (e.g., SDOX and Speece cone) could be applied to biological wastewater systems operated at high MLSS.

2.6.1 Membrane bioreactors

Among the commercially available activated sludge wastewater treatment technologies, MBRs are arguably the most suitable technology to be operated at high MLSS concentrations. Table 2.3 shows typical design parameters and performance data for MBRs (Metcalf and Eddy 2003).

Table 2.3 Typical operational and performance data for a membrane bioreactor (adapted from Metcalf and Eddy 2003)

Parameter	Unit	Range
Operating data		
COD** loading	kg m^{-3} d^{-1}	1.2 – 3.2
MLSS	mg L^{-1}	5,000 – 20,000
MLVSS	mg L^{-1}	4,000 – 16,000
F/M	g CODg $MLVSS^{-1}d^{-1}$	0.1 – 0.4
SRT	d	5 – 20
HRT	h	4 – 6
Flux	L m^{-2} d^{-1}	25 – 45.8
Applied vaccum	kPa	4 – 35
DO		0.5 – 1.0
Effluent concentration		
BOD	mg L^{-1}	<5
COD	mg L^{-1}	<30
Ammonia	mg L^{-1}	< 1
Total nitrogen	mg L^{-1}	< 10
Turbidity	NTU	< 1

COD**: Chemical oxygen demand

MBRs are usually operated at MLSS concentrations ranging from 8 to 18 g L^{-1} (Drews 2010), much higher compared to CAS system which is usually operated at approximately 3 to 5 g L^{-1}. The solid-liquid separation in MBRs is achieved by low pressure membrane filtration rather than by gravity settling. As such, the operation of MBRs is not affected by the settling characteristics of the sludge. Additional advantages of MBRs include the production of a clarified and mostly disinfected treated wastewater, the generation of less sludge compared to CAS systems and eventually mostly digested sludge when operating at longer SRTs, the easiness to operate at stable control conditions favouring setting ideal conditions for nutrient removal, the possibilities for handling shock loads, and the compliance with the strictest effluent discharge standards, among others (Fortunato et al. 2018; Henze et al. 2008; Khouni et al. 2020; Kim et al. 2019). Operating an MBR system at high MLSS concentrations, (i.e., MLSS concentrations above 15 g L^{-1}) can improve the treatment capabilities of MBR systems by handling even higher wastewater loading rates compared to conventional MBR systems, increasing the oxygen uptake rates in the systems leading to much higher biological degradation rates, reducing even further the system footprint requirements (lowering construction costs), and reducing the sludge generation and their respective handling and treatment costs (Barreto et al. 2017; Livingston 2010). This concept of an MBR operated at high MLSS concentrations (from approximately 15 to 40 g L^{-1}) was introduced by Kim et al. (2019) and presented as the HL-MBR. The possibility of operating an MBR system at such high MLSS concentrations

provides the opportunity to design more compact and containerized mobile wastewater treatment systems that can be suitable for on-site and/or decentralized municipal and/or industrial applications.

2.6.2 Aerobic digestion

Another activated sludge wastewater treatment technology is aerobic digestion to be operated at high MLSS concentrations. As a result of wastewater treatment, a big mass of excess sludge is constantly being produced. To stabilize the excess wasted sludge, aerobic digestion applied in medium-sized and small-sized WWTPs is employed because of its benefits in comparison with anaerobic digestion: simple operation, low capital (equipment) cost, safety issues, odorless end products, among others (WEF 2008). Aerobic digestion is similar to the activated sludge process. As the available substrate (food) is depleted, microorganisms begin to consume their own protoplasm to attain energy for cell maintenance reactions. When energy is obtained from cell tissue microorganisms are situated in the endogenous phase (Metcalf and Eddy 2003). That is, aerobic digestion serves to stabilize and minimize the excess sludge exposing it to endogenous decay by employing long-term aeration (WEF 2008). Cell tissue is oxidized aerobically to carbon dioxide, water, and ammonia. Actually, only about 75 to 80 percent of the cell tissue can be oxidized; the remained fraction is composed of inert components and organic compounds that are not biodegradable. The ammonia is subsequently oxidized to nitrate as digestion proceeds. Nonbiodegradable volatile suspended solids will remain as a final product from aerobic digestion (Metcalf and Eddy 2003). Aerobic digesters are operated at MLSS concentration of up to 30 g L^{-1} (Andreoli et al. 2007). Compared to anaerobic digestion, a well-known drawback of operating aerobic digester is higher operational cost due to extensive aeration conducted by diffused aeration that exhibits very low OTEs of approximately 1 to 5% per meter of reactor submergence. In this context, the supersaturated aeration technologies may be a candidate for reducing operating costs.

2.7 Factors affecting membrane fouling in membrane bioreactors

Membrane fouling in MBR systems is a phenomenon in which various types of materials (e.g., bio solids, colloidal species, scalants, or macromolecular species) present in the bulk mixed liquor reduce permeability [= flux divided by pressure expressed in L m^{-2} h^{-1} bar^{-1})] of the membrane by adsorption or deposition on the membrane surface, or by adsorption on the pore surface (Li et al. 2008; Stephenson et al. 2000). Typically, transmembrane pressure (TMP) increased to keep the flux at a constant level as an MBR operation progressed. Thus, membrane fouling reduces productivity of membranes as a result of TMP rise, which leads to an increase in maintenance (e.g., chemical cleaning) and operational costs, and ultimately a replacement of membranes. A description of membrane fouling is difficult due to the heterogeneity of the activated sludge that perform biodegradation of wastewater and follow the brownian motion (Li et al. 2008). Factors affecting the overall membrane fouling behavior in MBRs can be summarized as follows (Li et al. 2008).

1. Biomass characteristics
    - MLSS (activated sludge) concentrations can affect the fouling rate (Dvorak et al. 2011; Rosenberger et al. 2005; Yigit et al. 2008)
    - Characteristics of the mixed liquor (e.g. EPS - in particular, the soluble portion of the EPS (which is equal to SMP) influences the loss in permeability
    - Bulk characteristics such as viscosity, PSD, and hydrophobicity (Germain and Stephenson (2005))
2. Membrane and module characteristics
    - Pore size and shape
    - Surface characteristics such as polarity, hydrophobicity, surface topography, and porosity of the membrane as well as
    - Module geometry and dimensions
3. Operating conditions
    - Hydraulics, the most significant factor being the flux
    - F/M ratio (Dvorak et al. 2011)
    - Hydrodynamics: shear force, the cross-flow velocity or aeration rate (submerged membrane modules), flow rate, pulse rate, relaxation time, and so forth
    - Cleaning: for example, back-flush, physical cleaning, chemical cleaning, cleaning intervals

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Chapter 3

Limitations imposed by conventional fine bubble diffusers on the design of a high-loaded membrane bioreactor (HL-MBR)

This chapter is based on:

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Abstract

The operation of membrane bioreactors (MBR)s at higher than usual mixed liquor suspended solids (MLSS) concentrations may enhance the loading rate treatment capacity while minimizing even further the system's footprint. This requires operating the MBR at the highest possible MLSS concentration and biomass activity (e.g. at high loading rates and low solid retention times (SRTs)). Both a negative effect of the MLSS concentrations, and a positive effect of the SRT on the oxygen transfer have been reported when using conventional fine bubble diffusers. However, most of the evaluations have been carried out either at extremely high SRTs, or at low MLSS concentrations eventually underestimating the effects of the MLSS concentration on the oxygen transfer. This research evaluated the current limitations imposed by fine bubble diffusers in the context of the high-loaded MBR (HL-MBR) (*i.e.*, high MLSS and short SRT - the latter emulated by concentrating municipal sludge from a wastewater treatment plant (WWTP) operated at a short SRT of approximately five days). The high MLSS concentrations and the short SRT of the original municipal sludge induced a large fraction of mixed liquor volatile suspended solids (MLVSS) in the sludge, promoting a large amount of sludge flocs that eventually accumulated on the surface of the bubbles and reduced the free water content of the suspension. Moreover, the short SRTs at which the original municipal sludge was obtained eventually appear to have promoted the accumulation of surfactants in the sludge mixture. This combination exhibited a detrimental effect on the oxygen transfer. Fine bubble diffusers limit the maximum MLSS concentration for a HL-MBR at 30 g L^{-1}; beyond that point is either not technically or not economically feasible to operate; an optimum MLSS concentration of 20 g L^{-1} is suggested to maximize the treatment capacity while minimizing the system's footprint.

3.1 Introduction

The MBR has become a popular wastewater treatment technology. Alternatively to the gravity settlers installed in conventional activated sludge (CAS) systems for solid-liquid separation purposes, MBRs are provided with low pressure filtration membranes achieving higher solid-liquid separation efficiencies. As such, specific advantages of MBRs include: (i) a consistent and reliable high-quality effluent that can comply with the most strengthened discharge standards; (ii) low footprint; (iii) low production of highly digested sludge; (iv) stable control conditions for effective nutrient removal; and (v) robustness to handle shock loads; among others (Henze et al. 2008; Judd and Judd 2011; Mannina and Cosensza 2013; Mohammed et al. 2008; Mutamim et al. 2013; Pollice et al. 2008).

Moreover, to operate at MLSS concentrations even beyond the typical MBR MLSS range (e.g. >15 g L^{-1}) can lead to a HL-MBR which has additional advantages that include: (i) increased capacity to treat higher organic loading rates, (ii) increased oxygen uptake rates (OUR)s linked to higher chemical oxygen demand (COD) conversion rates, (iii) minimized footprint, reduced volume and therefore lower construction costs, and (iv) reduced waste solids generation and handling costs (Barreto et al. 2017; Livingstone 2010).Furthermore, these advantages may encourage the design of compact and containerized movable/portable MBRs for the treatment of municipal and industrial wastewaters in remote areas without access to sewer systems offering additional opportunities for water reuse (Hai and Yamamoto 2011; Hai et al. 2014); moreover, on-site/decentralized alternatives can be designed for sanitation provision under emergency situations originated by either natural or man-made disasters (Barreto et al. 2017). A HL-MBR operated at MLSS concentrations of up to 40-50 g L^{-1} can be accomplished by operating the MBR system at a high influent loading rate and at a relatively low or typical SRT (of approximately 5 to 20 days), resulting in a high MLSS concentration composed of primarily active biomass. By following this operation strategy, the treatment capacity of a MBR system can be enhanced reducing even further the footprint at a given loading rate or, alternatively, for a given footprint increasing the loading rate treatment capacity.

Several authors have evaluated the effects of the MLSS concentration on the oxygen transfer (alpha factor) being the alpha factor the oxygen mass transfer ratio of process-water to clean-water. Most of the studies were conducted at standard (CAS relevant) MLSS concentrations ranging from approximately 3 to 5 g L^{-1}. Only a few studies were indeed conducted at a high range of MLSS concentrations, up to approximately 39 g L^{-1} (Muller et al. 1995). Overall, those studies indicate that the main limitation to operate a MBR at such high range of MLSS concentrations seems to be the rather poor to negligible oxygen transfer efficiencies observed when using conventional diffused aeration systems (such as fine and coarse bubble diffusers) (Cornel et al. 2003; Durán et al. 2016; Germain et al. 2007; Henkel et al. 2011; Krampe and Krauth 2003; Muller et al. 1995). However, those few evaluations conducted at such high range of MLSS concentrations were carried out at extremely high (even infinite) SRTs; that is, an

opposite condition to that required to achieve a HL-MBR. In accordance to Rosso et al. (2008), the oxygen transfer efficiency is proportional to the SRT: the longer the SRT, the higher the oxygen transfer efficiency and the alpha factor. However, the beneficial effect of the SRT on the alpha factor was determined and reported mostly at low MLSS (CAS relevant) concentrations from approximately 3 to 6 g L^{-1}; and there is no information reported on the effects of the SRT on the alpha factors at high (HL-MBR relevant) MLSS concentrations. This suggests that the previously reported alpha factors may not be realistic and directly applicable when designing a HL-MBR with a short (or typical) SRT, an increased loading rate, and a minimized system footprint.

In addition, another discrepancy on the assessment of the alpha factor at different MLSS concentrations lies on the wide range of volumetric air flowrates (VAFRs) applied in previous studies that range from 3.3 up to even 60 $m^3 m^{-3} h^{-1}$ (Cornel et al. 2003; Gunder 2000; Krampe and Krauth 2003; Muller et al. 1995), resulting in different alpha factor values reported at similar MLSS concentrations. However, Germain et al. (2007) evaluated the effects of the VAFRs from 0.7 to 6 $m^3 m^{-3} h^{-1}$ on the alpha factors at an MLSS range from approximately 7 to 30 g L^{-1} and could not find any particular relationship between the VAFR and the alpha factor. Last but not least, all the previous work was carried out using air as the main oxygen source. To our knowledge, only Rodriguez et al. (2011) assessed the alpha factors in the context of MBRs operated with pure oxygen rather than air. When pure oxygen was supplied, they observed no major differences on the alpha factors compared to the studies performed with air. Designing a HL-MBR for maximizing the treatment capacity while minimizing the system's footprint requires to operate the biological system at the highest possible biomass activity; which corresponds to the highest biologically active MLVSS concentration obtained by operating the system at high loading rates and relatively low SRTs. This implies that the limitations imposed by conventional bubble diffusers (measured in terms of the alpha factor) at that particular set of operational conditions (high MLSS and low SRT) needs to be better understood. The few studies conducted at high MLSS concentrations, (which were also conducted at high SRTs), could have underestimated the effect of the MLSS concentration on the alpha factor. Moreover, the beneficial effect of the SRT on the alpha factor was determined and reported mostly at low MLSS (CAS relevant) concentrations from approximately 3 to 6 g L^{-1}; and consequently there is no information reported on the effects of the SRT on the alpha factors at high (HL-MBR relevant) MLSS concentrations. Therefore, there is a gap in the literature to better understand the effects of the high MLSS concentration on the alpha factor on a mixed liquor produced at relatively standard (low) SRT conditions when using conventional diffusers (within the context of the operational design conditions of the HL-MBR).

The present chapter was designed to test the hypothesis that an MBR provided with a conventional bubble aeration system cannot be operated at an MLSS higher than 20 g L^{-1}. This research aimed at evaluating the current limitations imposed by conventional bubble diffusers in the context of the HL-MBR. Particularly, this research investigated the effect of high MLSS

concentration on the alpha factor on municipal sludge obtained from a WWTP operated at a short SRT of approximately five days (that is, on a mixed liquor composition similar to the mixed liquor expected on a HL-MBR system); the impact of the different MLSS concentrations on the alpha factor at different VAFRs, oxygen sources, and at different sludge stabilization levels were evaluated. In addition, this research provides insight and guidelines on the design and operation of HL-MBR systems considering the limitations imposed by conventional diffusers.

3.2 Materials and methods

3.2.1 Design of experiments

To evaluate the performance of conventional bubble diffusers in the context of the HL-MBR operated at high MLSS (high active biomass) concentrations, the oxygen transfer performance of a fine bubble diffuser (SANITAIRE® Silver Series 2, Xylem, USA) was evaluated in mixed liquor at MLSS concentrations of approximately 4, 10, 20, 30, and 40 g L^{-1}. Fresh mixed liquor was taken from the municipal WWTP of city of Zagreb (Zagreb, Croatia), and concentrated up to the desired MLSS concentration value. The evaluation was carried out supplying either air or pure oxygen at different flow rates. Moreover, the aeration performance at each of the assessed MLSS concentrations was evaluated at different degrees of sludge stabilization by repeating the oxygen transfer evaluations after aerating the mixed liquor (sludge) for 24, 48, and 72 hours. At each of the evaluated experimental conditions, the overall oxygen mass transfer rate coefficient (K_La) was determined and reported at standard conditions. The $K_La$was also evaluated in clean water and reported at standard conditions. The K_La values were adjusted considering the oxygen intrusion from the atmosphere. The ratio of the K_La in mixed liquor and in clean water was calculated and reported as the alpha factor.

3.2.2 Analytical methods

MLSS and MLVSS were analysed according to the standard methods for the examination of water and wastewater as described in APHA (1998). The temperature and DO both in clean water and mixed liquor were determined with a DO probe (WTW Oxi 3310, Germany). The pH was determined with a pH probe (SI Analytics GmbH, Germany). Both the DO and pH determinations were adjusted by the temperature.

3.2.3 Oxygen uptake rate

The OUR determinations were carried out with a biological oxygen meter (BOM) based on the batch respirometric method (Kappeler and Gujer (1992)). As shown in Figure 3.1, the BOM consisted of a glass container equipped with a DO probe (WTW Oxi 3310, Germany), and a stirring plate (IKA® RH B2, Germany). A Master flex peristaltic pump (Cole-Parmer, U.S.A) recirculated the sludge from an aerobic reactor under evaluation through the BOM. When the BOM was filled with the sludge the pump stopped and the decrease in DO as a function of time was monitored and recorded by the DO probe. After determining the OUR, the sludge was

returned back to the reactor. A DO range from 6.5 to 2.5 mg $L^{-1}$was used to calculate the OURs. OURs were determined in triplicate before and after conducting each specific experiment. Since each experiment was also carried out in triplicate, a total of 12 OUR determinations were carried out for every single experimental condition. The average value of the calculated OUR from each experiment was used for the determination of the reported K_La.

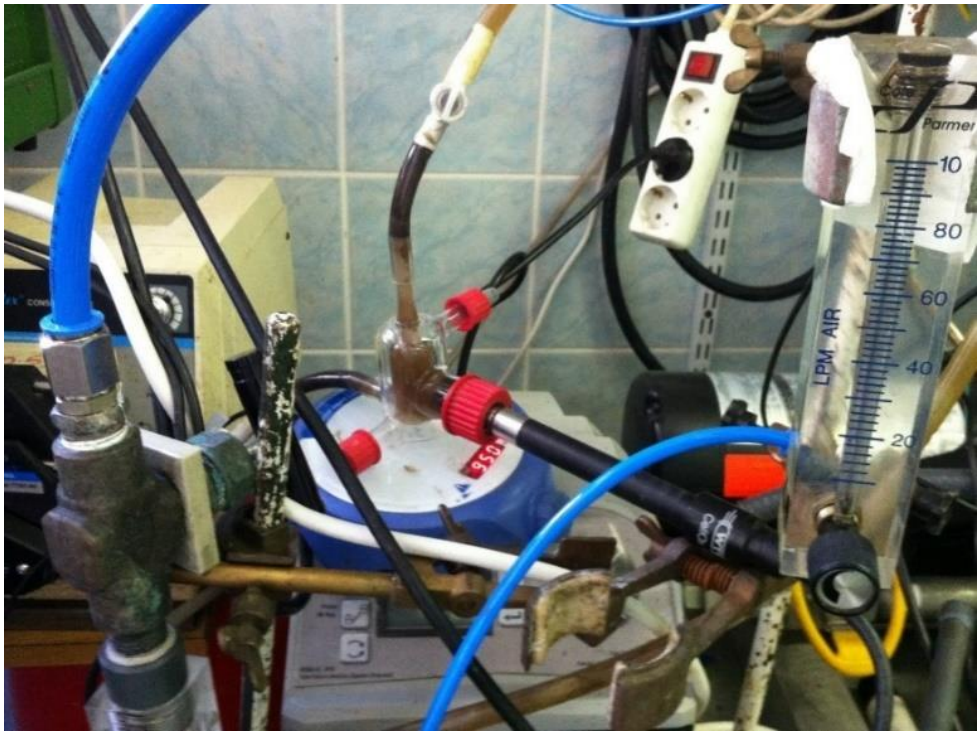

Figure 3.1 Biological oxygen meter experimental set-up for OUR determination (Photo by Sang Yeob Kim)

3.2.4 Particle size distribution and viscosity

The particle size distribution (PSD) was determined using a Malvern Mastersizer 2000 laser diffraction particle counter (Malvern Instruments Ltd, Malvern, UK). The apparent viscosity at a shear rate of 780 s^{-1} was measured at constanttemperature (20℃) using a viscometer Rheometric RM-180 (proRheo GmbH, Germany).

3.2.5 Experimental Procedures

3.2.5.1 Collection and preparation of the sludge

Fresh activated sludge was collected from the WWTP of city of Zagreb located in Zagreb, Croatia. The WWTP was designed only for carbon removal. The plant was operated as a CAS process at an SRT of approximately 5 days, and at an average MLSS concentration of approximately 4 g L^{-1}. The sludge was collected from one of the aerobic basins at the WWTP for the K_La determinations (Figure 3.2). The sludge was concentrated either by gravity settling or membrane filtration to reach the desired MLSS concentrations. For reaching the lower range of MLSS concentrations (for instance, 4 and 10 g L^{-1}) the sludge was concentrated mostly by

gravity settling at the WWTP facility (Figure 3.3). The 4 g L^{-1} MLSS concentration was directly prepared by sampling sludge from the aerobic basin without any further concentration step. To prepare the 10 g L^{-1} MLSS concentration approximately 100 L of sludge were sampled and introduced into 20 L containers. The mixture was settled for approximately 30 minutes until reaching the desired MLSS concentration by periodically removing the supernatant. The target MLSS concentration was confirmed by determining the total suspended solids (TSS) concentration at each sample. When the MLSS concentration exceeded the target value, the sludge was diluted with the supernatant to reach the desired final MLSS concentration.

To reach the higher range of evaluated MLSS concentrations (that is, 20, 30 and 40 g L^{-1}) the sludge was concentrated by membrane filtration. A rectangular based (24×24×93 cm) 40 L bench-scale MBR provided with hollow fibre membranes (ZenonZeeWee^{TM}-10, 0.4 μm pore size, 0.92 m^2 surface area) vertically submerged was used to concentrate the sludge. Sludge with a starting MLSS concentration of approximately 10 g L^{-1} (from the previously described gravity concentration step) was introduced into the MBR to achieve the desired sludge concentration. Sludge volumes of approximately 60, 90, and 120 L were introduced into the MBR to achieve MLSS of approximately 20, 30, and 40 g L-1, respectively. The target MLSS concentration was confirmed by determining the TSS concentrations. The sludge transport time from the WWTP to the laboratory, where the membrane concentration step was conducted, was less than an hour. The concentrated sludge was then aerated in the laboratory for approximately 24 hours before initiating the oxygen transfer evaluations.

Figure 3.2 Preparation of the sludge at the WWTP (Photo by Sang Yeob Kim)

Figure 3.3 Concentrating activated sludge by gravity settling at the WWTP facility (Photo by Sang Yeob Kim)

3.2.5.2 Experimental set up

As shown in Figure 3.4, the oxygen transfer performance experiments were conducted in a cylindrical plastic reactor with a total working volume of approximately 20 L. The reactor was equipped with a fine bubble diffuser (SANITAIRE® Silver Series 2, Xylem, USA) situated on the bottom of the reactor and a mixer with a propeller length of approximately 0.25 m (Heidolph Instruments GmbH, RZR 2102 control, Germany). A DO probe connected to a data logger (WTW Oxi 3310, Germany) was employed to monitor the DO concentration in the suspension. The reactor was aerated either using air or pure oxygen. The air was provided by a HIBLOW HP 80 air blower (Techno Takatsuki, Japan) for air flow rates (AFR)s from 0.1 to 1 $m^3 h^{-1}$ and by an AIRMAC air blower (Model number: DB 150, Taiwan) for an AFR of 4 $m^3 h^{-1}$. Pure oxygen was provided by means of a pure oxygen cylinder (MESSER, Croatia). Both the air and the pure oxygen were supplied to the reactor through the fine bubble diffuser. The air and oxygen gas flow rates were determined as follows: the flow rates ranging from 0.02 to 0.1 $m^3 h^{-1}$ were measured by a DK 800 series flowmeter (KROHNE Messtechnik GmbH, Germany); the flow rates ranging from 0.5 to 1 $m^3 h^{-1}$ were measured by a Cole-Parmer flowmeter (EW-32461-44, U.S.A); and the flow rate of 4 $m^3 h^{-1}$ was measured by a KING flowmeter (KING instrument, U.S.A).

Figure 3.4 Experimental setups for oxygen transfer determinations (Photo by Sang Yeob Kim)

3.2.5.3 Air intrusion experiments

The K_La due to the air intrusion in clean water was determined by the non-steady-state batch test in clean water (WEF and ASCE 2001). The experimental set up for air intrusion experiment is exhibited in Figure 3.5. Nitrogen was sparged into the reactor until reaching a DO concentration below approximately 0.5 mg L^{-1}. Then, the mixer was started at an identical mixing intensity as to be used in the oxygen transfer experiments. The DO concentration was continuously monitored and recorded until reaching a DO concentration of approximately the DO atmospheric saturation value. The K_La value was then calculated by a non-linear regression carried out with the Microsoft Excel software add-in SOLVER getting the best fit between the measured and calculated DO.

Figure 3.5 Experimental set up for air intrusion experiments (Photo by Sang Yeob Kim)

3.2.5.4 Oxygen transfer performance experiments in clean water

The K_La in clean water was determined by the non-steady-state batch test in clean water (WEF and ASCE 2001). The K_La in clean water was determined for all the evaluated flow rates and oxygen sources. For all evaluated experimental conditions as described in Table 3.1 the same experimental procedure was carried out as follows. The reactor was filled with 20 L of tap water. The DO concentration was depleted by sparging nitrogen gas until measuring a DO concentration below 0.5 mg L^{-1}. Then, oxygen was supplied at the desired flow rate by either supplying air or pure oxygen through the fine bubble diffuser. The DO concentration was continuously monitored and recorded until reaching a stable DO concentration. The K_La value was calculated as described in section 3.2.5.3. The oxygen intrusion from the atmosphere was taken into account for adjusting the K_La values in clean water. The experiments were conducted in triplicate, and an average K_La value at each experimental condition was reported.

Table 3.1 Evaluated experimental conditions

Experiment		Gas flow rates (m^3 h^{-1}) Air	Gas flow rates (m^3 h^{-1}) Oxygen	Oxygenation time before measurements (hours)
Clean water		0.1, 0.5, 1, 4	0.02, 0.1	-
Sludge MLSS (g L^{-1})	4			24, 48, 72
	10			
	20			
	30			
	40	0.5, 1, 4	0.1	

3.2.5.5 Oxygen transfer performance experiments in mixed liquor

The concentrated sludge collected from the WWTP was aerated overnight prior to the experiments. The K_La of the sludge at the evaluated concentrations was determined by the non-steady-state batch test under endogenous respiration conditions (WEF and ASCE 2001). For all the evaluated experimental conditions as described in Table 3.1 the same experimental procedure was carried out as follows. The reactor was filled with 20 L of mixed liquor at the desired concentration. The DO concentration was depleted by sparging nitrogen gas until the DO concentration was below 0.5 mg L^{-1}. Then, oxygen was supplied at the desired gas flow rate either supplying air or pure oxygen through the fine bubble diffuser. The DO concentration was continuously monitored and recorded until reaching an equilibrium DO concentration. The OURs were determined before and after each evaluation as described in section 3.2.3. Moreover, samples were taken at the end of each evaluation to determine both the PSD and viscosity. The K_La value was calculated by conducting a non-linear regression with the Microsoft Excel software add-in SOLVER as described in section 3.2.5.3; the values were corrected considering the oxygen intrusion from the atmosphere through the surface. The experiments were performed in triplicate and the average K_La was reported for each experimental condition. After conducting each test, the sludge was aerated for a period of 24 hours, and the experiments previously described were repeated; then this procedure was repeated again. Thereafter, the oxygen transfer performance was evaluated at a range of MLSS from 4 to 40 g L^{-1} using

different oxygen sources (air or pure oxygen) at different gas flow rates (from 0.02 to 4 $m^3 h^{-1}$) and at different degrees of sludge stabilization (after aerating the sludge for 24, 48, and 72 hours). All the determined K_La were corrected to 20°C temperature, and the alpha factors were calculated and reported. A summary of the entire evaluated experimental conditions is presented in Table 3.1.

3.3 Results and discussion

To evaluate the current limitations imposed by conventional bubble diffusers on the HL-MBR, the effect of the MLSS concentration on the alpha factor was evaluated on municipal sludge obtained from a WWTP operated at an SRT of approximately five days. The evaluation was carried out at different operational conditions including different oxygen sources (air and pure oxygen), and at different volumetric air/oxygen flow rates. In addition, the impact of the MLSS concentration on the alpha factor was determined at different levels of sludge stabilization indicated by the sludge specific OUR (SOUR). The results and discussion first introduces the impact of the MLSS concentration on the alpha factor at the evaluated oxygen sources and at the different air/oxygen flow rates. Then, the effect of the sludge stabilization on the alpha factor is introduced. Finally, a discussion is presented on the current limitations imposed by the bubble diffusers and possibilities for designing and operating the HL-MBR.

3.3.1 Impact of the MLSS concentration on the alpha factor at different air/oxygen flow rates

Figure 3.6 shows the effect of the MLSS concentration on the alpha factor when supplying either air (Figure 3.6a), or pure oxygen (Figure 3.6b) at different air/pure oxygen flow rates. Regardless the specific AFR, the alpha factor decreased as the MLSS concentration increased. Particularly, at an MLSS concentration of approximately 20 g L^{-1} non-detectable alpha factors were reported at a flow rate of 0.1 $m^3 h^{-1}$. Similarly, at an MLSS concentration of approximately 30 g L^{-1} non-detectable alpha factors were reported at AFRs of 0.1, 0.5, and 1 $m^3 h^{-1}$. In addition, at an MLSS concentration of approximately 40 g L^{-1} non-detectable alpha factors were reported for the entire range of evaluated AFRs. Figure 3.6b indicates the effect of the MLSS on the alpha factor at the evaluated pure oxygen flow rates (POFR)s of 0.02 and 0.1 $m^3 h^{-1}$. As observed as when supplying air (Figure 3.6a), the alpha factor decreased as the MLSS increased, regardless the POFR. However, at an MLSS concentration of approximate 20 g L^{-1} the alpha factors were detected at all the evaluated POFRs. At an MLSS concentration of 30 g L^{-1} non-detectable alpha factors were observed at the POFR of 0.02 $m^3 h^{-1}$. In addition, as observed when supplying air, at an MLSS concentration of approximately 40 g L^{-1}, non-detectable alpha factors were reported for the entire evaluated POFR range.

The overall trends in Figures 3.6a and 3.6b showed that the alpha factor decreased as the MLSS concentration increased. The higher the MLSS concentration, the more noticeable the effect of the suspended solids, limiting the oxygen diffusion from the fine bubbles into the liquid phase.

This observation is in accordance with previously reported studies investigating the relationship between the alpha factor and the MLSS concentration (Cornel et al. 2003; Germain et al. 2007; Gunder 2000; Henkel et al. 2009b; Krampe and Krauth 2003; Muller et al. 1995; Rosenberger 2003). These studies reported wide ranges of alpha factors at specific MLSS concentrations; alpha factors from approximately 0.5 to 1.0 were reported at an MLSS concentration of 5 g L^{-1}, while alpha factors from non-detectable to 0.3 were reported at an MLSS concentration of 40 g L^{-1}.

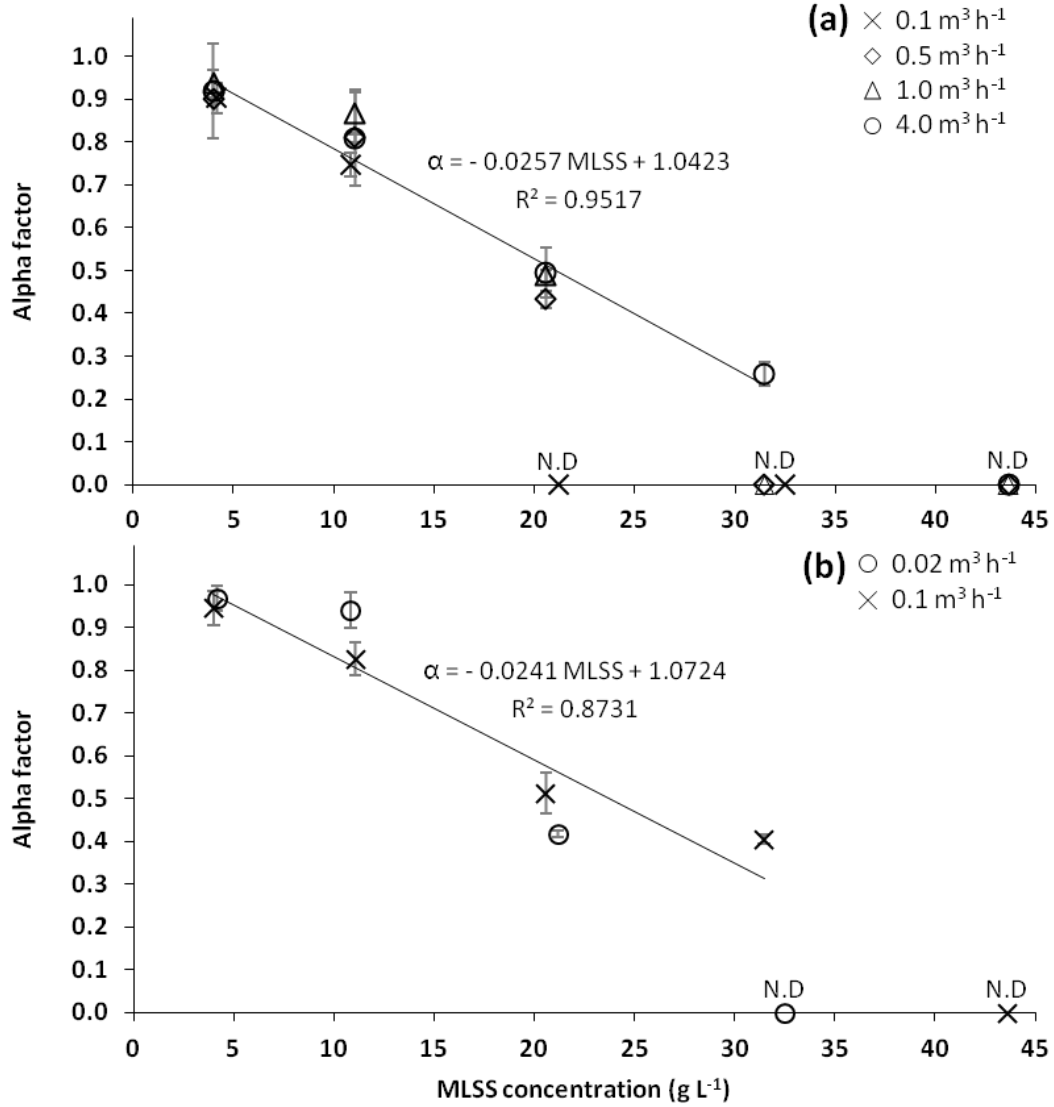

Figure 3.6 (a) Impact of the MLSS concentration on the alpha factor at different AFRs; the linear regression analysis corresponds to the average values of alpha factors determined at the evaluated AFRs of 0.1, 0.5, 1.0 and 4.0 m^3 h^{-1}; (b) Impact of the MLSS concentration on the alpha factors at different POFRs; the linear regression analysis corresponds to the average values of alpha factors determined at the evaluated POFRs of 0.02 and 0.1 m^3 h^{-1}

The alpha factors obtained in the present work as indicated in Figure 3.6 fitted well within the

ranges previously reported in literature at MLSS concentrations below 30 g L^{-1}. However, at MLSS concentrations higher than approximately 30 g L^{-1}, the alpha factors obtained in this research (mostly non-detectable) dropped below previously reported values (Cornel et al. 2003; Germain et al. 2007; Gunder 2000; Henkel et al. 2009b; Krampe and Krauth 2003; Muller et al. 1995; Rosenberger 2003). This means that a stronger negative impact of the MLSS concentration on the alpha factor was observed in this research compared to the literature. A linear regression analysis was carried out for determining the best expression that relates the alpha factor to the MLSS concentration; the linear regression results when supplying either air or pure oxygen are shown in Figures 1a and 1b, respectively.

Gunder (2000) and Muller et al. (1995) also carried out linear regression analyses to determine the best expression to relate the alpha factor to the MLSS concentration when supplying air; their main findings are reported below in Equation 3.1 and Equation 3.2, respectively. Particularly, when operating at a high MLSS concentrations of approximately 40 g L^{-1} (aim of this research), alpha factors of 0.036 and 0.25 are calculated when using the expressions reported by Gunder (2000) and Muller et al. (1995), respectively. When using the expression obtained in this research an alpha factor of 0.014 is obtained. That is, at high MLSS concentrations (i.e., higher than approximately 30 g L^{-1}) lower alpha factors were obtained in this research compared to the values reported by other authors such as Gunder (2000) and Muller et al. (1995). This research was conducted with sludge obtained from a WWTP working at a short SRT of approximately 5 days, while most of the research reported in the literature were carried out at very high (even infinite) SRTs. The negative effect of short SRTs on the alpha factor was reported by several authors (Gillot and Héduit 2008; Groves et al. 1992; Henkel et al. 2009a, 2011; Rieth et al. 1995; Rodriguez et al. 2012; Rosso et al. 2007; Rosso and Stenstrom 2005; US EPA 1989). However, previous studies were all conducted at low (CAS relevant) MLSS concentrations in the range from 3 to 6 g L^{-1} rather than at the high MLSS concentration range carried out in this research.

$$\alpha\ (Gunder\ 2000) = e^{-0.083\ MLSS} \tag{3.1}$$

$$\alpha\ (Muller\ et\ al.\ 1995) = 1.507e^{-0.0446\ MLSS} \tag{3.2}$$

α = Alpha factor (unitless)
MLSS = Mixed Liquor Suspended Solids (g L^{-1})

Moreover, most of the authors reported a negative exponential relationship between the alpha factor and the MLSS concentration (Cornel et al. 2003; Gunder 2000; Krampe and Krauth 2003). However, the results from this research indicated a negative linear relationship between the alpha factor and the MLSS concentration, as observed in Figure 3.6. A similar negative linear relationship was observed by Henkel et al. (2009b) who reported higher alpha factors compared to the literature at the evaluated MLSS concentrations. The authors claimed that since they were

working with grey water sludge, the sludge MLVSS/MLSS ratios were much lower compared to municipal sludge. Consequently, when reporting the alpha factors as a function of the MLVSS concentration rather than at the MLSS concentration, similar (lower) alpha factors as reported by other authors were obtained; in addition, probably the most important finding reported by Henkel et al. (2009b), a negative linear relationship between the alpha factor and the MLVSS concentration was observed. As such, the MLVSS, and not the MLSS, exhibited a direct impact on the oxygen transfer performance. Henkel (2010) reported that correlating the alpha factors to the MLSS led to a wide spread of the reported alpha factor at specific MLSS concentrations. In addition, the author correlated the alpha factors reported by others (Cornel et al. 2003; Germain et al. 2007; Krampe 2001; Rosenberger 2003) to the MLVSS concentrations (rather than to the MLSS concentrations) and obtained a negative direct linear relationship regardless the operational conditions (such as the SRT) at which these previous experiments were conducted. As observed in Figure 3.6, a similar negative linear trend was observed in the present study as reported by Henkel et al. (2009b); however, Figure 3.6 relates the alpha factor to the MLSS concentration rather than to the MLVSS concentration. The present work was conducted with fresh sludge obtained from a WWTP operated at an SRT of approximately 5 days; therefore, and as indicated in Table 3.2, the sludge exhibited relatively high MLVSS/MLSS ratios at the entire evaluated MLSS range. As such, most of the sludge consisted of MLVSS with a similar MLVSS/MLSS ratio for the entire evaluated MLSS range. This may eventually explain the negative linear relationship between the alpha factor and the MLSS concentration, as observed in Figure 3.6. The alpha factors in this research were also reported as a function of the MLVSS concentration (Figure 3.7). As expected, a similar negative linear trend was also obtained as both shown in Figure 3.6 and reported by Henkel et al. (2009b). Our results support the findings drawn by Henkel et al. (2009b), suggesting a direct negative relationship between the MLVSS and the alpha factor.

Table 3.2 Sludge properties at the evaluated MLSS concentration range

Target MLSS concentration ($g\ L^{-1}$)	Sludge characteristics						
				PSD (µm)			
	MLSS ($g\ L^{-1}$)	MLVSS ($g\ L^{-1}$)	MLVSS/MLSS	Dv 10	Dv 50	Dv 90	Viscosity (mPa s)
4	4.0	3.3	0.83	48.6	122.6	257.0	4.0
10	11.1	8.8	0.79	52.9	140.4	332.2	6.0
20	20.5	15.6	0.76	46.2	123.0	280.9	7.0
30	31.5	23.2	0.74	35.1	109.6	207.8	17.5
40	43.6	34.9	0.8	34.8	116.0	277.9	74.0

Dv: Volumetric particle diameter

Henkel (2010) indicated that the dependence of the alpha factor on the MLVSS rather than on the MLSS may be due to: (i) the reduction of the available gas/liquid interfacial area for the oxygen transfer due to the accumulation of sludge flocs (mostly MLVSS) on the surface of the gas bubbles; and (ii) the direct dependence of the sludge floc volume (determining the free water content of the solution) on the MLVSS content.

Henkel et al. (2009b) investigated the specific effect of the MLVSS on the gas/liquid bubble interface. Because of the partial hydrophobic surface of the sludge flocs and the hydrophobicity of the gas/liquid bubble interface, the sludge flocs tend to get attracted and accumulate on the gas bubble surface reducing the available gas/liquid interfacial area; this observation is regardless of the bubble size. Henkel et al. (2009b) observed a larger fraction of the bubble surface area covered with solids when working at an MLVSS concentration of 6.8 g L^{-1} compared to when working at an MLVSS concentration of 2.4 g L^{-1}. As the MLVSS increased, the surface area of the air bubbles was consistently more covered with flocs; therefore, reducing the net interfacial area available for the oxygen transfer, and increasing the difficulty for the oxygen molecules to diffuse into the liquid phase. Moreover, the MLVSS fraction directly correlates to the bacteria and extracellular polymeric substances (EPS) content of the sludge, which to a large extent consists primarily of water (Raszka et al. 2006). The more water bound in the sludge by the organic matter, the larger the volume that the floc occupies; therefore, the less free water is available for an undisturbed mass transfer from the gas to the liquid phase.

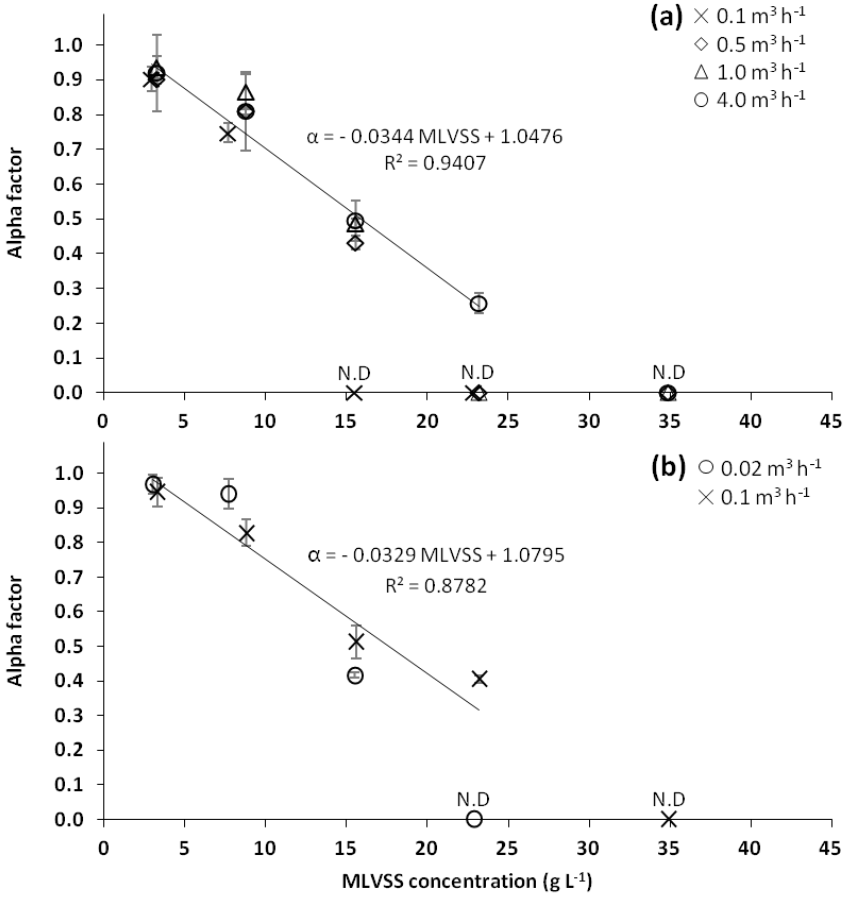

Figure 3.7 (a) Impact of the MLVSS concentration on the alpha factor at different AFRs; the linear regression analysis corresponds to the average values of alpha factors determined at the evaluated AFRs of 0.1, 0.5, 1.0 and 4.0 m^3 h^{-1}; (b) Impact of the MLVSS concentration on the alpha factors at different POFRs; the linear regression analysis corresponds to the average values of alpha factors determined at the evaluated POFRs of 0.02 and 0.1 m^3 h^{-1}

The MLSS and MLVSS concentrations only describe the sludge content in its dried form without considering the water bound in the sludge. The MLVSS concentration (not the MLSS) directly correlates with the free water content and the floc volume; an increase on the floc volume, decreases the free water content reducing the alpha factor in a linear way (Henkel 2010). The MLVSS component of the sludge not only directly interacts with the bubble (getting in contact with the bubble surface reducing the interfacial area between the liquid and the bubble), but also significantly contributes to the floc volume. The MLSS concentration is not the correct parameter to explain mechanisms that are related to floc volume phenomena. The MLVSS concentration better reproduces the free water content and floc volume than the MLSS concentration.

Most of the studies evaluating the impact of the MLSS concentrations on the alpha factors were carried out at long SRTs (Cornel et al. 2003; Gunder 2000; Henkel et al. 2009b; Muller et al. 1995); the higher the SRT, the lower the MLVSS/MLSS ratio due to the aerobic stabilization of the sludge. However, our research was conducted with sludge obtained from a WWTP operated at a short SRT of approximately 5 days; therefore, relatively high MLVSS/MLSS ratios were reported as described in Table 3.2. The higher the fraction of MLVSS in the sludge, both the higher the amount of sludge flocs accumulating in the surface of the bubbles, and the larger the floc volume decreasing the free water content of the suspension. Thus, the combination of these two effects has a negative impact on the oxygen transfer process explaining the low alpha factors determined in this research (conducted with sludge obtained from a WWTP operated at a short SRT of approximately 5 days) compared to the values reported on the literature (at high SRT) at similar MLSS concentrations. Therefore, under similar conditions, the lower the SRT, the higher the sludge floc concentration and MLVSS fraction on the sludge, and this contributes to a decrease in the alpha factor (as reported in this research). Consequently, operating an MBR system at high MLSS concentrations and short SRTs (HL-MBR concept) seems to be detrimental for the oxygen transfer process when using conventional bubble diffusers.

Zhang et al. (2015) reported higher concentrations of EPS when operating an MBR at a relatively short SRT of 10 days compared to when operating at SRTs of 30 and 90 days. Both the higher expected EPS concentrations, most likely to occur when working at short SRTs, together with the effect of operating a reactor at high MLSS concentrations may promote the agglomeration of sludge particles. This may probably modify the nature and structure of the flocs with a potential impact on both the accumulation of the flocs on the surface of the bubble, as well as on the floc volume; this has a residual effect on the oxygen transfer and alpha factor. However, as shown in Table 3.2 and Figure 3.8, relatively standard floc sizes were reported on this research of approximately 120 µm, and non-significant changes on the PSD were observed for the entire evaluated MLSS concentration range. These observations indicated the absence of agglomeration of flocs within the evaluated MLSS concentration range. Therefore, even though operating with sludge obtained from a WWTP operated at a short SRT of approximately

5 days and high MLSS concentrations may introduce a large amount of EPS (not measured in this research), agglomeration of the sludge was not observed that could have probably altered the effect of the MLSS concentrations on the oxygen transfer.

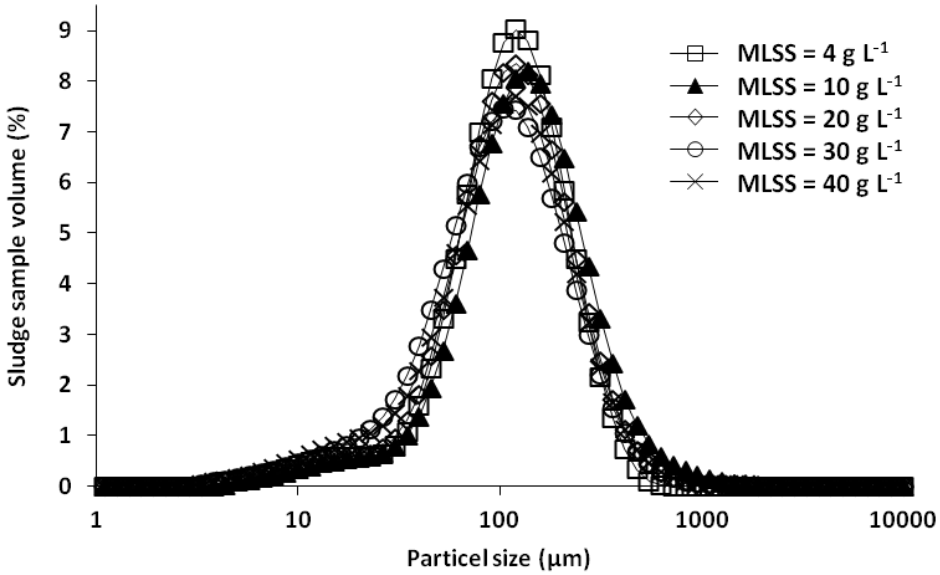

Figure 3.8 PSD of sludge at each MLSS concentration after 24 hours of oxygenation

The viscosity of the sludge was also determined at the evaluated MLSS concentrations and reported in Table 3.2. The viscosity exponentially increased with the MLSS concentration; similar trends were reported by Sato and Ishii (1991) and Itonaga et al. (2004). The adverse effects of the viscosity on the oxygen mass transfer performance were reported by several authors (Cornel et al. 2003; Germain and Stephenson, 2005; Gunder 2000; Krampe and Krauth 2003). Iorhemen et al. (2016) reported an additional increase of the viscosity when operating WWTPs at long SRTs due to the accumulation of non-biodegradable substances which contributed significantly to the overall viscosity. Pollice et al. (2008) reported similar findings when operating a bench scale MBR treating municipal wastewater at different MLSS concentrations (from 4 to 23 g L^{-1}) and SRTs (from 20 days to infinite). They observed a significant increase on the viscosity as the SRT increased from 20 days to infinite SRT. Consequently, operating at short SRTs seems to be beneficial in terms of lowering the viscosity with a positive impact on the oxygen mass transfer. However, short SRTs also increase the MLVSS/MLSS sludge ratio eventually overruling the positive effects of the reduced viscosity. Figure 3.9 describes more precisely the impact of air (Figure 3.9a) and pure oxygen (Figure 3.9b) flowrates on the alpha factor at the specific assessed MLSS concentrations. The alpha factor exhibited a much higher dependence on the MLSS concentration than on the air/oxygen flowrates. Similar alpha factors were reported at the specific MLSS concentrations, regardless the evaluated air/oxygen flowrate. At the largest flow rates for air and pure oxygen of 4 and 0.1 $m^3 h^{-1}$, respectively, alpha factors were detected even at an MLSS concentration as high as 30 g L^{-1}. However, alpha factors were not detected at the largest evaluated MLSS concentration of 40 g L^{-1}.

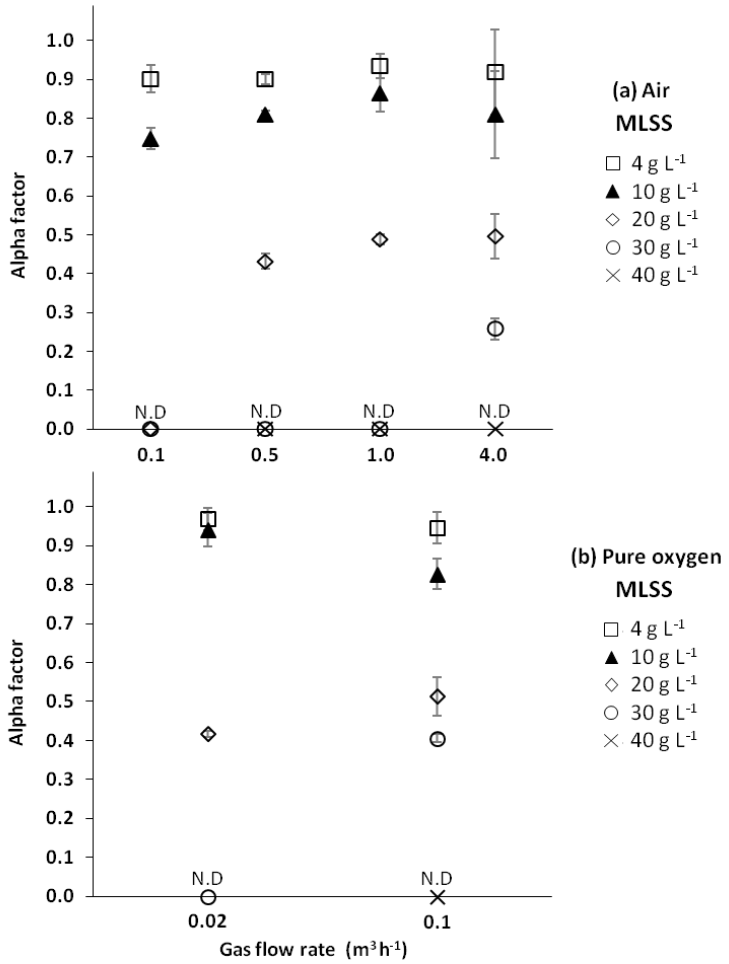

Figure 3.9 (a) Impact of the AFRs on the alpha factors at different MLSS concentrations; (b) Impact of the POFRs on the alpha factors at different MLSS concentrations

The flowrate has a direct impact on the mixing intensity. As reported by Benjamin and Lawler (2013), other factors being equal, the larger the mixing intensity, the larger the liquid exchange frequency in the proximity of the interfacial gas/liquid transfer layer, and the smaller the thickness of that interfacial layer. These effects cause an increase on the K_La. However, the K_La could have proportionally increased both in clean water and in process water at the evaluated flowrates; therefore, the alpha factors did not considerably change as the air/oxygen flowrate increased as observed in Figure 3.9. Similar findings were reported by Germain et al. (2007). The authors could not find any particular clear relationship between the alpha factor and the AFRs.

Similar alpha factors were reported when supplying either air or pure oxygen. When supplying pure oxygen, the gas bubbles consisted entirely of oxygen molecules, providing larger gas transfer interfacial areas per unit of volume and larger K_La values compared to when supplying air. However, the K_La could have proportionally increased both in clean and process water; therefore, the alpha factor remains unchanged regardless the supplied oxygen source (air or

pure oxygen). Most of the literature describing the effects of the MLSS concentrations on the alpha factor in the context of high MLSS concentrations was reported supplying air rather than pure oxygen. To our knowledge, Rodriguez et al. (2011) was the only research reporting alpha factors working at MLSS concentrations relevant for an MBR while supplying pure oxygen rather than air. The authors reported an alpha factor of approximately 0.03 at an MLSS concentration of 12.6 g L^{-1} in an MBR operated at an SRT of 40 days. This is a relatively low alpha factor compared to other authors working at similar MLSS concentrations that supplied air rather than pure oxygen. Although the oxygen transfer process strongly depends on the operational conditions, the only research reported where oxygen was supplied rather than air at a relatively high MLSS concentration did not show a significant advantage in terms of the oxygen transfer and alpha factor.

3.3.2 Effect of the sludge stabilization on the alpha factor

This particular phase aimed at evaluating the impact of the different MLSS concentrations at different degrees of sludge stabilization/activity (aerobically stabilized) as indicated by the sludge SOUR. The sludge at MLSS concentrations from 4 to 40 g L^{-1} was further oxygenated for periods of 24, 48, and 72 hours, and the alpha factors were determined. Figure 3.10 describes the alpha factors at the evaluated sludge samples expressed as a function of the MLVSS concentration when supplying air at a flowrate of 4 m^3h^{-1}.

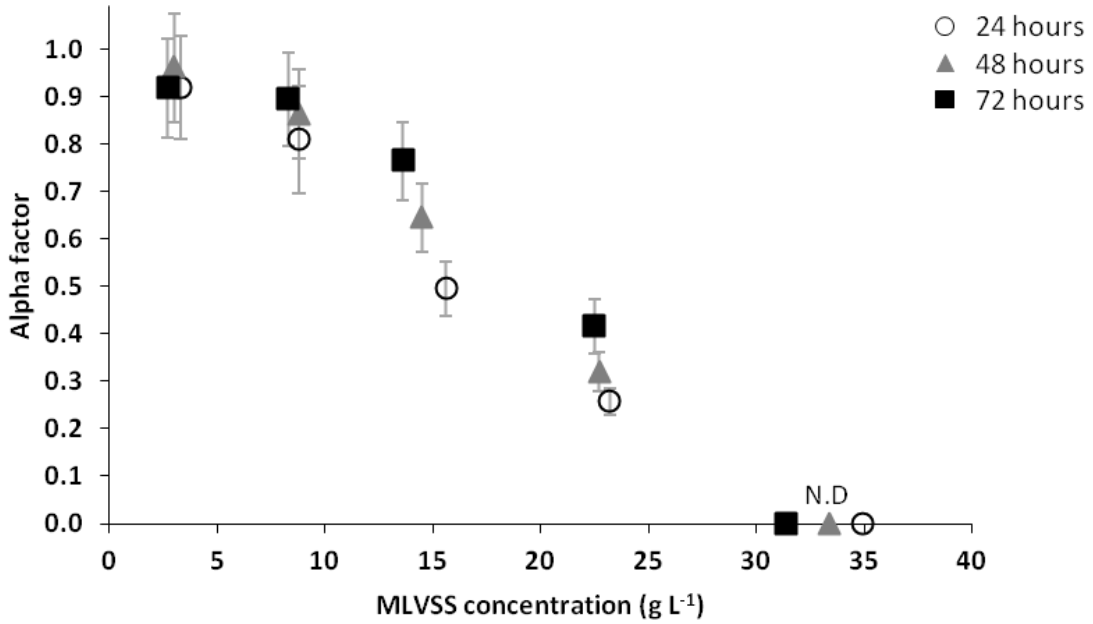

Figure 3.10 Alpha factor as a function of the MLVSS concentration evaluated at an AFR of 4 $m^3 h^{-1}$; unfilled symbols = 24 hours oxygenation; grey symbols = 48 hours oxygenation; black symbols = 72 hours oxygenation

The alpha factor followed a similar trend as previously described in Figures 3.6 and 3.7, regardless the degree of sludge stabilization. The alpha factors were determined at the entire

range of MLVSS concentrations and degrees of sludge stabilization, except at the largest evaluated MLSS concentration of approximately 40 g L^{-1} negligible alpha factors were reported. As indicated in Figure 3.10, the larger the degree of sludge stabilization at the specific evaluated MLVSS concentrations, the higher the alpha factor. Particularly, this trend is more pronounced at the highest used MLVSS concentrations. Table 3.3 indicates the precise MLVSS concentrations reported at each specific target MLSS concentration, as well as the overall sludge properties at which the sludge samples were evaluated.

Table 3.3 Sludge properties at the evaluated MLSS concentrations at different sludge stabilization times

Target MLSS concentration	Sludge stabilization	Sludge characteristics				
		MLSS	MLVSS	MLVSS/MLSS	OUR	SOUR
(g L^{-1})	(h)	(g L^{-1})	(g L^{-1})		(mg O_2 L^{-1} h^{-1})	(mg O_2 $gMLVSS^{-1}$ h^{-1})
4	24	4.0	3.3	0.83	29.4	7.61
	48	3.8	3.0	0.79	26.4	7.31
	72	3.6	2.7	0.75	20.4	6.21
10	24	11.1	8.8	0.79	72.0	7.97
	48	10.8	8.6	0.80	51.0	5.87
	72	10.4	8.3	0.80	42.6	4.91
20	24	20.6	15.6	0.76	76.2	4.88
	48	19.2	14.5	0.76	50.4	3.54
	72	19.1	13.6	0.71	37.2	2.79
30	24	31.5	23.2	0.74	108.6	4.83
	48	31.4	22.7	0.72	72.6	3.40
	72	31.7	22.5	0.71	54.6	2.58
40	24	43.6	34.9	0.80	198.0	5.70
	48	44.3	33.4	0.75	153.0	4.62
	72	43.9	31.4	0.72	87.0	2.82

The results observed in Figure 3.10 clearly indicate considerable differences on the reported alpha factors at similar MLVSS concentrations. Particularly, at the target MLSS concentration of 30 g L^{-1} (with an MLVSS concentration of approximately 23 g L^{-1}) the alpha factors ranged from 0.26 to 0.46. Similarly, at the target MLSS concentration of 20 g L^{-1} (and an MLVSS concentration of approximately 15 g L^{-1}) the alpha factors ranged from 0.47 to 0.64. The differences were not that evident when working at the lowest range of the target MLSS concentration (4 g L^{-1}). Therefore, the results clearly indicated that in addition to the negative effects exerted directly by the MLVSS on the oxygen transfer and alpha factors (reported in Section 3.3.1), there are other causes strongly influencing the oxygen transfer that may not depend that directly on the MLVSS concentration.

Henkel (2010) reported that the presence of surfactants such as surface active long chain fatty acids (LCFAs) may also negatively affect the oxygen transfer performance; particularly, when these substances are adsorbed to the sludge (not on their soluble form). Rosso et al. (2006) have also reported on the adverse effects of surfactants on the oxygen transfer. Dignac et al. (2000) and Quemeneur and Marty (1994) reported that the surface active substances commonly found

in municipal wastewater are due to the presence of fatty acids in lipids. Lipids may count for approximately 20 to 25% of the organic material in domestic wastewater (Quemeneur and Marty 1994). Activated sludge flocs are able to trap (adsorb) low water soluble organic compounds such as LCFA surfactants (Struijs et al. 1991). Henkel (2010) reported the presence of LCFA surfactants adsorbed to the sludge when working at short SRTs (as short as 2 days) and low oxygen transfer efficiencies most likely due to the presence of these compounds adsorbed to the sludge. Since surfactants are mostly biodegradable, their accumulation on the sludge (and their negative effect on the oxygen transfer) is more noticeable at short SRTs. As the SRT increases these compounds are prone to be biodegraded, and their effects on the oxygen transfer should be less noticeable. The trends observed in our research might be eventually explained by the presence of biodegradable surfactants. As observed in Figure 3.10, when increasing the sludge oxygenation time from 24 to 72 hours the alpha factor (and the oxygen transfer performance) increased at the specific evaluated target MLSS concentrations. The larger the sludge oxygenation time, the higher the possibilities for the biodegradable surfactants to be removed out of the sludge alleviating the negative effects on the oxygen transfer.

The analytical determination of surfactants was not carried out in this research; however, the OUR of the sludge was determined at the different stages of sludge stabilization at the evaluated MLSS concentrations. Figure 3.11 describes the alpha factor as a function of the SOUR at the evaluated range of MLSS concentrations. The OUR values as well as the overall evaluated sludge parameters are presented in Table 3.3. Similarly, as reported in Figure 3.10, at the low range of evaluated MLSS concentrations (4 and 10 g L^{-1}) similar alpha factors were reported regardless the SOUR. However, at MLSS concentrations of 20 and 30 g L^{-1}, the alpha factor significantly increased as the SOUR decreased. The MLVSS concentrations did not significantly vary at each target MLSS concentration at the different sludge stabilization stages (24, 48, and 72 hours), as shown in Figure 3.10. Therefore, the decrease on the reported SOUR could have been due to the removal of biodegradable substances (e.g. biodegradable surfactants). This implies that the increase on the alpha factor as the SOUR decreased was not in this case due to the effects of the MLVSS concentration (as reported in Section 3.3.1), but due to the removal of biodegradable compounds present in the sludge mixture. As the sludge aerobic stabilization progressed, the reduction of the SOUR indicated the biodegradation of organic compounds alleviating their negative impact on the oxygen transfer. Therefore, other factors being equal, the larger the sludge aerobic stabilization time, (usually provided when working at large SRTs) the better the oxygen transfer performance.

Based on the results obtained in this research, the most significant negative effect to the oxygen transfer is probably still given by the MLVSS concentration. As observed in Figure 3.11 at the same SOUR of approximately 4.5 mg O_2 g $MLVSS^{-1}$ h^{-1}, the alpha factors are significantly reduced when going from an MLSS concentration of 4 g L^{-1} to 40 g L^{-1}. However, not only should the effects of the MLVSS concentration be considered when evaluating the potential impact on the oxygen transfer, but also the presence of specific organic substances (such as

surfactants) which may also hinder the oxygen transfer performance. The SOUR seems like a promising good indicator together with the MLVSS concentration to better assess and predict the oxygen transfer performance of a biological wastewater treatment system.

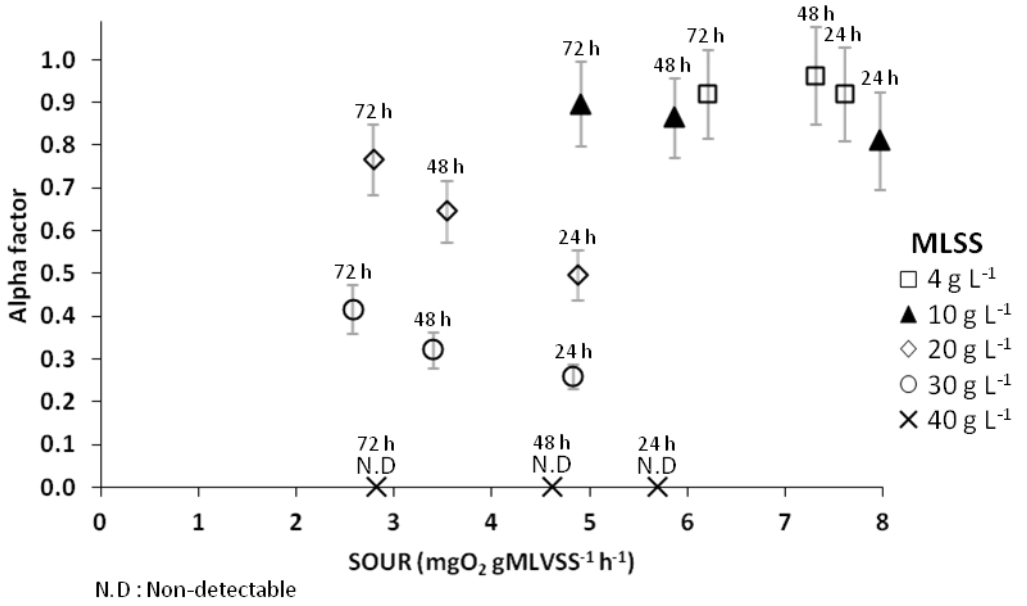

Figure 3.11 Alpha factors as a function of the SOUR at each MLSS concentration at an AFR of 4 m^3 h^{-1}

The goal of this research was to assess the limitations imposed by conventional bubble diffusers in the context of the HL-MBR. The concept of a HL-MBR for maximizing the treatment capacity while minimizing the system footprint requires operating the system at the highest achievable biologically active MLSS concentration obtained by operating the system at high loading rates and low SRTs. Our results indicated a negative impact of both high MLSS concentrations and short SRTs (emulated by taking and concentrating municipal sludge from a WWTP operated at a short SRT of approximately 5 days) on the oxygen transfer performance of conventional bubble diffusers. This may limit the design and operation conditions of the HL-MBR provided with conventional bubble diffusers.

3.3.3 Current limitations imposed by conventional diffused aeration on the HL-MBR

This section aims at both presenting the advantages of designing and operating a HL-MBR, as well as providing guidelines on the current limitations imposed by conventional diffused aeration on this system. Figure 3.12a describes some of the advantages of a HL-MBR system, while Figure 3.12b describes the limitations of these systems imposed by the conventional aeration systems.

Figure 3.12a captures the most relevant design advantages of a hypothetical HL-MBR designed and operated at the conditions described in Table 3.4. Figure 3.12a shows the volume

requirements and treatment capacities of the hypothetical system when operated at an MLSS concentration that ranges from 3 to 40 g L^{-1} and at an SRT of 10 days. As the MLSS concentration increases from 3 to 40 g L^{-1}, the volume requirements of the system dramatically decrease from approximately 2,500 to 190 m^3, while the volumetric organic loading rates (Vol OLRs) to the system considerably increase from approximately 1.5 to 14 kg bCOD m^{-3} d^{-1}. Moreover, the sludge wastage flow rates decrease from approximately 10 to 0.8 m^3h^{-1} at MLSS concentrations of 3 and 40 g L^{-1}, respectively. That is, Figure 3.12a describes the operational unique advantages of the HL-MBR. When operating at high MLSS concentrations and relatively standard (short) SRTs, high loading rates can be treated while minimizing the footprint needed by the system. Moreover, the sludge wastage flow can also be considerably decreased. The hypothetical system exhibits a biological oxygen demand of 2,530 kg O_2 d^{-1}; which indicates that approximately 950 g bCOD can be removed per kg of oxygen consumed by the system without considering the oxygen transfer inefficiencies introduced by the bubble diffused aeration systems. This implies that in the example presented in Figure 3.12a, a standard oxygen transfer efficiency (SOTE) of 100% in process water was considered. Moreover, the hypothetical example assumed both complete biodegradation of the influent biodegradable COD (bCOD), as well as a full nitrification of the influent total nitrogen at the selected SRT of 10 days.

Table 3.4 Wastewater characteristics and bio-kinetic designed parameters

Wastewater characteristics		
Influent flowrate	(m^3 d^{-1})	2,000
Influent biodegradable COD	(g COD m^{-3})	1,200
Influent unbiodegradable particulate COD	(g COD m^{-3})	20
Influent total suspended solids	(g TSS m^{-3})	500
Influent volatile suspended solids	(g VSS m^{-3})	400
Influent total Kjeldahl nitrogen	(g TKN m^{-3})	120
Bio-kinetic design parameters		
Substrate half saturation constant (*Ks*)	(g COD m^{-3})	20
True Yield (*Y*)	(g VSS g COD^{-1})	0.45
Specific biomass decay rate (*b*)	(g VSS g VSS^{-1} d^{-1})	0.24
COD to VSS ratio of the sludge (*fcv*)	(g COD g VSS^{-1})	1.48
Inorganic content of active biomass (f_{iOHO})	(g ISS g VSS^{-1})	0.15
Endogenous residue fraction (f_H)	(Unitless)	0.20

Figure 3.12b describes the treatment capacities of the hypothetical HL-MBR, but now adding

the oxygen transfer inefficiencies imposed by the conventional diffused aeration on the HL-MBR operational conditions as investigated in this research. Both the high concentration of MLVSS as well as the potential accumulation of surfactants, most likely to occur at the designed operational conditions of the HL-MBR (high loading rate and short SRT), introduce a serious limitation on the oxygen transfer performance. The hypothetical example presented in Figure 3.12b considered a SOTE of 5% per meter of submergence in clean water for a 4 m depth reactor (equivalent to a total SOTE in clean water of 20%). In addition, the alpha factors obtained in the present work were selected when working in wastewater. Overall SOTEs in process water of 19, 18, 16, 9, 4 and 0% were selected for MLSS concentrations of 3, 5, 10, 20, 30 and 40 g L^{-1}, respectively. As observed in Figure 3.12a, Figure 3.12b also shows the Vol OLR, as well as the amount of bCOD removed per amount of oxygen at an MLSS concentration range from 3 to 40 g L^{-1} and SRT of 10 days. Moreover, Figure 3.12b also introduces the oxygen specific Vol OLR parameter describing the amount of COD that can be removed per volume occupied by the system and per oxygen consumed by the system. The same volume requirements (not shown in Figure 3.12b) and Vol OLRs as described in Figure 3.12a apply to the HL-MBR system when considering the oxygen transfer inefficiencies. The first main difference on the performance of the HL-MBR system when considering the oxygen transfer inefficiencies (as reported in Figure 3.6) is that the system cannot be operated at MLSS concentrations higher than 30 g L^{-1}, since negligible alpha factors were reported at those MLSS concentrations; therefore, it is not possible to supply DO at those operational conditions when using conventional diffused aeration systems. Moreover, even though the biological oxygen demand of the system remained identical as presented in Figure 3.12a (of 2,530 kg O_2 d^{-1} and 950 g bCOD removed per kg of oxygen consumed) the amount of oxygen that needs to be supplied increased dramatically considering the oxygen transfer inefficiencies of the bubble diffusers at the reported MLSS concentrations. As seen in Figure 3.12b, the amount of COD removed per oxygen supplied considerably decreased as compared to Figure 3.12a following a direct linear negative relationship with the MLSS concentration; even reaching a value of zero at an MLSS concentration of 40 g L^{-1}. This implies that the hypothetical system can handle the same volumetric treatment loads as presented in Figure 3.12a. However, the aeration system introduces such enormous inefficiencies on the oxygen transfer performance requiring the supply of extremely large amounts of oxygen to satisfy the oxygen biological needs of the systems to maintain aerobic conditions in the reactor.

Moreover, Figure 3.12b introduces another parameter aiming at finding the optimal operational set point of the HL-MBR considering the oxygen transfer inefficiencies introduced by the diffused aeration systems. The oxygen specific Vol OLR parameter is introduced describing the amount of COD that can be removed per volume occupied by the system and per oxygen consumed by the system. The higher the value of this indicator, the higher the treatment capacity of the system at the lower footprint and oxygen consumption. As observed in Figure 3.12b a maximum value is reached at an MLSS concentration of 20 g L^{-1} corresponding to 225

g COD removed per cubic meter of the reactor and per ton of oxygen supplied. The fine bubble diffused aeration system introduces a severe limitation on the design conditions of a HL-MBR. MLSS concentrations higher than 30 g L^{-1} cannot be achieved since it would not be technically feasible to introduce DO; moreover, an optimum design MLSS concentration of 20 g L^{-1} was calculated considering maximizing the amount of COD that can be treated per unit of system footprint and per unit of oxygen consumption.

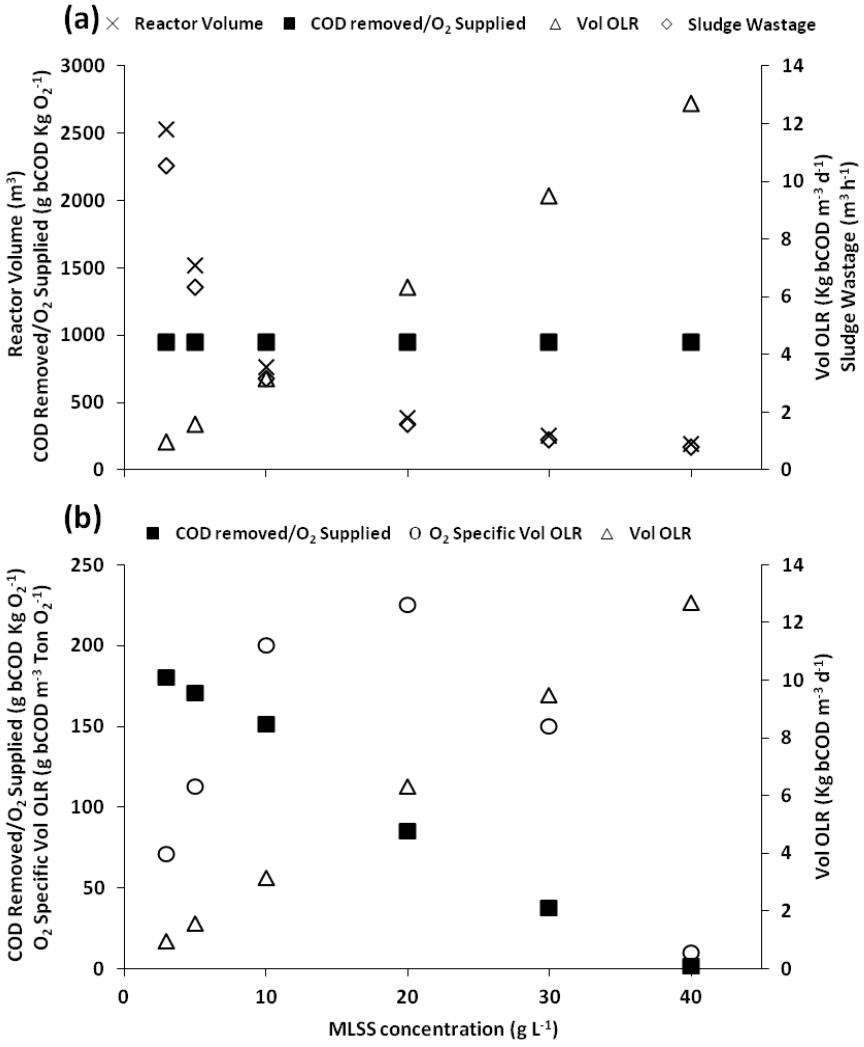

Figure 3.12 (a) Most relevant design advantages of a HL-MBR as a function of the MLSS concentration without considering oxygen transfer inefficiencies introduced by fine bubble diffusers; (b) HL-MBR performance as a function of the MLSS concentration considering the process water SOTE introduced by conventional fine bubble diffusers as investigated in this research

This research was carried out using fine bubble diffusers for supplying DO into the system. The current evaluation did not consider the performance of coarse bubble diffusers on the HL-MBR system. Coarse bubble diffusers would eventually yield higher alpha factors compared to fine bubble diffusers; however, coarse bubble diffusers experienced overall low SOTEs than fine

bubble diffusers. Therefore, even though coarse bubble diffusers could have performed better compared to fine bubble diffusers in terms of alpha factors, the overall SOTE in activated sludge would not considerably change and similar results can be expected.

This research evaluated the current limitations imposed by fine bubble diffused aeration on the HL-MBR; however, there may be other technological options for supplying DO at much more efficient SOTEs that may eventually uncap the current limitations imposed by fine bubble diffused aeration systems. Concentrated oxygen delivery systems (superoxygenation systems) are able to deliver DO at approximately 100% SOTEs (Barreto et al. 2018); however, the precise performance of these systems still needs to be properly evaluated at the operational conditions required by the HL-MBR (like high MLSS concentrations and short SRTs).

Moreover, this research did not evaluate the impact of such high MLSS concentrations on the membrane filtration performance. However, Barreto et al. (2017) reported no significant additional sludge filterability difficulties when operating an MBR at an MLSS concentration of 30 g L^{-1} compared to when operating at a lower MLSS concentration of approximately 8 g L^{-1}. Moreover, ceramic membranes can be used instead of polymeric membranes increasing the conventional standard fluxes allowed through the membranes when operating at higher than usual MLSS concentrations. This research was conducted in the framework of exploring the limitations of conventional diffusers on the design of a HL-MBR; however, the experiments were conducted in batch reactors without considering the dynamic effects of the membrane filtration process on the sludge. The characteristics of the biomass may eventually differ from what was observed in this research, and the results may not be linearly extrapolated to MBR systems.

3.4 Conclusions

The impact of the MLSS concentration on the alpha factors is more pronounced when working at short SRTs (evaluated in this research by using sludge obtained from a WWTP operated at a short SRT of approximately 5 days). At short SRTs, a direct negative linear relationship between the alpha factor and the MLSS concentration can be observed. Other factors being equal, the shorter the SRT, the higher the MLVSS fraction and the lower the alpha factor. The gas flow rate and oxygen source (either air or pure oxygen) have just a marginal effect on the alpha factor at the evaluated operational conditions. The more stabilized the sludge, the lower the potential presence of biodegradable substances such as surfactants; thus, having a positive impact on the oxygen transfer (and alpha factor). The provision of fine bubble diffusers limits the maximum MLSS concentration that can be achieved on the HL-MBR concept at 30 g L^{-1}; beyond that point is either not technically or not economically feasible to supply DO. An optimum MLSS concentration of 20 g $L^{-1}$is suggested for designing the HL-MBR, maximizing the treatment capacity while minimizing both the footprint needs as well as the oxygen consumption.

3.5 Acknowledgments

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3.7 Appendix 3A：K_La determinations

To exclude the oxygen transferred through the surface of the water in the tank, DO concentration increase after sparging the water with nitrogen gas was measured in the clean water without aeration, but with mixing turned on and then $K_La_{,int}$ was calculated. K_La was then calculated for each experiment by applying Equations 2-1 for air and 2-2 for pure oxygen, respectively. The K_La values were determined by using parameter estimation with the aid of Microsoft Excel software add-in called SOLVER which can get the best fit between the measured DO and the calculated DO.

$$C_{(t)} = C_{S,Air} - \left(C_{S,Air} - C_{O2,1}\right)e^{(K_La+K_La_{,int})(t_1-t)} \quad 2\text{-}1$$

$$C_{(t)} = \left(\frac{(K_LaC_{S,O2}+K_La_{,int}C_{S,Air}}{K_La+K_La_{,int}}\right)\left(1 - e^{(K_La+K_La_{,int})(t_1-t)}\right) + \left(C_{O2,1}e^{(K_La+K_La_{,int})(t_1-t)}\right) \quad 2\text{-}2$$

Where $C_{(t)}$ is the DO concentration in the reactor at time t and $C_{S,Air}$ and $C_{S,O2}$ are the saturation DO concentration of air and pure oxygen in the clean water, respectively. $C_{O2,1}$ is the initial DO concentration at time t_1 and $K_La_{,int}$ is the oxygen transfer coefficient for air from the atmosphere with mixing and without aeration. The t_1 is the starting time of the K_La experiment.

The $C_{S,Air}$ values of DO in the clean water under the atmosphere of air at each temperature were taken from literature (Tchobanoglous et al. 2003). On the other hand, the $C_{S,O2}$ values for pure oxygen were established experimentally with the 0.02 and 0.1 $m^3\ h^{-1}$ of pure oxygen flow rates by measuring saturation DO concentration. Afterward, the SOLVER estimated the value of K_La with those new $C_{S,O2}$ attained. Determination of K_La of the sludge at each MLSS concentration was then conducted in the same way as with clean water. To calculate the K_La of sludge for both air and pure oxygen, equations of 2-3 for air and 2-4 for pure oxygen were introduced.

$$C_{(t)} = \left(C^*_{S,Air} - \left(\frac{OUR}{K_La+K_La_{,int}}\right) - \left(C^*_{S,Air} - \left(\frac{OUR}{K_La+K_La_{,int}}\right) - C_{O2,1}\right)\right)e^{(K_La+K_La_{,int})(t_1-t)} \quad 2\text{-}3$$

$$C_{(t)} = \left(\frac{(K_LaC^*_{S,O2}+K_La_{,int}C^*_{S,Air}-OUR}{K_La+K_La_{,int}}\right)\left(1 - e^{(K_La+K_La_{,int})(t_1-t)}\right) + C_{O2,1}e^{(K_La+K_La_{,int})(t_1-t)} \quad 2\text{-}4$$

Where $C^*_{S,Air}$ and $C^*_{S,O2}$ are the saturation, DO concentrations of air and pure oxygen, respectively, obtained by multiplication of values for clean water by a beta factor of 0.95. Since WWTP are receiving impurities such as surfactants and salt etc. along with influent wastewater,

the β factor characterized by the influence of such constituents needs to be taken into account when estimating K_La values. The βfactor is defined as below (Metcalf and Eddy 2003).

$$\beta = \frac{C^*_{wastewater}}{C^*_{cleanwater}}$$

Where $C^*_{wastewater}$ is the saturated dissolved oxygen concentration in wastewater and $C^*_{cleanwater}$is the saturated dissolved oxygen concentration in the clean water. The $C_{S,O2}$ value for aeration with pure oxygen for each temperature of the sludge suspension employed was obtained by Henry's constant using Van't Hoff equations

As the K_La experiments were performed at the slightly different temperatures, K_La at each temperature of the test were corrected by standardisation to 20 ℃ as followed the equation 2-5 and are referred as K_La_{20}. All the K_La determinations were done in triplicates.

$K_La_{(T)} = K_La_{(20℃)} \bullet 1.024^{(T-20)}$ 2-5

Where T is the temperature (℃) and θ is constant. Typical θ values are between 1.015 and 1.040, with 1.024 being the ASCE standard (Rodriguez et al. 2010). The alpha factor ($K_La_{20,MLSS}/K_La_{20,clean\ water}$) for all experiments was calculated as the ratio of K_La_{20} in the particular MLSS concentrations to K_La_{20} in the clean water.

3.8 Appendix 3B：K_La values at each MLSS

<MLSS of 4 g L^{-1}>

		C_{water}	STDV	24 h	STDV	48 h	STDV	72 h	STDV
Air	0.1 m^3 h^{-1}	11.0192	0.0063	9.9427	0.0034	8.9174	0.0031	8.0415	0.0041
	0.5 m^3 h^{-1}	22.9767	0.0044	20.6987	0.0023	21.3903	0.0094	22.0066	0.0044
	1 m^3 h^{-1}	31.9060	0.0103	29.8553	0.0134	30.2727	0.0245	31.9438	0.0175
	4 m^3 h^{-1}	66.9220	0.1196	61.5015	0.0522	64.3437	0.0547	61.4516	0.0364
Oxygen	0.02 m^3 h^{-1}	6.5220	0.0021	6.3170	0.0023	6.0407	0.0073	5.2115	0.0041
	0.1 m^3 h^{-1}	7.0444	0.0032	6.6630	0.0037	6.8989	0.0019	7.2842	0.0055

<MLSS of 10 g L^{-1}>

		C_{water}	STDV	24 h	STDV	48 h	STDV	72 h	STDV
Air	0.1 m^3 h^{-1}	11.0192	0.0063	8.2378	0.0018	8.5229	0.0015	7.7602	0.0099
	0.5 m^3 h^{-1}	22.9767	0.0044	18.6108	0.0023	18.9969	0.0229	21.8658	0.0149
	1 m^3 h^{-1}	31.9060	0.0103	27.6312	0.0250	28.6532	0.0560	32.1220	0.0334
	4 m^3 h^{-1}	66.9220	0.1196	54.1693	0.0807	57.7931	0.0126	59.8855	0.0274
Oxygen	0.02 m^3 h^{-1}	6.5220	0.0021	6.1343	0.0042	5.6597	0.0070	6.1273	0.0047
	0.1 m^3 h^{-1}	7.0444	0.0032	5.8296	0.0036	6.3779	0.0113	6.9075	0.0075

<MLSS of 20 g L^{-1}>

		C_{water}	STDV	24 h	STDV	48 h	STDV	72 h	STDV
Air	0.1 m^3 h^{-1}	11.0192	0.0063	ND	-	ND	-	4.9068	0.0021
	0.5 m^3 h^{-1}	22.9767	0.0044	9.9290	0.0074	12.9678	0.0220	14.4766	0.0124
	1 m^3 h^{-1}	31.9060	0.0103	15.5653	0.0047	19.7581	0.0089	22.9061	0.0059
	4 m^3 h^{-1}	66.9220	0.1196	33.1587	0.0241	43.1548	0.0224	51.1597	0.0086
Oxygen	0.02 m^3 h^{-1}	6.5220	0.0021	2.7192	0.0000	3.3871	0.0039	5.3413	0.0037
	0.1 m^3 h^{-1}	7.0444	0.0032	3.6128	0.0055	4.8535	0.0067	5.8686	0.0028

<MLSS of 30 g L^{-1}>

		C_{water}	STDV	24 h	STDV	48 h	STDV	72 h	STDV
Air	0.1 m^3 h^{-1}	11.0192	0.0063	ND	-	ND	-	ND	-
	0.5 m^3 h^{-1}	22.9767	0.0044	ND	-	ND	-	11.8918	0.0085
	1 m^3 h^{-1}	31.9060	0.0103	ND	-	12.8265	0.0198	14.6627	0.0088
	4 m^3 h^{-1}	66.9220	0.1196	17.2626	0.0032	21.4386	0.0262	27.7781	0.0398
Oxygen	0.02 m^3 h^{-1}	6.5220	0.0021	0.0000	0.0000	3.5731	0.0039	3.2527	0.0039
	0.1 m^3 h^{-1}	7.0444	0.0032	2.8599	0.0001	4.7332	0.0005	4.7676	0.0034

<MLSS of 40 g L^{-1}>

		C_{water}	STDV	24 h	STDV	48 h	STDV	72 h	STDV
Air	0.1 m^3 h^{-1}	11.0192	0.0063	ND	-	ND	-	ND	-
	0.5 m^3 h^{-1}	22.9767	0.0044	ND	-	ND	-	ND	-
	1 m^3 h^{-1}	31.9060	0.0103	ND	-	ND	-	ND	-
	4 m^3 h^{-1}	66.9220	0.1196	ND	-	ND	-	ND	-
Oxygen	0.02 m^3 h^{-1}	6.5220	0.0021	ND	-	ND	-	ND	-
	0.1 m^3 h^{-1}	7.0444	0.0032	ND	-	ND	-	2.7778	0.0031

3.9 Appendix 3C : Alpha factors at each MLSS

<MLSS of 4 g L^{-1}>

		24h	STDV(α)	48h	STDV(α)	72h	STDV(α)
Air	0.1 m^3 h^{-1}	0.9023	0.0361	0.8093	0.0324	0.7298	0.0337
	0.5 m^3 h^{-1}	0.9009	0.0119	0.9310	0.0268	0.9578	0.0158
	1 m^3 h^{-1}	0.9357	0.0311	0.9488	0.0495	1.0012	0.0383
	4 m^3 h^{-1}	0.9190	0.1091	0.9615	0.1141	0.9183	0.1037
Oxygen	0.02 m^3 h^{-1}	0.9686	0.0280	0.9262	0.0696	0.7991	0.0406
	0.1 m^3 h^{-1}	0.9458	0.0405	0.9793	0.0310	1.0340	0.0545

<MLSS of 10 g L^{-1}>

		24h	STDV(α)	48h	STDV(α)	72h	STDV(α)
Air	0.1 m^3 h^{-1}	0.7476	0.0275	0.7735	0.0278	0.7042	0.0589
	0.5 m^3 h^{-1}	0.8100	0.0110	0.8268	0.0605	0.9517	0.0403
	1 m^3 h^{-1}	0.8660	0.0499	0.8981	0.1067	1.0068	0.0657
	4 m^3 h^{-1}	0.8094	0.1130	0.8636	0.0933	0.8949	0.0990
Oxygen	0.02 m^3 h^{-1}	0.9406	0.0428	0.8678	0.0664	0.9395	0.0469
	0.1 m^3 h^{-1}	0.8275	0.0381	0.9054	0.0994	0.9806	0.0691

<MLSS of 20 g L^{-1}>

		24h	STDV(α)	48h	STDV(α)	72h	STDV(α)
Air	0.1 m^3 h^{-1}	ND	-	ND	-	0.4453	0.0191
	0.5 m^3 h^{-1}	0.4321	0.0200	0.5644	0.0579	0.6301	0.0331
	1 m^3 h^{-1}	0.4878	0.0129	0.6193	0.0206	0.7179	0.0178
	4 m^3 h^{-1}	0.4955	0.0574	0.6449	0.0720	0.7645	0.0823
Oxygen	0.02 m^3 h^{-1}	0.4169	0.0081	0.5193	0.0371	0.8190	0.0379
	0.1 m^3 h^{-1}	0.5129	0.0485	0.6890	0.0601	0.8331	0.0326

<MLSS of 30 g L^{-1}>

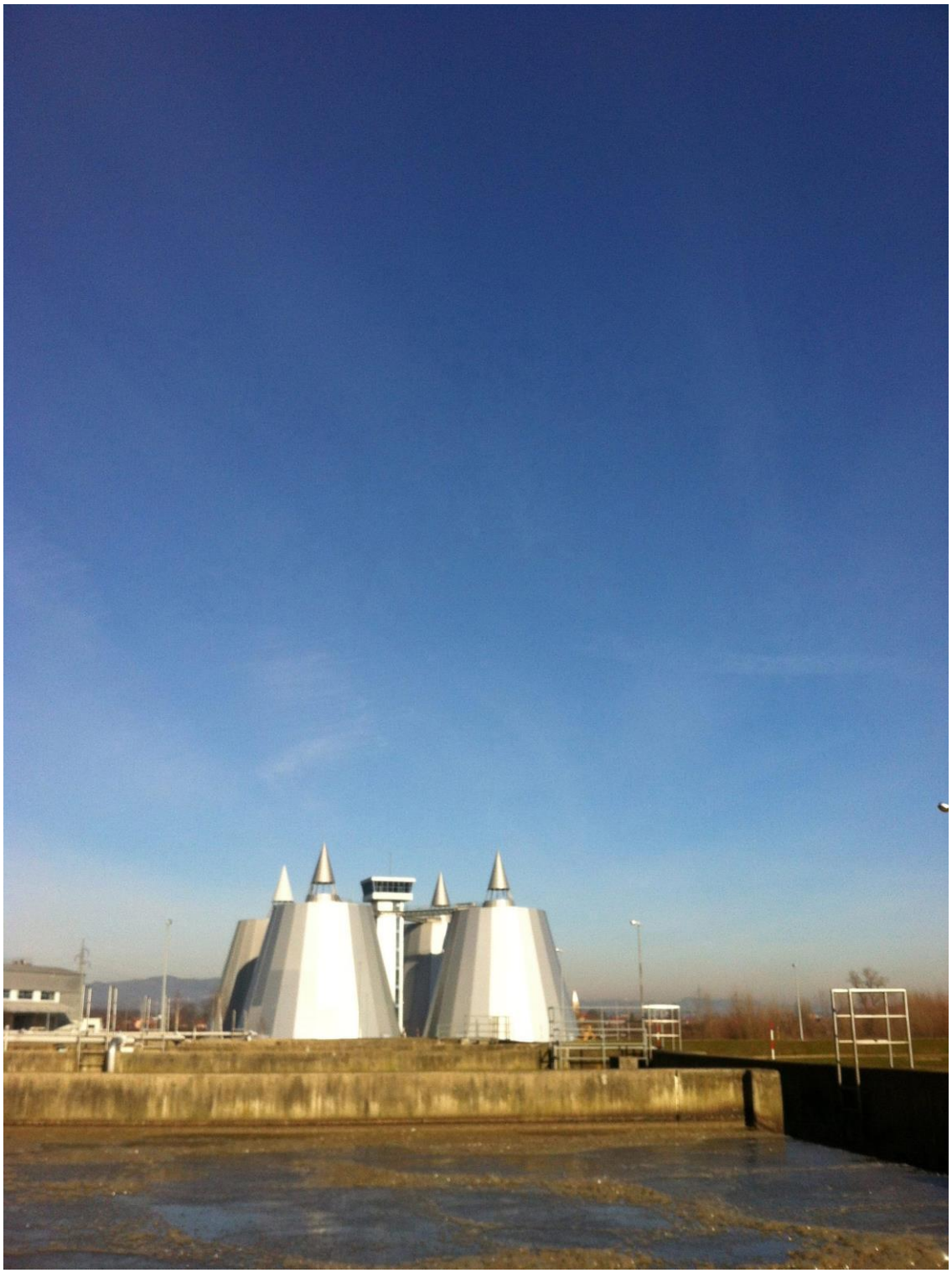
		24h	STDV(α)	48h	STDV(α)	72h	STDV(α)
Air	0.1 m^3 h^{-1}	ND	-	ND	-	ND	-
	0.5 m^3 h^{-1}	ND	-	ND	-	0.5176	0.0230
	1 m^3 h^{-1}	ND	-	0.4020	0.0381	0.4596	0.0188
	4 m^3 h^{-1}	0.2580	0.0278	0.3204	0.0416	0.4151	0.0571
Oxygen	0.02 m^3 h^{-1}	0.0000	-	0.5479	0.0372	0.4987	0.0370
	0.1 m^3 h^{-1}	0.4060	0.0109	0.6719	0.0186	0.6768	0.0345

<MLSS of 40 g L^{-1}>

		24h	STDV(α)	48h	STDV(α)	72h	STDV(α)
Air	0.1 m^3 h^{-1}	ND	-	ND	-	ND	-
	0.5 m^3 h^{-1}	ND	-	ND	-	ND	-
	1 m^3 h^{-1}	ND	-	ND	-	ND	-
	4 m^3 h^{-1}	ND	-	ND	-	ND	-
Oxygen	0.02 m^3 h^{-1}	ND	-	ND	-	ND	-
	0.1 m^3 h^{-1}	ND	-	ND	-	0.3943	0.0281

3.10 Appendix 3D: Basic parameters for steady-state modeling (for Figure 3.12)

CAS Standard	**3 g/L**	**5 g/L**	**10 g/L**	**20 g/L**	**30 g/L**	**40 g/L**
Q influent	2000 m^3/d	2000 m^3/d	2000 m^3/d	2000 m^3/d	2000 m^3/d	2000 m^3/d
bCOD	1200 g/m^3	1200 g/m^3	1200 g/m^3	1200 g/m^3	1200 g/m^3	1200 g/m^3
nb COD	20 g/m^3	20 g/m^3	20 g/m^3	20 g/m^3	20 g/m^3	20 g/m^3
TKN	120 g/m^3	120 g/m^3	120 g/m^3	120 g/m^3	120 g/m^3	120 g/m^3
TSS	500 g/m^3	500 g/m^3	500 g/m^3	500 g/m^3	500 g/m^3	500 g/m^3
VSS	400 g/m^3	400 g/m^3	400 g/m^3	400 g/m^3	400 g/m^3	400 g/m^3
Load	2400 Kg bCOD/d	2400 Kg bCOD/d	2400 Kg bCOD/d	2400 Kg bCOD/d	2400 Kg bCOD/d	2400 Kg bCOD/d
Volumetric organic loading rate (Vol OLR)	**0.95 Kg bCOD/m^3- d**	**1.58 Kg bCOD/m^3- d**	**3.17 Kg bCOD/m^3- d**	**6.33 Kg bCOD/m^3- d**	**9.49 Kg bCOD/m^3- d**	**12.70 Kg bCOD/m^3- d**
COD removed / O2 Consumption	948.6 g bCOD/Kg O_2	948.6 g bCOD/Kg O_2	948.6 g bCOD/Kg O_2	948.6 g bCOD/Kg O_2	948.6 g bCOD/Kg O_2	948.6 g bCOD/Kg O_2
Oxygen specific Vol OLR	0.38 Kg b COD/m^3-ton O_2	0.63 Kg b COD/m^3-ton O_2	1.25 Kg b COD/m^3-ton O_2	2.50 Kg b COD/m^3-ton O_2	3.75 Kg b COD/m^3-ton O_2	5.02 Kg b COD/m^3-ton O_2
SRT	10 days	10 days	10 days	10 days	10 days	10 days
MLSS	3000 g/m^3	5000 g/m^3	10000 g/m^3	20000 g/m^3	30000 g/m^3	40000 g/m^3
Volume	**2525 m^3**	**1515 m^3**	**758 m^3**	**379 m^3**	**253 m^3**	**189 m^3**
HRT	30 hours	18 hours	9 hours	5 hours	3 hours	2 hours
MLVSS/MLSS	0.67	0.67	0.67	0.67	0.67	0.67
fav	0.62	0.62	0.62	0.62	0.62	0.62
F_{XT}	758 Kg/d	758 Kg/d	758 Kg/d	758 Kg/d	758 Kg/d	758 Kg/d
Qw	253 m^3/d	152 m^3/d	76 m^3/d	38 m^3/d	25 m^3/d	19 m^3/d
	10.5 m^3/hr	6.3 m^3/hr	3.2 m^3/hr	1.6 m^3/hr	1.0 m^3/hr	0.8 m^3/hr
Foc	2530 Kg O_2/d	2530 Kg O_2/d	2530 Kg O_2/d	2530 Kg O_2/d	2530 Kg O_2/d	2530 Kg O_2/d
Fine bubble diffuser 2-7%/m 4 m	0.2	0.2	0.2	0.2	0.2	0.2
	0.95	0.9	0.8	0.45	0.2	0.01
	13315.8 Kg O_2/d	14055.6 Kg O_2/d	15812.5 Kg O_2/d	28111.1 Kg O_2/d	63250.0 Kg O_2/d	1265000.0 Kg O_2/d
Considering SOTE						
COD removed / O2 Consumption	**180.2 Kg bCOD/Ton O_2**	**170.8 Kg bCOD/Ton O_2**	**151.8 Kg bCOD/Ton O_2**	**85.4 Kg bCOD/Ton O_2**	**37.9 Kg bCOD/Ton O_2**	**1.9 Kg bCOD/Ton O_2**
Oxygen specific Vol OLR	**71.4 gr b COD/m^3-ton O_2**	**112.7 gr b COD/m^3-ton O_2**	**200.2 gr b COD/m^3-ton O_2**	**225.3 gr b COD/m^3-ton O_2**	**150.0 gr b COD/m^3-ton O_2**	**10.0 gr b COD/m^3-ton O_2**



Wastewater treatment plant of city of Zagreb located in Zagreb, Croatia. The wastewater treatment plant was designed only for carbon removal. The plant was operated as a conventional activated sludge process at a solid retention time of approximately 5 days, and at an average mixed liquor suspended solids concentration of approximately 4 g L^{-1} (Photo by Sang Yeob Kim)

Chapter 4

Oxygen transfer performance of a supersaturated oxygen aeration system (SDOX) evaluated at high biomass concentrations

This chapter is based on:

Kim SY, Garcia HA, Lopez-Vazquez CM, Milligan C, Herrera A, Ćurko J, Matošić M, Brdjanovic D (2020) Oxygen transfer performance of a supersaturated oxygen aeration system (SDOX) evaluated at high biomass concentrations. *Process Safety and Environmental Protection* 139:171–181. https://doi.org/10.1016/j.psep.2020.03.026

Abstract

Oxygen transfer in wastewater treatment is significantly influenced by the mixed liquor suspended solids (MLSS). The effect is more pronounced at MLSS concentrations higher than 20 g L^{-1} when supplying air by conventional diffused aeration systems. The oxygen transfer performance of a supersaturated oxygenation technology (i.e., the supersaturated dissolved oxygen(SDOX)system) was evaluated in clean water and at MLSS concentrations from 4 to 40 g L^{-1} as a promising technology for uncapping such limitation. The SDOX exhibited oxygen mass transfer rate coefficients(K_La) values in clean water lower than for fine bubble diffusers. However, higher oxygen transfer rates (OTR)s and alpha factors (mass transfer ratio of process-water to clean-water) as a function of the MLSS concentration were observed. A standard oxygen transfer efficiency (SOTE) of approximately 100% in clean water was reported. The SDOX technology can be presented as a promising alternative for supplying dissolved oxygen (DO)into mixed liquor solutions; particularly, at the high MLSS concentrations required by the high-loaded membrane bioreactor systems (HL-MBR) and aerobic digesters.

4.1. Introduction

Supplying DO into conventional activated sludge (CAS) wastewater treatment plants (WWTP) is an inefficient and costly process. It may represent up to 75% of the total operational costs of a WWTP (Reardon, 1995; Rosso et al. 2008). The oxygen transfer in CAS systems is highly influenced by the MLSS and other substances present in the liquid phase. Particularly, this negative effect has been clearly observed and reported when supplying air into CAS systems utilizing conventional diffused aeration systems (e.g. fine and coarse bubble diffusers) (Cornel et al. 2003; Durán et al. 2016; Germain et al. 2007; Henkel et al. 2011; Krampe and Krauth 2003; Muller et al. 1995). In particular, at MLSS concentrations higher than 20 gL^{-1}, the alpha factor is severely affected (Cornel et al. 2003; Durán et al. 2016; Germain et al. 2007; Henkel et al. 2011; Kim et al. 2019; Krampe and Krauth 2003; Muller et al. 1995). Beyond that MLSS concentration it is either not technically feasible (due to hardware limitations) or extremely inefficient to supply DO (because of the higher associated costs).

Operating an activated sludge WWTP at high MLSS concentrations may introduce certain benefits compared to CAS systems. Among others: (i) higher organic loading rates can be efficiently treated; (ii) footprint can be reduced; and (iii) longer solid retention times (SRT)s can be applied. Membrane bioreactor (MBR) systems are arguably the most suitable technology to be operated at high MLSS concentrations. Advantages of MBRs include: (i) the production of a high quality treated wastewater able to comply with strict effluent discharge standards; (ii) lower generation of digested sludge (compared to CAS systems) at longer SRTs; and (iii) more robust systems able to handle severe shock loads (Henze et al. 2008; Mannina and Cosensza, 2013; Pollice et al. 2008). Moreover, if, for instance, MBRs can be operated at higher than usual MLSS concentrations (e.g. higher than 20 gL^{-1}) the system footprint and sludge generation can be further reduced lowering the capital and operational costs (Barreto et al. 2017; Livingston, 2010). This concept of an MBR operated at high MLSS concentrations (from approximately 15 to 40 g L^{-1}) was introduced by Kim et al. (2019) and presented as the HL-MBR. A HL-MBR can also bring the opportunity to design more compact and containerized mobile wastewater treatment systems that can be suitable for on-site and/or decentralized municipal and/or industrial wastewater treatment applications. Also, such containerized HL-MBR systems can be considered as an alternative for the provision of sanitation after the occurrence of natural disasters (Barreto et al. 2017; Zakaria et al. 2015). However, Kim et al. (2019) reported that, if conventional aerations systems are used, it is neither technically nor economically feasible to operate such systems at MLSS concentrations higher than 20 g L^{-1}. Notwithstanding the intrinsic benefits offered by both conventional MBR and HL-MBR, there is a need for more efficient oxygen supply systems able to work at MLSS concentrations higher than 20 g L^{-1} in an economic manner. Similar constraints and needs can be found when applying other aerobic biological wastewater treatment systems designed to be operated at high sludge concentrations (such as aerobic digesters).

Different innovative, non-conventional aeration technologies have been recently proposed to enhance the oxygen transfer process. Aeration processes such as the deep-shaft (U-Tube contactor or vertical shaft), high purity oxygen (HPO) aeration systems, and pressurized oxygenation systems (supersaturated oxygen aeration systems) have been developed to enhance the OTR and oxygen transfer efficiency (OTE) (Xu et al. 2016). Most of these systems rely on increasing the amount of DO in the liquid phase by increasing the partial pressure of oxygen in the gas phase (Gray, 2004). Such systems can achieve high OTEs of up to 90% (Mueller et al. 2002). The disadvantages of these technologies historically include the high capital, operation, and maintenance costs. Besides, most of them have not been tested at MLSS concentrations higher than 20 g L^{-1} (Ball and Humenick, 1972; Bernat et al. 2017; Singh, 2017).

Among the non-conventional aeration systems, the supersaturated oxygen aeration systems have been developed for working with HPO and at high-pressure conditions achieving higher OTRs (Berktay and Ellis, 1997; Jin et al. 2010). The two most relevant supersaturated oxygen aeration technologies include the Speece cone technology and the SDOX system. The Speece cone technology consists of a down flow conical bubble contact chamber connected to an HPO source. The Speece cone technology was first developed for lake and river restoration (Ashley et al. 2008). Recently, Barreto et al. (2017, 2018) evaluated the Speece cone as an alternative technology for supplying DO on biological wastewater treatment applications. The authors evaluated the performance of an MBR provided with a Speece cone system at several operational conditions in clean water and fed municipal wastewater. The Speece cone system appears as a promising technology for supplying DO at high MLSS concentrations in biological wastewater treatment systems. However, the oxygen transfer performance of such technology needs to be further evaluated at a high MLSS concentration range. The SDOX system is a novel alternative to supply DO into biological wastewater treatment systems. It consists of a pressurized chamber operated at a high pressure (> 800 kPa) connected to an HPO source. A stream of the mixed liquor to be oxygenated is recirculated through the pressurized chamber where it gets in contact with the HPO at the high-pressure conditions in the chamber (CDM Smith, 2012). The influent stream enters at the top of the pressurized chamber, where a large gas-liquid interface is created between the wastewater and pure oxygen. Under pressure, the oxygen is quickly and efficiently dissolved into the wastewater. The oxygen-supersaturated stream is returned back to the receiving basin through specially designed distribution pipes. The high-pressure conditions exerted in the pressurized chamber allows reaching DO concentrations of up to 350 mg L^{-1} (Jones, 2010), higher than other technologies. OTEs higher than 95% have been reported for the SDOX system (https://www.blueingreen.com 2018).However, the SDOX technology has been mostly evaluated for lake and river restoration. Thus, no information has been reported in the literature regarding the performance of the SDOX system in activated sludge mixed liquors, despite the potential advantages and benefits that this technology can offer in terms of (i) reaching highly-supersaturated DO concentrations, (ii) higher OTE, (iii) easiness to install, and (iv) relatively lower maintenance and operational needs than other aeration systems. As such, there is a need to evaluate the performance of the SDOX at higher

MLSS concentrations (> 20 g L^{-1}) in biological wastewater treatment systems, and this research addressed those needs.

The main objective of this research was to evaluate the oxygen transfer performance of an SDOX system at a high MLSS concentration range of 4 to 40 g L^{-1}. The K_La, the maximum standard oxygen transfer rates (SOTR)s, the SOTE, and the alpha factors were determined. Moreover, the energy requirements of the SDOX system as a function of the MLSS concentration are presented and compared to the energy requirements of conventional diffused aeration systems. If the SDOX technology is successful at such MLSS concentration range, the limitations imposed by conventional diffused aeration for working at high MLSS concentrations may be uncapped, promoting the implementation of HL-MBR units and achieving the benefits that such systems can bring.

4.2 Materials and Methods

4.2.1 SDOX unit modification

The most important part of this experiment was that the pressure in the SDOX pressurized chamber must be kept constant so that the OTE can be accurately calculated. Prior to experiments for data analysis, the SDOX unit was inspected through preliminary experiments. As the injected oxygen was leaked out of the system frequently through the pipelines connected to the SDOX system, the entire system was repaired. As shown in Figure 4.1, the entire system, including the SDOX pressurized chamber, was originally made of metal materials. All metal materials were replaced with polyurethane tubes, and the leakage in the SDOX pressurized chamber itself was repaired by welding. Figure 4.1 shows the overall repair process for the SDOX system.

4.2.2 Design of experiments

The oxygen transfer performance of the SDOX system was evaluated in clean water and in activated sludge mixed liquor at MLSS concentrations of approximately 4, 10, 20, 30, and 40 g L^{-1}. Fresh mixed liquor (activated sludge) was taken from the municipal WWTP of the city of Zagreb (Zagreb, Croatia). The initial and original concentration was approximately 4 g L^{-1}. Thus, the sludge was concentrated up to the desired target MLSS concentrations. At each of the evaluated experimental conditions, the oxygen transfer performance of a bench-scale SDOX system was assessed determining the K_La, the maximum SOTR, and the alpha factors. Moreover, the SOTE of the SDOX system was also determined in clean water. In all the evaluations, the oxygen intrusion from the atmosphere was also evaluated and incorporated into the oxygen transfer performance assessment.

4.2.3 Analytical methods

The MLSS and mixed liquor volatile suspended solids (MLVSS) concentrations were analysed according to Standard Methods (APHA, 1998). The temperature and DO were determined with

a DO probe (WTW Oxi 3310, Germany). The pH was determined with a pH probe (SI Analytics GmbH, Germany). Both the DO and pH determinations were corrected by the actual temperature. The particle size distribution (PSD) was determined using a Malvern Mastersizer 2000 laser diffraction particle counter (Malvern Instruments Ltd, Malvern, UK).

Figure 4.1 Repairing the SDOX unit

4.2.4 Oxygen uptake rate

The oxygen uptake rate (OUR) determinations were carried out with a biological oxygen meter (BOM) based on the batch respirometric method (Kappeler and Gujer (1992)). The BOM consisted of a glass container equipped with a DO probe (WTW Oxi 3310, Germany), and a stirring plate (IKA® RH B2, Germany). A Master flex peristaltic pump (Cole-Parmer, U.S.A) recirculated the sludge from the aerobic reactor under evaluation through the BOM. When the BOM was filled with the activated sludge, the pump was stopped and the decrease of the DO as a function of time was monitored and recorded by the DO probe. After determining the OURs, the sludge was returned back to the reactor. A DO range from 6.5to 2.5 mg $L^{-1}$was used to calculate the OURs. OURs were determined in triplicate before and after conducting each specific experiment. The average value of the calculated OUR from each experiment was used for the determination of the reported K_La.

4.2.5 Experimental procedures

4.2.5.1 Collection and preparation of the sludge

Fresh activated sludge was collected from the WWTP of the city of Zagreb in Croatia. The WWTP was designed only for organic matter removal. The plant was operated as a CAS process at an SRT of approximately 5days and at an average MLSS concentration of approximately 4 g L^{-1}. As shown in Figure 4.2, the sludge was collected from one of the aerobic basins at the WWTP. The sludge was thickened by either gravity settling or membrane filtration to reach the desired MLSS concentrations. For reaching the lower range of MLSS concentrations (i.e., 4 and 10 g L^{-1}) the sludge was concentrated mostly by gravity settling at the WWTP facility. To reach the higher range of evaluated MLSS concentrations (i.e., 20, 30 and 40 g L^{-1}) the sludge was thickened by membrane filtration. A rectangular based (24×24×93 cm) 40 L bench-scale MBR provided with vertically submerged hollow fibre membranes (Zenon ZeeWee^{TM}-10, 0.4 µm pore size, 0.92 m^2 surface area) was used to concentrate the sludge. Sludge with a starting MLSS concentration of approximately 10 g L^{-1} achieved by gravity settling was introduced into the MBR and concentrated to the desired sludge concentration. The sludge transport time from the WWTP to the laboratory, where the sludge concentration step was conducted, was less than an hour.

4.2.5.2 Experimental setup

The schematic experimental setup is described in Figure 4.3. The setup consisted of a biological reactor with a working volume of approximately 5 L. The biological reactor was equipped with a mixer that had a propeller length of approximately 0.25 m (Heidolph instruments GmbH, RZR 2102 control, Germany). The reactor was provided with a DO probe connected to a data logger (WTW Oxi 3310, Germany) and with a pH probe (SI Analytics GmbH, Germany). The BOM equipment was placed next to the biological reactor to determine the OUR. The DO was supplied to the biological reactor by means of a bench-scale SDOX system. The bench-scale SDOX system consisted of a pressurized chamber connected to an HPO source (Figure 4.3).

Figure 4.2 Sludge preparation

A sludge stream was recirculated from the biological reactor through the SDOX system; the sludge stream was supersaturated with pure oxygen at the high-pressure conditions in the pressurized chamber. The supersaturated sludge stream was then released from the pressurized chamber back into the biological reactor introducing in such way the DO into the reactor. The pressurized chamber had a total volume of approximately 2.75 L. Approximately 40% of that volume (1.1 L) was occupied by the solution to be oxygenated, while the 60% remaining (1.65 L) consisted of the headspace of the pressurized chamber. The pressure at the pressurized chamber was set at 500kPa for the entire series of experiments carried out. Figure 4.4 displays a bench-scale of SDOX pressurized chamber.

The pressurized chamber was provided with two analogic pressure gauges (McDaniel Controls, USA). Moreover, both a pressure digital sensor (SICK AG, Germany) and a level digital sensor (Setra Systems, USA) were also located at the pressurized chamber. An electro-pneumatic valve (NVF3-MOH-5/2-K-1/4-EX, FESTO, Germany) was also placed at the effluent drainage of the pressurized chamber. The pressure sensors, level sensors, and the electro-pneumatic valve were used to monitor and control the level and pressure of the pressurized chamber by the aid of a program logic controller (PLC) system.

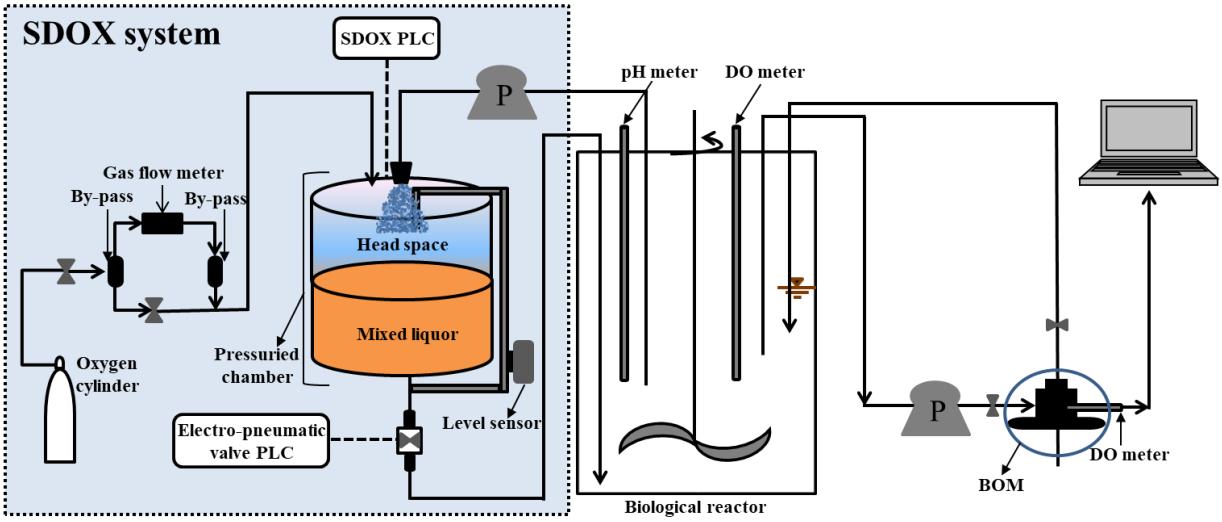


Figure 4.3 Schematic diagram of the SDOX system with a bioreactor using pure oxygen used in this study

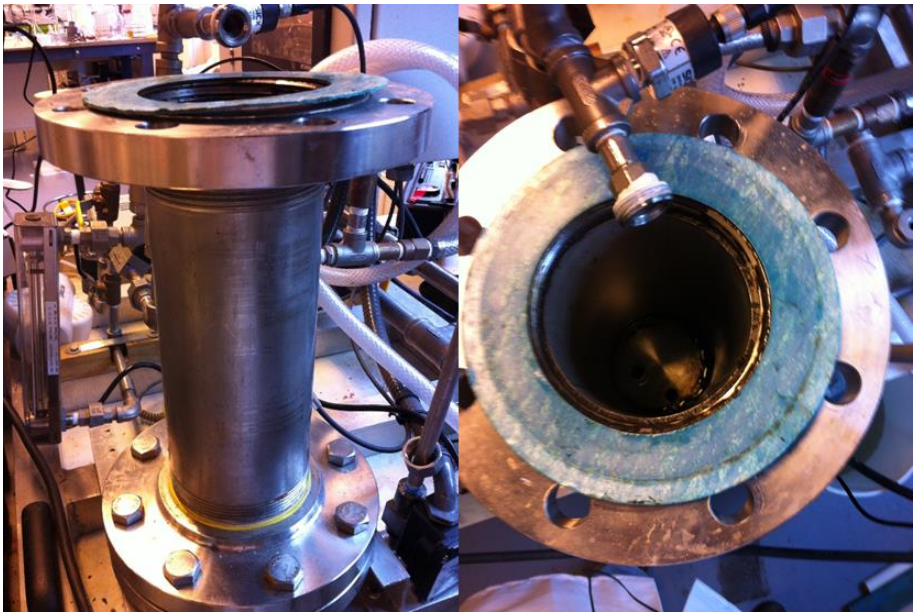


Figure 4.4 Bench-scale of SDOX pressurized chamber

The sludge stream was introduced into the pressurized chamber of the SDOX system through a 6 mm orifice (as shown in Figure 4.5) by a high-pressure peristaltic pump (EW-74203-24, Cole-Palmer, USA). A flowrate of approximately 0.825 L min^{-1} was set on the peristaltic pump for all the evaluated experimental conditions. The supersaturated sludge was released back to the biological reactor on a semi-continuous way by the action of the electro-pneumatic valve connected to the PLC system. The opening intervals of the valve were properly adjusted to maintain a constant flow of the sludge out of the pressurized chamber, so a constant level could be maintained in the pressurized chamber. The pure oxygen was supplied into the pressurized chamber from a pure oxygen cylinder (MESSER, Croatia) through a gas flow meter provided

with mass totalizer capacities (Model # 32908-59, Cole-Palmer, USA). In practice, the SDOX system is operated in a continuous fashion, constantly pumping water through the saturation vessel and constantly discharging the oxygenated solution back into the process.

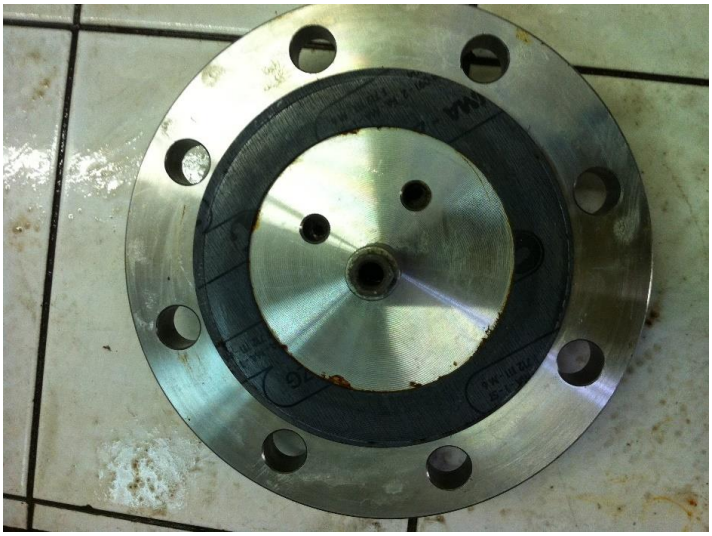


Figure 4.5 Upper part of SDOX pressurized chamber with 6 mm orifice

In general, the smaller the orifice size, the smaller droplets are formed, resulting in higher oxygen transfer. Before proceeding with oxygen transfer experiment, a nozzle was attached to the orifice (Figure 4.6, upper), but the nozzle was frequently blocked by impurities (Figure 4.6, bottom). In the case of lab-scale unit, the nozzle size is so small that this blockage occurs, but which will not occur at either pilot-scale or full-scale since the nozzle size is much bigger than that of lab-scale.

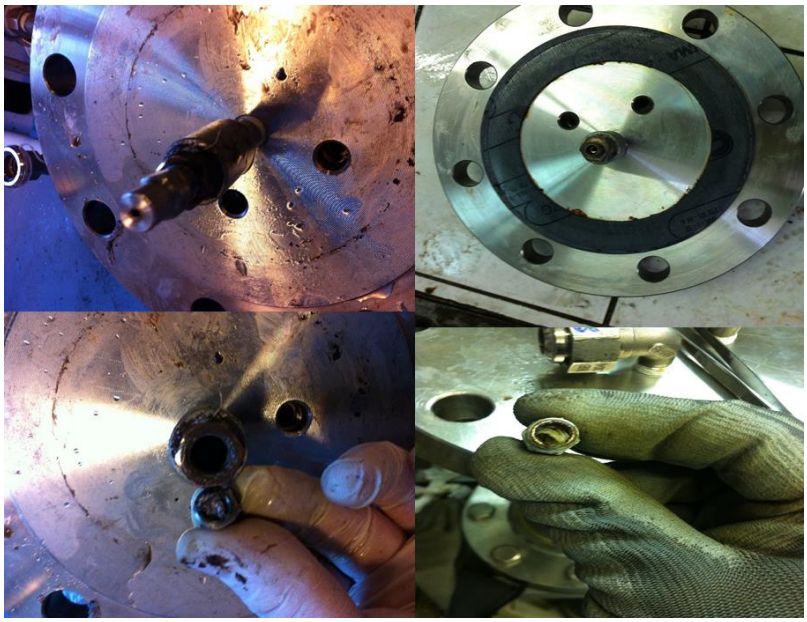


Figure 4.6 SDOX pressurized chamber with different nozzles (upper) and nozzles clogged with impurities (bottom)

The oxygen transfer performance of the SDOX system was evaluated by measuring the DO transfer performance in the biological reactor operated with clean water and then with sludge at MLSS concentrations of 4, 10, 20, 30, and 40 g L^{-1} To determine the SOTE of the SDOX system in clean water some minor modifications were introduced to the experimental setup. A 100 L biological reactor was used to monitor the OTE on the system for a longer period. Moreover, the recirculation flowrate from the biological reactor to the SDOX system was set at 0.225 L min^{-1}. All the rest of the operational conditions remained unchanged.

4.2.5.3 Air intrusion experiments

The oxygen intrusion from the atmosphere into the biological reactor was evaluated and considered in the subsequent calculations. The K_La due to air intrusion in clean water was determined by the non steady-state batch test in clean water (WEF and ASCE 2001). Nitrogen was sparged into the reactor until reaching a DO concentration below approximately 0.5 mg L^{-1}. Then, the mixer was started at an identical mixing intensity as to be used in the oxygen transfer experiments. The DO concentration was continuously monitored and recorded until reaching a DO concentration of approximately the DO atmospheric saturation value. The K_La value was then calculated by a non-linear regression carried out with the aid of the Microsoft Excel software add-in SOLVER getting the best fit between the measured and calculated DO as described in Barreto et al. (2018).

4.2.5.4 Oxygen transfer performance experiments in clean water

The K_La values in clean water were determined by the non-steady state batch test in clean water (WEF and ASCE 2001). The biological reactor was filled with tap water. The DO concentration was depleted by sparging nitrogen gas until measuring a DO concentration below 0.5 mg L^{-1}. Then, the SDOX unit was started to supply the DO into the biological reactor. The DO concentration was continuously monitored and recorded in the biological reactor until reaching a stable DO concentration. The K_La value was calculated as described in section 4.2.5.3 Air intrusion experiments. The oxygen intrusion from the atmosphere was taken into account for adjusting the K_La values in clean water. The experiments were conducted in triplicate, and an average K_La value was reported. The SOTEs were determined and reported when using the 100 L biological reactor as described in Barreto et al. (2018).

4.2.5.5 Oxygen transfer performance experiments in the mixed liquor

The sludge collected from the WWTP and concentrated up to the desired MLSS concentration was aerated overnight prior to the experiments. The values of K_La of the sludge at the evaluated concentrations were determined by the non steady-state batch-test under endogenous respiration conditions (WEF and ASCE 2001). The experiments were conducted from the most concentrated MLSS concentration (approximately 40 g L^{-1}) to the most diluted MLSS concentration (approximately 4 g L^{-1}). For all the evaluated experimental conditions, the same experimental procedure was carried out as follows. The reactor was filled with mixed liquor at the desired MLSS concentration. The DO concentration was depleted by sparging nitrogen gas

until the DO concentration dropped below 0.5 mg L^{-1}. Then, the SDOX unit was started thus introducing DO into the biological reactor. The DO concentration was continuously monitored and recorded in the biological reactor until reaching a stable DO concentration. The OURs were determined before and after each evaluation as described in Section 4.2.4 Oxygen uptake rate. Moreover, samples were taken at the end of each evaluation to determine the MLSS, MLVSS, and PSD. The K_La value was calculated by conducting a non-linear regression with the aid of the Microsoft Excel software add-in SOLVER as described in Section 4.2.5.3 Air intrusion experiments. Thus, the values were corrected considering the oxygen intrusion from the atmosphere. The experiments were performed in triplicate and the average K_La was reported for each experimental condition. All the determined K_La values were corrected to the standard environmental temperature (20 ℃). The alpha factors and the maximum SOTR were calculated and reported as described in Barreto et al. (2018). Figure 4.7 shows the SDOX oxygen transfer experimental set up used in the actual experiment.

Figure 4.7 SDOX oxygen transfer experimental set up

4.3 Results and Discussion

The objective of this research was to evaluate the oxygen transfer performance of the SDOX system at different MLSS concentrations. The K_La, maximum SOTR, SOTE, and alpha factors were determined. The energy requirements of the SDOX system as a function of the MLSS concentration are presented and compared to the energy requirements of conventional diffused aeration systems.

4.3.1 Impact of sludge concentrations on the oxygen transfer parameters of SDOX system

The K_La values and SOTR (Figure 4.8a) were determined both in clean water and at each of the evaluated MLSS concentrations. The values reported at an MLSS concentration of zero g L^{-1} corresponds to the evaluations carried out in clean water. Both the K_La value and SOTR (Figure 4.8a) decreased exponentially as a function of the MLSS concentrations.

A K_La value of approximately 2.6 h^{-1} was obtained for the SDOX system when working in clean water (Figure 4.8a) at the evaluated experimental conditions. The K_La values in clean water were also determined on previous research conducted by the same authors (Kim et al. 2019) carried out at the same experimental conditions used in this research, but using a fine bubble diffuser (SANITAIRE® Silver Series 2, Xylem, USA). Kim et al. (2019) reported K_La values in clean water of 11, 23, 32, and 64 h^{-1} at the specific airflow rates (AFRs) of 5, 25, 50, and 200 m^3_{AIR} m^{-3} h^{-1}, respectively. That is, higher K_La values in clean water were reported when using fine bubble diffusers as compared to this research with the SDOX system.

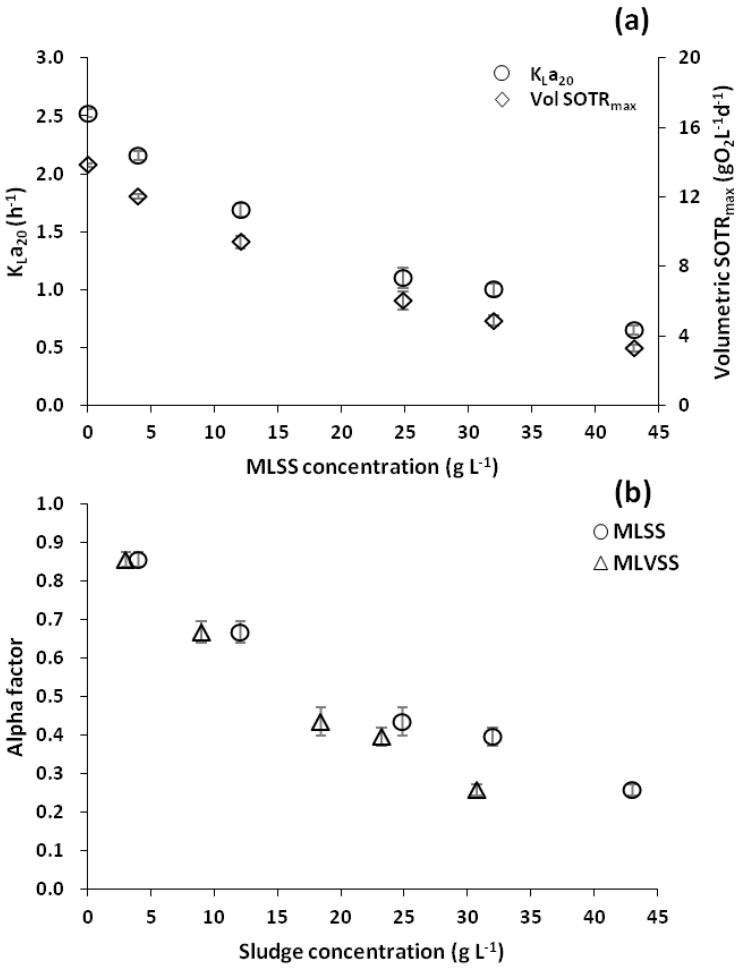


Figure 4.8 (a) Oxygen mass transfer rate coefficient (K_La) and maximum volumetric standard oxygen transfer rates(SOTRs) as a function of the MLSS concentrations; (b)Alpha factors as a function of MLSS and MLVSS concentrations

However, the evaluation carried out with fine bubble diffusers were performed at specific AFRs ranging from 5 to 200 m^3_{AIR} m^{-3} h^{-1} that are higher than the specific AFRs commonly used in full-scale WWTPs (typically ranging from approximately 1 to 7 m^3_{AIR} m^{-3} h^{-1}) (Cornel et al. 2003; Krause et al. 2003). When comparing the K_La value obtained in this research with the K_La value obtained by Kim et al. (2019) at the lowest evaluated specific AFR of 5 m^3_{AIR} m^{-3} h^{-1} (typical AFRs applied in full-scale systems), still, higher K_La values were reported when using the fine bubble diffusers (11 h^{-1}) compared to the SDOX system (2.6 h^{-1}); however, the differences are not that considerable. Therefore, the SDOX system in clean water exhibited a K_La value lower than the K_La values reported for fine bubble diffusers at full-scale relevant specific AFRs. Henkel (2010) also reported the K_La values in clean water when introducing DO by means of both fine and coarse bubble diffusers at specific AFRs ranging from 2 to 5 m^3_{AIR} m^{-3} h^{-1}. When using fine bubble diffusers the K_La values reported were similar to those observed by Kim et al. (2019). However, when using coarse bubble diffusers lower K_La values were reported (4 h^{-1} at a specific AFR of 3 m^3_{AIR} m^{-3} h^{-1}) closer to the K_La values reported for the SDOX system (2.6 h^{-1}). Therefore, the K_La values obtained for the SDOX system in clean water were lower than the commonly reported K_La values for fine bubble diffusers in clean water and similar to the K_La values reported for coarse bubble diffusers. The K_La values in clean water have also been evaluated and reported for other supersaturated oxygen delivery technologies such as the Speece cone system (Barreto et al. 2018). Barreto et al. (2018) evaluated the oxygen transfer performance of a Speece cone system and the reported K_La value of approximately 2.0 h^{-1} in clean water, which is similar to the K_La value obtained for the SDOX system (2.6 h^{-1}).

The maximum SOTR was also determined in clean water and reported as the volumetric maximum SOTR (Figure 4.8a). A volumetric maximum SOTR of 14 g O_2 L^{-1} $d^{-1}$was observed in clean water at the evaluated operational conditions. Kim et al. (2019) reported volumetric maximum SOTR in clean water of 2.4, 5.0, 7.0, and 14.6 g O_2 L^{-1} d^{-1} at specific AFRs of 5, 25, 50, and 200 m^3_{AIR} m^{-3} h^{-1}, respectively, at the same experimental conditions but using a fine bubble diffuser. Despite that the SDOX system exhibited lower K_La values than the fine bubble diffuser, higher volumetric maximum SOTRs were obtained,in particular, when comparing to the lowest (and more realistic) specific AFRs evaluated by Kim et al. (2019). At a specific AFR of 5 m^3_{AIR} m^{-3} h^{-1}, Kim et al. (2019) observed a volumetric SOTR of 2.4 g O_2L^{-1} d^{-1} and a K_La of 11 h^{-1} compared to a volumetric SOTR of 14 g O_2 L^{-1} d^{-1} obtained with the SDOX at a K_La of 2.6 h^{-1}. The SDOX system was operated with pure oxygen under pressurized conditions, while the fine bubble diffuser reported by Kim et al. (2019) was operated with air at approximately atmospheric pressure. These differences may explain the higher volumetric maximum SOTR of the SDOX system. Without considering any energy consumption or OTE aspects (discussed later on in this manuscript), the advantages introduced by the SDOX system capable of working at high-pressure conditions and fed pure oxygen may overcome the lower K_La values (when compared to the fine bubble diffusers). In this regard, the SDOX system can reach higher OTRs compared to conventional bubble diffusers, regardless the K_La values.

The alpha factors of the SDOX system were determined as a function of the MLSS and MLVSS concentrations (Figure 4.8b). As expected, the alpha factors followed a similar trend like the K_La values presented in Figure 4.8a. Alpha factors of approximately 0.9 and 0.3 were reported at the MLSS concentrations of approximately 5 and 45 g L^{-1}, respectively. The alpha factors exponentially decreased as a function of the MLSS concentration, while they linearly decreased as a function of the MLVSS concentration (Figure 4.8b).

As observed in Figures 4.8a and 4.8b, the K_La values, and consequently the alpha factors, were negatively affected by the MLSS concentration. The impact is more noticeable at the highest evaluated MLSS concentrations. Particularly, the higher the concentration of the suspended solids in the mixed liquor, the higher the limitations imposed for the oxygen to diffuse from the gas phase (pure oxygen) into the liquid phase (mixed liquor). This observation is in line with previously reported studies evaluating the relationship between the oxygen transfer (expressed as alpha factor) and the MLSS concentration for conventional diffusers, both at the very same experimental conditions as in this research (Kim et al. 2019), as well as at other different experimental conditions (Cornel et al. 2003; Germain et al. 2007; Gunder 2000; Henkel et al. 2009a; Krampe and Krauth 2003; Muller et al. 1995). Most of the authors concluded that the oxygen transfer is considerably inhibited by the presence of high MLSS concentrations, although an exact correlation could not be established due to differences in the operational conditions such as the AFRs, reactor configurations, sludge characteristics, types of influent wastewater and aeration systems, among others.

Generally, the larger the MLSS concentration, the more noticeable the impact of the suspended solids impeding the oxygen molecules in the gas phase to diffuse into the liquid phase. However, Henkel (2010) concluded, and as observed in our research, that the volatile fraction of the MLSS concentration (i.e., the MLVSS) tends to limit the oxygen transfer process. Moreover, the author reported a direct correlation between the alpha factor and the MLVSS concentration. Firstly, the author reported a reduction in the available gas/liquid interfacial oxygen transfer area due to the accumulation of volatile solids on such transfer area. Henkel et al. (2009b) examined the particular impacts of the volatile suspended solids of the sludge flocs on the gas-liquid interface. The sludge flocs are inclined to make contact with the gas surface area because of the inherent partially hydrophobic surface of the sludge flocs and the hydrophobicity of the gas-liquid interface. The authors observed that as the MLVSS concentrations increased, the gas-liquid interface area was covered with a higher amount of sludge flocs. This reduces the net interfacial area available for the oxygen transfer. Secondly, there is a direct dependence of the sludge floc volume determining the free water content of the solution. The MLVSS concentration relates to the microorganisms and extracellular polymeric substances (EPS) content of the sludge, which consists primarily of water (Raszka et al. 2006). The more water bound in the sludge by the organic matter, the larger the volume that the floc occupies and the less free water available for the undisturbed oxygen transfer from the gas to the liquid phase. The MLVSS component of the sludge not only reduces the net interfacial area available for the

oxygen transfer to occur but also increases the difficulty for the oxygen molecules to diffuse into the liquid phase. Therefore, the MLVSS concentration tends to exhibit a direct negative impact on the oxygen transfer rather than the MLSS concentration. Similar findings were obtained in our research. Figure 4.8b shows an exponential decrease of the alpha factor as the MLSS concentration increases. However, Figure 4.8b shows a direct negative relationship between the alpha factor and the MLVSS confirming the direct impact of the volatile solids fraction, as reported by Henkel (2010) and Henkel et al. (2009b).

4.3.2 Impact of different aeration systems (SDOX *versus* fine bubble diffuser) on the alpha factor

Figure 4.9 shows a comparison between the alpha factors obtained in the current research when the DO is supplied with an SDOX system, and the alpha factors obtained in the research performed by Kim et al. (2019) working in the same experimental conditions but supplying oxygen by means of a fine bubble diffuser. The same sludge was used in both evaluations (in the present research and by Kim et al. 2019), so the comparison of the alpha factor as a function of the MLVSS concentration between the two studies is not influenced by the characteristic of the sludge. Almost the same alpha factors were reported at MLSS concentrations below 20 g L^{-1}. However, above that MLSS concentration higher alpha factor values were reported by the SDOX system compared to the fine bubble diffusers, even at the highest specific AFRs provided by the fine bubble diffusers.

Regarding the alpha factors, Figure 4.9 shows a higher performance of the SDOX system compared to the use of fine bubble diffusers. The better performance could be inherent to the SDOX technology used in this study, which is conceptually and technologically different than diffused aeration systems as described previously. However, despite the potential technological advantages exhibited by the SDOX system, the K_La values reported in clean water for the SDOX system were not higher than those of fine bubble diffusers. Rather, lower K_La values were reported for the SDOX system when compared to fine bubble diffusers, but similar to coarse bubble diffusers. Therefore, the technological features of the SDOX system seemed not to enhance the oxygen mass transfer performance from the mass transfer rate coefficient perspective (compared to fine and coarse bubble diffusers), but the SDOX seems to reduce the negative effects of the mixed liquor on the oxygen transfer (as reflected by the higher alpha factors observed at higher concentrations). Moreover, because the SDOX system can work with pure oxygen and under pressurized conditions, it can reach higher OTRs than fine bubble diffusers in spite of the lower K_La values.

In the SDOX system, the structure and morphology of the sludge can change due to the high-pressure conditions set in the SDOX chamber, and due to the high shear effects at which the sludge is exposed (when pumping the sludge into and out of the pressurized compartment). These changes on the sludge properties could have a strong influence on the oxygen transfer process. Figure 4.10 shows the changes in the PSD of the sludge as a function of the exposure

time inside the SDOX system at different MLSS concentrations. As observed in Figure 4.10, a considerable reduction of the average particle size was observed at all the evaluated MLSS concentrations. Specifically, the exposure of the sludge mixture to the conditions of the SDOX system creates a shift in the PSD of the sludge decreasing substantially the average size of the flocs.

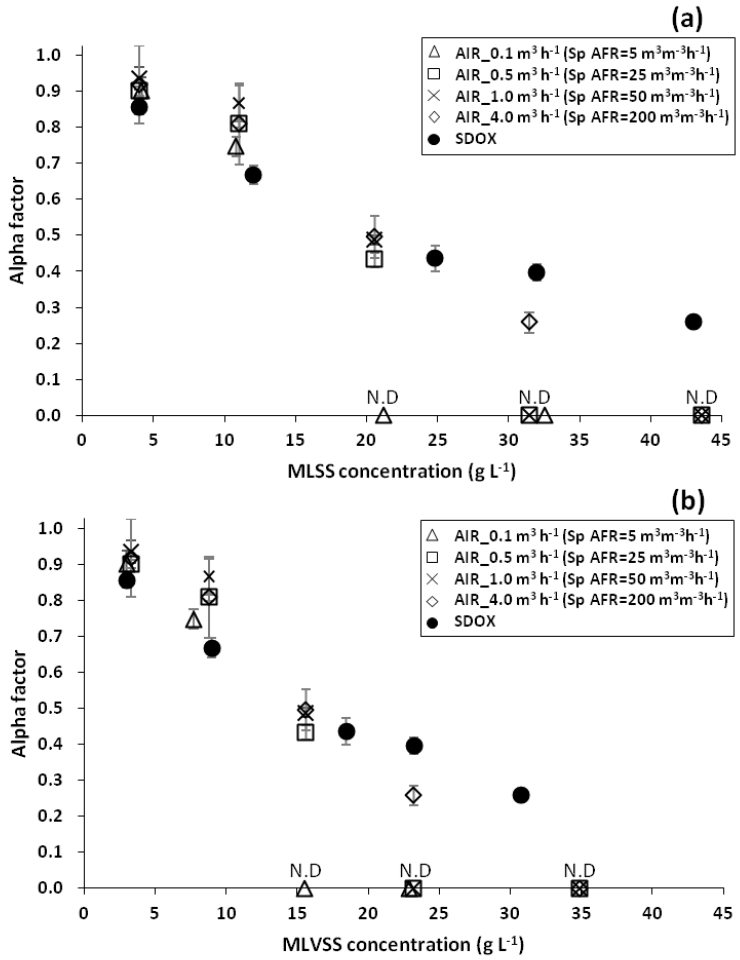


Figure 4.9 Alpha factors determined in this study as a function of the MLSS concentration by the SDOX system compared to the alpha factors reported by Kim et al. (2019) as a function of the MLSS concentration obtained by fine bubble diffusers at AFR of 0.1, 0.5, 1.0, and 4.0 m^3 h^{-1} (specific AFRs of 5, 25, 50, and 200 m^3_{AIR} m^{-3} h^{-1})

As such, the average sludge floc size decreased approximately ten times from approximately 200 µm to 30 µm in all the evaluated conditions. The "smashing" effects of the SDOX system may not only reduce the size of the flocs but eventually reduce its water content. Therefore, this effect could be the reason why the oxygen transfer increases by (i) reducing the specific area of the flocs that "obstruct" the gas/liquid oxygen transfer area; and (ii) increasing the free water available for an undisturbed oxygen transfer between the gas phase and liquid phase due to the reduction of the water content of the flocs. The effects of the reduction of the particle size are shown in Figure 4.9 where alpha factor values were almost undetectable in the fine bubble

diffuser system at MLSS concentrations higher than 20 g L^{-1}, while alpha factors ranging from approximately 0.4 to 0.2 were obtained in the SDOX system within the same MLSS concentrations range. Therefore, the SDOX system can deliver DO at higher OTRs, and at the same time reach alpha factor values higher than those reached with fine bubble diffusers at high MLSS concentrations.

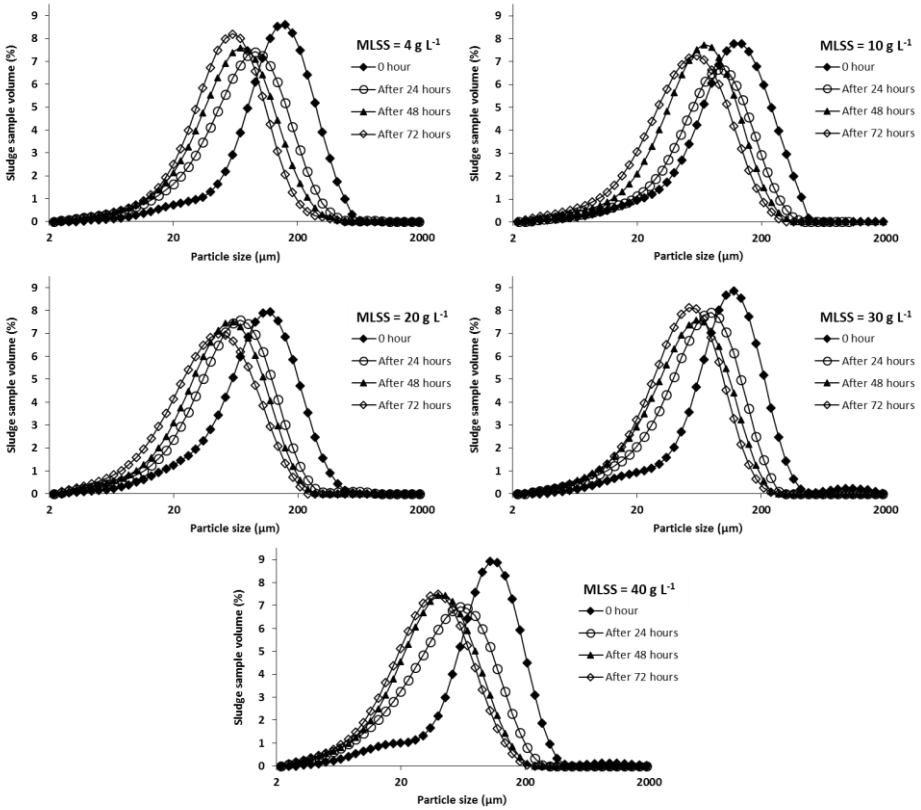


Figure 4.10 Particle size distribution (PSD) of the sludge at each MLSS concentration as a function of the oxygenation time in the SDOX system

Several authors have reported on the effects of the MLSS concentration on the alpha factor at MLSS concentrations of up to approximately 40 g L^{-1} on a wide range of experimental wastewater treatment setups (from laboratory-scale reactors to full-scale plants) provided with diffused aeration systems (Cornel et al. 2003; Germain et al. 2007; Gunder 2000; Krampe and Krauth 2003; Muller et al. 1995). Remarkably, the alpha factors reported in this research (Figure 4.8b) are higher than those reported in literature. For instance, Muller et al. (1995) and Gunder (2000) reported the highest alpha factor values as a function of the MLSS concentration. Muller et al. (1995) observed alpha factors of 0.50, 0.30, and 0.20, while Gunder (2000) alpha factors of 0.27, 0.12, and 0.04 at the MLSS concentrations of 16, 26, and 39 g L^{-1}, respectively.

Muller et al. (1995) did not indicate what type of bubble diffusers were used in their study, while Gunder (2000) operated pilot-scale MBRs with both fine and coarse bubble diffusers. In this research, as observed in Figure4.8b, alpha factors of approximately 0.6, 0.45, and 0.32 for

the SDOX system were determined at the MLSS concentrations of 16, 26, and 39 g L^{-1}, respectively (i.e., at the same MLSS concentrations reported by Muller et al. (1995) and Gunder (2000)). Moreover, the studies of Muller et al. (1995) and Gunder (2000) applied more favourable conditions than those used in this research to increase the oxygenation capacity: infinite SRTs (without waste of sludge) that promote the removal of surfactants (fatty acids and lipids commonly found in municipal wastewater) and lead to lower MLVSS fractions. Rosso and Stenstrom (2006) reported on the negative impact of surfactants on the oxygen transfer and the benefits of longer SRT on the aeration efficiency. On the opposite, this research was conducted with sludge obtained from a WWTP operated at a short SRT of approximately 5 days. That is a less favourable set of conditions regarding the oxygen transfer; nevertheless, the alpha factors reported in this research are higher to those reported using bubble diffusers.

Figure 4.11 compares the values of the alpha factors obtained in this research (with the SDOX system) *versus* the alpha factors reported by Germain et al. (2007) as a function of the MLSS and MLVSS concentrations. Germain et al. (2007) investigated the effect of the MLSS concentration on the oxygen transfer in fine bubble diffusers systems using sludge from full and pilot-scale municipal and industrial MBRs. Specifically, Germain et al. (2007) evaluated the oxygen transfer performance under standard conditions, and not at infinite SRTs (arguably unrealistic conditions) like those applied by Muller et al. (1995) and Gunder (2000). Similar alpha factors were obtained in this research (with the SDOX system) and in that one of Germain et al. (2007) up to sludge concentrations slightly lower than 10 g L^{-1}. However, at higher sludge concentrations, higher alpha factors were obtained in this research compared to those reported by Germain et al. (2007). Therefore, the SDOX system can reach higher alpha factors than those obtained with conventional bubble diffusers under similar experimental conditions (particularly, at similar sludge characteristics).

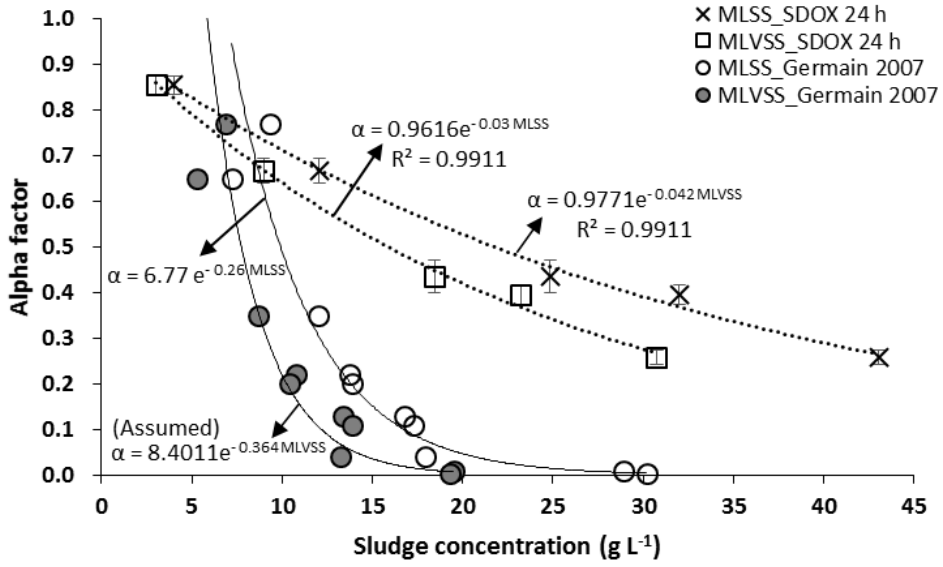


Figure 4.11 Comparison of alpha factor between conventional aeration systems and SDOX at different sludge concentrations

In addition, the OTE of the SDOX system in clean water was evaluated by measuring with a mass flow controller the amount of oxygen diffused by the SDOX system, and by determining the amount of oxygen actually dissolved into the system. Figure 4.12 shows the SOTE obtained for the SDOX system in clean water as a function of time. The results clearly indicate an OTE of almost 100% for the evaluated period at the evaluated conditions. That is, the SDOX system on top of achieving a higher SOTR, and exhibiting much higher alpha factors compared to fine bubble diffusers at high MLSS concentrations, also exhibited an almost 100% OTE. This represents a major advantage for the SDOX technology compared to conventional diffused aeration systems. The K_La exhibited by the SDOX system in clean water was not higher (actually even lower) than the K_La reported for fine bubble diffusers. However, the higher achievable OTRs, the higher reported alpha factors as a function of the MLSS concentration, and the higher observed SOTE (approximately 100% in clean water) compared to conventional diffused aeration may position the SDOX technology as a promising alternative for DO supply into mixed liquors solutions.

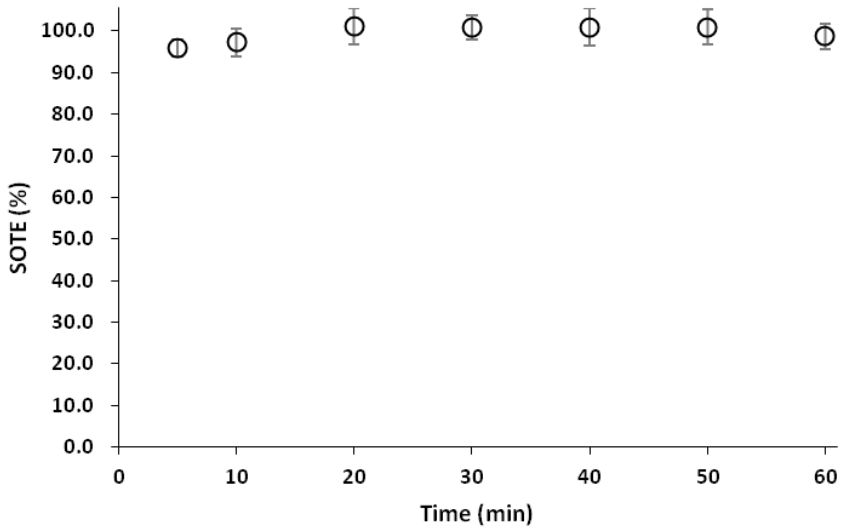


Figure 4.12 Standard oxygen transfer efficiency (SOTE) for the SDOX system as a function of time in clean water

4.3.3 Evaluation on energy requirements of SDOX in comparison with energy requirements of fine and coarse bubble diffusers as a function of MLSS concentrations

This research indicates that the SDOX technology exhibits: (i) lower K_La compared to fine bubble diffuser systems operated at realistic specific AFRs; (ii) higher OTRs due to the possibility to operate with pure oxygen at pressurized conditions; (iii) higher alpha factors than fine bubble diffusers (particularly at high MLSS concentrations); and (iv) very high SOTEs in clean water of approximately 100%. In this respect, the SDOX technology has several advantages in terms of oxygen transfer; however, the technology requires to operate with pure oxygen and to recirculate (pump) the mixed liquor through a pressurized vessel, which may introduce considerable operational (energy) costs to drive the SDOX system. Therefore, to

better assess the applicability of the SDOX technology (or the niche is the technology may be applied) an evaluation on the energy requirements of the system was carried out at the entire range of MLSS concentrations evaluated in this research. Moreover, the energy needs for the SDOX system were compared to the energy needs for conventional fine and coarse bubble diffused aeration systems.

The evaluation was carried out on the hypothetical wastewater treatment system proposed by Kim et al. (2019). Specifically, a middle-size MBR system exhibits a biological oxygen demand of 2,530 kg O_2 d^{-1}. The MBR system can operate, like in that example, within a broad range of MLSS concentrations from approximately 4 to 40 g L^{-1} exhibiting different alpha factors at each of the hypothesized MLSS concentration operational set points. Three different aeration systems were compared: fine bubble diffusers, coarse bubble diffusers, and the supersaturated oxygen system (SDOX technology). For each of the evaluated systems, three scenarios were evaluated at a low, middle, and high standard aeration efficiencies(SAE)s (Henze et al. 2008; https://www.blueingreen.com, accessed on July 2017). The power requirements of each system were calculated at the evaluated range of MLSS concentrations from 4 to 45 g L^{-1}. The alpha factors selected for this evaluation for the fine and coarse bubble diffusers were taken from literature from alpha factors measured at high MLSS concentrations as follows: (i) for the fine bubble diffusers the alpha factors were taken from Germain et al. (2007), and Kim et al. (2019), and (ii) for the coarse bubble diffusers the alpha factors were taken from Gunder (2000).Germain et al. (2007) evaluated the oxygen transfer performance of fine bubble diffusers on such high MLSS range on sludge obtained from full-scale and pilot plants (i.e., these alpha factors were obtained at more realistic full-scale conditions). Kim et al. (2019) operated at the same experimental conditions like in this research (SDOX research), but introducing the DO using a fine bubble diffuser (i.e., same sludge and experimental conditions like those applied in this research). The alpha factors obtained by Kim et al. (2019) at the more realistic operational conditions at a specific AFR of 5 m^3_{AIR} m^{-3} h^{-1} were considered in this evaluation. Gunder (2000) operated pilot-scale MBRs with both fine and coarse bubble diffusers on sludge obtained from a plant operated at an infinite SRT (i.e., these alpha factors represent one of the highest reported alpha factor in the literature). For the SDOX system, the alpha factors obtained in this research were selected for the current evaluation. Moreover, to estimate the energy needs for the SDOX system, it was assumed that pure oxygen is delivered using an on-site oxygen generator with an additional power consumption of 50 kW for the amount of oxygen delivered in this evaluation (https://www.pcigases.com, accessed on August 2019).

The results of the evaluation are presented in Table 4.1. As observed when working at standard CAS relevant concentrations of approximately 4 g L^{-1}, fine bubble diffusers demand less power (28 kW at SAE of 4.2kg/kWh) compared to coarse bubble diffusers (147 kW at SAE of 1.0 kg/kWh) and to the SDOX system (80 kW at SAE of 4.1 kg/kWh) at all the evaluated SAE conditions. However, it is important to highlight that the SDOX system requires less power to operate than the coarse bubble diffusers. It should be noted, the alpha factors stated above for

bubble diffusers systems are higher than reported in studies from full-scale operating WWTPs. For example, Rosso et al. (2005), based on operating data from approximately 30 WWTPs, reported an average alpha factor of 0.3 for systems operating at low SRTs. Bubble diffuser systems are prone to fouling when operated in biological systems, and it is common practice to apply a fouling factor when estimating performance of bubble diffusion systems. Considering the alpha factors suggested by Rosso et al. (2005), applying such fouling factor for long-term operations, fine bubble diffusers may demand similar power (84 kW at SAE of 4.2kg/kWh) to the SDOX system (80 kW at SAE of 4.1 kg/kWh) at CAS relevant MLSS concentrations. At a sludge concentration of 10 g L^{-1} (i.e., a standard MBR concentration range), fine bubble diffusers (33 kW at SAE of 4.2 kg/kWh) demand less energy than both coarse bubble diffusers (242 kW at SAE of 1.0 kg/kWh) and SDOX system (86 kW at SAE of 4.1 kg/kWh). At this operational condition, the differences compared to the SDOX system are not large; the SDOX system requires less power to operate compared to coarse bubble diffuser systems. However, at this MLSS concentration (i.e., standard for MBR systems), fine bubble diffusers seem to be more efficient in terms of power requirements than the other evaluated technologies.

That said, considering the same alpha factors suggested by Rosso et al. (2005) and applying a fouling factor for long term operation, fine bubble diffusers may demand more power (99 kW at SAE of 4.2kg/kWh) compared to the SDOX system (80 kW at SAE of 4.1 kg/kWh). At the 20 g L^{-1} MLSS concentration, the SDOX system (99 kW at SAE of 4.1 kg/kWh) outperforms significantly both the fine (672 kW at SAE of 4.2 kg/kWh) and coarse bubble (554 kW at SAE of 1.0 kg/kWh) aeration systems. Moreover, the operation at this point would not be even practically feasible with fine bubble diffusers at standard specific AFRs. Therefore, based on this evaluation, the SDOX technology has key advantages with regard to operational power requirements compared to conventional bubble diffusers at an MLSS concentration range between 10 and 20 g L^{-1}, potentially applicable for biological systems operated at higher organic loading rates. This MLSS concentration range represents biological wastewater treatment system working at higher than usual MLSS concentrations, like for instance the HL-MBR concept introduced by Kim et al. (2019). Beyond the 20 g L^{-1} MLSS concentration (i.e., at 30 and 40 g L^{-1}) the differences are even more noticeable. Above 20 g L^{-1} the first observation is that is not even feasible to introduce DO by fine bubble diffusers since non-detectable alpha factors have been reported by Germain et al. (2007) and Kim et al. (2019). Therefore, in that range not only the SDOX technology would be more efficient with regard to energy consumption than fine bubble diffusers, but also would not be even possible to supply DO by means of fine bubble diffusers. With respect to coarse bubble diffusers, the SDOX technology also needs less power in this MLSS range. This operational MLSS range fits well with the HL-MBR concept described by Kim et al. (2019) and eventually, it could be an appropriate technology to supply DO to certain aerobic digester systems.

In Table 4.1 the SDOX technology was only compared to conventional diffused aeration systems since those are the most widely used systems to provide DO into engineered wastewater

treatment system (Mueller et al. 2002). This comparison did not include other systems such as underground systems (the deep shaft reactor), HPO activated sludge systems, Praxair I-SO systems, UNOX system, OASES system, among others. Furthermore, the evaluation was carried out for a medium size MBR system with a biological oxygen demand of 2,530 kg of dissolved O_2 per day. Results may differ when considering systems of different scales. Moreover, the alpha factors considered for coarse bubble diffusers reported by Gunder (2000) were obtained on sludge from pilot plants operated at infinite SRTs. Therefore, the alpha factors for the coarse bubble diffusers were probably overestimated. Besides, on this comparison, only energy (power) requirements were discussed, and additional costs for maintenance activities were not considered. The SDOX technology may require less maintenance compared to diffused aeration system representing other potential advantages for that system that may prove the system competitive on the lowest range of evaluated MLSS concentration and expand even beyond the advantages in the high MLSS concentration range.

Additionally, the evaluation only presents and considers the energy needs for introducing the DO without considering the effect of the SDOX technology on the biological activity of the system or on the downstream unit operations in a WWTP. For instance, the shear forces and high-pressure effects at which the sludge is exposed on the SDOX system may affect the biological performance of the sludge. Moreover, the observed reduction in the PSD may influence the post sedimentation of the sludge in the secondary clarifiers or the membrane filtration performance in MBR systems. Therefore, further research is needed to address these pending aspects and provide a full evaluation of the advantages and disadvantages of the SDOX system.

Table 4.1 Comparison of the energy requirement for each of the aeration systems as a function of MLSS concentration

	Type of aeration systems															
	Fine bubble diffuser								Coarse bubble diffuser				SDOX			
			Power required (kW)							Power required (kW)				Power required (kW)		
MLSS (gL^{-1})	Alpha factor		Low SAE (3.6)		Mid SAE (4.2)		High SAE (4.8)		Alpha factor	Low SAE (0.6)	Mid SAE (1.0)	High SAE (1.5)	Alpha factor	Low SAE (2.7)	Mid SAE (4.1)	High SAE (5.5)
	Ger*	Kim	Ger*	Kim	Ger*	Kim	Ger*	Kim	Gunder				SDOX			
4	1.00	0.90	29	33	25	28	22	24	0.72	245	147	98	0.85	96	80	72
10	0.50	0.75	58	39	50	33	44	29	0.44	403	242	161	0.71	105	86	77
20	0.04	ND	784	-	672	-	588	-	0.19	924	554	370	0.53	124	99	86
30	ND	ND	-	-	-	-	-	-	0.08	2,119	1,271	848	0.39	150	116	99
45	ND	ND	-	-	-	-	-	-	0.02	7,359	4,416	2,944	0.25	207	153	127

Ger *: Germain et al. (2007)

4.4 Conclusions

- The SDOX system exhibits a K_La of 2.6 h^{-1} in clean water similar to the ones observed for coarse bubble diffusers (4 h^{-1}) and lower than for fine bubble diffusers (11 h^{-1}) at standard specific AFRs. Moreover, similar K_La values were reported for the SDOX system in clean water compared to other supersaturated oxygen delivery systems such as the Speece cone system.
- Higher OTRs were reported for the SDOX system (14 g O_2 L^{-1} d^{-1}) compared to fine bubble diffusers (2.4 g O_2 L^{-1} d^{-1}at AFR of 5 m^3_{AIR} m^{-3} h^{-1}) in clean water at the experimental conditions evaluated in this research; operating the SDOX system with pure oxygen at pressurized conditions contributed significantly on obtaining such high OTRs.
- Considerably higher alpha factors were reported for the SDOX system compared to both fine and coarse bubble diffusers; particularly at MLSS concentrations higher than 20 g L^{-1}.
- SOTEs of approximately 100% were reported for the SDOX system in clean water; i.e., much higher SOTEs compared to conventional diffused aeration.
- At an MLSS concentration of 10 g L^{-1} and below, fine bubble diffusers may have a lower energy demand depending on actual alpha factors achieved and amount of fouling considered.
- Within an MLSS concentration range between 10 and 20 g L^{-1}, the energy needs of the SDOX system are similar, or less depending on actual alpha factors achieved and amount of fouling considered to the energy needs of conventional diffused aeration systems.
- Above 20 g L^{-1}, the SDOX system demands much less energy compared to conventional diffused aeration systems.
- The higher operational MLSS concentration range can be a niche for the application of the SDOX system in the HL-MBR concept and aerobic digesters.

4.5 Acknowledgments

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4.7 Appendix

4.7 A Data analysis and oxygen transfer parameter estimation

4.7 A-1 Determination of the intrusion oxygen mass transfer rate coefficient ($K_La_{Intrusion}$)

DO data recorded during the air intrusion experiments were fitted to Eq. (1) by means of a numerical integration method. The $K_La_{Intrusion}$ were calculated by a non-linear regression carried out with the aid of Microsoft Excel software add-in SOLVER. The endogenous respiration (OUR_{endo}) term was only taken into account when performing the oxygen transfer determinations with mixed liquor; the term indicated zero for the clean water experiments. The calculated $K_La_{Intrusion}$ values were incorporated into the following mass balance in Eq. (2), (3), (4) to exclude the oxygen transferred through the surface of the water in the reactor.

$$V\left(\frac{dC_{Intrution}}{dt}\right) = K_La_{Intrusion}(C_s - C_{Reactor}) \times V - OUR_{endo} \quad (1)$$

4.7 A-2 Determination of the net oxygen transfer rate

DO values obtained through the oxygen transfer determinations of clean water and mixed liquor were fit to the Eq. (2) to calculate the net oxygen transfer rate signifying the observed oxygen transfer rate (OTR gO_2d^{-1}) achieved by the SDOX system. The $K_La_{Intrusion}$ calculated in Eq. (1) was considered. The endogenous respiration term (OUR_{endo}) was only taken into consideration on the oxygen transfer tests with mixed liquor in which microbial activity is present. That is, this term does not exist in a clean water test. Only DO values in the range of 10% to 75% of the value of Cs were used for the calculation. With regard to DO concentrations for the OTR calculation, only the measured DO values in the range of 10 to 75% of the atmospheric Cs value was considered (Boyd, 1986; Casey, 1997; Mueller et al. 2002).

$$V\left(\frac{dC_{Reactor}}{dt}\right) = \text{Net } OTR_{Reactor} + [K_La_{Intrusion}(C_s - C_{Reactor})] \times V - OUR_{endo} \quad (2)$$

4.7 A-3 Determination of the overall oxygen mass transfer rate coefficient $K_La_{Transference}$ in clean water and mixed liquor

The DO profiles from the experiments performed both in clean water and in mixed liquor were fitted to Eq. (3) and (4). The values for $K_La_{Transference}$ were calculated by a non-linear regression

carried out with MS Excel software add-in SOLVER. The DO concentration range of 10 to75% of the atmospheric Cs was also used for $K_La_{Transference}$ calculations as mentioned in section 4.7 A-2. Also, as indicated in Eq. (5), the endogenous respiration term (OUR_{endo}) and beta factor of 0.95 were only considered for the oxygen transfer tests with mixed liquor. The driving force for operating the SDOX depends on the disparity between the oxygen saturation concentration inside the SDOX pressurized chamber (C_{sSDOX}) and the DO concentration in the aerobic reactor ($C_{Reactor}$). The C_{sSDOX} was calculated considering pressure in the SDOX (P_{SDOX}), saturated DO concentration in clean water (Cs), and oxygen gas purity (O_2F) inside the SDOX as indicated

in Eq. (5). All the determined K_La valueswere corrected to 20℃ temperature as described in Eq. (6).

$$V\left(\frac{dC_{Reactor}}{dt}\right) = [K_La_{Transference}(C_{SDOX} - C_{Reactor})] \times V + [K_La_{Intrusion}(C_s - C_{Reactor})] \times V \quad (3)$$

$$V\left(\frac{dC_{Reactor}}{dt}\right) = [K_La_{Transference}(\beta C_{SDOX} - C_{Reactor})] \times V + [K_La_{Intrusion}(C_s - C_{Reactor})] \times V - OUR_{endo} \quad (4)$$

$$C_{s\_SDOX} = P_{SDOX} \times C_s \times O_2F \quad (5)$$

$$K_La_{(T)} = K_La_{(20℃)}1.024^{(T-20)} \quad (6)$$

4.7 A-4 Determination of the observed maximum standard oxygen transfer rate

The amount of oxygen that can be supplied by SDOX to the receiving basin can be calculated using Eq. (7).

$$SOTR_{max} = K_La_{Transference20} \times C_{sHPO} \times V \quad (7)$$

4.7 A-5 Determination standard oxygen transfer efficiency

Considering the concept of the SDOX, there is no chance for oxygen to be escaped from the SDOX pressurized chamber, meaning that the SDOX unit achieves 100 percent of OTE. The following form of a mass balance was employed to determine the OTE. The amount of oxygen provided (that is, oxygen entering into the SDOX unit provided by the oxygen cylinder measured by the mass flow meter) is equal to the sum of the amount of oxygen dissolved in the reactor minus the oxygen supplied from the surface of the reactor (intrusion). When determining SOTE of the SDOX, oxygen intrusion from the atmosphere should be considered. Although the $K_La_{Intrusion}$ term through the air intrusion experiments was already calculated and incorporated in the mass balance, Eq. (8) was applied to better elucidate the effect of air intrusion in adjacent range of the measured DO in the whole range of DO measured.

$$K_La_{,int} = \left(V_R K_La_{,Int}(C_{s,Air} - (\frac{DO_t + DO_{t1}}{2}))\right)(t_1 - t) \quad (8)$$

Where the V_R is the volume of mixed liquor in the reactor and $C_{s,Air}$ is the saturation DO concentration of air in clean water. The DO_t and DO_{t1} are the DO concentration at time t and time t_1 of the starting time for the oxygen intrusion calculation, respectively.

Chapter 5

Supersaturated-oxygen aeration effects on a high-loaded membrane bioreactor (HL-MBR): Biological performance and microbial population dynamics

This chapter is based on:

Kim SY, Lopez-Vazquez CM, Curko J, Matosic M, Svetec IK, Stafa A, Milligan C, Herrera A, Maestre JP, Kinney KA, Brdjanovic D, Garcia HA (2021) Supersaturated-oxygen aeration effects on a high-loaded membrane bioreactor (HL-MBR): Biological performance and microbial population dynamics. *Science of the Total Environment* 771:144847. https://doi.org/10.1016/j.scitotenv.2020.144847

Abstract

Conventional diffused aeration systems (such as fine-bubble diffusers) exhibit a poor oxygen transfer in wastewater treatment plants (WWTPs), particularly when operating at sludge concentrations higher than 15 g L^{-1}. The supersaturated dissolved oxygen (SDOX) system has been proposed as an alternative for supplying dissolved oxygen (DO) at high mixed liquor suspended solids (MLSS) concentrations. The advantages introduced by such technology include the possibility of operating WWTPs at much higher than usual MLSS concentrations, increasing the treatment capacity of WWTPs. Recent studies have demonstrated that the SDOX system has higher oxygen transfer rates (OTRs) and oxygen transfer efficiencies (OTEs) relative to fine-bubble diffusers. However, it is unknown if the high-pressure conditions introduced by SDOX may possibly impact the biological performance of WWTPs. In this study, the effects of SDOX technology on the biological performance of a membrane bioreactor (MBR) were evaluated. The MBR was operated at an MLSS concentration of approximately 15 g L^{-1} in four phases as follows: (P1) with bubble diffusers, (P2) with an SDOX unit, (P3) with the bubble diffusers, and (P4) with the SDOX unit. The performance of the MBR was assessed by monitoring the sludge concentration, as well as changes in the particle size distribution (PSD), sludge activity, organic matter removal and nitrification performance, and changes in the microbial community within the MBR. The operational conditions exerted by the SDOX technology did not affect the concentration of active biomass during the study period. The biological performance of the MBR was not affected by the introduction of the SDOX technology. Finally, the microbial community was relatively stable although some variations at the family and genus level were evident during each of the study phases. Therefore, the SDOX system can be proposed as an alternative technology for DO supply in WWTPs increasing the overall treatment capacity.

5.1 Introduction

Operating an activated sludge WWTP at the highest possible active MLSS concentration is highly desirable, since the treatment capacity of the WWTP can be increased almost proportionally to the increase on the active MLSS concentration. The higher the active MLSS concentration, either the higher the influent flowrate that a WWTP can handle (at a given footprint), or the lower the footprint needs (at a given flowrate); in addition, the higher the MLSS concentrations, the lower the sludge production. However, there are some limitations for reaching high MLSS concentrations in activated sludge WWTPs, mostly introduced by commonly used aeration technologies (e.g. fine and coarse bubble diffusers).

Membrane bioreactors (MBRs) are arguably the most suitable and available activated sludge wastewater treatment (WWT) technology to operate at high MLSS concentrations. MBRs combine biological processes with membrane filtration. The operation of MBRs is not affected by the settling characteristics of the sludge as in conventional activated sludge (CAS) processes. Therefore, MBRs are mostly operated at higher MLSS concentrations of approximately 10 g L^{-1} (Hai et al. 2019) compared to CAS systems regularly operated at approximately 3 g L^{-1}. In addition, advantages of MBRs compared to CAS systems include: a consistently high quality solids-free effluent, the capacity to handle high organic loading rates, a low footprint, and low sludge production, among others (Bagheri et al. 2019; Kim et al. 2019). Operating MBRs at even higher than usual MBR MLSS concentrations (i.e., higher than 10 g L^{-1}) increases their treatment capacity and reduces even further the system footprint and sludge production (Barreto et al. 2017; Livingston, 2010). Furthermore, this may encourage the design of containerized and movable MBR systems suitable for the provision of on-site decentralized WWT (Zakaria et al. 2015). Such concept of an MBR operated at higher than usual MBR MLSS concentrations (from approximately 15 to 40 g L^{-1}) was introduced by Kim et al. (2019) as the high-loaded MBR (HL-MBR). The HL-MBR exhibits all the advantages previously described of an MBR operated at high MLSS concentrations. However, there are severe limitations for reaching such high MLSS concentrations when applying aeration technologies commonly used in activated sludge WWTPs (fine and coarse bubble diffusers).

Innovative aeration technologies have been developed for achieving more effective and efficient oxygen transfer when working at high MLSS concentrations of above 20 g L^{-1}. Among them, the supersaturated dissolved oxygen (SDOX), a supersaturated-oxygen aeration technology, has demonstrated promising advantages. The SDOX system consists of a pressurized chamber (operated at approximately 0.8 MPa) connected to a high-purity oxygen (HPO) source. The mixed liquor to be oxygenated is recirculated through the pressurized chamber where it gets in contact with pure oxygen under high-pressure conditions. A large gas-liquid interface is created between the mixed liquor (reaching the SDOX at the top of the pressurized chamber) and the pure oxygen; such high-pressure conditions in the SDOX allow DO concentrations to reach up to 350 mg L^{-1} in clean water (Jones, 2010). Kim et al. (2020)

evaluated the oxygen transfer performance of the SDOX system at MLSS concentrations from approximately 4 to 45 g L^{-1}. Slightly lower oxygen mass transfer rate coefficients (K_La) were observed in clean water with the SDOX system (2.6 h^{-1}) compared to diffused aeration systems (4 h^{-1} and 11 h^{-1} for coarse and fine-bubble diffusers, respectively); but, the SDOX system showed higher oxygen transfer rates (OTR) (14 g O_2 L^{-1} d^{-1}) compared to fine-bubble diffusers (2.4 g O_2 L^{-1} d^{-1}). Also, the SDOX system reached oxygen transfer efficiencies (OTEs) of approximately 100% in clean water, much higher than the approximate 5% per meter of submergence usually reported for fine-bubble diffusers. In particular, at MLSS concentrations higher than 20 g L^{-1}, the SDOX system exhibited considerably higher alpha factors (mass transfer ratio of process water to clean water) and demanded less energy than fine-bubble diffusers. Such advantages position the SDOX technology as a promising alternative for supplying DO in activated sludge WWT systems operated at high MLSS concentrations. However, the evaluations carried out so far with the SDOX system did not assess the potential negative effects on the biological activities (Kim et al. 2019; Kim et al. 2020). For instance, the shear forces and high-pressure conditions at which the sludge is exposed in the SDOX system may affect the biological activity, thus influencing the performance of WWTPs.

High-pressure conditions may negatively influence the cell structure of bacteria as well as their metabolic processes and survival capacity (Bartlett, 2002). Microorganisms are adversely impacted by the high-pressure conditions, depending on the intensity of such pressure (Picard and Daniel, 2013). However, certain studies have reported the effects of high-pressure conditions on the performance of diverse biological WWT systems indicating that the biological removal processes were not affected but even improved at high-pressure conditions (Ellis et al. 1992; Jin et al. 2010; Xu et al. 2016; Zhang et al. 2014; Zhang et al. 2016). Nevertheless, most such studies were conducted in pressurized batch reactors exposing the biomass continuously and completely to high-pressure conditions, using diffused aeration systems, and treating specific types of wastewater (e.g. industrial wastewater or synthetic saline wastewater). Neither any of the previously reported studies were carried out in WWT systems operated at high MLSS concentrations. Moreover, no such studies included a supersaturated-oxygen aeration technology (such as the SDOX system) as the main source of DO. The SDOX technology exposes part of the sludge to the high-pressure conditions and shear effects in a completely different manner than diffused aeration systems. Thus, the impacts of such technology on the sludge activity and microbial population dynamics may be completely different and need to be evaluated.

In this study, the effects of the SDOX technology on the performance of a biological WWT system were evaluated. An MBR was operated at a relatively high MLSS concentration of approximately 15 g L^{-1}. For comparison purposes, the MBR system was evaluated in four different phases with either fine-bubble diffusers or using an SDOX unit for DO supply. The performance of the MBR system was assessed by monitoring changes in the sludge concentration and particle size distribution (PSD), the sludge activity in terms of the oxygen

uptake rates (OURs), the organic matter removal and nitrification performance, and overall variations in the microbial population communities when exposing the sludge to the SDOX technology. The SDOX technology has already demonstrated a much better oxygen transfer performance (e.g. alpha factors, OTEs, and energy consumption) at high MLSS concentrations compared to diffused aeration systems. If successful, this research will demonstrate the absence of major negative effects on the biological performance of a WWT system equipped with an SDOX system. Therefore, positioning the SDOX technology as a feasible and energy efficient alternative for operating WWTPs at higher than usual MLSS concentrations increasing the WWTPs treatment capacity (i.e., increasing the receiving wastewater flowrates at a given footprint, or lowering the footprint requirements at a giving flowrate).

5.2 Materials and methods

5.2.1 Design and production of a lab-scale membrane bioreactor (MBR)

In preliminary experiments, an MBR working volume of 20 L was used, much larger than an MBR working volume of 6.5 L used in this study. When operating the MBR (20L working volume) with SDOX, roughly 30% of the oxygen supplied by SDOX. There was an internal debate in terms of the amount of oxygen delivered by SDOX when working with MBR-SDOX. On the one hand, most of the oxygen does not have to be supplied by SDOX, if we just consider the high-pressure effect. On the other hand, oxygen delivery should be mostly performed by SDOX. Eventually, we came to the conclusion that most oxygen transfer should occur by SDOX. Accordingly, a lab-scale MBR working volume of 6.5 L was designed and used for a long-term MBR experiment to make sure that most of oxygen transfer is done by SDOX when MBR is operated with SDOX. The MBR was designed so that a flat-sheet membrane (XJ3 module by Kubota) can be located within the MBR but with little space (approximately 1 cm on both sides of membrane) and simultaneously to have the smallest working volume. Figure 5.1 shows the sketches for the lab-scale MBR design, and Figure 5.2 shows the floor plan specified for the actual production.

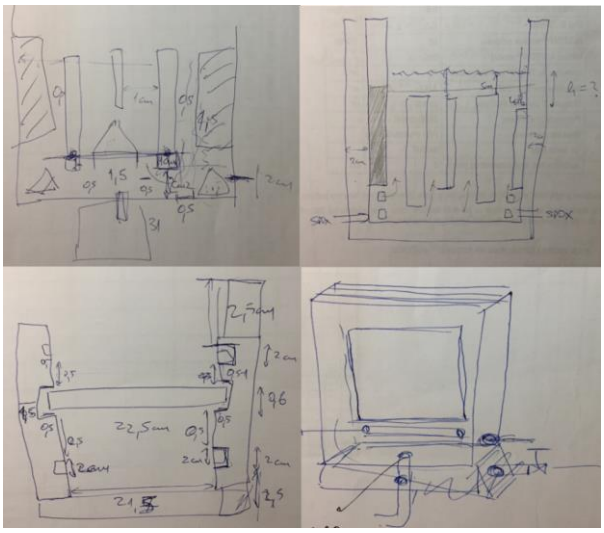

Figure 5.1 Sketches of a lab-scale membrane bioreactor (MBR) (Drawing: Marin Matosic)

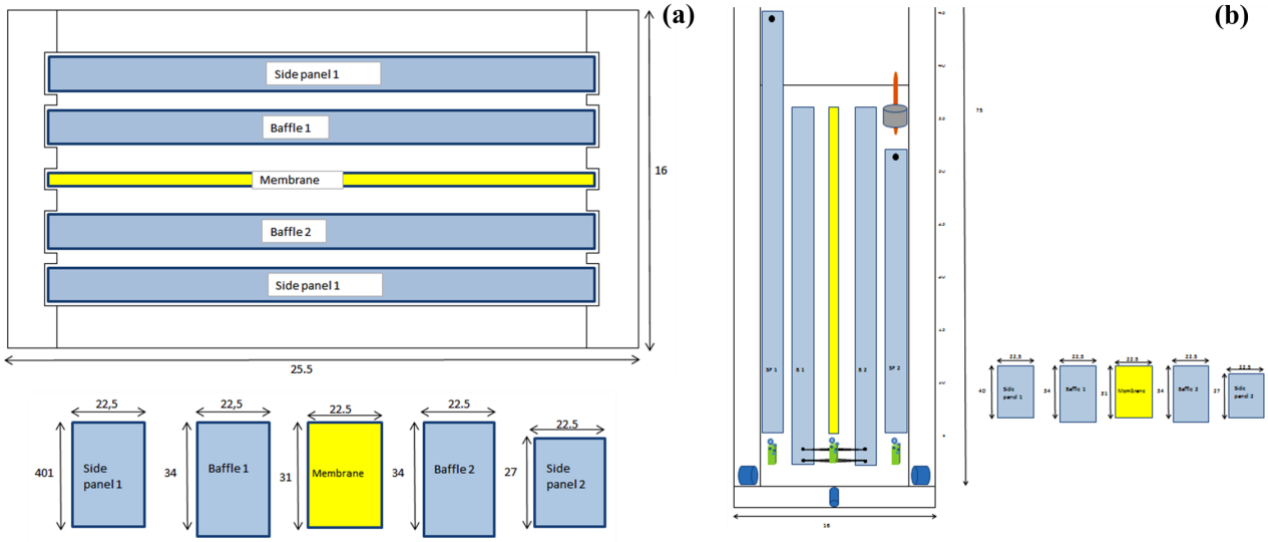

Figure 5.2 The conceptual design of the lab-scale membrane bioreactor (MBR) (Drawing: Sang Yeob Kim)

Figure 5.3 shows the process of the actual lab-scale MBR production.

Figure 5.3 Preparation of a lab-scale membrane bioreactor (MBR) (Photo by Sang Yeob Kim)

5.2.2 Long-term effect of SDOX technology on microorganisms

5.2.2.1 Design of the experiment

A bench-scale MBR was continuously operated for 80 days and fed with synthetic wastewater.

The MBR was equipped with either fine-bubble diffusers or with a bench-scale SDOX unit, for the provision of DO. The MBR was inoculated with fresh activated sludge from the municipal WWTP of the city of Zagreb (Zagreb, Croatia) and concentrated up to approximately 10 g L^{-1}. The system was operated in four phases: phase one (P1) using bubble diffusers (days 0 to 40); phase two (P2) with the SDOX unit (days 41 to 56); phase three (P3) bubble diffusers (days 57 to 74); and, phase four (P4) SDOX unit (days 75 to 80).

Thus, after inoculation, in P1 the MBR was operated with the fine-bubble diffusers for 40 days to acclimatize the biomass. On day 41, P2, the SDOX unit was introduced and the MBR was operated under identical operational conditions to P1 for 16 days; P2 aimed at investigating the potential influence of the high-pressure conditions and shear effects on the biomass. Then, in P3, the SDOX unit was taken out, and the MBR operated again with fine-bubble diffusers for 18 days. P3 was included to investigate the effects of the sludge and of the MBR system when exposed again to bubble diffusers (since the sludge could have been damaged after being exposed to the SDOX unit). Finally, in P4, the aeration system was replaced one more time by the SDOX unit to confirm the effect of high-pressure conditions for a further six days. In P3 and P4, full stabilized reactor conditions cannot be entirely claimed. These phases were carried out mostly to confirm the previous trends observed in P1 and P2.

A solution containing the concentrated organic components of the synthetic wastewater (glucose, acetate, peptone, and yeast) was fed to the MBR by gravity drips using a gravity medical infusion unit operated at a flowrate of 1 L d^{-1}. A second solution containing the inorganic components of the synthetic wastewater was added through a piston fluid-metering pump (FMI PM6014 RHV, Fluid Metering Inc, USA) at a flowrate of 39.6 L d^{-1}. That is, the total influent flowrate to the MBR was set at 40.6 L d^{-1} delivering the wastewater composition of the synthetic wastewater to the MBR system described in Table 5.1 Such a flowrate established a total hydraulic retention time (HRT) of approximately 4 hours and a membrane flux of 15 L m^{-2} h^{-1}. The solid retention time (SRT) was set at 10 days by withdrawing 0.65 L d^{-1} of sludge from the MBR. Samples of the MBR sludge, influent, and effluent were regularly collected and analyzed for the determination of water quality parameters, sludge characteristics, and changes in the microbial populations.

Table 5.1 Characterization of the synthetic wastewater reaching the MBR system

Chemical compounds	Concentration (mg L^{-1})	Chemical compounds	Concentration (mg L^{-1})
$C_6H_{12}O_6$	421.88	$FeCl_3 \cdot 6H_2O$	19.36
$C_2H_3NaO_2$	571.28	$C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$	30.00
Peptone	260.00	$MnCl_2 \cdot 4H_2O$	0.74
Yeast	40.00	$ZnSO_4 \cdot 7H_2O$	2.50
NH_4Cl	65.69	$CuSO_4 \cdot 5H_2O$	0.61
KH_2PO_4	48.33	$CoCl_2 \cdot 6H_2O$	2.09
$NaHCO_3$	251.95	$Na_2MoO_4 \cdot 2H_2O$	0.26
$CaCl_2$	40.37	H_3BO_3	0.13
$MgSO_4$	65.65	$NiSO_4 \cdot 7H_2O$	0.29

5.2.2.2 Experimental setup

The setup consisted of an MBR equipped with either fine-bubble diffusers (Figure 5.4a, and also displayed in Figure 5.5) or the SDOX unit (Figures 5.4b and 5.7), for introducing the DO. The MBR basin was made of transparent acrylic glass with a total volume of 30.6 L (16 × 25.5 × 75 cm), and it was operated at a working volume of 6.5 L. A flat-sheet membrane (XJ3 module by Kubota) made of chlorinated polyethylene was immersed in the middle and lower part of the MBR basin. The membrane had an effective filtration area of 0.11 m^2 with a nominal pore size of 0.4 μm. A coarse bubble diffuser (Uxcell, model number: US-SA-AJD-231698, Hong Kong) was placed at the bottom of the MBR for membrane scoring. Air was supplied by a blower (HIBLOW HP 80, Techno Takatsuki, Japan) which was operated to satisfy the specific membrane scouring aeration needs of 2 m^3 m^{-2} h^{-1}. The permeate was taken out of the MBR system through a piston fluid metering pump (FMI PM6014 RHV, Fluid Metering Inc, USA).

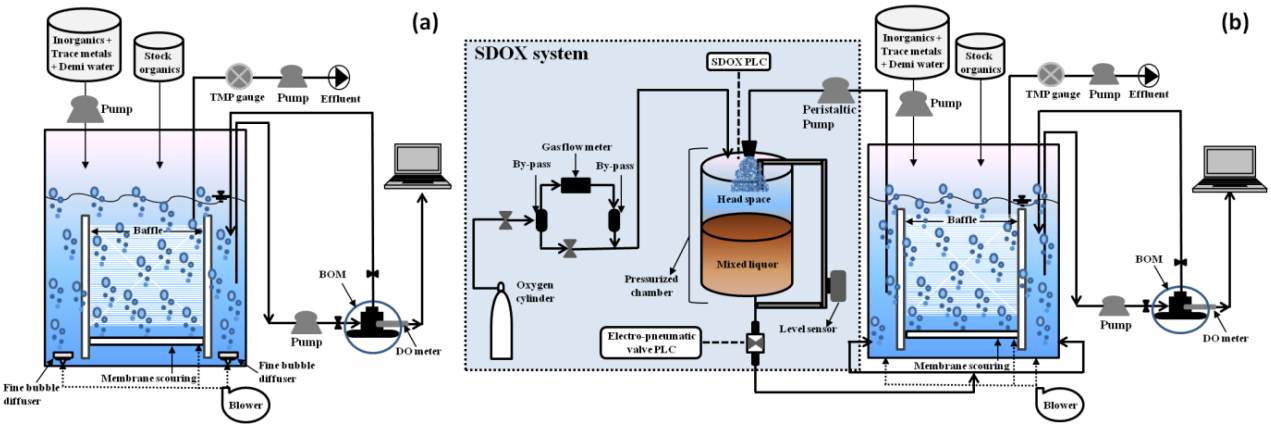

Figure 5.4 Experimental setup of the MBR system equipped with (a) bubble diffusers and (b) the SDOX system

During P1 and P3, the DO was supplied by fine-bubble diffusers (Hydrofarm, Inc, USA) placed at the bottom of the MBR basin (Figure 5.4a). The fine-bubble diffusers were operated at air flow rate (AFR) values of approximately 0.5 m^3 h^{-1}. Also, two baffles were placed, one at either side of the immersed membrane, to provide a uniform distribution of the aeration. During P2 and P4, the DO was supplied by a bench-scale SDOX unit (Figure 5.4b). The bench-scale SDOX unit consisted of a pressurized chamber connected to an HPO source (oxygen cylinder (MESSER, Croatia)). The pressurized chamber had a total volume of 2.75 L. Approximately 20% of that volume (0.55 L) was occupied by the sludge solution to be oxygenated, while the 80% remaining (2.20 L) consisted of the headspace. The pressure in the SDOX unit was set at 0.69 MPa. The pressurized chamber operated with two analogic pressure gauges (McDaniel Controls, USA). Moreover, both a pressure digital sensor (SICK AG, Germany) and a level digital sensor (Setra Systems, USA) were placed inside the pressurized chamber.

An electro-pneumatic valve (NVF3-MOH-5/2-K-1/4-EX, FESTO, Germany) was introduced at the effluent drainage of the pressurized chamber. The pressure sensors, level sensors, and the

electro-pneumatic valve was used to monitor and control the level and pressure of the pressurized chamber by the aid of a program logic controller (PLC) system (SIMATIC S7-1200, Siemens, Germany). Pure oxygen was supplied into the system through a gas flowmeter equipped with a mass totalizer (Model # 32908-59, Cole-Palmer, USA). The sludge stream was introduced into the SDOX system through a 6 mm orifice by a high-pressure peristaltic pump (EW-74203-24, Cole-Palmer, USA) operated at a flowrate of 0.3 L min^{-1}. The supersaturated sludge stream was then released back into the MBR basin, thus introducing oxygen into the MBR system. The sludge from the pressurized chamber was released at the bottom of the MBR basin, contributing to the mixing of the MBR system.

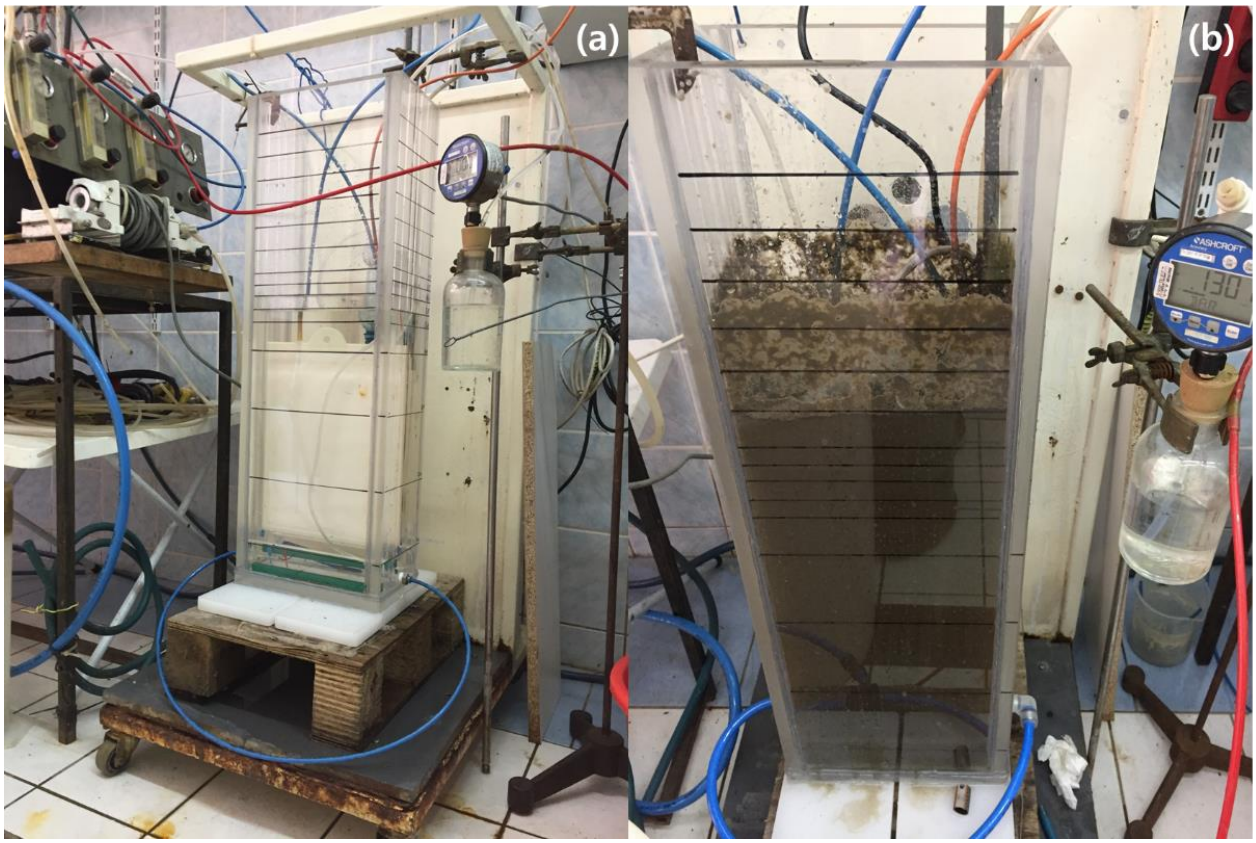

Figure 5.5 Experimental setup of the MBR with clean water (a) and the MBR inoculated with activated sludge (b) (Photo by Sang Yeob Kim)

Also, as displayed in Figure 5.6, two baffles were placed on both sides and above the membrane to provide uniform aeration for the membrane.

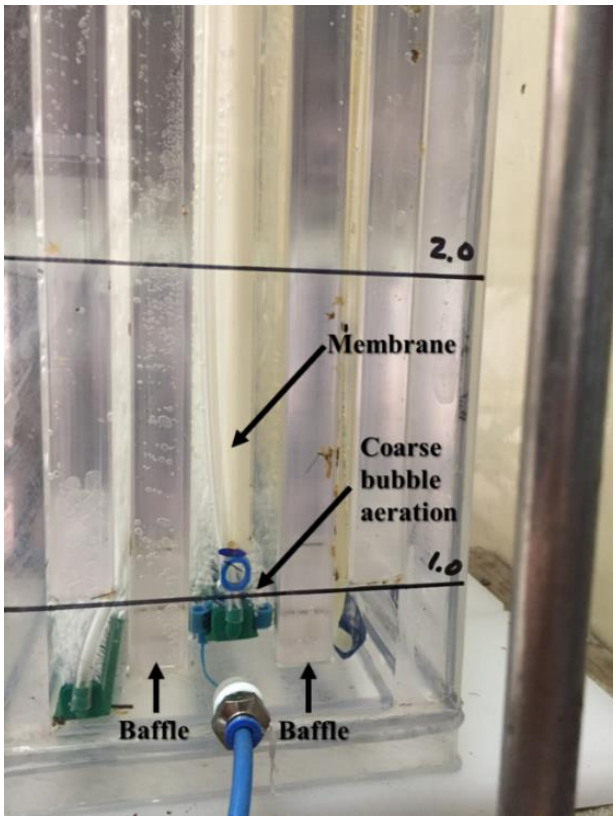

Figure 5.6 The MBR equipped with two baffles, coarse bubble diffuser, and a flat-sheet membrane (XJ3 module by Kubota) (Photo by Sang Yeob Kim)

Figure 5.7 MBR-SDOX setup (Photo by Sang Yeob Kim)

5.2.3 Analytical methods

The MBR effluent and influent samples were analyzed to determine the chemical oxygen demand (COD), NH_4-N, NO_2-N, NO_3-N, total nitrogen (TN), PO_4-P, and total phosphorus (TP) using the Hach Lange Cuvette Tests (LCK 238, 303, 304, 314, 339, 342, 350, 514). Composite permeate samples were collected within 24 h and were analyzed daily. The MLSS and mixed liquor volatile suspended solids (MLVSS) concentrations were determined following the standard methods for the examination of water and wastewater (APHA, 2017). The temperature and DO of the MBR system were measured using a DO probe (WTW Oxi 3310, Germany). The pH was measured with a pH probe (SI Analytics GmbH, Germany). Both the DO and pH determinations were corrected by the actual temperature. The PSD was measured using a Malvern Mastersizer 2000 laser diffraction particle counter (Malvern Instruments Ltd, Malvern, UK). The Mann-Whitney U test was carried out to assess significant differences on the performance of the MBR between P1 and P2 for the evaluated key performance indicators such as the PSD, specific OURs (SOURs), COD, NH_4, and PO_4; in addition, the average values and standard deviations for such parameters were also determined.

5.2.4 Oxygen uptake rate

The OUR determinations were carried out with a biological oxygen meter (BOM) based on the batch respirometric method (Kim et al. 2020). The BOM consisted of a glass container equipped with a DO probe (WTW Oxi 3310, Germany) and a stirring plate (IKA® COLOR SQUID, Germany). A Master flex peristaltic pump (Cole-Parmer, USA) recirculated the sludge from the MBR under evaluation through the BOM. When the BOM was filled with the activated sludge, the pump was stopped and the decrease in the DO as a function of time was monitored and recorded by the DO probe. After determining the OUR values, the sludge was returned to the MBR. A DO range from 6.5 to 2.5 mg L^{-1} was used to calculate the OUR values. OURs were determined in triplicate, and an average value of the calculated OURs was reported.

5.3 High-throughput sequencing analysis

5.3.1 DNA isolation, PCR, and sequencing

A total of 19 sludge samples were analyzed throughout P1 and P2 to explore the response of the microbial community structure when switching between the two aeration systems. The initial sample (day 0) represented the sludge taken from the WWTP. Eight sludge samples were collected during P1 (on days 16, 28, 30, 32, 34, 36, 38, and 40) to assess the MBR operation with fine-bubble diffusers, while ten sludge samples were collected in P2 (on days 41, 43, 45, 47, 49, 50, 51, 53, 54, and 55) to study the operation of the MBR with the SDOX unit.

The samples for deoxyribonucleic acid (DNA) extraction were obtained by pelleting 2 mL of the sludge by centrifugation (10,000 g for 5 min) and removing the supernatant. The DNA was extracted from the pellets (0.25-0.30 g pellets) using the PowerSoil DNA Isolation Kit (MO BIO Laboratories, CA, USA). The sludge samples were added to a bead beating tube provided with the PowerSoil DNA Isolation Kits. The cell lysis was achieved by multidirectional beating

in a homogenizer set, following the manufacturer's recommendations (30 s at 5.0 m s^{-1}). The DNA was eluted in 100 µL solution of C6. After the extraction, the DNA integrity was checked by running 1 µL of all the samples using 0.8% agarose gel and storing the extracted DNA at -20 ℃. Negative controls were included in this study to account for background noise from possible material and reagent contamination.

The bacterial DNA was analyzed at the Genomic Sequencing and Analysis Facility (GSAF) at the University of Texas at Austin (Austin, TX, USA) for Illumina® paired-end (2250) sequencing on the MiSeq platform. The first-round polymerase chain reaction (PCR) (19 cycles) was used to amplify the V4/V5 regions of the 16S ribosomal ribonucleic acid (rRNA) gene using the primers 515F (5'-GTGYCAGCMGCCGCGGTA-3') (Baker et al. 2003) and 909R (5'-CCCCGYCAATTCMTTTRAGT-3') (Wang and Qian, 2009). These primers included appropriate Illumina adapters with reverse primers which also had an error-correcting 12-bp barcode unique to each sample to permit multiplexing of the samples. After the PCR amplification, samples were prepared for their Illumina® sequencing run. This first round of PCR amplification was run in triplicate for each sample, pooled, and then cleaned using AMPure beads (New England Biolabs, Ipswich, MA). A second-round PCR amplification (11 cycles) was performed with hybrid primers that added sample-specific barcodes. Both rounds of the PCR amplification used Taq polymerase NEB Q5 (New England Biolabs, Ipswich, MA). The final PCR products for each sample after both rounds of amplification were again size-purified by removing amplicons less than 300 bp in length using AMPure beads (New England Biolabs, Ipswich, MA) and quantified using PicoGreen (Life Technologies, Carlsbad, CA). Samples were then normalized by amplicon mass and pooled for the Illumina® run. In addition, a random subset of samples was assessed on an Agilent BioAnalyzer (Agilent Technologies, Santa Clara, CA) to ensure correct amplicon size. Negative PCR controls (negative template) were included to test for contamination during amplification and sequencing processes. However, no sequences were obtained from these controls.

5.3.2 Sequence processing and statistical analysis

Bacterial DNA sequences were processed and analyzed in QIIME v.1.8 (Caporaso et al. 2010). Sequences were demultiplexed and forward and reverse reads were merged using FLASH v.1.2.11 (Magoč and Salzberg, 2011) with maximum overlap of 250bp. Sequences were quality-filtered (-q 19), and chimeras were removed via QIIME and USEARCH (Edgar, 2010). High-quality sequences were clustered into operational taxonomic units (OTUs) at 97% similarity using QIIME's USEARCH-based open-reference OTU clustering workflow (pick_open_reference_otus.py). Global singleton OTUs were removed, and OTU proportions were standardized to the total number of high-quality reads. Taxonomy was assigned using the Ribosomal Database Project (RDP) classifier (Wang et al. 2007) with the reference database Greengenes13_8 16s rRNA (McDonald et al. 2012). All the samples were rarefied to the least number of sequences present in any individual sample as is commonly done in microbiome studies. All statistical analyses were performed in the R environment (www.r-project.org). Pair-

wise dissimilarities between communities were calculated using both unweighted and weighted UniFrac (Lozupone and Knight, 2005). The Mann-Whitney U test was carried out to assess significant differences on the taxonomic ranks between P1 and P2.

5.3 Results and discussion

5.3.1 Effects of the SDOX system on the sludge concentration

The effects of the SDOX unit on the sludge concentration were evaluated. Figure 5.8 describes the changes in the MLSS and MLVSS concentrations, and the MLVSS/MLSS ratio as a function of the exposure time. After inoculation, the initial MLSS concentration was approximately 10 g L^{-1}. The operational conditions in the MBR (including the composition of the synthetic wastewater, HRT, and SRT) were designed to achieve a sludge concentration of approximately 15 g L^{-1}, which was reached during P1.

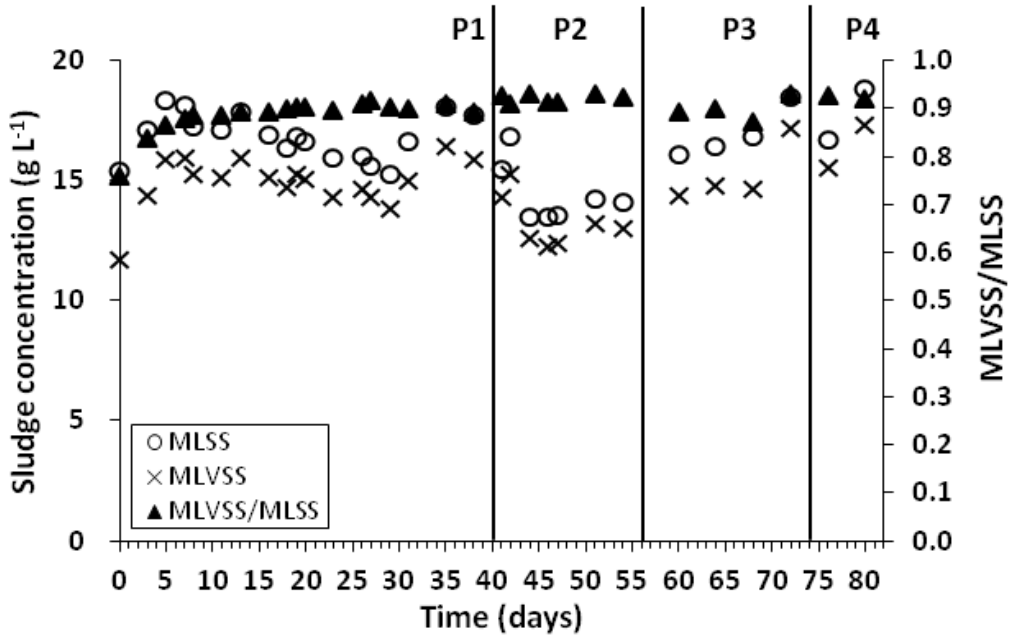

Figure 5.8 Sludge MLSS and MLVSS concentrations and MLVSS/MLSS ratio (P1: aerated with diffusers, P2: aerated with SDOX, P3: aerated again with diffusers, P4: aerated again with SDOX)

On the operational day 41, the SDOX unit was introduced (P2), and a decrease in the sludge concentration was immediately observed. It continued to decrease for the next three consecutive days until reaching an MLVSS concentration of 12.6 g L^{-1}; after that, it stabilized (and even slightly increased) until the end of phase P2 (day 56). The reduction in the MLSS concentration observed when incorporating the SDOX unit in P2 mostly occurred due to a dilution observed in the MBR basin. When the SDOX unit was introduced, it was filled with sludge, thus reducing the level in the MBR basin. This resulted in more influent wastewater coming into the MBR to reach the operational MBR level setpoint established by the automatization system, thus diluting the sludge in the MBR basin. Such an effect could have contributed with approximately

a 0.85 dilution factor to the lowering of the MLVSS concentration to approximately 12.7 g L^{-1}, similar to the observed MLVSS concentration of 12.6 g L^{-1}on operational day 43 (Figure 5.8). Therefore, the decrease in the MLVSS concentration was mostly due to the dilution rather than to a deleterious effect caused by the SDOX unit (e.g. cell lysis that could have reduced the sludge concentration).

Thereafter in P3 (days 57 to 74), the SDOX unit was removed, and the MBR was operated again with only bubble diffusers. During this phase, the sludge concentration returned back up to approximately the original MLVSS concentration of 15 g L^{-1}. In P4 (days 75 to 80), the SDOX unit was again introduced; however, during this phase a decrease in the sludge concentration was not observed. When moving from P3 to P4 (that is, when switching again from the bubble diffusers to the SDOX unit), the level setpoint control in the automatization system was modified to avoid such a dilution effect as observed when moving from P1 to P2
In addition, the MLVSS/MLSS ratio was monitored (Figure 5.8). During the first 10 days of operation in P1, when the sludge in the MBR was getting acclimated to the new synthetic wastewater and operational conditions, the MLVSS/MLSS ratio increased from approximately 0.76 to 0.90. In this study, a readily biodegradable synthetic wastewater was provided to the system. So, during such a period, fresh active biomass grew contributing to the increase in MLVSS and the MLVSS/MLSS ratio. The MLVSS/MLSS ratio remained constant during the entire evaluation period, indicating that the SDOX unit did not induce major damage to the cells. If this had happened then a consequent reduction in the MLVSS concentration would have been observed, contributing significantly to lowering the MLVSS/MLSS ratio.

5.3.2 Effects of the SDOX system on the PSD

The effects of the SDOX system on the PSD of the sludge were determined. Figure 5.9a indicates the changes in the PSD in the sludge from the inoculation of the MBR until the end of P2 (SDOX evaluation).

When inoculated, the sludge exhibited an average particle size (Dv50) of 114 µm (at day 0) which was reduced down to 39.8 µm towards the end of P1 (day 40). During P1 the sludge was mostly acclimating to the MBR system conditions and to the new synthetic wastewater. Such a reduction in the PSD and average particle size was caused by the effects of the turbulence and mixing provided by the bubble diffusers in the MBR basin, and possibly by the effects of the pressure exerted on the surface of the membrane. Zhang et al. (2015) reported that the sludge flocs get smaller in aerobic basins due to the shear forces generated by diffused aeration systems. This means that a noticeable reduction in the average size of the particles was observed without taking the effects of the SDOX system into account.

After introducing the SDOX unit (P2), a further decrease in the average particle size was observed down to 27.8 µm at the end of P2 (day 54 in Figure 5.9a). The Mann-Whitney U test indicated significant differences ($p \leq 0.02$) in the average particle size between P1 and P2. The

changes in the PSD from day 40 to day 54 were attributed to the effects of high-pressure and shear exerted by the SDOX unit. Figure 5.9b shows the changes in the PSD and average particle size immediately after using the SDOX unit on the first five consecutive operational days in P2 (day 41 to day 45). The PSD and average particle size of sludge decreased from 43.0 µm (day 41 right after introducing the SDOX unit) until 24.9 µm (day 45). The average particle size stabilized at the end of P2 as observed in Figure 5.9a at an average particle size of 27.8 µm (day 54). The high-pressure conditions and shear effects introduced by the SDOX system contributed to reducing the PSD of the sludge; however, such a decline in the PSD occurred right after the SDOX unit was introduced and the effects stabilized with the exposure time. When the SDOX unit was removed and the MBR was operated one more time with the bubble diffusers (P3), the PSD shifted back to larger particles, and an average particle size of 49.3 µm was reported at the end of P3 (day 65) (Figure 5.9c). As the high-pressure conditions and shear effects imposed by the SDOX unit ceased, the sludge flocs became larger again. In phase P4, the MBR system was operated again with the SDOX unit, and the average particle size decreased to 44.7 µm (day 76) (Figure 5.9c).

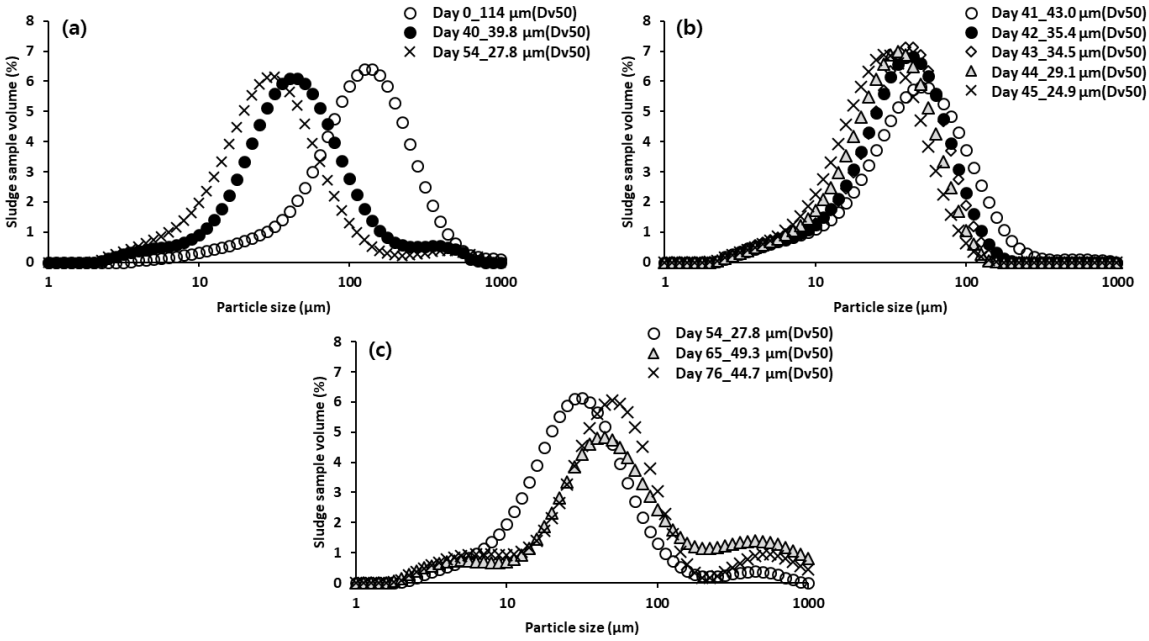

Figure 5.9 Changes in PSD: (a) when acclimating the sludge and switching from bubble diffusers to the SDOX unit (phases P1 and P2); (b) after introducing the SDOX (phase P2); and (c) when switching from the SDOX unit to bubble aeration and back to the SDOX unit (phases P2, P3, and P4)

Overall, the SDOX system tended to decrease the PSD of the sludge. In particular, the effects were more pronounced during the first days after introducing the SDOX system until the PSD stabilized. The reduction in the PSD did not have any critical effect on the sludge concentration of the MBR system or on the MLVSS/MLSS ratio. Consequently, it can be considered that the high-pressure conditions and shear effect did not appear to produce any substantial cell lysis nd/or cell inactivation with subsequent losses of volatile suspended solids in the sludge.

5.3.3 Effects of the SDOX system on the sludge activity

The effects of the SDOX unit on the biological sludge activity in the MBR were also evaluated. Figure 5.10 presents the OUR and SOUR when the MBR was provided with bubble diffusers (P1) and with the SDOX unit (P2) until the operational day 56.

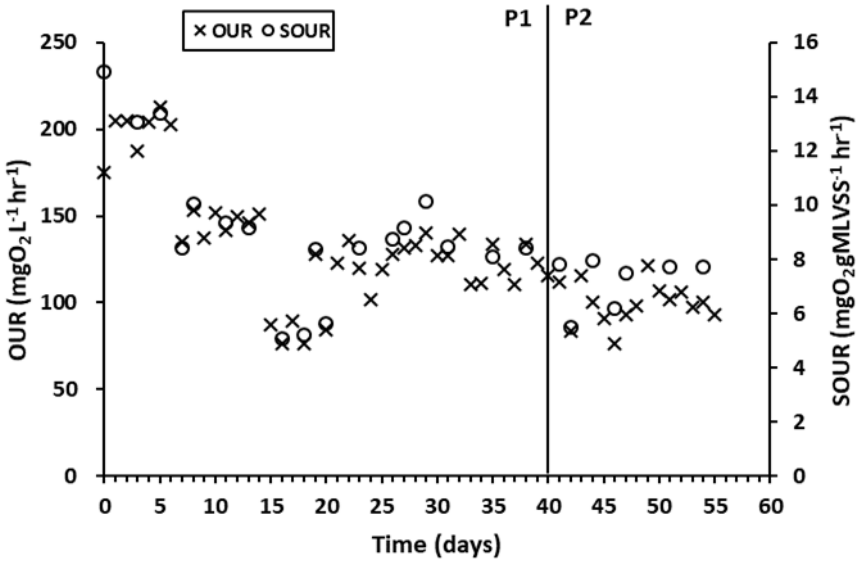

Figure 5.10 OUR and SOUR for the experiments with bubble diffusers and SDOX (P1: aerated with diffusers, P2: aerated with SDOX)

In the first 20 days of operation, both the OUR and SOUR halved. During P1, the sludge was adapting to the MBR operational conditions and the synthetic wastewater. In particular, the SRT of the sludge changed from 5 days (operational SRT at the local WWTP) to 10 days (SRT set for the MBR evaluation), explaining such a reduction in the OUR and SOUR values. After the operational day 20, the OUR and SOUR stabilized until the end of the phase. No major differences were observed in the reported values when switching the aeration systems from the bubble diffuser to the SDOX unit (i.e., from P1 to P2) as indicated in Figure 5.10. Average SOUR values of 8.0 ± 1.6 and 7.2 ± 1.0 mg O_2 L^{-1} hr^{-1} were obtained for P1 and P2, respectively. In addition, the Mann-Whitney U test indicated no significant differences ($p \leq 0.02$) in the SOUR values between P1 and P2. There was a slight decrease in the OUR values due to the losses of sludge at the beginning of P2 due to the dilution effect previously described. However, the SOUR did not considerably change. Then, as determined by the OUR, switching to the SDOX system did not affect the biological activity.

5.3.4 Effects of the SDOX system on COD removal, nitrification, and phosphorus removal

The effects of the SDOX unit on the biological performance of the MBR system were determined by evaluating the COD removal performance. Figure 5.11a indicates the COD removal for the entire evaluated period. The system was fed with synthetic wastewater at an influent concentration of approximately 1,000 mg L^{-1}. The effluent COD concentration

remained below 60 mg L^{-1}, showing an average COD removal efficiency higher than 95%. As observed in Figure 5.11b, after the introduction of the SDOX unit, the effluent COD concentration remained unchanged compared to the performance in P1 at approximately 40 mg L^{-1}. Later on, towards the end of P2, a slight increase in the effluent COD up to approximately 60 mg L^{-1} was observed. This increase in the COD in the effluent could have been caused by changes in the PSD of the sludge, producing possibly some colloidal materials with a particle size lower than the pore size of the microfiltration membrane (0.4 µm) that could have escaped the MBR. Average COD removal values of 96.8 ± 0.8 and 96.2 ± 1.5 % were obtained for P1 and P2, respectively. In addition, the Mann-Whitney U test indicated no significant differences ($p \leq 0.02$) in the effluent COD concentration between P1 and P2. Certainly, it can be concluded that the introduction of the SDOX unit did not affect the performance of the MBR system regarding the removal of COD, and the MBR exhibited overall an excellent COD removal efficiency of above 95% on average. Therefore, this suggests that the functionality of the microbial community responsible for the decomposition of organic matter was not affected when introducing the SDOX system. The effects of the SDOX unit on the biological performance of the MBR were also evaluated by determining the nitrification performance of the system.

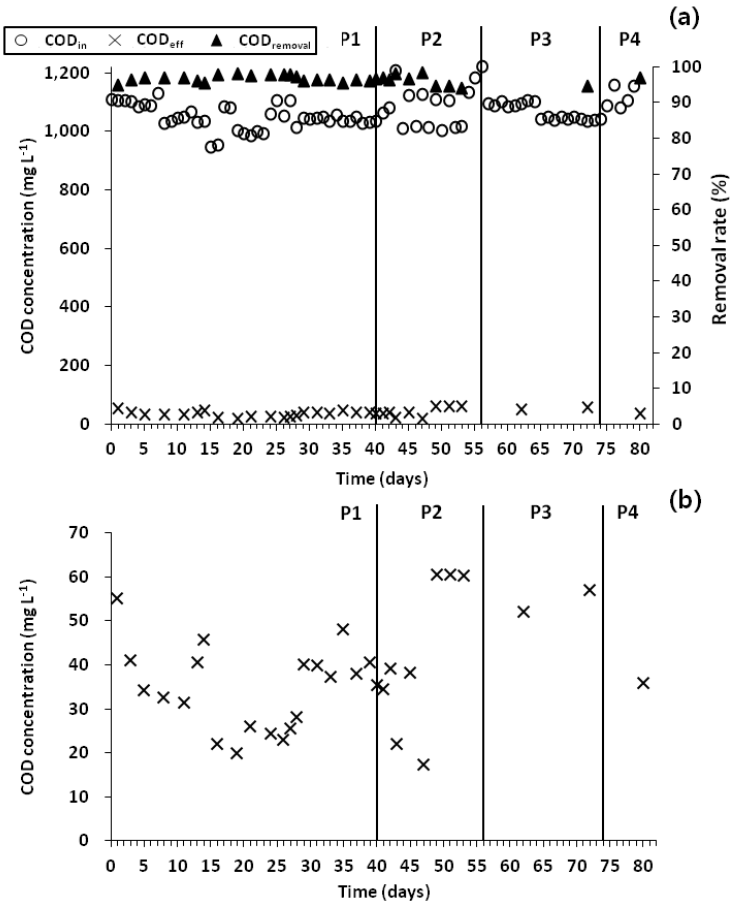

Figure 5.11 (a) Influent and effluent COD concentration and removal efficiency, (b) effluent COD concentration (P1: aerated with diffusers, P2: aerated with SDOX, P3: aerated again with diffusers, P4: aerated again with SDOX)

Figures 5.12a and 5.12b show the influent and effluent ammonia and nitrate concentration, respectively, for the evaluated period. An influent ammonia concentration of approximately 20 mg L^{-1} was continuously added to the MBR system. Complete ammonia removal was observed (Figure 5.12a) with the subsequent formation of nitrate (Figure 5.12b), already immediately after inoculating the MBR with the sludge from the WWTP (P1). This indicates the presence of nitrifying microorganisms in such sludge. Moreover, when switching to the SDOX unit (P2), the ammonia removal performance and nitrate generation of the system remained unchanged. Average NH_4 removal values of 98.6 ± 3.1 and 99.4 ± 0.2 % were obtained for P1 and P2, respectively. In addition, the Mann-Whitney U test indicated no significant differences ($p \leq 0.02$) in the effluent NH_4 concentration between P1 and P2. Similar observations were observed in P3 and P4. Therefore, as observed with the organic matter removal organisms, there is a clear indication that the ammonia oxidizing populations were not affected by the high-pressure conditions and shear effects that the SDOX system could have created and led to biomass lysis. Figure 5.12c shows the concentrations of phosphate in the influent and effluent of the MBR. An influent phosphate concentration of approximately 12 mg L^{-1} was fed to the MBR system. The MBR system was not designed for enhanced biological phosphorous removal (EBPR), and chemical phosphate removal was not applied. Therefore, phosphate was mostly removed for biomass growth requirements. Moreover, phosphate release was not observed after introducing the SDOX unit. Thus, this is another indication that the SDOX system did not contribute significantly to cell lysis that could have released phosphate into the system. Average PO_4 removal values of 71.1 ± 16.0 and 67.1 ± 16.7 % were obtained for P1 and P2, respectively. In addition, the Mann-Whitney U test indicated no significant differences ($p \leq 0.02$) in the effluent PO_4 concentration between P1 and P2.

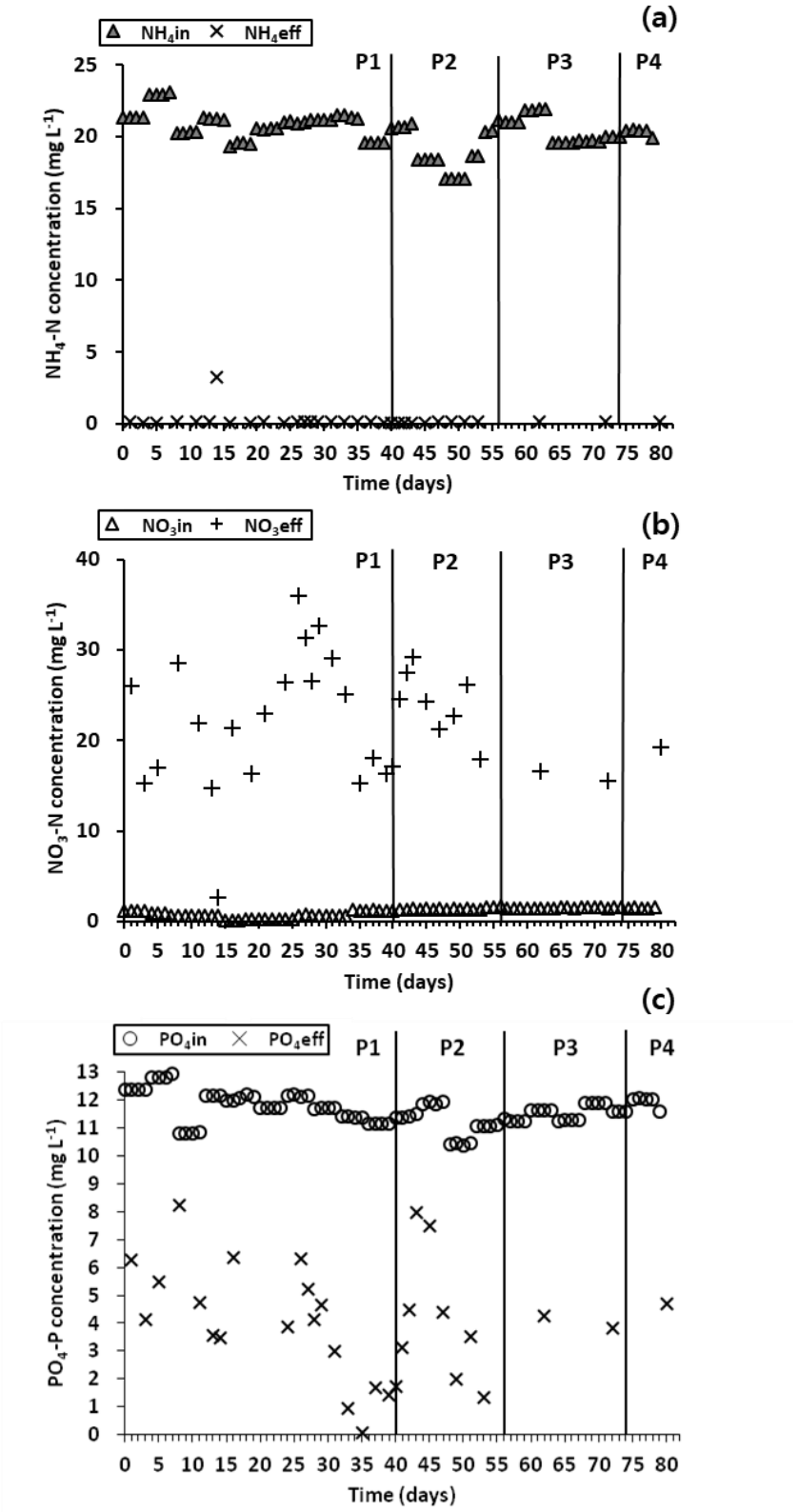

Figure 5.12 Influent and effluent concentration of NH_4-N (a), NO_3-N, and PO_4-P (c) (P1: aerated with diffusers, P2: aerated with SDOX, P3: aerated again with diffusers, P4: aerated again with SDOX)

5.3.5 Effects of the SDOX system on the microbial community in the MBR system

The effects of the SDOX system on the microbial community structure in the MBR system were evaluated via high-throughput DNA sequencing. The similarities between the different microbial communities when switching from diffused aeration to the SDOX unit (P1 and P2, respectively) were visualized via principal coordinate analysis (PCoA) of the unweighted and weighted UniFrac dissimilarities as shown in Figures 5.13a and 5.13b, respectively. Several sludge samples were analyzed covering the entire P1 (bubble diffusers – days 0 to 40) and P2 (SDOX unit – days 41 to 56). During P1, when the MBR was equipped with bubble diffusers, the sludge was acclimating to the operational conditions and synthetic influent wastewater in the MBR system. As time progressed during P1, the sludge sample communities shifted in both the weighted and unweighted PCoA diagrams (Figure 5.13). Such trends suggest a slight change in microbial community structures, although the variability in the ordinates represents only 11.4 and 19.8% of the total variability for the unweighted and weighted PCoA diagrams, respectively. Some changes in the microbial communities were expected during this time since the sludge was acclimating to the environmental conditions within the MBR. However, when the aeration systems were switched from bubble diffusers to the SDOX system (from P1 to P2), more significant shifts in the microbial community were immediately evident in both the weighted and unweighted plots. These results suggest that the introduction of the SDOX unit yielded more substantial shifts in the membership (unweighted) and structure (weighted) of the bacterial community than the acclimatization of the sludge did to the MBR operational conditions. However, such differences become less pronounced at the end of P2, when the systems are becoming acclimated to the SDOX aeration system.

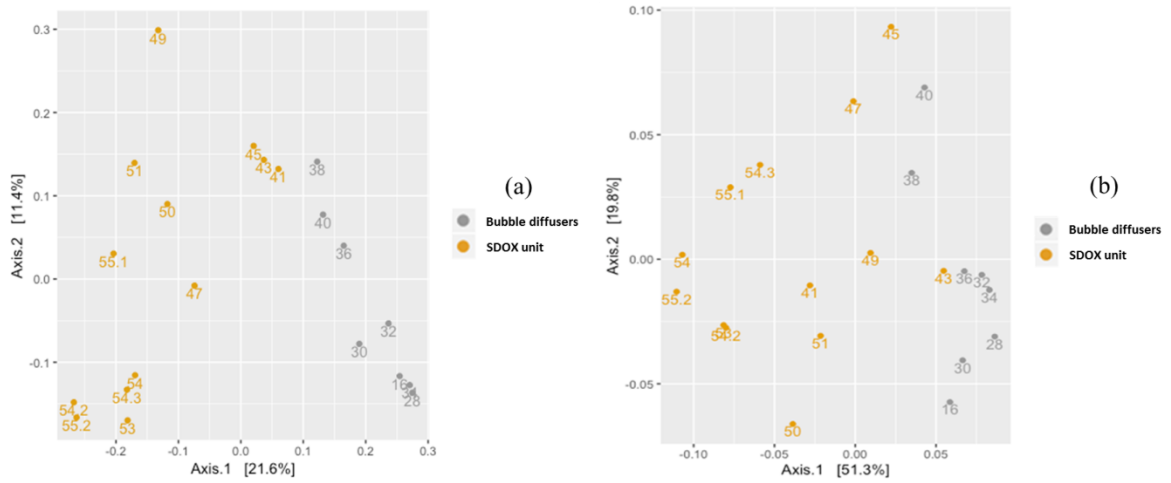

Figure 5.13 (a) PCoA unweighted UniFrac, and (b) weighted visualization of the microbial community structure of sludge samples under two different aeration systems. The numbers in the data points in the figures represent the day of operation. When more than one sample was analyzed for the same operational day, a dot followed by the sample number was added. For instance, the data points 55.1 and 55.2 in Figure 5.13 (a) describes the first and second samples taken on the operational day 55, respectively

Also, as shown in Figure 5.14, visual observations of the changes in activated sludge were carried out as a part of this research, indicating the color of the sludge changed from dark brown to light brown, which is the nature of the sludge (e.g. physical features and/or their physiology) or species changes can be expected to occur.

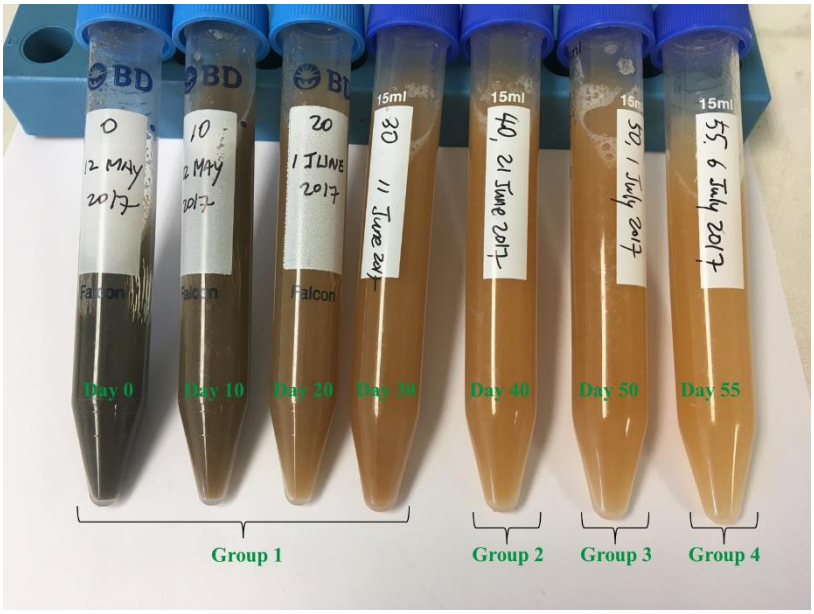

Figure 5.14 Visual changes in activated sludge during the MBR experiments

The relative abundances of the taxon assignments at the level of phylum, class, family, and genus for each sludge sample collected throughout P1 and P2 are presented in Figure 5.15. With respect to the phylum level, a total of 24 different phyla were detected in the 19 analyzed sludge samples corresponding to P1 (diffused aeration – days 0 to 40) and P2 (SDOX unit – days 41 to 56). As indicated in Figure 5.15a, only a small number of bacterial phyla constituted the majority of the bacterial communities in P1 and P2. The dominant phyla were the *Proteobacteria* and *Bacteriodetes* bacteria, comprising between 49.2-64.8% and 23.4-39.8% of the total bacterial sequences, respectively. These two phyla have been reported to be dominant in biological WWT systems regardless of the specific WWT technology deployed (Nascimento et al. 2018; Xu et al. 2018). The phyla composition did not change after switching the aeration system from diffused aeration to the SDOX unit (on day 41). After introducing the SDOX unit the *Proteobacteria* and *Bacteriodetes* abundance remained at 86% of the total bacterial sequences compared to the 89% reported for the diffused aeration. In addition, the Mann-Whitney U test indicated no significant differences ($p \leq 0.02$) in the abundance between P1 and P2 for *Proteobacteria* and *Bacteriodetes*. As such, the high-pressure conditions and shear effects introduced by the SDOX unit did not change the microbial community composition at the phyla level. Subdominant phyla accounting for more than 1% of the total bacterial sequences included *Acidobacteria* (1.4-6.2%), *Actinobacteria* (1.1-5.7%), *Plactomycetes* (1.0-4.6%), *Gemmatimonadetes* (0.1-4.1%), and *Chloroflexi* (0.2-1.1%). These phyla have also been proved to be abundant in biological WWTP systems, even though the percentage of each

phylum has considerably varied among the different published studies (Hu et al. 2012; Nascimento et al. 2018; Xu et al. 2018; Yadav et al. 2014; Zhang et al. 2017).
At the class level, *Alphaproteobacteria* and *Gammaproteobacteria* (both *Proteobacteria*) were the dominant class at 20.6-38.4 and 11.2-31.1% of the total bacterial sequences, respectively. *Saprospirae* (*Bacteriodetes*) accounted for 11.0-26.9% of all the sequences. The abundance of these three classes was similar after switching the aeration system from diffused aeration to the SDOX unit. The Mann-Whitney U test indicated no significant differences ($p \leq 0.02$) in the abundance between P1 and P2 for these three classes. Classes above 1% included *Cytophagia* (1.0-7.1%), *Flavobacteria* (1.0-8.3%), *Acidobacteria-6* (1.2-4.4%), *Actinobacteria* (1.0-5.7%), *Deltaproteobacteria* (2.2-6.3%), *Gemmatimonadetes* (0.1-4.1%), *Sphingobacteriia* (0.9-6.2%), *Betaproteobacteria* (0.6-5.1%), *Planctomycetia* (0.6-4.3%), and *Chloracidobacteria* (0.1-2.4%). Some minor fluctuations of specific classes were noticed. However, most of the classes related to the phyla previously described supporting the presence of communities commonly abundant in municipal WWTP systems. The introduction of the SDOX unit (on day 41) did not induce changes at the class level as observed in Figure 5.15b and as previously noticed at the phyla level.

At the family level, *Chitinophagaceae* was the subdominant group with an abundance of 10.3-24.7% of the total bacterial sequences, followed by *Thiotrichaceae* (4.5-20.3%), *Xanthomonadaceae* (4.8-15.0%), and *Sphingomonadaceae* (2.4-17.4%). The abundance of *Chitinophagaceae* remained mostly unchanged during the evaluated period, although a slight decrease was observed at the end of the SDOX period (on day 54 in P2). The abundance of *Caulobacteraceae*, gram negative bacteria affiliated to the *Proteobacteria* phylum, also gradually declined shortly after starting the MBR operation with the pressured aeration system, suggesting that these families could be vulnerable to the high-pressure conditions exerted by the SDOX unit. The opposite trend was observed for *Thiotrichaceae* and *Sphingomonadaceae* where the abundance of these two families increased after the introduction of the SDOX unit. Additionally, the abundance of *Saprospiraceae* (*Sphingobacteriales* class) increased after introducing the SDOX system. However, the Mann-Whitney U test indicated no significant differences ($p \leq 0.02$) in the abundance between P1 and P2 for the families previously described.

Finally, at the genus level, 4.5-20.3% of the total identified bacterial sequences corresponded to the genus *Thiothrix*, followed by *Sphingopyxis* (2.1-17.4%) and *Niabella* (1.6-13.4%). Overall, and as reported for the other bacterial community levels, there were no major changes when incorporating the SDOX unit, although some variations were observed as follows. The presence of the *Thiothrix* genus (*Proteobacteria*) slightly increased after introducing the SDOX unit towards the end of this phase. However, the Mann-Whitney U test indicated no significant differences ($p \leq 0.02$) in the abundance between P1 and P2 for this genus. The *Thiothrix* genus is characterized by a group of filamentous bacteria commonly found in WWTPs (Nielsen et al. 2000). The *Thiothrix* genus has been related to carbon removal and nitrification processes in WWTPs (Nierychlo et al. 2020). The *Thiothrix* genus may have better resisted the high-pressure

conditions and shear effects exerted by the SDOX unit. The relative abundances of *Thiothrix* during P1 and P2 were on average 7.8 ± 1.9 % and 14.3 ± 5.1%, respectively. The *Sphingopyxis* genus (*Sphingomonadaceae* class) exhibited a similar trend to the *Thiothrix* genus. The Mann-Whitney U test indicated no significant differences ($p \leq 0.02$) in the abundance between P1 and P2 for the *Sphingopyxis* genus. The *Sphingopyxis* genus can resist high osmotic pressure conditions (Verma et al. 2020); the authors also reported that *Sphingopyxis* have been involved in the degradation of aromatic compounds (Verma et al. 2020). The presence of *Niabella* originally decreased at the beginning of the MBR adaptation phase (P1), and then gradually increased even after introducing the SDOX unit. The relative abundances of *Niabella* during P1 and P2 were on average 4.4 ± 2.7 % and 10.6 ± 2.3%, respectively. The Mann-Whitney U test indicated significant differences ($p \leq 0.02$) in the abundance between P1 and P2 for the *Niabella* genus. The presence of *Niabella* was detected in conventional WWTP systems provided with standard diffused aeration systems (Jiao et al. 2016; Starke et al. 2017), and they have been found to participate in the nitrification process (Bucci et al. 2020); however, this genus has not been reported when operating at high-pressure conditions (Zhang et al. 2016; Zhang et al. 2017).

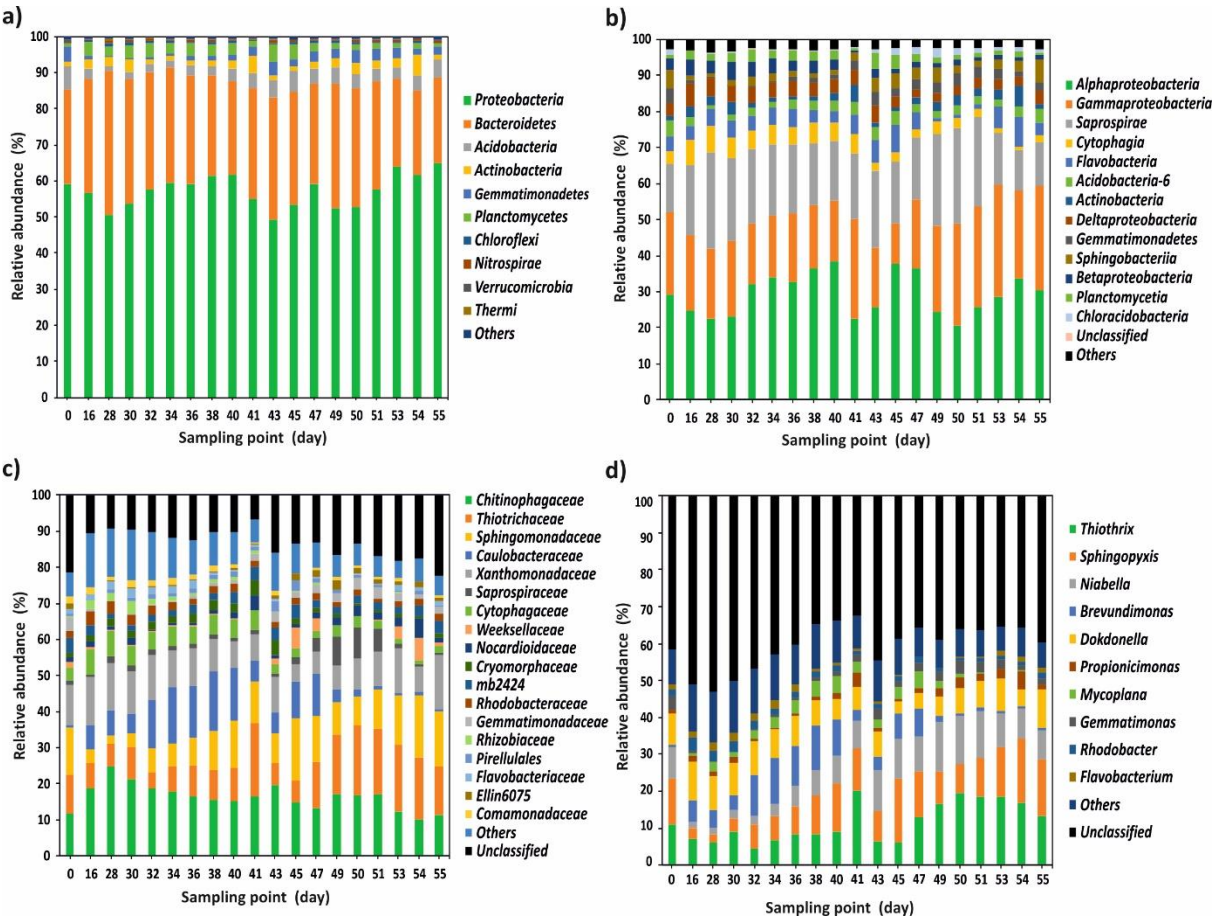

Figure 5.15 Bacterial community abundance for the first 55 days of the MBR operation at the level of (a) phylum, (b) class, (c) family, and (d) genus. Minor taxa classified as less than 1.0% of total sequences are grouped as "others", and those not classified are noted as "unclassified"

Only a few other studies have evaluated changes in microbial communities under high pressure-conditions in the context of biological WWT (Zhang et al. 2016; Zhang et al. 2017). However, such studies were carried out in systems fed with high saline wastewater (approximately 3.0%). To the best of our knowledge, this is the first study reporting on the changes in microbial communities at high-pressure conditions in the context of biological WWT systems. The results of the current study indicate that at the phylum, class and family levels, the major components of the microbial community remained stable throughout the bubble diffusion and SDOX operating periods. However, the weighted and unweighted UniFrac analyses indicate that there was a shift in the microbial community over time, first during the acclimation period of P1 and more significantly following the change to the SDOX system during P2. Regardless, the overall performance of the WWT system remained consistent, indicating that while the high-pressure conditions and shear effects introduced by the SDOX system may have altered some membership within the microbial community, the changes were insufficient to change the overall performance of the system.

The SDOX technology exhibited both much higher alpha factors and energy efficiencies when operated at high MLSS concentrations compared to diffused aeration (Kim et al. 2020), and also did not affect the biological performance of the system. Therefore, the SDOX technology can be proposed as an alternative for DO supply in activated sludge WWTPs. A WWTP equipped with the SDOX technology can either increase the receiving wastewater flowrate (for a given footprint), or decrease the footprint needs (for a given flowrate). During this research, the system reached a pseudo steady-state conditions; particularly, in phase P2, the variation of key performance indicator parameters (e.g. MLSS, MLVSS, MLVSS/MLSS, SOUR, COD, NH_4, and PO_4) were lower than 10% in consecutive days. However, further research would be needed to explore the long-term effects of the SDOX unit on the biological activities of the sludge at a complete stabilized (steady-state) conditions. In addition, a synthetic wastewater simulating a municipal wastewater was used in this study for feeding the MBR; thus, further research would be needed to confirm such same effects on real municipal and/or industrial wastewater. In this context, additional research is needed to evaluate the impact of the operational conditions of the SDOX system on other biological processes such as denitrification and biological phosphorous removal (i.e., EBPR). Moreover, the impact of the SDOX system on the subsequent solid-liquid separation processes (such as sludge settling and/or membrane filtration) needs to be further evaluated. The experimental design of such future evaluations may consider also the possibility of evaluating biological systems in parallel equipped either with fine-bubble diffusers, or with an SDOX unit.

5.4 Conclusions

- The concentration of active biomass was not impacted by the introduction of the SDOX unit. The PSD was reduced by the action of the SDOX unit, although the MLVSS

concentration and the MLVSS/MLSS ratio were not affected by the introduction of the SDOX technology in the MBR system.

- The biological performance of the MBR system was not influenced by the introduction of the SDOX system. The COD removal, ammonia removal and nitrification activities were not modified by the introduction of the SDOX system. In addition, the sludge activity measured as the OUR and SOUR remained unchanged after introducing the SDOX unit.
- The microbial community in the MBR system shifted over time during the diffused aeration operating period and more substantially following the introduction of SDOX. However, the major taxa in the community (including many involved in key biological wastewater degradation processes) remained relatively stable throughout both operating periods, indicating that the community was sufficiently robust to handle the high-pressure conditions of the SDOX system.
- The SDOX technology is a promising technology for supplying DO in biological WWT systems, particularly when working at high MLSS concentrations. The treatment capacity of WWT systems can be eventually expanded by incorporating such aeration technology.

5.5 Acknowledgments

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Chapter 6

Effects of a sidestream concentrated oxygen supply system on the membrane filtration performance of a high-loaded membrane bioreactor

This chapter is based on:

Kim SY, Garcia HA, Lopez-Vazquez CM, Ćurko J, Matošić M, Brdjanović D (*In preparation*) Effects of a sidestream concentrated oxygen supply system on the membrane filtration performance of a high-loaded membrane bioreactor

Abstract

To investigate the influence of high-pressure and shear effects on the membrane filtration performance, a bench-scale of membrane bioreactor (MBR) fed artificial municipal wastewater was continuously operated for 80 days in four phases: (P1) bubble diffusers (days 0 to 40), (P2) supersaturated dissolved oxygen (SDOX) (days 41 to 56), (P3) bubble diffusers (days 57 to 74), and (P4) SDOX (days 75 to 80). Several sludge parameters, visual inspection of membrane, and permeability test were carried out. Our results demonstrated that the high-pressure effects contributed to severe membrane fouling compared to bubble diffuser aeration system. Biofouling seemed the principal contributor to the cake layer when using bubble diffusers, whereas organic fouling seemed to be the primary contributor to the cake layer when using concentrated oxygen supply system (i.e., SDOX). It is plausible that small fractions of particle size distribution (PSD) would be a main parameter affecting the intensive membrane fouling (e.g., formation of a dense and thin cake layer). However, notwithstanding several possibilites, PSD itself alone cannot unquestionably elucidate the deteriorated membrane fouling propensity. Therefore, presumably, a combination of several factors (certainly including PSD) resulted in the serious membrane fouling imposed by the high-pressure and shear effect.

6.1 Introduction

Membrane bioreactors (MBRs) combine the advantages of biological treatment with membrane filtration. Benefits of MBRs compared to conventional activated sludge (CAS) systems include: (i) the production of a reliable high-quality effluent satisfying the most strengthened discharge standards; (ii) the operation at much higher mixed liquor suspended solid (MLSS) concentrations reducing the system footprint; (iii) the possibility to operate at much higher solid retention times (SRTs) producing low amounts of stabilized sludge; and (iv) handling unexpected high organic loads and shock loads without compromising the system performance (Kim et al. 2019).

MBRs are usually equipped with conventional diffused aeration systems, fine and/or coarse bubble diffusers, to provide the dissolved oxygen (DO) needs for the biological process and membrane scouring. It has been widely reported that the poor oxygen transfer performance exhibited by diffused aeration systems (Cornel et al. 2003; Duran et al. 2016; Germain et al. 2007; Henkel et al. 2011; Kim et al. 2019; Kim et al. 2020; Kim et al. 2021; Krampe and Krauth 2003; Muller et al. 1995). The oxygen transfer performance of diffused aeration systems is severely affected by the MLSS concentration in the reactor. Conventional MBRs operate at higher MLSS concentration (approximately 10 g L^{-1}) compared to CAS systems (approximately 3 g L^{-1}). Thus, the inefficiency introduced by conventional diffused aeration system is more notorious in MBRs than in CAS systems. Operating MBRs at higher than usual MLSS concentrations, (i.e., MLSS concentrations higher than 10 g L^{-1}), is highly desirable to increase the treatment capacity of such systems and/or to reduce even further the system's footprint. Such concept of an MBR operated at MLSS concentrations higher than 10 g L^{-1} was introduced by Kim et al. (2019) as the high-loaded MBR (HL-MBR). Significantly, the negative effects exerted by the high MLSS concentration on the oxygen transfer when using diffused aeration system are more noticeable in such systems. Therefore, the operation of conventional MBRs beyond MLSS concentrations of 10 g L^{-1} is either not technically feasible, or extremely energy inefficient (Kim et al. 2019).

Innovative oxygenation technologies have been recently developed to enhance the oxygen transfer process in biological wastewater treatment systems. Among them, the concentrated oxygen supply systems such as the supersaturated dissolved oxygen (SDOX) system appears as a promising technology. The SDOX system consists of a pressurized chamber operated at a pressure of approximately eight bars. A high purity oxygen (HPO) source is introduced into the pressurized chamber. A stream of the mixed liquor from the biological reactor of the wastewater treatment system is recirculated through the pressurized chamber where it gets in contact with the HPO source at high-pressure conditions. Consequently, concentrated DO concentrations can be achieved, for instance, DO concentrations of up to 350 mg L^{-1} in clean water can be reached (Kim et al. 2020). The concentrated and/or supersaturated mixed liquor is released back to the biological reactor introducing in such way large amounts of concentrated DO. Kim et al.

(2020) assessed the oxygen transfer performance of the SDOX system at MLSS concentrations ranging from approximately 4 to 45 g L^{-1}, and it was compared to the oxygen transfer performance of conventional diffused aeration systems. The SDOX showed much higher oxygen transfer rates (OTRs) (14 g O_2 L^{-1} d^{-1}) compared to diffused aeration (fine-bubble diffusers) (2.4 g O_2 L^{-1} d^{-1}). Moreover, the SDOX system reached oxygen transfer efficiencies (OTEs) of approximately 100% in clean water. Fine-bubble diffusers exhibited an OTE of approximately 5% per meter of submergence (Kim et al. 2019). Besides, the authors reported much higher alpha factors (mass transfer ratio of process-water to clean-water) for the SDOX system than for the fine-bubble diffusers. The SDOX system demonstrated a much better oxygen transfer performance compared to fine-bubble diffusers, particularly, when working at MLSS higher than 10 g L^{-1} (i.e., in the HL-MBR operational range). Thus, the SDOX system overcomes the oxygen transfer limitations imposed by conventional diffused aeration systems for MBRs working at high MLSS concentrations.

The SDOX technology exposes the mixed liquor to high pressure-conditions and shear forces. Hence, the biological activity of the sludge in the biological systems might be impaired. Kim et al. (2020) evaluated the influence of the SDOX system on the biological performance of an MBR system. Specifically, the authors assessed the biological carbon removal and nitrification performance of a lab-scale MBR treating synthetic municipal wastewater equipped either with a fine-bubble diffuser, or with the SDOX unit. The authors concluded that the biological performance of the system was not affected by the introduction of the SDOX unit (i.e., high pressure conditions and shear forces). In addition, the taxa in the sludge community remained relatively unchanged; particularly, the taxa related to the key biological wastewater treatment processes were investigated.

Overall, the SDOX technology has shown a better oxygen transfer performance compared to diffused aeration systems, and the biological wastewater treatment processes were not affected by the action of the SDOX unit. On the other hand, the shear effects and high-pressure conditions exerted by the SDOX technology could modify the properties of the sludge. Thus, such changes on the sludge properties could eventually influence the performance of downstream solid-liquid separation processes observed in wastewater treatment processes such as gravity settlers and/or membrane filtration. For instance, Zhang et al. (2015) reported that shear forces generated by conventional diffused aeration systems already contributed considerably to the modification of particle size distribution (PSD) of sludge affecting the sludge settleability. In addition, changes in the PSD of the sludge significantly affect the membrane filtration performance in membrane filtration processes (Fortunato et al. 2018; Shen et al. 2015). Particularly, the sludge flocs are attracted and accumulated onto the membrane surface contributing to the formation of a cake layer reducing the membrane filtration performance. The smaller the sludge particle size, the more compact the cake layer affecting the membrane filtration performance (Hennemann et al. 2021; Meng et al. 2006; Meng et al. 2007a; Meng et al. 2007b; Temmerman et al. 2015). The shear effects and high-pressure

conditions introduced by the SDOX technology can contribute to lowering the PSD of the sludge, eventually worsening subsequent membrane filtration separation processes. Moreover, the breakage of sludge-flocs due to the shear forces and high-pressure condition may aid to release compounds such as extracellular polymeric substances (EPS) and soluble microbial products (SMP). These compounds have been reported to exert a negative effect on the membrane filtration process (Chang et al. 2002; Le-Clech et al. 2006).

Notwithstanding the promising benefits offered by the SDOX technology mentioned above, the potential impact of the SDOX technology on the subsequent solid-liquid separation processes has not been yet investigated. Particularly, MBR systems seem to be the proper niche for the SDOX technology when working at higher than usual MLSS concentrations as in the HL-MBR concept (i.e., MLSS concentrations higher than 10 g L^{-1}). The SDOX technology is an innovative process for supplying DO and the technology has been mostly evaluated in the context of clean water including bioremediation processes, aquaculture applications, river restorations, and odor control processes, among others. Only a few studies have been reported utilizing the SDOX system in the context of biological wastewater treatment (Kim et al. 2019; Kim et al. 2020; Kim et al. 2021). To the best of the authors' knowledge, the impact of the SDOX technology on the membrane filtration process of MBR systems working at high MLSS concentrations has not been assessed. This study will therefore address such needs directly.

This research aimed at evaluating the potential impacts of the SDOX technology on the membrane filtration performance of an MBR system operated at high MLSS concentrations. Sludge properties including total suspended solids (TSS), volatile suspended solids (VSS), PSD, SMP, and EPS were determined and linked to the membrane filtration performance. In addition, scanning electron microscope (SEM) images of the membranes were evaluated and energy dispersive X-ray (EDX) analysis were also carried out for characterizing the surfaces of membranes to better determine the causes affecting the membrane filtration process due to the presence of the SDOX technology.

6.2 Materials and Methods

6.2.1 Design of experiments

A bench-scale MBR was operated for 80 days fed synthetic wastewater. The MBR was provided with either conventional fine bubble diffusers (supplying air), or with a bench-scale SDOX unit (supplying pure oxygen). The MBR was inoculated with fresh activated sludge from the municipal wastewater treatment plant (WWTP) of the city of Zagreb (Zagreb, Croatia). The system was operated in four phases as follows: phase one (P1) bubble diffusers (day 0 to 40), phase two (P2) SDOX unit (day 41 to 56), phase three (P3) bubble diffusers (day 57 to 74), and phase four (P4) SDOX unit (day 75 to 80). Both the transmembrane pressure (TMP) as a function of the exposure time, as well as the membrane permeability were continuously monitored to assess the membrane fouling and membrane filtration performance of the two

different evaluated aeration systems (diffusers and SDOX). In addition, sludge properties (e.g., TSS, VSS, PSD, SMP, and EPS) were determined. Moreover, SEM images coupled with EDX analysis were carried out for characterizing the surfaces of the virgin and fouled membranes.

6.2.2 Experimental setup

A bench-scale MBR was equipped with either conventional fine bubble diffusers (Figure 6.1a), or the SDOX unit (Figure 6.1b) for introducing DO. The MBR was made of transparent acrylic glass with a total volume of 30.6 L (16 × 25.5 × 75 cm), and it was operated at a working volume of 6.5 L. A flat-sheet membrane (XJ3 module by Kubota) made of chlorinated polyethylene was submerged in the middle and lower part of the MBR basin. The membrane had an effective filtration area of 0.11 m^2 with a nominal pore size of 0.4 µm. A coarse bubble diffuser (Uxcell, model number: US-SA-AJD-231698, Hong Kong) was placed at the bottom of the MBR basin to continuously scour the membrane. Air was supplied by a blower (HIBLOW HP 80, Techno Takatsuki, Japan) operated to satisfy the specific membrane scouring aeration needs (also known as specific aeration demand (SAD)) of 2 $m^3/m^2/h$ (i.e., the membrane was continuously scoured with a tangential air flowrate of 0.22 m^3/h). A piston fluid metering pump (FMI PM6014 RHV, Fluid Metering, Inc, USA) was provided to extract the permeate from the MBR.

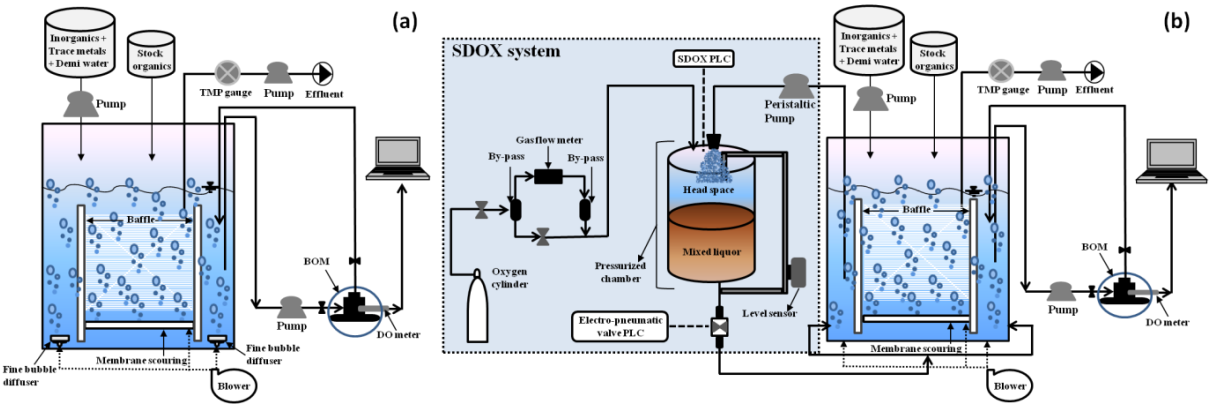

Figure 6.1 Experimental setup of the membrane bioreactor system provided with (a) bubble diffusers and (b) SDOX system

To escape the pressure effect when discharging supersaturated mixed liquor from the SDOX pressurized chamber, the discharge line was situated under the coarse bubble diffuser, as exhibited in Figure 6.2. Considering that the diameter of the orifice connected to the discharge line is about 1cm, the height difference between the coarse bubble aeration and the orifice is about 2cm. The released mixed liquor from the SDOX pressurized chamber did not affect coarse bubble aeration for membrane scouring.

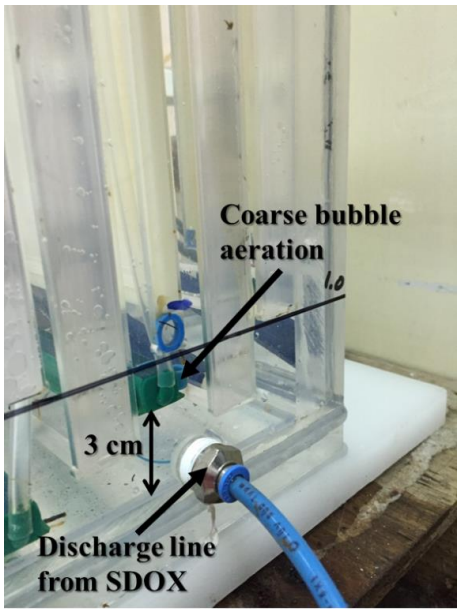

Figure 6.2 Discharge line from the SDOX pressurized chamber under coarse bubble aeration

During the operational phases P1 and P3, the DO was supplied by conventional fine bubble diffusers (Hydrofarm, Inc, USA). The diffusers were placed at the bottom of the MBR, and they were operated at an air flowrate of approximately 0.5 m^3/h; the fine bubble diffusers served as the primary source of oxygen (Figure 6.1a). In addition, two baffles were placed at both sides of the immersed membrane to secure an uniform distribution of the airflow. The membrane surface was continually air-scoured. The TMP of membrane was continuously monitored by a digital gauge (Ashcroft 2274, USA) fitted to the permeate line and connected to a data acquisition system. During the operational phases P2 and P4, the DO was supplied by a bench-scale SDOX unit (Figure 6.1b). The bench-scale SDOX unit consisted of a pressurized chamber connected to an HPO source (pure oxygen cylinder (MESSER, Croatia)). The pressurized chamber had a total volume of 2.75 L. Approximately 20% of the total volume (0.55 L) was occupied by the mixed liquor sludge solution to be oxygenated, while the 80% remaining (2.20 L) consisted of the headspace. The pressure in the SDOX pressurized chamber was set at 6.9 bars. The pressurized chamber was provided with two analogic pressure gauges (McDaniel Controls, USA), a digital pressure sensor (SICK AG, Germany), and a level digital sensor (Setra Systems, USA). An electro-pneumatic valve (NVF3-MOH-5/2-K-1/4-EX, FESTO, Germany) was introduced at the effluent drainage of the pressurized chamber. The pressure sensors, level sensors, and the electro-pneumatic valve were used to monitor and control the level and pressure of the pressurized chamber by the aid of a program logic controller system (SIMATIC S7-1200, Siemens, Germany). The HPO was supplied into the SDOX system through a gas flowmeter provided with mass totalizer capacities (Model # 32908-59, Cole-Palmer, USA). The sludge stream was introduced into the SDOX system through a 6 mm orifice by a high-pressure peristaltic pump (EW-74203-24, Cole-Palmer, USA) at a flowrate of 0.3 L min^{-1}. The supersaturated sludge stream was released back into the MBR introducing in such way DO into

the MBR. Such stream was released at the bottom of the MBR basin providing also mixing to the MBR system. The coarse bubble diffuser was cleaned periodically by 1% of NaOH followed by 1% of HCl (Figure 6.3).

Figure 6.3 Coarse bubble diffuser cleaning

6.2.3 Experimental procedure

The MBR was inoculated with fresh activated sludge from the aerobic basin of the municipal WWTP located in the city of Zagreb in Croatia. The WWTP was operated as a CAS process and designed only for carbon removal. The plant was operated at an SRT of approximately five days at an average MLSS concentration of approximately 4.0 g L^{-1}. The sludge was filtered through a 500 μm sieve and thickened up to an MLSS concentration of approximately 15 g L^{-1} first by gravity settling (carried out at the WWTP facility) followed by membrane filtration thickening (carried out at the laboratory facilities of the faculty of food technology and biotechnology at the University of Zagreb).

After inoculating the MBR system, it was then operated with the fine bubble diffusers for 40 days (P1). On P1, the biomass was mostly acclimating to the synthetic influent wastewater and operational conditions in the MBR. As such, the baseline conditions regarding membrane fouling in the MBR could be established. On day 41, the aeration system was switched to the SDOX unit and the MBR was operated under identical operational conditions as in P1 for 16 days (P2). P2 aimed at investigating the potential effects of the SDOX system (high-pressure conditions, shear effects, among others) on membrane fouling. Then, the SDOX unit was replaced again by the fine bubble diffusers, and the system was operated for 18 additional days (P3). P3 was included to monitor the changes in membrane fouling when the system was exposed again to bubble diffusers. Finally, the aeration system was again replaced by the SDOX

unit, and the evaluation was continued for six additional days (P4) to confirm the effects of the high-pressure conditions on membrane fouling. The fouled membranes during the entire evaluated period were replaced by a virgin membrane once the TMP exceeded the value of 0.45 bars. In this study, membrane relaxation and/or membrane backwashing were not applied. That is, the membrane was continuously permeating the treated effluent to maximize the visualization of the potential fouling effects on the membrane (i.e., pushing the limits of the membrane regarding membrane fouling and membrane filtration performance).

The MBR was fed synthetic wastewater. The organic constituents included glucose, acetate, peptone, and yeast, were added to the MBR by gravity drips using a gravity medical infusion at a flowrate of 1 L d^{-1}. A second solution containing the inorganic components of the synthetic wastewater was added through a piston fluid metering pump (FMI PM6014 RHV, Fluid Metering, Inc, USA) at a flowrate of 39.6 L d^{-1}. That is, the total influent flowrate to the MBR was set at 40.6 L d^{-1} delivering the wastewater composition of the synthetic wastewater to the MBR system as describe in Table 6.1. Such a flowrate established a total hydraulic retention time of approximately 4 hours and a membrane flux (i.e., the amount of permeate produced per membrane surface area per time) of 15 L m^{2-} h^{-1} (generally abbreviated as LMH). The SRT was set to 10 days by withdrawing 0.65 L d^{-1} of sludge from the MBR.

Table 6.1 Characterization of the synthetic wastewater reaching the membrane bioreactor system

Chemical compounds	Concentration (mg L^{-1})	Chemical compounds	Concentration (mg L^{-1})
$C_6H_{12}O_6$	421.88	$FeCl_3 \cdot 6H_2O$	19.36
$C_2H_3NaO_2$	571.28	$C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$	30.00
Peptone	260.00	$MnCl_2 \cdot 4H_2O$	0.74
Yeast	40.00	$ZnSO_4 \cdot 7H_2O$	2.50
NH_4Cl	65.69	$CuSO_4 \cdot 5H_2O$	0.61
KH_2PO_4	48.33	$CoCl_2 \cdot 6H_2O$	2.09
$NaHCO_3$	251.95	$Na_2MoO_4 \cdot 2H_2O$	0.26
$CaCl_2$	40.37	H_3BO_3	0.13
$MgSO_4$	65.65	$NiSO_4 \cdot 7H_2O$	0.29

6.2.4 Samples collection and analytical methods

6.2.4.1 Membrane fouling evaluation (transmembrane pressure and membrane permeability determination)

The membrane permeability was measured twice in demineralized water: (i) before exposing/submerging each new membrane into the MBR; and (ii) after the membrane was completely fouled (i.e., when TMP of membrane reached a value of 0.45 bars). The membranes were submerged in a separate MBR with a working volume of 31.7 L (14 × 22 × 103 cm) filled with demineralized water. The permeability was determined by measuring the stabilized TMP

at different permeate fluxes. The permeate was extracted by a piston fluid metering pump (FMI PM6014 RHV, Fluid Metering, Inc, USA). The TMP was monitored by a digital gauge (Ashcroft 2274, USA) fitted to the permeate line. The flowrate was controlled by a flowmeter controller (FMI V200, Fluid Metering, Inc, USA) connected to the piston fluid metering pump. The flux was calculated by dividing the measured flowrate by the membrane filtration area, and the permeability was obtained by dividing the calculated flux by the TMP. The permeability was determined using no less than four data points – fluxes vs stabilized TMPs. The flux was gradually increased and the corresponding stabilized TMP values were recorded. Flowrates ranging from approximately 0.7 to 2.2 L h^{-1} were selected providing fluxes ranging from approximately 6.6 to 22.0 L m^{2-} h^{-1} (LMH). The permeability was calculated determining the slope when plotting the flux as a function of the stabilized TMP. The slow, fast, and total membrane fouling rates were calculated based on the instantaneous changes of the TMP as a function of time. The slow membrane-fouling rate was calculated until the TMP reached a value of 0.06 bar, while the fast fouling rate was calculated from the moment the TMP exceeded the value of 0.06 bar until reaching the maximum allowed TMP value of 0.45 bar.

6.2.4.2 Total and volatile suspended solids determination

The TSS and VSS concentrations were determined following the standard methods for the examination of water and wastewater (APHA, 2017). The determination of TSS and VSS was carried out between 2 to 3 times a week.

6.2.4.3 Particle size distribution and diluted sludge volume index

The PSD of the sludge was determined using a Malvern Mastersizer 2000 (Malvern Instruments Ltd, Malvern, UK) with laser diffraction functionalities. The PSD results are reported as the value of the particle size at 10% (D10), 50% (D50), and 90% (D90) cumulative distribution. The D50 is also reported as the median particle size (MPS). That is, D50 indicates that 50% of the total sludge particles are less than or equal to the D50 value. Similarly, D10 indicates that 10% of the total sludge particles are less than or equal to the D10 value. The PSD determination was carried out between 2 to 3 times a week. The PSD determinations were carried out in triplicate, and the average value of PSD was reported.

Settleability tests were performed to determine the sedimentation of the sludge when exposed either to the conventional diffusers, or to the SDOX system. The diluted sludge volume index (DSVI) were determined following the method reported by Ekama et al. (Ekama et al. 1997). The settled sludge volume after a 30 min sedimentation period should be between 150 and 250 mL L^{-1}. Permeate was used to carry out the dilutions. The DSVI is usually utilized to determine the settleability of concentrated sludge (e.g., above 15 g L^{-1} of TSS). The DSVI determinations were conducted between 2 to 3 times a week.

6.2.4.4 Extraction and analytical determination of soluble microbial products and extracellular polymeric substances (EPS)

The SMP and EPS analytical determinations were carried out following the method described

by Le-Clech et al. (2006). Mixed liquor samples containing a volume of 60 mL were centrifuged for 5 min at 5,000g using a Rotina 35 centrifuge (Hettich, Germany). The supernatant was then filtered through a 1.2 µm Minisart® syringe filter (Sartorius, Germany). The filtrate represented the SMP solution. The SMP was determined as reported by Jarusutthirak and Amy (2006) both by measuring the total organic carbon (TOC) content using a TOC analyzer (TOC-5000A, Shimadzu, Japan) as non-purgeable organic carbon, and by measuring the ultraviolet absorbance at 254 nm (UV_{254}) using a spectrophotometer UNICAM Helios Beta (Thermo Fisher Scientific, USA). The samples were filtered through a 0.45 µm polypropylene filter (Whatman, USA) to determine both the TOC and UV_{254}. Therefore, the measured TOC values represented the dissolved organic carbon (DOC) values. The specific ultraviolet absorbance ($SUVA_{254}$) was calculated dividing the UV_{254} by the DOC. Since SMPs are characterized by major components of dissolved organic matter in wastewater, the $SUVA_{254}$ was reported as the SMPs introduced by Jarusutthirak and Amy (2006).

After removing the supernatant from the sample for the SMP determination, the remaining pellet retained at the bottom of the centrifuge tube was re-suspended with demineralized water. The mixture was then heated for 10 min at a temperature of 80 °C in a water bath (Memmert, Germany), which was then centrifuged for 10 min at 7,000g. The supernatant was then filtered through a 1.2 µm Minisart® syringe filter (Sartorius, Germany). Such filtrate contained the EPS compounds. The EPS can be further classified into carbohydrate EPS (EPS_c) and protein EPS (EPS_p). The EPSc was determined following a photometric method performing a H_2SO_4/phenol oxidation followed by a colorimetric determination method using a DR3900 spectrophotometer (Hach, USA) (Lowry et al. 1951); the EPSp was determined following the Folin–Ciocalteu method (Dubois et al. 1956). Both SMP and EPS were determined between 2 to 3 times a week. Figure 6.4 exhibits samples of EPSc (left) and EPSp (right) during their analyses.

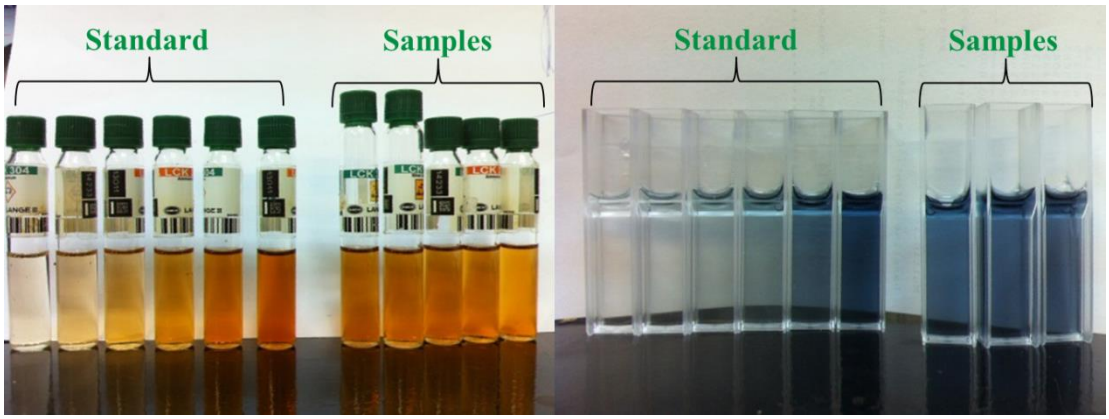

Figure 6.4 EPS samples with the addition of chemicals: EPSc (left), EPSp (right)

6.2.4.5 Determination of the characteristics and elemental composition of the compounds deposited on the membrane surface

After determining the permeability of the fouled membrane in demineralized water, the membranes were dried at atmospheric conditions. Then, membrane fragments of approximately

1 cm^2 were prepared. Such membrane fragments were later observed under the microscope (JEOL JSM-7500F Field Emission SEM, Japan) to determine the characteristics of the compounds that were deposited on the surface of the membrane. In addition, the elemental composition of such compounds were determined. Each sample was coated with gold (Au) by using a JFC-1300 high-vacuum auto fine sputter coater (JEOL, Japan) connected to a DUOLINE vacuum pump (Pfeiffer vacuum GmbH, Germany). The coated samples were placed on a sample holder, and the membrane surfaces were scanned using a JSM-7500F Field Emission SEM (JEOL, Japan). Each sample was photographed using secondary electrons (SE) at 5,000x magnification at 5 kV. For characterizing the chemical elemental composition of the compounds deposited on the membrane surface, an EDX spectroscopy (Noran system 6, Thermo Fisher Scientific, USA) was employed with the SEM images taken at the low magnifications of 5,000x. The determination of the characteristics and elemental composition of the compounds deposited on the membrane surface was performed on the following membranes: an unused membrane, two membranes used during P1, and three membranes used during P2.

6.3 Results and discussion

6.3.1 Effect of the SDOX system on the transmembrane pressure and membrane permeability

The MBR operation right after inoculation (day 1) was started with a new (unused) membrane. During the entire evaluated period, the membranes were replaced every time the TMP exceeded the value of 0.45 bars. That is, 13 new membranes were used to carry out the entire evaluation. Figure 6.5 presents the evolution of the TMP as a function of the operational time. In addition, Table 6.2 describes the TMP increment rates for each membrane (slow, fast, and total), the permeability for each virgin and fouled membrane, and the loss of permeability. Each membrane was identified with a unique number and code as indicated in Table 6.2. The first and second column in Table 6.2 display the membrane number (in a chronological order as used in this research) and the code assigned to each membrane, respectively. The MBR was continuously operated at the same effluent (permeate) flowrate of 40.6 L d^{-1} setting a membrane flux of approximately 15 L m^{2-} h^{-1}. Therefore, the TMP values reported in Figure 6.5 and Table 6.2 were obtained at the very same flux for all the evaluated membranes. Usually, MBR systems provided with flat sheet (Kubota) membranes (as used in this research) are operated in cycles introducing relaxation phases in between the filtration phases to enhance the membrane filtration performance. In this evaluation, to push the fouling limits of the membrane filtration process, the relaxation phase was not included in between the filtration phases.

At the startup of the MBR system during the phase P1 as shown in Figure 6.5, the TMP of the first membrane (M#1) sharply increased after only two days of operation. In addition, Table 6.2 exhibits higher slow, fast, and total fouling rates experienced for M#1 compared to M#2. During phase P1, the system was equipped with the fine bubble diffusers. The sludge taken from the

municipal WWTP for inoculating the MBR system was concentrated from 4 g L^{-1} (sludge concentration at the WWTP in Zagreb) to 15 g L^{-1} (sludge concentration at the startup of the MBR). In addition, at the startup of the MBR, the MBR system was fed synthetic influent wastewater whose characteristics differed from the real municipal wastewater at which the sludge was already exposed and acclimated. The sludge needed to be acclimatized again to a new set of operational conditions. Therefore, during the first few days of operation the biomass could have been stressed eventually causing a detrimental effect on the membrane filtration processes (Shah et al. 2021; Wu et al. 2011).

In addition, while concentrating the sludge, some sludge flocs-breakage (sludge disintegration) could occur contributing to the presence of large amounts of small-size loose particles that could also affect the membrane filtration processes (Temmerman et al. 2015; Wisniewski and Grasmick 1998). Both the stress exerted on the biomass, as well as the potential presence of biomass fragments could eventually explain such a pronounced increase on the observed TMP values during the initial operational days. After reaching the TMP value of 0.45 bar, M#1 was replaced by M#2. The MBR system was operated with M#2 for approximately 25 days before experiencing a severe increase on the TMP; that is, a much better membrane filtration performance was observed compared to M#1, also indicated in Table 6.2 as a lower fouling rate for M#2 (slow, fast, and total) compared to M#1. Nevertheless, a pronounced and fast fouling was also observed on M#2 after 25 days of operation; at this point, M#2 was replaced by a new membrane (M#3). The MBR system was then operated for additional 12 days during which membrane fouling was not observed.

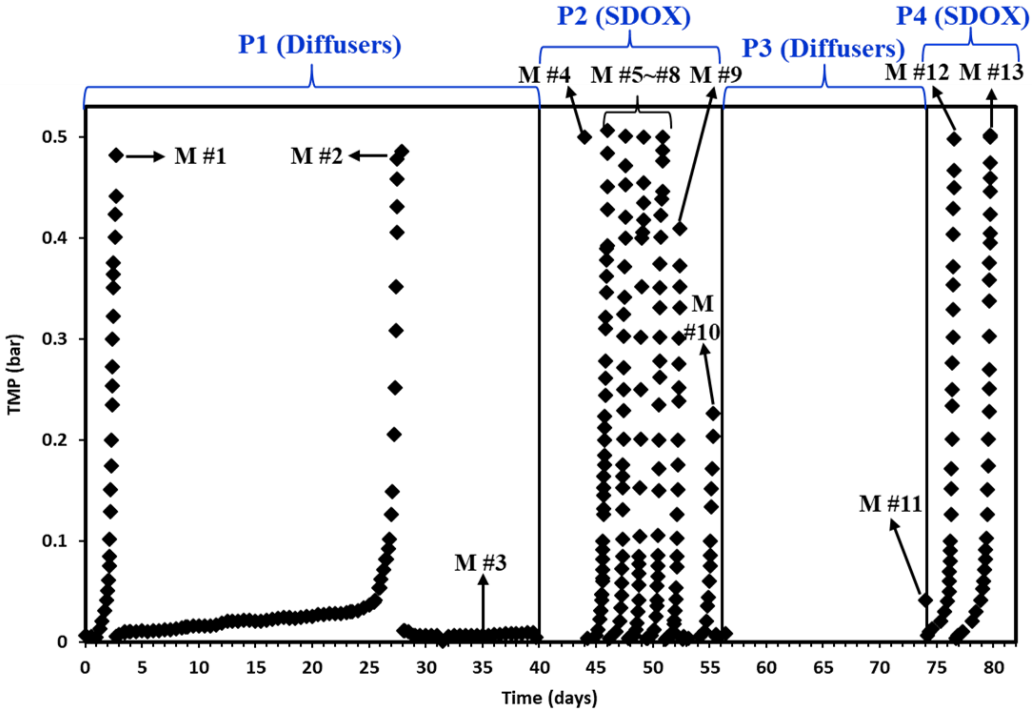

Figure 6.5 Transmembrane pressure profile as a function of the exposure time. M#1 to M#13 identifies the 13 different new membranes used in this research. The four phases of this research are indicated in the figure

Table 6.2 Transmembrane pressure increment rates and membrane permeability for the evaluated membranes

Membrane number	Membrane code	Operational days	Days of exposure	dTMP/dt (bar/day)			Permeability (K) (L m^{-2} h^{-1} bar^{-1})		Loss of permeability (%)
				Slow	Fast	Total	Clean	Fouled	
1	DIFF1	0 to 2.75	2.75	0.0262	0.6230	0.1728	7529.2	96.1	98.7
2	DIFF2	2.95 to 28.06	25.11	0.0024	0.2375	0.0192	6946.7	58.7	99.2
3	DIFF3	28.26 to 39.74	11.48	-	-	-	9505.5	1840.2	80.6
4	SDOX1	39.94 to 44.23	4.29	-	-	0.1155	7816.3	51.3	99.3
5	SDOX2	44.43 to 46.24	1.81	0.0422	0.9247	0.2773	7816.3	77.6	99.0
6	SDOX3	46.44 to 47.84	1.40	0.0511	1.3232	0.3554	8016.4	65.5	99.2
7	SDOX4	48.04 to 49.45	1.41	0.0555	0.9616	0.3511	7103.5	70.0	99.0
8	SDOX5	49.65 to 51.06	1.41	0.0543	0.9617	0.3511	8462.0	64.9	99.2
9	SDOX6	51.26 to 52.58	1.32	0.0432	0.9228	0.3079	8739.9	113.0	98.7
10	SDOX7	52.78 to 55.52	2.74	0.0087	0.3416	0.0820	9696.1	423.9	95.6
11	DIFF4	55.72 to 74.16	18.44	-	-	0.0020	5523.4	527.0	90.5
12	SDOX8	74.36 to 76.7	2.34	0.0229	0.9913	0.2097	5891.8	130.7	97.8
13	SDOX9	76.90 to 79.94	3.04	0.0228	0.7646	0.1633	5829.6	92.1	98.4

On day 41, the aeration system was changed from the bubble diffusers to the SDOX system indicating the beginning of the phase P2; a new membrane (M#4) was placed to better observe the effects of the SDOX system on the membrane filtration performance. After approximately 4 days the maximum allowed TMP value was reached, as it was also observed at the beginning of P1. Eventually, the sludge was adapting to the new conditions introduced by the SDOX system. As the MBR continued to run with the SDOX system, a rise in the TMP values for all the subsequent evaluated membranes was also noticed. Six additional unused membranes were introduced (M#5 to #10), and all of them lasted for approximately 1.5 days. As observed in Figure 6.5 and Table 6.2, the TMP increase over time during P2 was much more pronounced than during P1. On day 53, the SAD was increased from 2.0 to 2.5 m^3/m^2 /h to evaluate the possibilities of achieving a more prolonged membrane operational period. Indeed, such operational change seemed to play a certain positive effect on delaying the replacement of the membranes; e.g., membrane #10 lasted for almost three days compared to the 1.5 days of the previous membranes (M#5 to #9). However, such improvements on the membrane filtration were still below the performance obtained in P1 where the membrane was operating for 25 days before reaching the maximum TMP value. The fouling rates observed in P2 were higher than in P1 for all the evaluated membranes confirming a worse membrane filtration performance in P2 than in P1. Thus, it can be inferred that the SDOX system introduced changes on the sludge characteristics in the MBR with a negative short-term impact on the membrane filtration performance.

Right before M#10 reached the maximum allowed TMP value, the phase P3 was initiated; that is, the aeration system was switched back from the SDOX system to the bubble diffusers. The phase P3 was evaluated, started with a new membrane in the MBR (M#11). A marginal increase on the TMP was observed during phase P3, and the system was operated all the time with the same membrane (M#11) until reaching operation day 74. The negative membrane filtration effects introduced by the SDOX system observed in P2 were not noticeable in P3. This was also observed on the total fouling-rate as shown in Table 6.2 exhibiting almost the lowest fouling-rate values comparable to those observed during P1. The bubble diffusers operated almost at atmospheric pressure and with the absence of the high shear forces introduced by the SDOX. That is, the sludge characteristics were much less affected and thereby yielding a better membrane performance compared to when the system was equipped with the SDOX system.

Right after the initiation of the phase P4 on day 75, a new membrane was introduced into the MBR (membrane M#12) to evaluate the effects of re-introducing the SDOX system on the membrane filtration performance. Increments on the TMP values were observed in P4, although the TMP values were lower than the values observed in P2 when the MBR was also equipped with the SDOX unit. The M#12 only lasted for little longer than two days, when a new membrane was introduced (membrane M#13). Both P2 and P4 exhibited almost the same fouling pattern. Therefore, it can be concluded that the SDOX aeration system had a detrimental effect on the membrane filtration performance observed as a fast increase on the TMP values.

In addition, Table 6.2 describes the permeability of each clean and fouled membrane and the loss of permeability expressed as a percentage. The loss of permeability was almost the same for all the evaluated membranes, since the permeability was measured when each membrane reached its limit of functionality. Certainly, the SDOX system exhibited a negative effect on the membrane filtration performance. When the MBR was equipped with the SDOX unit, the sludge was recirculated through the SDOX system by a high-pressure peristaltic pump through a small-diameter piping (6 mm). The sludge was introduced to the SDOX pressurized-chamber through a small orifice in the SDOX system (6 mm), and exposed to high-pressure conditions (6.9 bars) inside the pressurized-chamber of the SDOX unit. Therefore, the sludge was exposed to high shear forces and friction that could have some immediate influence on the structure and nature of the sludge flocs. Consequently, changes on the size distribution of the sludge were expected, as reported later in this study, eventually negatively affecting the membrane filtration performance. Nevertheless, the biomass activity was not affected with respect to organic matter removal and nitrification (not reported in this study but thoroughly discussed in Kim et al. (2021); however, such high stress conditions at which the microorganisms were exposed, could have contributed to changes on the sludge characteristics with a negative impact on the membrane filtration performance.

6.3.2 Effects of the SDOX system on the sludge physical-chemical properties

6.3.2.1 Total suspended solids and volatile suspended solids concentration

Figure 6.6 describes the changes on the TSS and VSS concentrations as well as the VSS/TSS ratio as a function of the operational time. During P1, the TSS and VSS concentrations increased right after inoculating the reactor until reaching stable TSS and VSS concentrations by the end of the phase P1 at approximately 16.9 and 14.9 g L^{-1}, respectively. The VSS/TSS ratio also increased until reaching a 0.89 value towards the end of P1. At the beginning of P2 an operational problem occurred with the level sensor of the MBR allowing an excess of influent wastewater to reach the MBR and therefore to slightly dilute the mixed liquor. The TSS and VSS concentrations dropped to approximately 13.5 and 12.6 g L^{-1}, respectively. Such a decrease on the TSS and VSS concentrations was not due to the action of the SDOX system (i.e., shear forces and high-pressure conditions), but rather to the dilution effect. The TSS and VSS concentration increased towards the end of P2 reached TSS and VSS values of 14.1 and 13.0, respectively. During P3, the TSS and VSS concentrations kept increasing reaching concentrations on average of 18.5 and 17.2 g L^{-1}, respectively. Finally, during P4 similar TSS and VSS concentrations as in P3 were reported confirming that the SDOX system did not contribute to reduce the TSS and/or the VSS concentration or to change the VSS/TSS ratio. During the entire evaluated period, the TSS and VSS concentration ranged from 13.5 to 18.8 and from 11.7 to 17.4 g L^{-1}, respectively. Even though some variation on the TSS and VSS were reported, those changes in the TSS and VSS concentration could not explain the different membrane filtration performance observed on the different phases as discussed in previous section 3.1. Likewise, the VSS/TSS ratio adopted values from 0.76 to 0.93 for the entire evaluated period. Accordingly, the VSS/TSS ratio did not reflect major changes on the organic fraction content of the sludge.

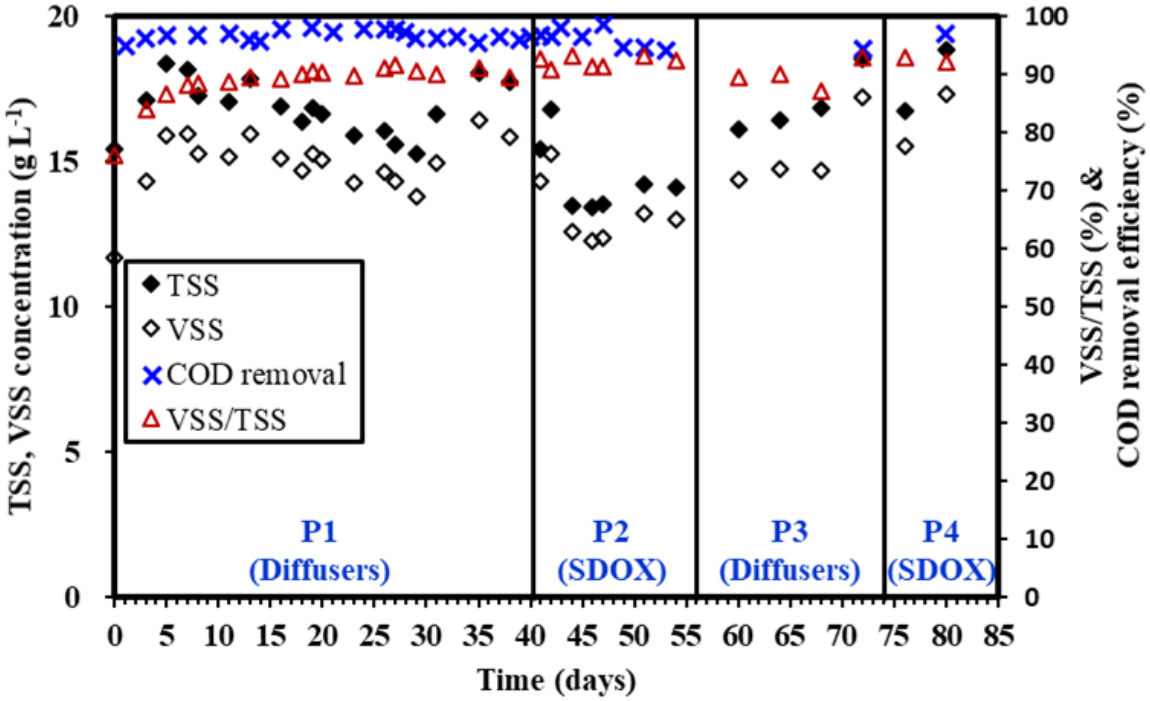

Figure 6.6 Total suspended solids (TSS), volatile suspended solids (VSS) concentrations, VSS/TSS ratio, and chemical oxygen demand removal efficiency as a function of the operational time

Although not reported in this research, the biological performance of the MBR was also evaluated and reported in Kim et al. (2021). The biological performance regarding COD removal and nitrification did not vary during the evaluated period, confirming that the activity of the sludge was not affected depending on the utilized aeration system. That is, the deterioration on the membrane performance observed primarily in P2 cannot be explained due to changes on the TSS and/or VSS concentrations in the mixed liquor, or due to the changes on the biological activity of the sludge.

6.3.2.2 Particle size distribution, median particle size, and diluted sludge volume index

The PSD of the sludge has been considered one of the most critical sludge properties affecting the membrane filtration performance (Diaz et al. 2016; Drews 2010; Shen et al. 2015). Figure 6.7 shows the MPS as a function of the operational time. Right after inoculating the MBR, the sludge exhibited an MPS of approximately 114 μm. During P1 the MPS continuously decreased until reaching a value of approximately 39.8 μm towards the end of P1. Such a reduction on the MPS during P1 was only due to the action of the shear forces introduced by the bubble diffusers and the filtration process. The sludge was taken from a municipal WWTP, so during the acclimation period to the MBR such a reduction on the MPS was expected due to the action of the shear forces (Stricot et al. 2010). Noticeably, as described in Section 3.1 such shift on the PSD of sludge towards smaller particle sizes did not have a detrimental effect on the membrane filtration performance during P1. On the other hand, the membrane filtration exhibited a better performance at the end of P1compared to at the beginning of P1. On the day 41, the SDOX system was introduced initiating the phase P2. The PSD kept shifting towards the low size particle range. As shown in Figure 6.7, the MPS further decreased from 39.8 μm at the beginning of P2 to 28.9 μm by the end of the P2. The reduction on the MPS was not as evident during P2 as compared to during P1. However, P2 started at a much lower MPS than P1; the sludge in P2 was already acclimatized to the operational conditions in the MBR. In this regard, the changes on the MPS on P2 were mostly due to the action of the SDOX unit. Even though the starting MPS was smaller (40 μm) than the MPS at the start of P1 (114 μm), the MPS kept decreasing during P2 until reaching an MPS of 28.9 μm. Significantly, during P2 the membrane filtration performance was negatively affected as delineated in Section 3.1. Thus, the changes on the PSD on P2 could eventually contribute to such reduced membrane filtration performance.

When the SDOX system was replaced again by the diffuser (P3), the MPS of the sludge increased in the MBR; some re-flocculation of the sludge could eventually take place. During P3 a better membrane filtration performance was observed than during P2. Therefore, there is a potential indication that the PSD of the sludge may exhibit a key role on the performance of the membrane filtration. The SDOX unit could introduce an adverse effect on lowering the size of the sludge particles, and ultimately exhibiting a negative effect on the membrane filtration performance. The SDOX unit could introduce an adverse effect on lowering the size of the sludge particles, and ultimately exhibiting a negative effect on the membrane filtration

performance. However, when the high shear effects introduced by the SDOX system were no longer present, the MPS of the sludge increased improving the membrane filtration performance. When changing the aeration system back to the SDOX system in P4 the filtration performance of the new membranes was again strongly affected. The MPS sharply decreased immediately after introducing again the SDOX unit, and the membrane filtration performance was negatively affected. However, towards the end of P4 the MPS gradually increased. This was also noticed at the end of P2. The fact that the MPS was increasing towards the end of the evaluation in P2 and P4 could imply that the long-term exposure of the sludge to the SDOX unit (not evaluated in this study) may not be that much negative in terms of the reduction of the MPS and membrane filtration performance. However, more research would be needed to confirm that hypothesis.

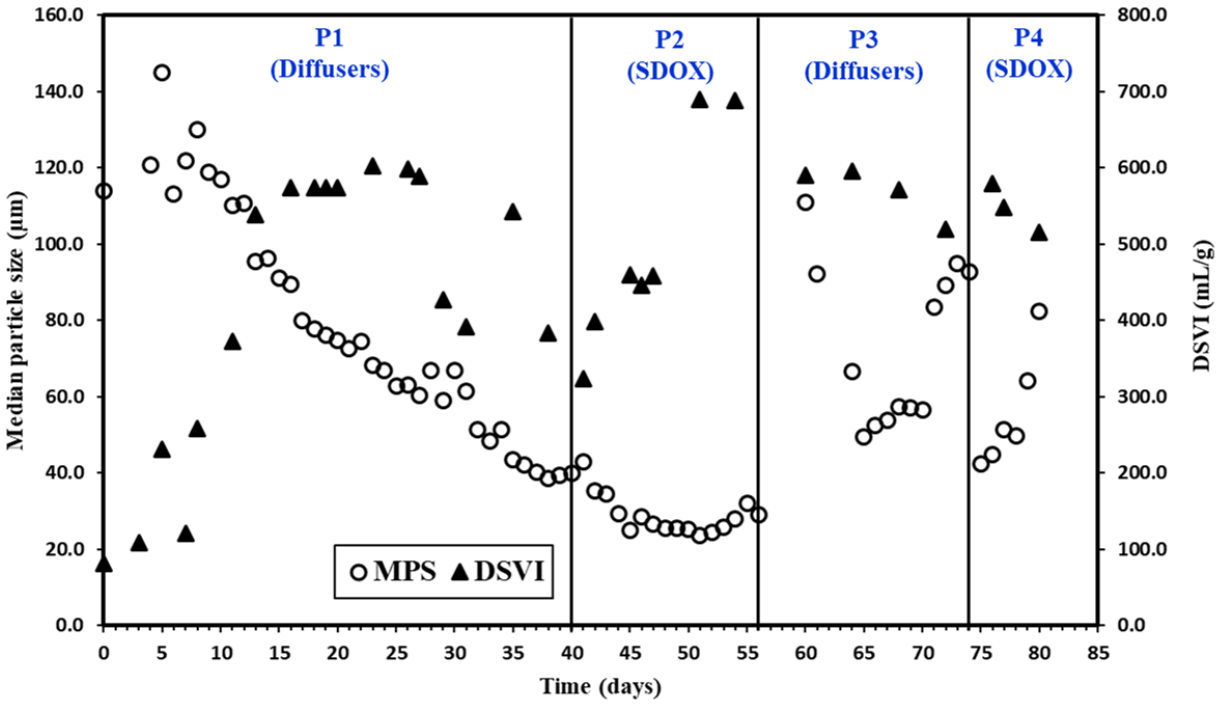

Figure 6.7 Median particle size and diluted sludge volume index of the sludge as a function of the operational time

Figure 6.8 shows the PSD of the sludge evaluated during phases P1 (black dots) and P2 (red dots). The PSD continuously shifted towards the low particle size range (left side of the Figure 6.8). That is, the fraction of small-sized particles in the sludge gradually increased. Particularly, during P1 an increase on the proportion of particles with a particle size range from approximately 10 to 100 µm was observed. However, during P2 the shift of the PSD occurred at lower particle sizes compared to P1, increasing the ratio of particles in the sludge with particle sizes lower than 10 µm. Such an increase on the fraction of particles with sizes lower than 10 µm was quite notorious when looking at the left side of Figure 6.8 during P2. The presence of a left shoulder in Figure 6.8 can be observed indicating an increase on the high rate of particles with a particle size lower than 10 µm.

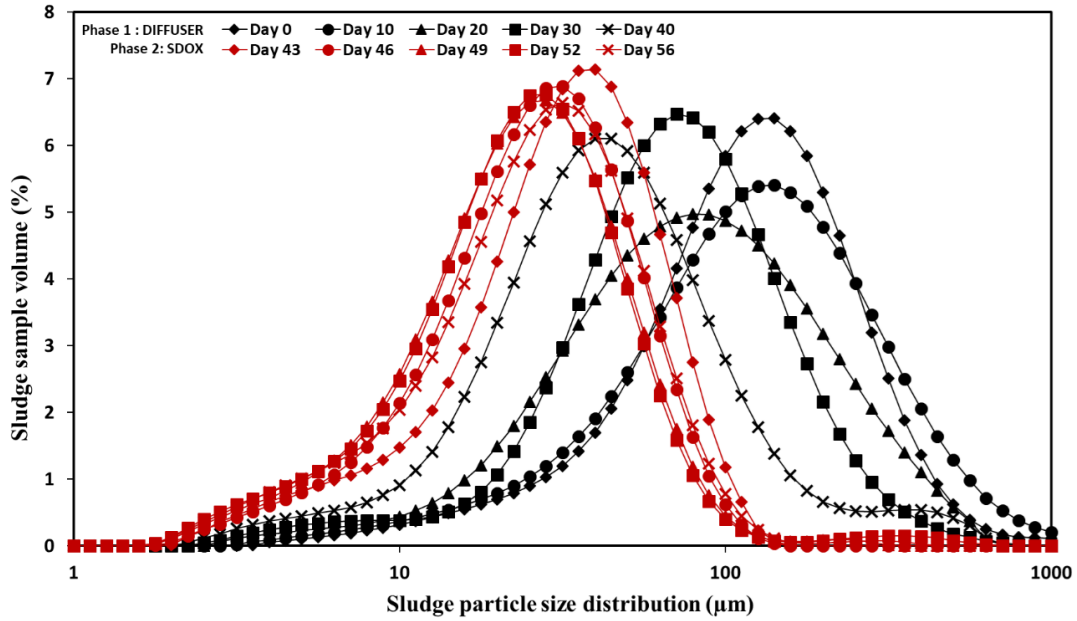

Figure 6.8 Particle size distribution of the activated sludge during the experiment

Based on Figure 6.8, a much larger fraction of small particles was present during P2 (SDOX unit) as compared to during P1 (bubble diffusers). Guo et al. (2012) reported that particulate and colloidal solids contributed significantly to pore blocking leading to a reduced membrane filtration performance. Small particles can easily adhere to the surface of the membrane due to their inherent low diffusive back-transport forces (Belfort et al. 1994). That is, lower reverse transport velocities from the cake layer to the bulk mixed liquor solution occurred for small particles than for large particles. This phenomenon could be explained considering that the scouring effect of the fluid when passing through the membrane surface is not as effective for removing small particles as for removing large particles. As a result, the cake layer on the surface of the membrane would consist mostly of small particles forming a thin and compact cake layer that cannot be effectively removed by air scouring (Park et al. 2015), and thereby contributing to deteriorate the membrane filtration performance.

The MPS, also known as the D50, represents the value of the particle size at 50% in the cumulative distribution. Lin et al. (2010) could not establish a clear relation between the MPS and the membrane filtration performance. However, the authors observed a link between the D10, the value of the particle size at 10% in the cumulative distribution, and the membrane filtration performance. Particularly, the authors reported that the membrane filtration performance was affected when increasing the fraction of particles with a particle size smaller than 10 µm. In addition, Bai and Leow (2010) and Qi et al. (2016) had shown that membrane filtration was strongly affected by sludge flocs sizes less than 50 µm. Similar findings were observed in this research. Table 6.3 indicates the fraction of particles organized in two categories: (i) 1-50 and 50-100 µm, and (ii) 1-10 and 10-100 µm. As observed in Table 6.3, when focusing on the 1-50 µm range fraction, the operation during P1 increased such range fraction from approximately 13.8%, when the MBR system was just inoculated, up to 56.1% at

the end of P1. However, as soon as the SDOX system was introduced, the 1-50 μm fraction range sharply increased reaching a maximum value of 85.4% during P2. That is, the SDOX system indeed exerted a strong influence increasing the fraction of particles within the 1-50 μm range, and that was detrimental for the membrane filtration performance. Similar effects were observed when focusing on the 1-10 μm range. The incorporation of the SDOX unit increased the fraction of small particles from 6.1% at the end of P1, up to a maximum of 15.5% at P2. As previously reported by Lin et al. (2010), large fractions of particles with diameters lower than 10 μm could be adverse impact on the membrane filtration performance.

Table 6.3 also indicates that as soon as the SDOX system was taken out of the MBR and replaced by the bubble diffuser, both the 1-50 μm fraction as well as the 1-10 μm fraction decreased back to similar values as observed during P1. That is, the fraction of small particles in the mixed liquor decreased during P3. This is reflected in an improved membrane filtration performance during P3. Finally, when the SDOX system is introduced back in P4, again the fraction of both the 1-50 μm and 1-10 μm ranges increased with a consequent deterioration of the membrane filtration performance. Therefore, the amount of small particles present in the mixed liquor sludge had a detrimental effect on the membrane filtration, and the high shear forces introduced by the SDOX system contributed to create that shift on the PSD increasing the proportion of small particles.

Table 6.3. Fractions of sludge particle sizes organized in two different ranges for all the evaluated phases

Sampling points (days)		Proportion (%)			
		Particle size (1-50 μm)	Particle size (50-1000 μm)	Particle size (1-10 μm)	Particle size (10-1000 μm)
Inoculated sludge	0	13.8	85.8	1.56	98.3
DIFFUSER (Phase 1)	10	15.9	83.5	2.1	97.7
	20	29.1	71.0	2.9	97.5
	30	29.1	71.1	3.5	96.8
	40	56.1	43.9	6.1	94.8
SDOX (Phase 2)	43	72.9	27.1	10.9	90.6
	46	81.8	18.2	12.5	89.7
	49	85.3	14.7	15.2	87.4
	52	85.4	14.6	15.5	87.0
	56	80.0	20.0	14.3	87.7
DIFFUSER (Phase 3)	60	24.1	70.9	4.8	90.6
	64	36.8	59.6	6.8	90.1
	68	36.7	58.9	7.6	88.5
	71	29.8	64.0	5.4	88.7
	74	27.8	61.5	4.3	85.4
SDOX (Phase 4)	76	48.3	50.3	9.9	89.5
	77	42.7	57.4	9.4	91.4
	78	44.4	53.9	9.2	89.9

Kim et al. (2001) also reported on the influence of the shear effect on the membrane filtration performance of MBRs. The authors evaluated the impacts of the shear effects created by two different types of pumps, a centrifugal pump and a rotary pump, on the membrane filtration performance of a crossflow MBR. The authors concluded that the rotary pump imposed greater shear to the microbial flocs than the centrifugal pump. The percentage of flocs below 10 μm increased from 23% to 61% in the rotary pump compared to the centrifuge pump. Thus, lower fluxes were obtained when operating with the rotary pump (20 L m^{2-} h^{-1}) compared to when operating with the centrifuge pump (36 L m^{2-} h^{-1}) after only six days of operation. Likewise, as observed in our research, the shear effects exerted an impact on increasing the fraction of small particles with a detrimental effect on the membrane filtration processes. Similarly, Wisniewski and Gramsick (1998) also operated an MBR exposing the sludge at different shear forces by increasing the cross flow velocity. As the cross flow velocity increased, the fraction of small particles with average sizes below 10 μm increased, showing detrimental effects on the membrane filtration performance. In addition, higher resistance to filtration was reported when operating at cross flow velocities of 5 m/s than at 0.5 m/s. Therefore, indeed the introduction of the SDOX system increased the shear on the sludge shifting the PSD of the sludge to the low-size range of the distribution, increasing the percentage of small particles existed in the sludge. Consequently, the presence of a large fraction of small particles contributed to the formation of a more compact cake layer (less permeable) worsening the membrane filtration performance as observed during P2 and P4 in this research.

Figure 6.7 also indicates the DSVI of the sludge as a function of the operational time. The DSVI is utilized to determine the settleability of concentrated sludge. Although the solid-liquid separation in MBRs is achieved by a membrane filtration process and not by gravity settling (Van den Broeck et al. 2012), an increased on the DSVI values could indicate some deterioration of the membrane filtration performance. At the beginning of P1, good settleabilities of the sludge were observed with DSVI values lower than 100 mL g^{-1}; afterward, the DSVI increased indicating a poor settleability of the sludge. The deterioration of the sludge settleability was observed when the MPS decreased below 100 μm. However, at that point, still during P1, a deterioration on the membrane performance was not observed. After the introduction of the SDOX unit (beginning of P2), the PSD kept shifting to the lower side of the range, and the sludge settling properties became progressively worse in such period. The increase on the DSVI implies deflocculation of the sludge shifting the PSD towards low particles sizes (i.e., increasing the fraction of small particles in the sludge). The presence of a non-settleable sludge could also possibly indicate a reduced membrane filtration performance (Ognier et al. 2002; Rosenberger et al. 2006). The DSVI during P3 also exhibited a better sludge settleability compared to P2, and it kept improving towards the end of the phase. Thus, the results may suggest that the sludge originally exposed to high extra shear conditions could recover in terms of membrane filtration performance once the conditions causing the high shear are eliminated. During P4 an increase on the fraction of small particles were observed; however, no major changes on the DSVI were noticed.

6.3.2.3 Presence of EPS and SMP

Organic components such as EPS and SMP are regarded as the main contributors to membrane fouling (Drews 2010; Shah et al. 2021); the membrane pore blocking process is also intimately associated with the presence of EPS and SMP compounds (Guo et al. 2012; Zhang et al. 2015). EPS can be described as a mixture of high molecular polymers. Proteins, polysaccharides, humic acids, lipids, and nucleic acids, are the major constituents of EPSs (Frolund et al. 1996). EPS can make up to 50 to 80% of the total sludge floc weight (Meng et al. 2016). Because of their strong adhesive and cohesive characteristics, EPS acts as a bridge to allow bacteria and their surrounding particles to clump together (Wingender et al. 1999). SMP consists of soluble organic compounds generated because of the bacterial metabolism and autolysis; they can also be present in the influent wastewater (Barker and Stuckey 1999).

The concentrations of EPS and SMP were determined during the evaluated period, and they are presented in Figure 6.9. EPS_p and EPS_c concentrations of 78.9 and 32.5 mg L^{-1}, respectively were observed right after inoculating the MBR at the beginning of P1. The EPS_p decreased towards the end of P1 reaching a concentration of approximately 50.7 mg L^{-1}, while the EPS_c did not fluctuate much during the P1 observing an EPS_c concentration of 33.9 mg L^{-1} at the end of P1. Right after introducing the SDOX unit during P2, no major changes on the EPS concentrations were noticed. Similar EPS concentration as in P2 were reported for P3 and P4. It can be concluded that after the sludge was acclimated to the new operational conditions in the MBR, similar EPS concentrations were observed for the entire evaluated period.

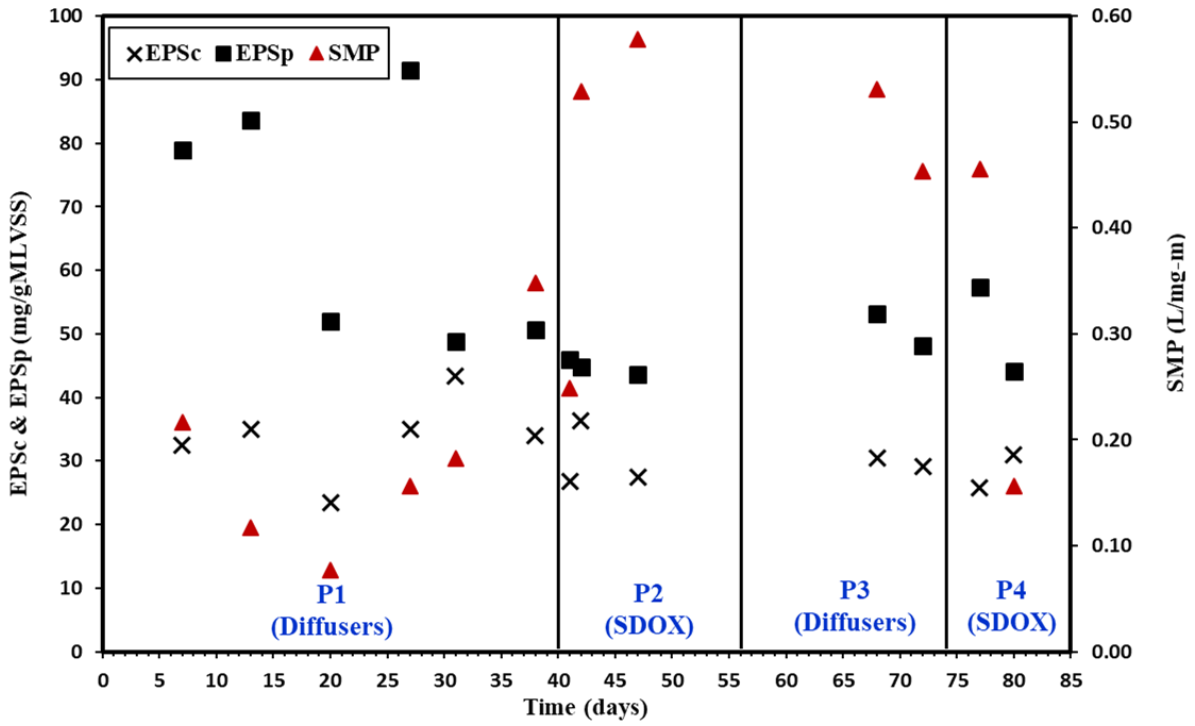

Figure 6.9 Extracellular polymeric substances and soluble microbial products presence in the activated sludge during the evaluated period

Judd and Judd (2011) reported severe fouling at EPS concentrations ranging from 20 to 80 mg g $MLVSS^{-1}$. On the contrary, Geng and Hall (2007) reported the absence of a correlation between membrane fouling and the presence of EPS. The authors claimed that the presence of SMP in the mixed liquor floc was more influential to membrane fouling than the presence of EPS. In our study, the EPS values were within the range reported by Judd and Judd (2011). The membrane filtration performance was not much affected during P1 and P3, in spite of the reported EPS concentrations, whereas the membrane filtration was severely affected during P2 and P4. Therefore, in our study the presence of EPS could not be linked to the membrane filtration performance. The sludge flocs during P2 and P4 were exposed to high-shear conditions; thus, EPS could have been released into the sludge mixture. However, marginal changes on the EPS concentrations were observed during P2 and P4 disregarding such a hypothesis. The SDOX unit shifted the PSD of the sludge to smaller-size particles. However, such changes on the PSD could not be reflected on the increase on the EPS concentrations that could have affected the membrane filtration performance.

The SMP value gradually decreased during the acclimatization period in P1 right after inoculating the MBR. However, after day 20, the SMP concentration continuously increased until the end of P1. In P2, the SDOX unit was introduced and the SMP concentration rapidly increased approximately doubling the SMP values from 0.25 to 0.53 L mg^{-1} m^{-1}. During P3, the SMP values slightly decreased, although showing similar values compared to P2. At the start of phase P4, similar SMP values as observed in P3 were reported. However, the SMP concentration largely dropped at the end of P4.

The increase in the SMP values during P2 was consistent with the increase in the TMP as reported in Figure 6.5. That is, the presence of such SMPs values during P2 could contribute to a reduced membrane filtration performance. The SMPs produced by the microbial metabolism, although not fully characterized during this research, consists of dissolved macromolecules and colloids surrounding the sludge flocs. As the SMPs penetrate through the membrane surface, such substances could be readily adsorbed onto the membrane pores. Thereby, they may accumulate on the membrane surface, eventually forming a gel layer. The gel layer can bring more foulants such as sludge flocs. Particularly, small-sized sludge particles can be easily adhered to the membrane surface, forming a cake, which may ultimately lead to a higher degree of irreversible membrane fouling (Zhang et al. 2015). It is generally known that a cake layer plays a larger role than the internal membrane pore clogging in terms of membrane fouling (Park et al. 2015). The membrane filtration performance was deteriorated during P2, and that could be eventually related to the presence of SMP. However, same SMP values were reported during phase P3, and the membrane filtration performance was not worsened. In this context, the membrane filtration performance cannot be directly linked to the presence of SMP.

6.3.3 Effects of the SDOX system on the membrane surface

Figure 10a shows the images of the fouled membranes when the MBR was equipped with the

diffuser aeration system (M#1 to M#3) or with the SDOX unit (M#4 to M#9). Membrane fouling can be expressed by the overall resistance to filtration composed of three different resistances: the membrane intrinsic resistance, the cake layer resistance, and the pore blocking resistance. Membrane fouling in a submerged MBR stems from a combination of cake layer formation and pore blocking (Chen et al. 2017), both of which always coincide because of the interaction between the biomass metabolism and the membrane (Meng et al. 2007a). Among the two phenomena, the cake layer formation on the surface of the membrane has been considered the primary membrane fouling-causing factor (Hu et al. 2016; Turken et al. 2019); the cake layer accounts for approximately 90% of the total resistance to filtration (Guo et al. 2012). Meng et al. (2007b) in a study aimed at evaluating the characterization of the cake layer in submerged MBRs reported that the cake layer resistance contributed the most to the overall resistance. The authors reported resistances of approximately 8.7, 84, and 7.3% for the membrane intrinsic, cake layer, and pore blocking resistances, respectively. Thus, the cake layer resistance contributed by far the most to the membrane fouling in submerged MBRs. The cake layer resistance can be caused by the presence of: (i) microorganisms (biofouling); (ii) biopolymers or organic matter (organic fouling); and/or (iii) inorganic matter (inorganic fouling). The authors reported that the cake layer fouling in submerged MBRs consisted of sludge – biomass/VSS (63%), inorganic compounds (23%), solutes (8%), and colloidal material (6%). The last two exhibited a higher tendency to membrane fouling by pore blocking (Du et al. 2020; Meng et al. 2007b).

The larger the particles, the easier to detached from the membrane surface and not contributing much to the cake layer resistance, or forming a loose cake layer. On the other hand, the smaller the particles, the stronger the tendency to deposit onto the membrane surface and create a compact cake later; i.e., the accumulation of small particles on the surface of the membrane contributes to form a more compact cake layer decreasing the cake layer porosity and thereby contributing to membrane fouling (Chen et al. 2022).

In addition, solutes (macromolecules) and colloidal material can be adsorbed onto the cake layer and/or are directly deposited on the surface of the membrane contributing also to the formation of a less permeable cake layer. In addition, macromolecules and colloidal material can easily penetrate into the membranes pores and lead to severe membrane pore blocking. Meng et al. (2007b) reported that the causes of biofouling, organic fouling, and inorganic fouling could coexist in the cake layer resistance; the authors observed bacteria clusters covered with biopolymers/organic matter in the cake layer. Mostly, the biopolymers consisted of macromolecules such as polysaccharides. In addition, the presence of inorganic compounds could contribute to precipitate out certain biopolymers having ionic constituents such as SO_4^{-2}, CO_3^{-2}, PO_4^{-3} and OH^-. Cations such as Ca^{+2}, Mg^{+2}, Al^{+3}, and Fe^{+2} could origin the precipitation of such substances contributing to inorganic fouling. In addition, the presence of carbonate species (due to the constant production of CO_2 due to the aerobic respiration) can contribute as well as to inorganic fouling. Thus, there is a synergistic interaction in the cake layer of bacterial,

colloids, macromolecules, and inorganic elements all contributing to the cake layer resistance and membrane fouling. Biopolymers (colloids and macromolecules – such as polysaccharides) have the strongest effect on membrane fouling (Kim et al. 2001; Wang and Li 2008). The provision of aeration (membrane scouring) partially contributes to remove the cake layer, although cannot be completely removed; particularly, the more loose the compact layer, the better the performance of the membrane scouring on preventing membrane fouling.

At the beginning of the evaluation, during P1 when the MBR was provided with the bubble diffuser aeration, the material attached to the surface of the fouled membrane exhibited a dark brown color as observed in images M#1, M#2, and M#3 in Figure 10a. The MPS and PSD described in Figures 6.7 and 6.8, respectively indicate the presence of relatively large-size particles in the sludge. Thus, the cake layer observed in Figure 10a probably consisted mostly of biomass (VSS) as previously described by Meng et al. (2007b) and Bell et al. (2016); thus, the cake layer was not much compacted yielding a relatively porous cake layer. That was confirmed considering the relatively good membrane filtration performance described in Figure 6.5 and Table 6.2, also considering that a relaxation phase was not included in the membrane filtration cycles. In addition, Figure 10a (images M#1, M2, and M#3) show on the left and right sides of the membrane more biomass deposited and accumulated on the surface of the membrane than on the center of the membrane. This could also indicate the presence of a relatively loose cake layer since the provision of the membrane air scouring was able to remove partially the cake layer; particularly, the cake layer located in the center of the membrane where the air scoring seemed to be more intense. Thus, biofouling seemed to account as the major fouling mechanisms in P1 contributing to the cake layer resistance.

The cake layer appearance on the membranes during P2, i.e., M#4 to M#9 in Figure 10a, differs from the membranes during P1 - M#1 to M#3. A most homogeneous cake layer could be observed on the membranes in P2. In addition, the cake layer in P2 seemed thinner than the cake layer observed in P1. In essence, the cake layer in P2 looks more compact than in P1. When looking at the MPS and PSD described in Figures 6.7 and 6.8, respectively, an important reduction on the particle size of the sludge was observed during P2. Such a reduction on the particle size was due to the strong shear forces introduced by the SDOX system. Therefore, there were higher fractions of small-sized particles present in the sludge mixture eventually contributing to the formation of a more compact cake layer. This was also noticed by a decrease on the membrane filtration performance as indicated in Figure 6.5 and Table 6.2, and the presence of a more frequent fouling. In addition, the exposure of the sludge mixture to such high shear forces introduced by the SDOX unit could promote the release and/or generation of colloidal material and macromolecules that could be adsorbed onto the cake layer/membrane surface promoting a less permeable cake layer (Judd and Judd 2011; Stricot et al. 2010). Moreover, such substances could easily penetrate through the membrane pores causing severe membrane pore blocking (Guo et al. 2012). Thus, the presence of higher concentrations of small particles, colloidal material and macromolecules compared to P1 seemed to contribute to

membrane fouling deteriorating in such a way the membrane filtration performance during P2. The main contributor to membrane fouling in the cake layer during P2 seemed to be the organic fouling (macromolecules and small particles); the provision of air membrane scouring seemed not to play a major effect to prevent fouling as was the case in P1.

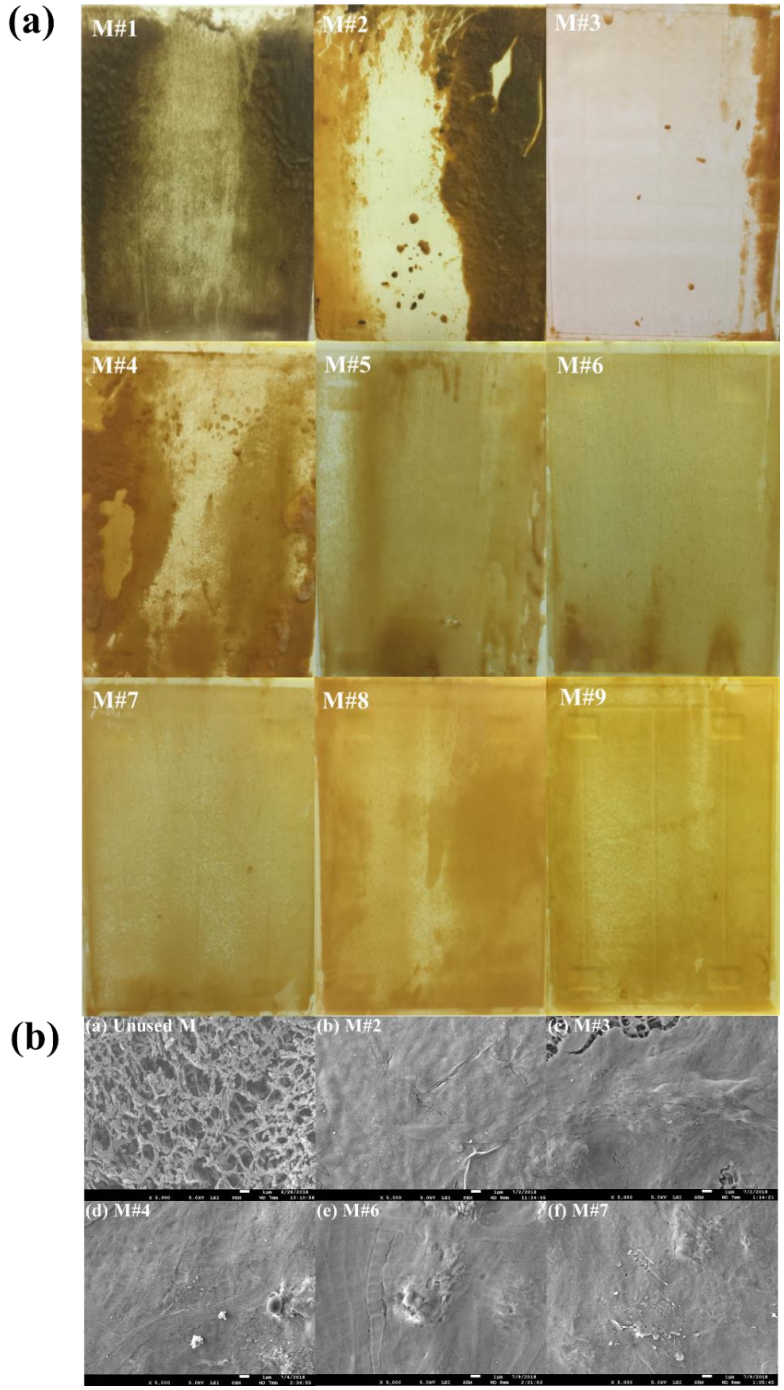

Figure 10 (a) Images of the fouled membranes for the membrane bioreactor equipped with bubble diffusers (M#1 to M#3) and with the supersaturated dissolved oxygen unit (M#4 to M#9); and (b) Scanning electron microscope images of the fouled membranes: Unused membrane (a), M#2 (b), M#3 (c), M#4 (d), M#6 (e), and M#7 (f)

Figure 10b shows the SEM images of the selected membranes photographed at ×5,000 resolution to investigate the morphological features of the cake layers. The unused membrane, Figure 10b (a), exhibited a clean surface with the membrane pores clearly visible on the membrane surface. The rest of the SEM photographs show the membrane surface completely covered by the cake layer. M#3, Figure 10b (c) exhibits some of the membranes pores visible together with the cake layer. Similar observations are shown in Figure 10a for the same membrane. Not much difference was observed on the SEM photographs for the evaluated membranes. Certainly, the fouling was associated with the presence of a cake layer in all the evaluated membranes.

The elemental composition of the surface of the fouled membranes was also evaluated by conducting EDX analyses, and the results are presented in Table 6.3. The filtration membrane was made of chlorinated polyethylene, and the elemental composition presented in Table 6.3 for the unused membrane was in accordance showing the presence of C, O, and Cl. The membranes analyzed during P1 exhibited a changed on the elemental composition with respect to the unused membrane. M#2 and M#3 still exhibited the presence of C, and O; however, higher percentages of O were reported than in the unused membrane (13.56% in M#3 compared to 1.26% in the unused membrane), and the presence of N was observed (10.61% in M#3) but not present in the unused membrane. A low proportion of metallic elements along with non-metallic elements such as Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, and Fe, were present on the membrane surface. The presence of inorganic elements except Cl and Sc was in line with the results from Meng et al. (2007b) when operating a submerged MBR treating synthetic wastewater. Thus, the presence of C, O, N, and trace of inorganic elements in the EDX analysis of the surface of the cake layer is in agreement with the findings reported in Figure 10. Such findings could support the presence of biomass – VSS in the cake lake formation in the membranes during P1, and thereby also contributing to support that biofouling could have been the main cause of fouling during P1.

The EDX analysis of the evaluated membranes during P2 exhibited some changes compared to the EDX analysis of the membranes during P1. A higher proportion of C and O than in P1 was reported as described in Table 6.3. Moreover, N was no longer detected, and the proportion of inorganic elements increased. The absence of N could indicate that the biomass and VSS were no longer the major contributors to the cake layer; in addition, the larger proportion of C and O could also suggest the presence of biopolymers such as polysaccharides as reported by Meng et al. (2007b). Particularly, the high shear effects introduced by the SDOX unit were eventually favoring the deposit of such macromolecules in the cake layer rather than biomass. In addition, the increase on the proportion of inorganic elements occupying the fouled membranes could also influence the cake layer by promoting the precipitation of macromolecules and by introducing a bridging effect (Hong and Elimelech 1997; Seidal and Elimelech 2002). Thus, the EDX analysis of the elemental composition of the surface of the membranes also suggested some changes on the cake layer structure supporting the membrane filtration performance

findings previously reported. The high shear forces introduced by the SDOX unit introduced changes on the sludge mixture reducing the particle size of the mixture and promoting a different composition and structure of the cake layer. The cake layer changed from P1 to P2 from a more loose cake layer to eventually a more compact layer. The presence of biomass as the main component of the cake layer during P1 was most likely replaced by biopolymers. Thus, the major fouling contributor due to the cake layer seemed to change from biofouling in P1 to organic fouling in P2. However, due to the strong reduction on the particle size, and the presence of macromolecules and colloidal mater, membrane pore blocking cannot be rejected as an important contributor to membrane fouling during P2.

Table 6.3 Elemental composition of the surface of the selected evaluated membranes

Element	Weight (%)					
	Unused membrane	M#2	M#3	M#4	M#6	M#7
C	74.57	62.95	65.57	74.79	70.07	74.38
N		13.19	10.61			
O	1.26	11.88	13.56	20.47	24.54	20.22
Na	0.07	0.37	0.05	0.38	0.33	0.66
Mg		0.1	0.16	0.52	0.93	0.38
Al		0.01				
Si		0.1			0.09	
P			0.29	1.51	1.24	1.53
S				0.07	0.04	
Cl	24.1	11.15	8.81	0.4	0.22	1.29
K		0.09	0.63	0.86	0.7	0.8
Ca		0.13	0.18	0.67	1.59	0.48
Sc		0.03				
Fe			0.13	0.33	0.24	0.25
Total	100	100	100	100	100	100

6.3.4 Limitations and future directions on the SDOX-MBR concept

This study aimed at evaluating the membrane filtration performance of an MBR when equipped with an innovative oxygen transfer technology supplying concentrated oxygen, the SDOX system. Concentrated oxygen supply systems have been widely used in water remediation applications and in aquaculture systems for supplying DO; however, they were barely used in wastewater treatment applications. Previous studies (Kim et al. 2019) indicated that the operation of MBRs is limited by inefficiencies introduced by conventional bubble-diffuser aeration systems. Conventional bubble diffusers exhibit an inefficient oxygen transfer performance at the MLSS concentrations higher than 10 g L^{-1}, commonly reported for operating MBR systems. The oxygen transfer inefficiencies are exacerbated when working at even higher MLSS concentrations limiting either expanding the treatment capacity, or reducing the footprint requirements of MBR systems. Concentrated oxygen supply technologies, such as the SDOX system, can uncap such limitations imposed by conventional bubble diffusers. Higher OTRs,

higher alpha factors, and higher OTEs were reported for the concentrated oxygen supply system compared to bubble diffusers (Kim et al. 2020). Particularly, the higher the MLSS concentration in the MBR, the better the oxygen transfer performance of the concentrated oxygen supply system compared to the bubble diffusers (Kim et al. 2020). In addition, the biological performance of the MBR was not negatively affected by the action of the concentrated oxygen supply system (Kim et al. 2021); similar performance in terms of carbon removal and nitrification was reported by Kim et al. (2021) in an MBR operated either with bubble diffusers or with the SDOX system. Moreover, no major changes in the microbial population dynamics were reported by the authors. Therefore, concentrated oxygen supply systems, such as the SDOX system, introduce major advantages for operating biological wastewater treatment system, particularly MBR systems, uncapping their operational limitations and increasing the overall energy efficiency due to the improved oxygen transfer. However, this study demonstrated, at the evaluated experimental conditions in this research, that the membrane filtration performance could be negatively affected by the shear forces and high-pressure conditions introduced by the concentrated oxygen supply systems. The changes in the PSD increasing the concentration of particles with diameters less than 50 and 10 μm exhorted a detrimental effect on the membrane filtration performance. Nevertheless, the present study was carried out using a bench scale SDOX system provided with small size diameter tubing and a small orifice at the inlet of the SDOX; these conditions imposed additional shear forces that would not have been observed when operating a full-scale SDOX system, thereby calling for large-scale experiments to support the absence of lower intensity of shear forces. In addition, only one type of membrane was used in this research and backwash was not possible to perform. Moreover, to push the limits of the membrane filtration a relaxation phase in between filtration phases was not added. Besides, this study only evaluated the short-term exposure effect of the membrane to the SDOX systems. During P2 and P4, it was observed that towards the end of these phases the MPS increased (or at least stopped decreasing), so the membrane filtration performance could recover during a long-term exposure to the SDOX unit; this, however, was not evaluated in this research. Therefore, further research is required to explore membrane fouling propensity of MBR operated with SDOX under following conditions (i): long-term periods (at least 3 times SRTs); (ii) different membrane types (hollow fiber and ceramic membranes); (iii) under relaxation and backwash modes; and (iv) real municipal and/or industrial wastewater.

6.4 Conclusions

- The membrane filtration performance at the experimental conditions evaluated in this research was negatively affected by the short-term exposure of the membranes to the concentrated oxygen supply system. In this evaluation, the potential fouling conditions were maximized by not including membrane relaxation periods in the membrane filtration cycle.

- The membrane filtration performance could be recovered when the membranes were no longer exposed to the concentrated oxygen supply system (i.e., high-pressure and high shear forces conditions).
- The concentrated oxygen supply system reduced the average particle size of the mixed liquor increasing the fraction of small particles (1 – 10 and 1 – 50 μm range). The presence of high ratio of small size particles exhibited a detrimental effect on the membrane filtration performance. When the mixed liquor was no longer exposed to the concentrated oxygen supply system, and was exposed back to the bubble diffusers, the PSD switched back to large size particles improving the membrane filtration performance.
- It was not possible to determine a clear relationship between the presence of EPS and SMP and the membrane filtration performance. Eventually, the effect of the presence of high fractions of small particles exerted a stronger negative effect on the membrane filtration performance compared to the presence of EPS and SMP.
- The formation of a cake layer was observed on the fouled membranes exposed to the concentrated oxygen supply system contributing to the deterioration of the membrane filtration performance. Biofouling seemed the major contributor to the cake layer resistance when the membranes were not exposed to the concentrated oxygen supply system, while organic fouling seemed to be the primary contributor when the membranes were exposed to the concentrated oxygen supply system

6.5 Acknowledgments

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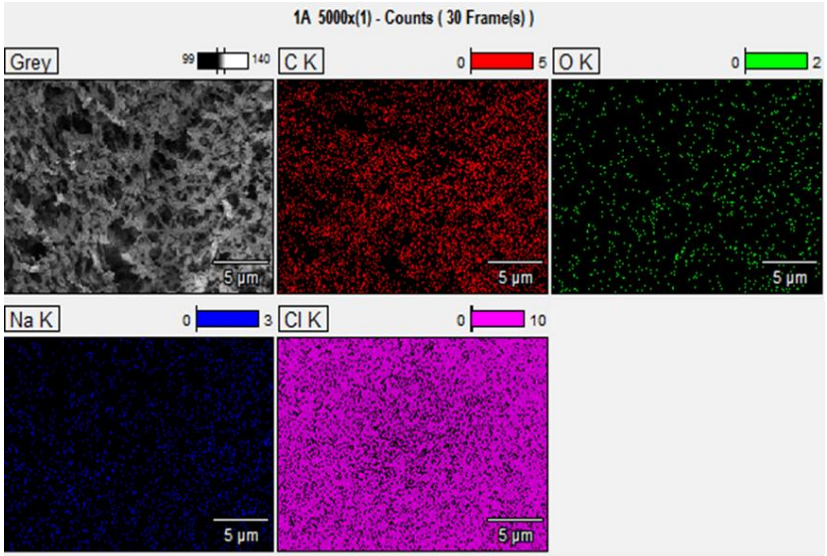
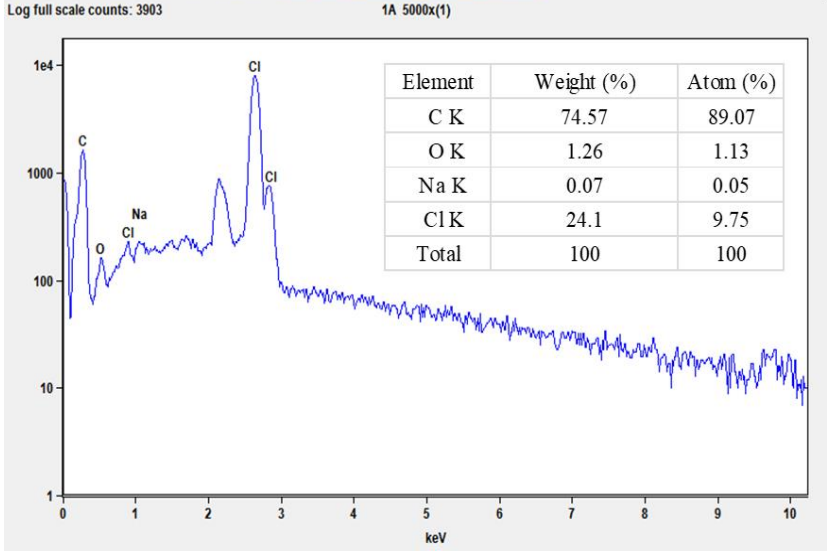
6.7 Appendix

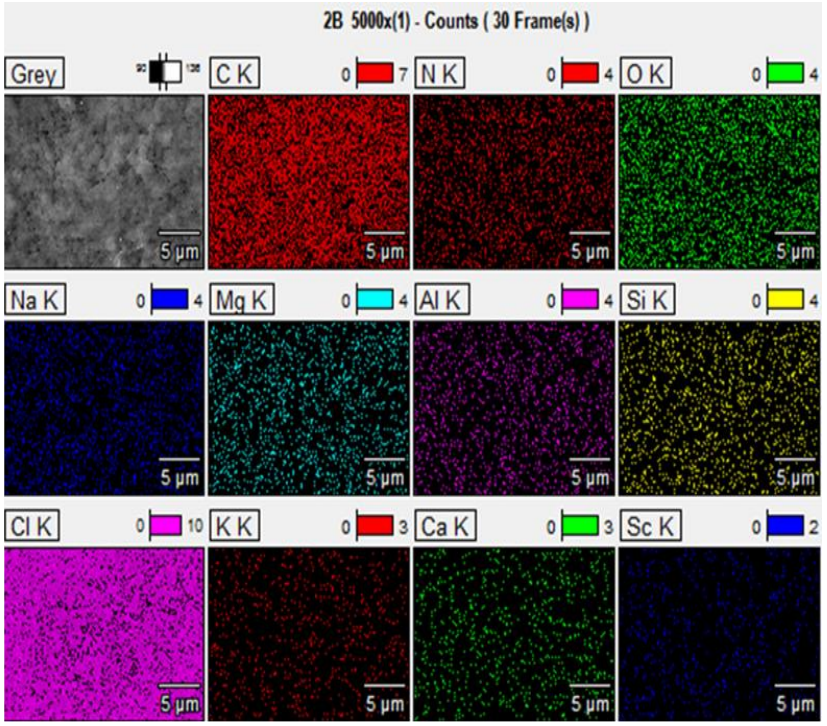
Sampling points : B(right middle), D(upper middle), E(middle bottom)

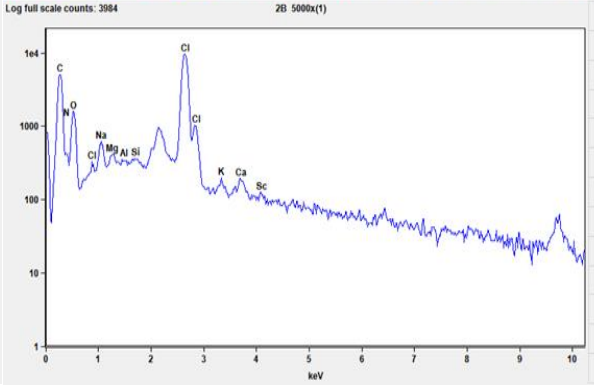
List of samples
Sample of 1A : clean membrane
Samples of 2B, 2D, 2E : 2nd fouled membrane with diffuser
Samples of 3B, 3D, 3E : 3rd fouled membrane with diffuser
Samples of 4B, 4D, 4E : 1st fouled membrane with SDOX
Samples of 5B, 5D, 5E : 2nd fouled membrane with SDOX
Samples of 6B, 6D, 6E : 3rd fouled membrane with SDOX
Samples of 7B, 7D, 7E : 4th fouled membrane with SDOX



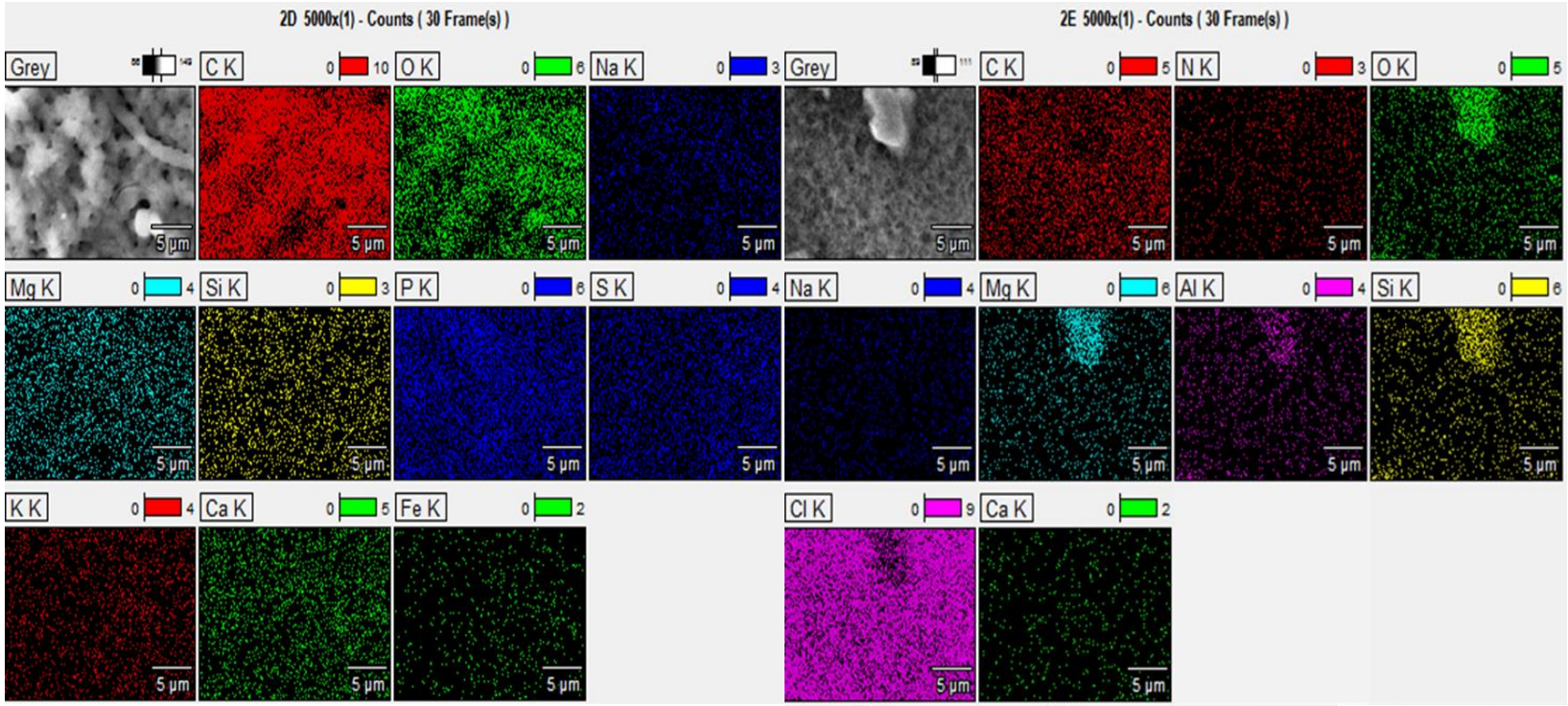


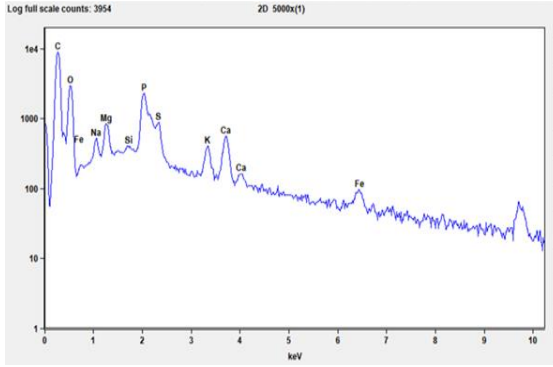
Element	Weight (%)	Atom (%)
C K	74.57	89.07
O K	1.26	1.13
Na K	0.07	0.05
Cl K	24.1	9.75
Total	100	100



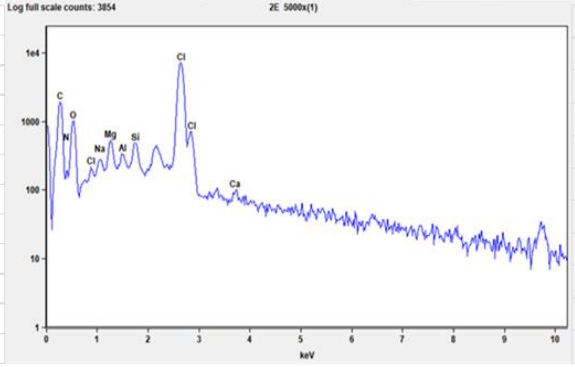


Element	Weight (%)	Atom (%)
C K	62.95	72.09
N K	13.19	12.95
O K	11.88	10.22
Na K	0.37	0.22
Mg K	0.1	0.05
Al K	0.01	0.01
Si K	0.1	0.05
Cl K	11.15	4.33
K K	0.09	0.03
Ca K	0.13	0.05
Sc K	0.03	0.01
Total	100	100

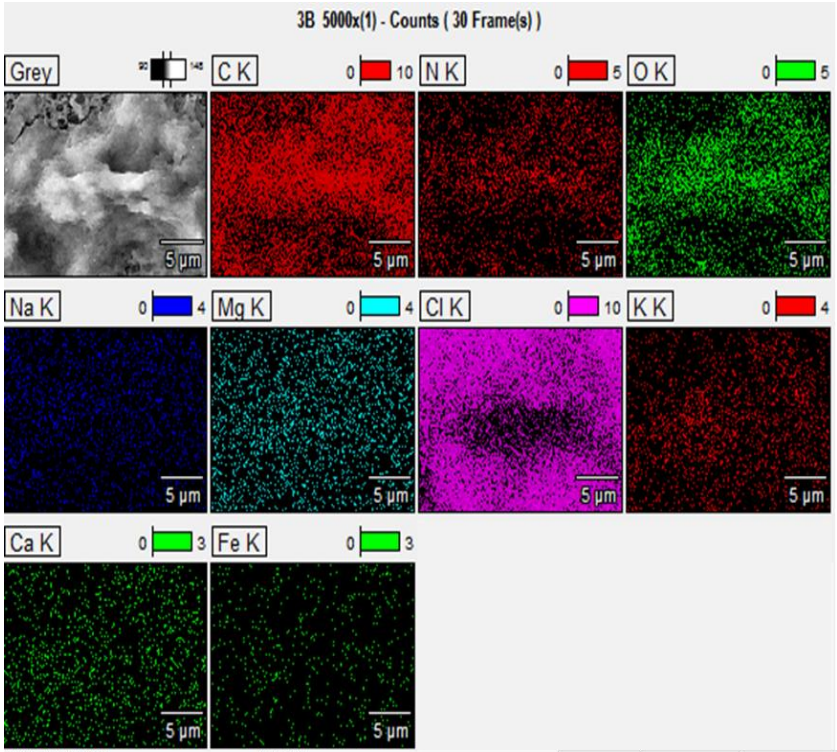


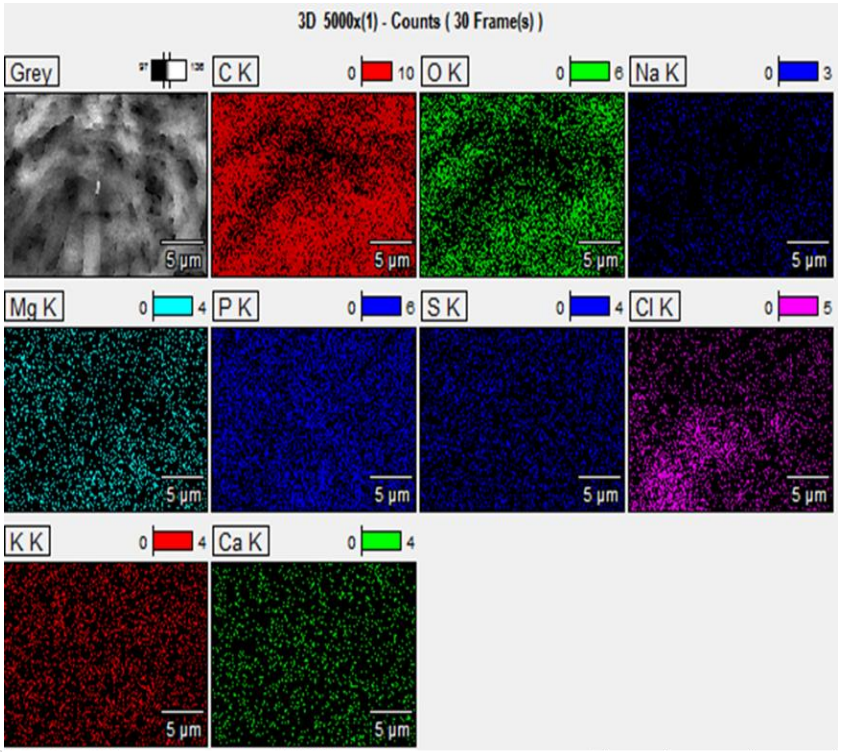


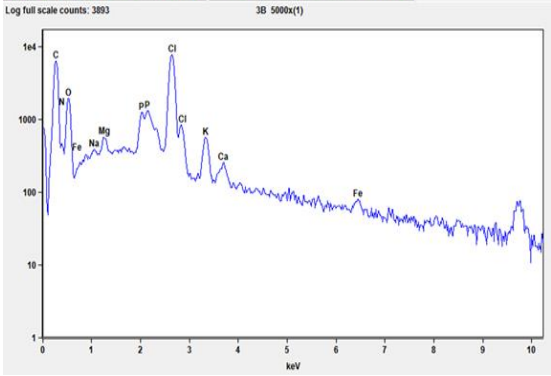
Element	Weight (%)	Atom (%)
C K	73.39	80.24
O K	21.58	17.72
Na K	0.4	0.23
Mg K	0.51	0.28
Si K	0.1	0.05
P K	1.82	0.77
S K	0.36	0.15
K K	0.46	0.16
Ca K	0.98	0.32
Fe K	0.39	0.09
Total	100	100



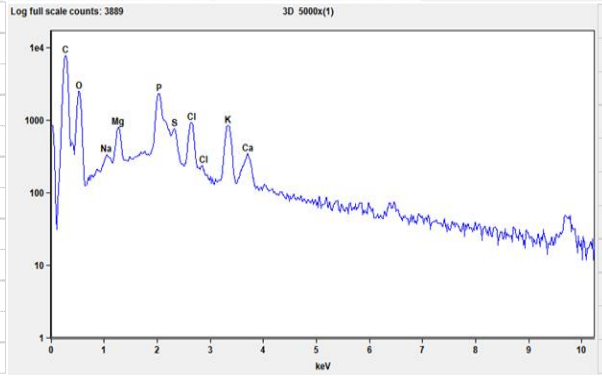
Element	Weight (%)	Atom (%)
C K	61.96	73.78
N K	6.14	6.27
O K	14.08	12.59
Na K	0.15	0.09
Mg K	0.36	0.21
Al K	0.17	0.09
Si K	0.49	0.25
Cl K	16.56	6.68
Ca K	0.1	0.04
Total	100	100



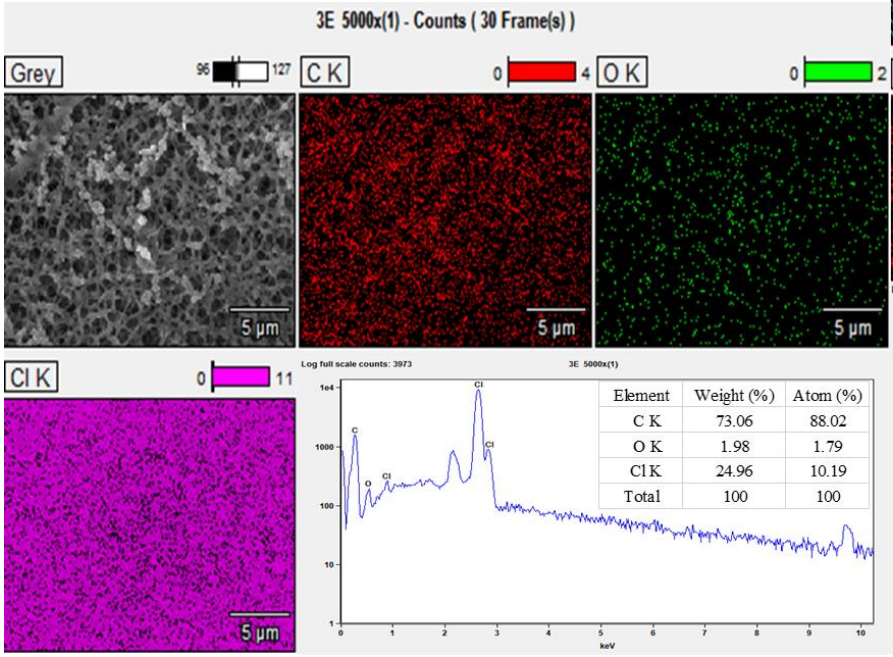




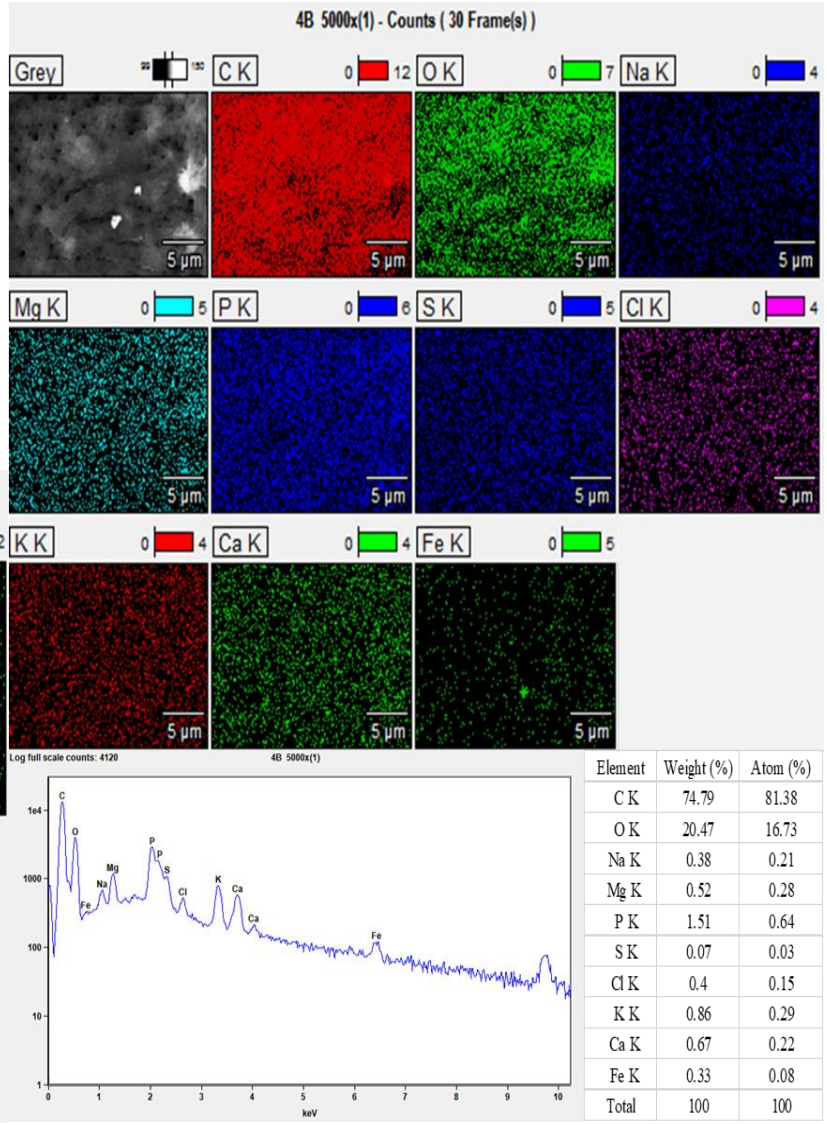
Element	Weight (%)	Atom (%)
C K	65.57	74.23
N K	10.61	10.3
O K	13.56	11.53
Na K	0.05	0.03
Mg K	0.16	0.09
P K	0.29	0.13
Cl K	8.81	3.38
K K	0.63	0.22
Ca K	0.18	0.06
Fe K	0.13	0.03
Total	100	100



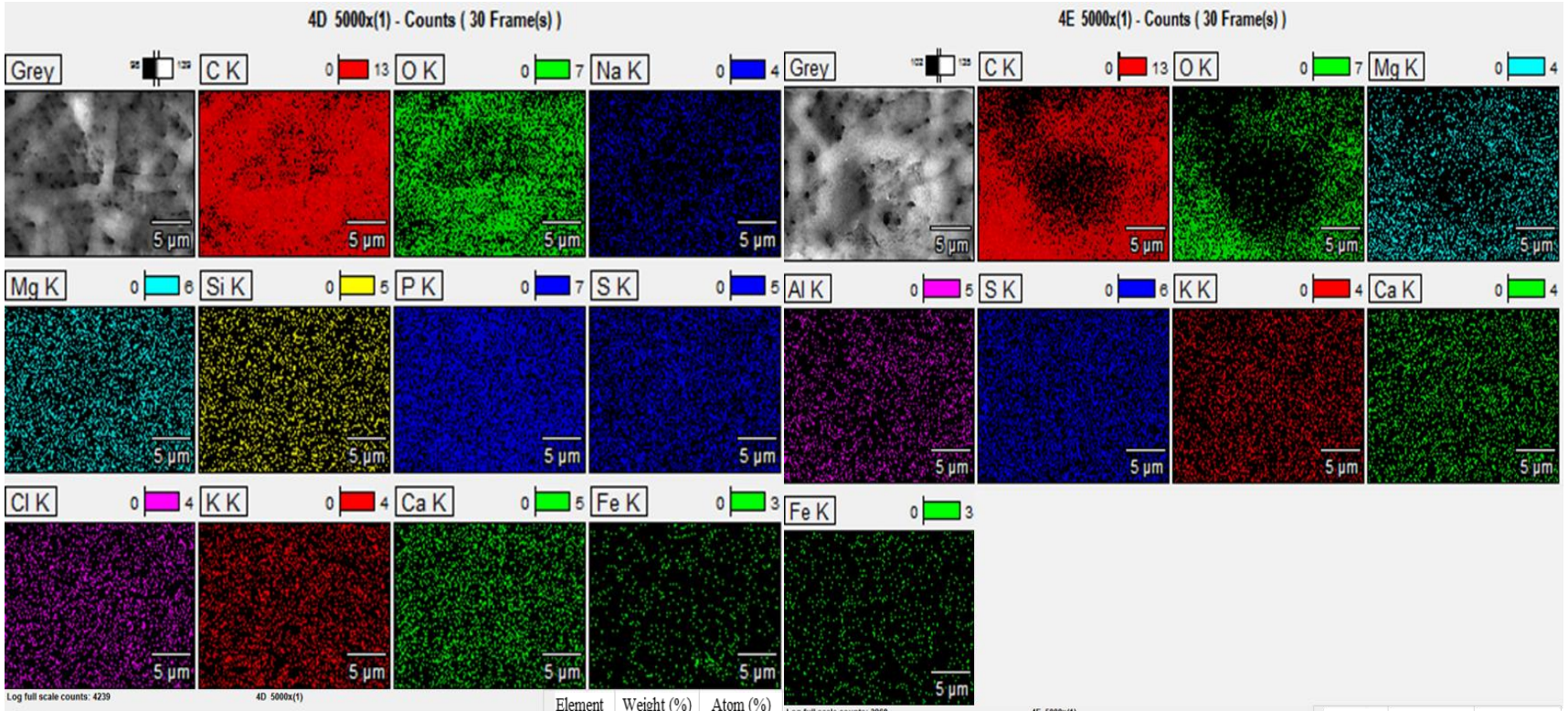
Element	Weight (%)	Atom (%)
C K	74.36	81.62
O K	19.2	15.82
Na K	0.17	0.1
Mg K	0.51	0.28
P K	2.07	0.88
S K	0.29	0.12
Cl K	1.37	0.51
K K	1.5	0.5
Ca K	0.52	0.17
Total	100	100

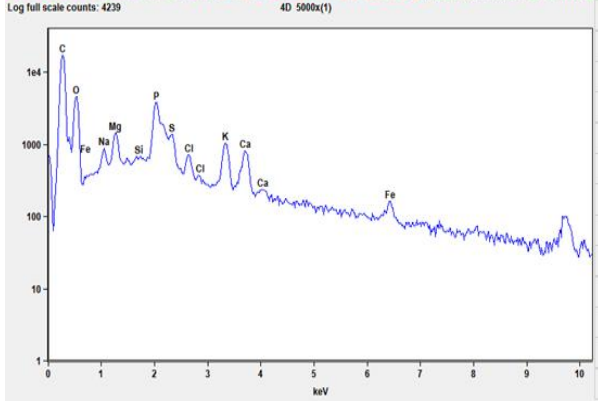


Element	Weight (%)	Atom (%)
C K	73.06	88.02
O K	1.98	1.79
Cl K	24.96	10.19
Total	100	100

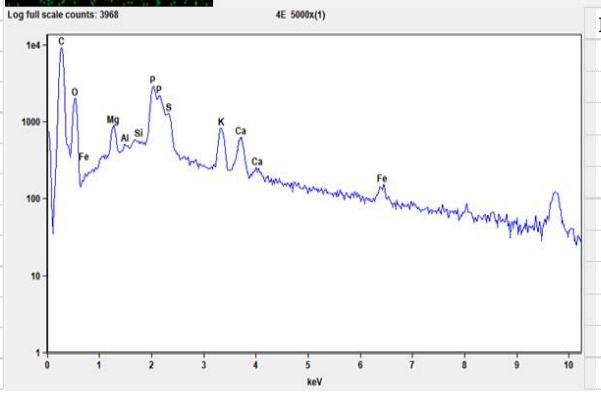


Element	Weight (%)	Atom (%)
C K	74.79	81.38
O K	20.47	16.73
Na K	0.38	0.21
Mg K	0.52	0.28
P K	1.51	0.64
S K	0.07	0.03
Cl K	0.4	0.15
K K	0.86	0.29
Ca K	0.67	0.22
Fe K	0.33	0.08
Total	100	100

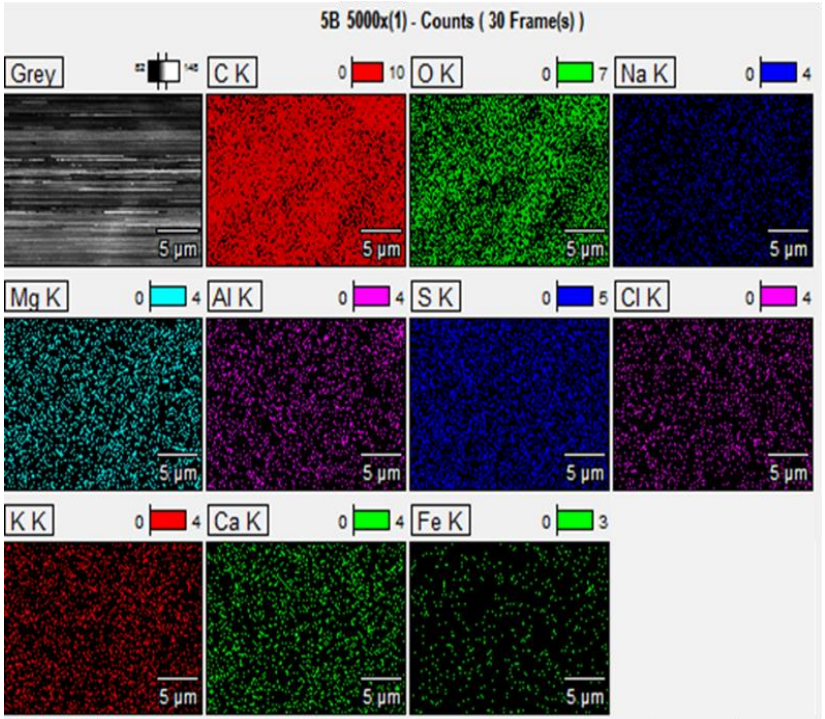


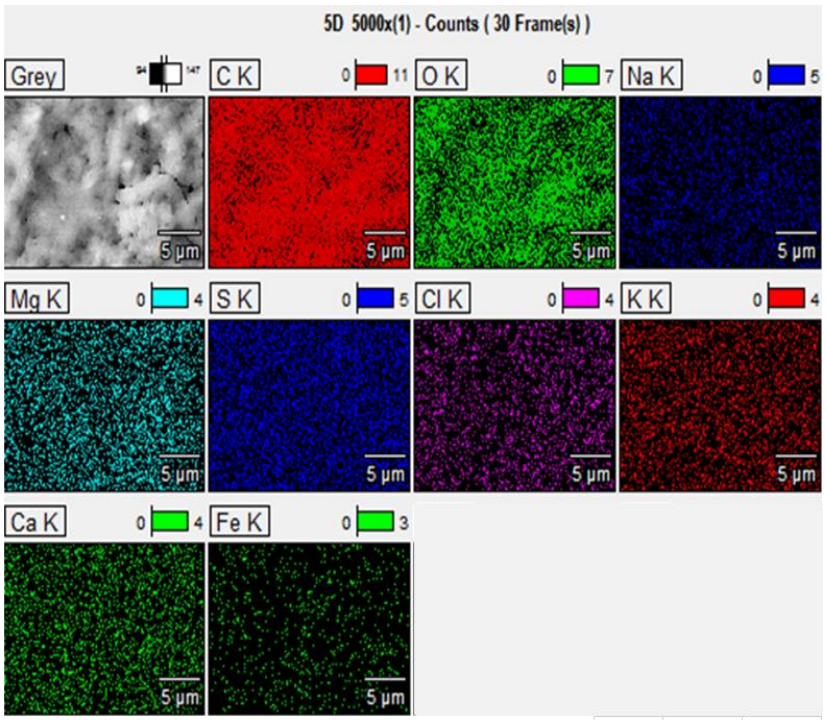


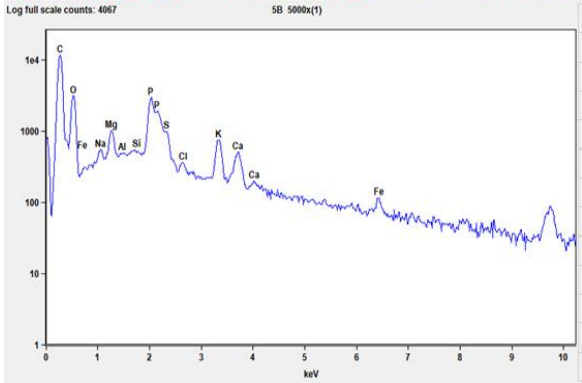
Element	Weight (%)	Atom (%)
C K	75.9	82.48
O K	18.96	15.46
Na K	0.36	0.2
Mg K	0.48	0.26
Si K	0.07	0.03
P K	1.66	0.7
S K	0.24	0.1
Cl K	0.44	0.16
K K	0.85	0.29
Ca K	0.76	0.25
Fe K	0.29	0.07
Total	100	100



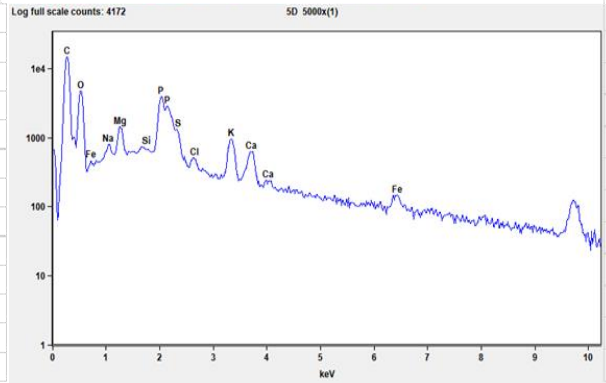
Element	Weight (%)	Atom (%)
C K	78.64	85.04
O K	15.88	12.89
Mg K	0.45	0.24
Al K	0.01	0
Si K	0.13	0.06
P K	1.93	0.81
S K	0.26	0.1
K K	1.3	0.43
Ca K	0.97	0.31
Fe K	0.45	0.1
Total	100	100



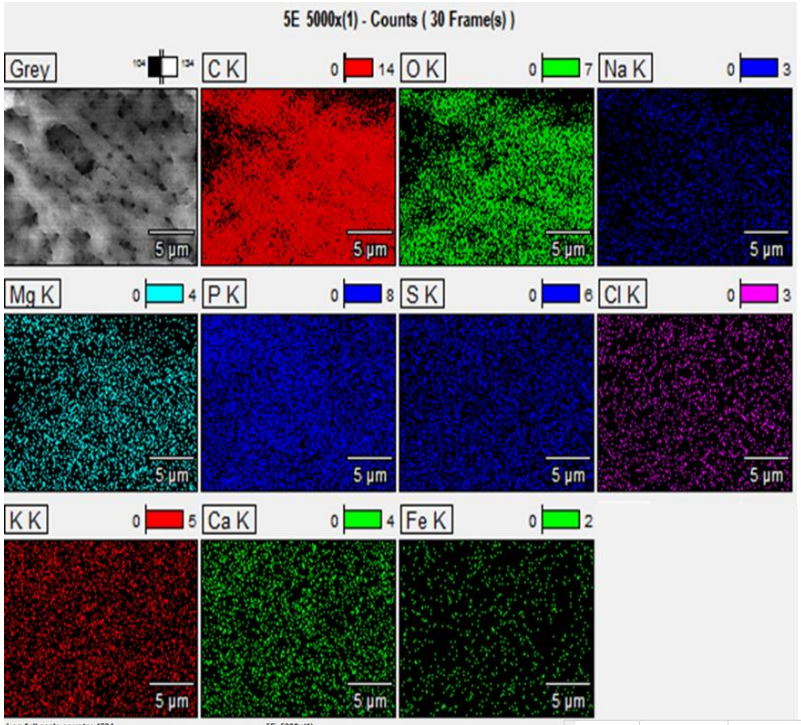




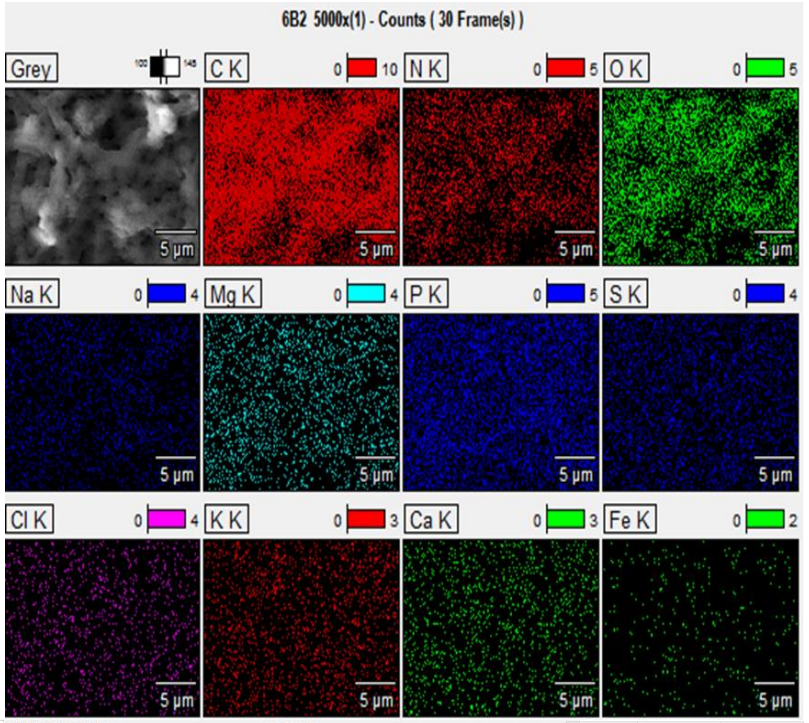
Element	Weight (%)	Atom (%)
C K	76.12	82.43
O K	19.43	15.8
Na K	0.24	0.13
Mg K	0.48	0.26
Al K	0.01	0.01
Si K	0.1	0.04
P K	1.62	0.68
Cl K	0.22	0.08
K K	0.88	0.29
Ca K	0.65	0.21
Fe K	0.24	0.06
Total	100	100



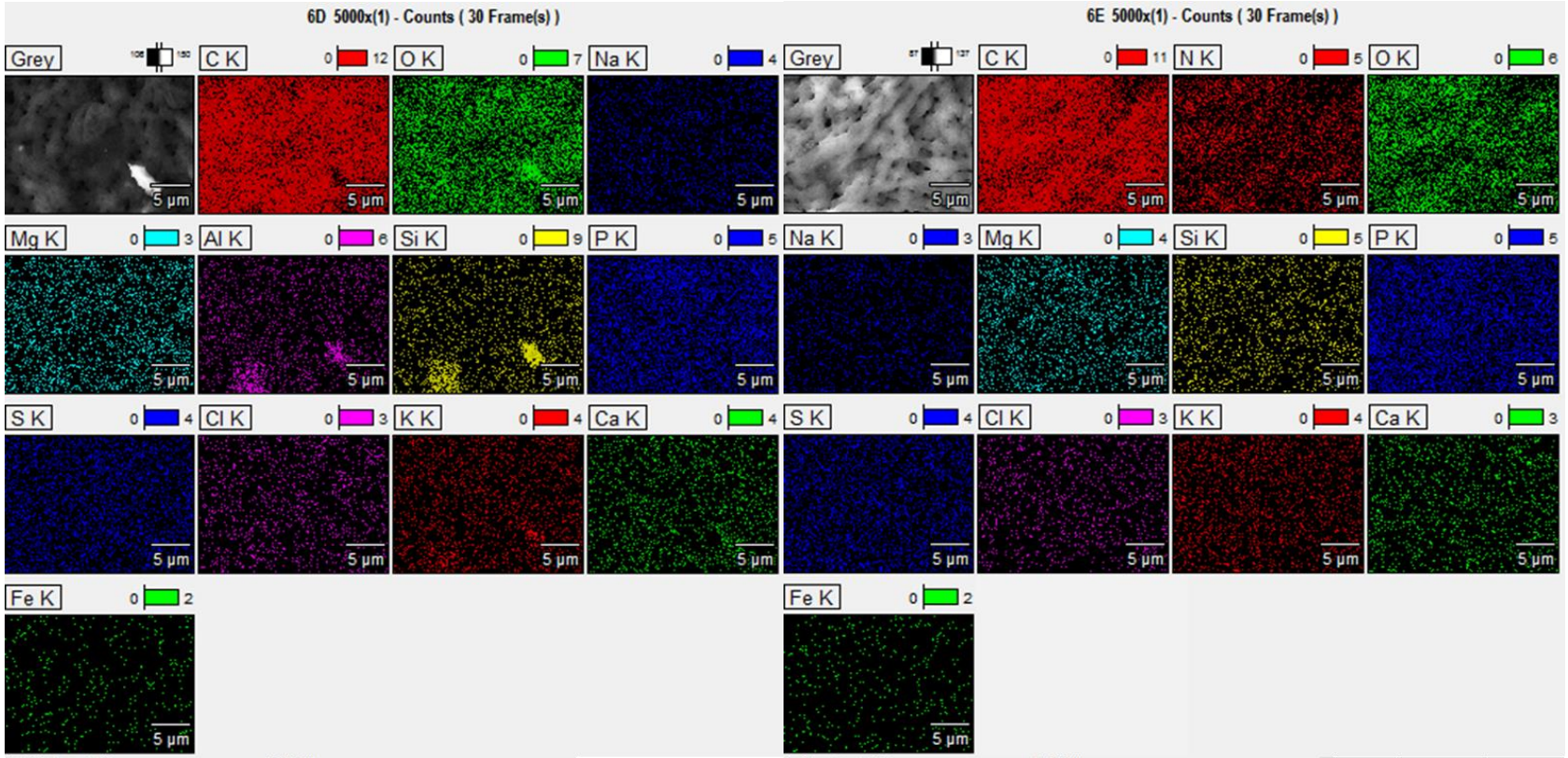
Element	Weight (%)	Atom (%)
C K	73.81	80.51
O K	21.48	17.59
Na K	0.34	0.19
Mg K	0.54	0.29
Si K	0.11	0.05
P K	1.59	0.67
Cl K	0.29	0.11
K K	0.92	0.31
Ca K	0.62	0.2
Fe K	0.31	0.07
Total	100	100

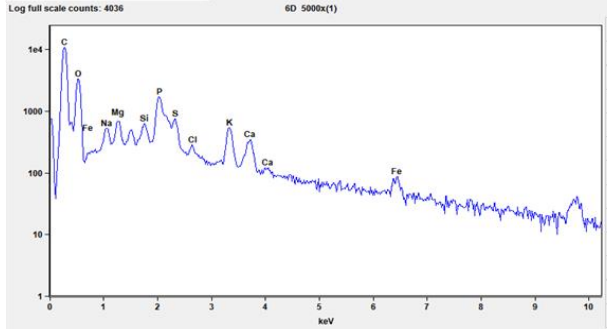


Element	Weight (%)	Atom (%)
C K	77.39	83.57
O K	18.09	14.66
Na K	0.14	0.08
Mg K	0.42	0.22
P K	1.76	0.74
S K	0.25	0.1
Cl K	0.12	0.04
K K	0.94	0.31
Ca K	0.59	0.19
Fe K	0.3	0.07
Total	100	100

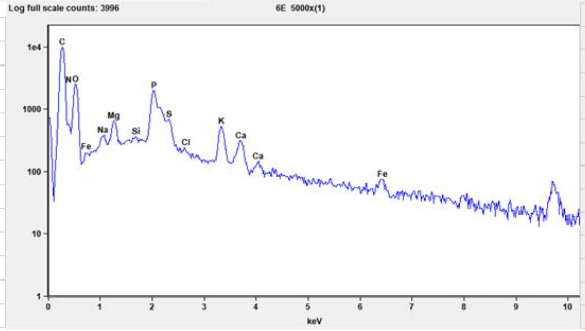


Element	Weight (%)	Atom (%)
C K	62.25	68.42
O K	15.02	14.16
Na K	19.46	16.06
Mg K	0.37	0.21
Si K	0.32	0.17
P K	1.28	0.55
S K	0.07	0.03
Cl K	0.16	0.06
K K	0.52	0.18
Ca K	0.38	0.12
Fe K	0.17	0.04
Total	100	100

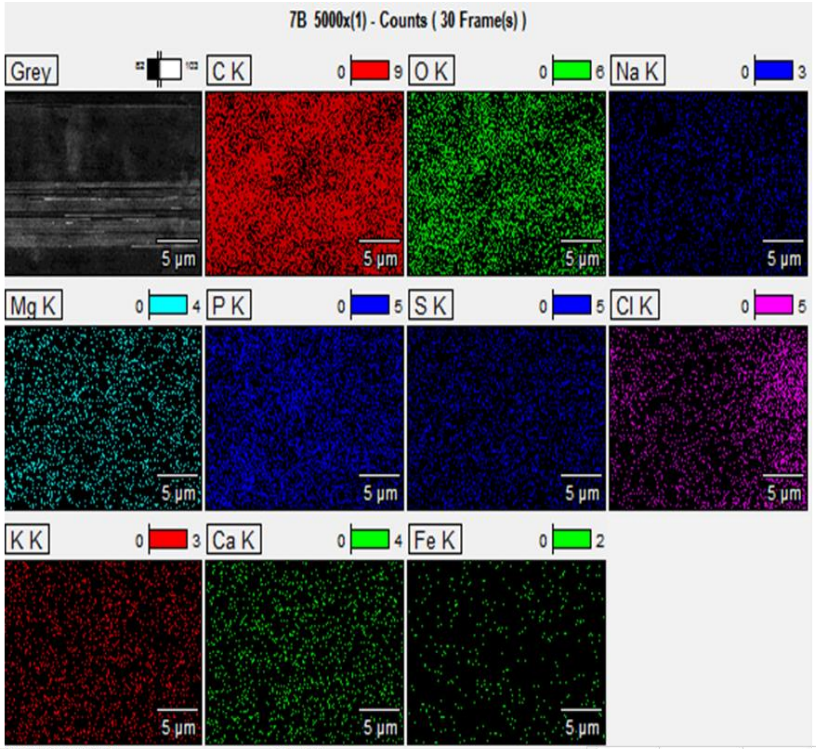


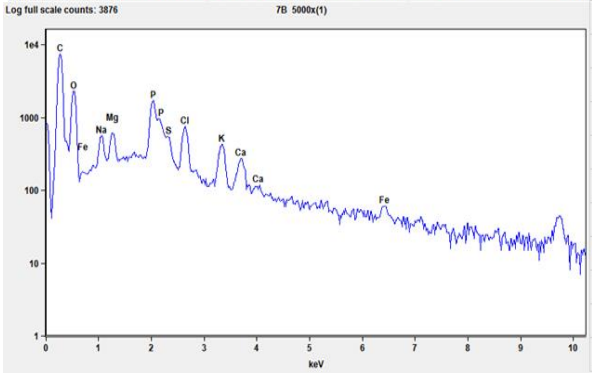


Element	Weight (%)	Atom (%)
C K	74.46	80.76
O K	21.74	17.7
Na K	0.49	0.28
Mg K	0.32	0.17
Si K	0.14	0.07
P K	1.02	0.43
S K	0.21	0.09
Cl K	0.17	0.06
K K	0.66	0.22
Ca K	0.49	0.16
Fe K	0.29	0.07
Total	100	100

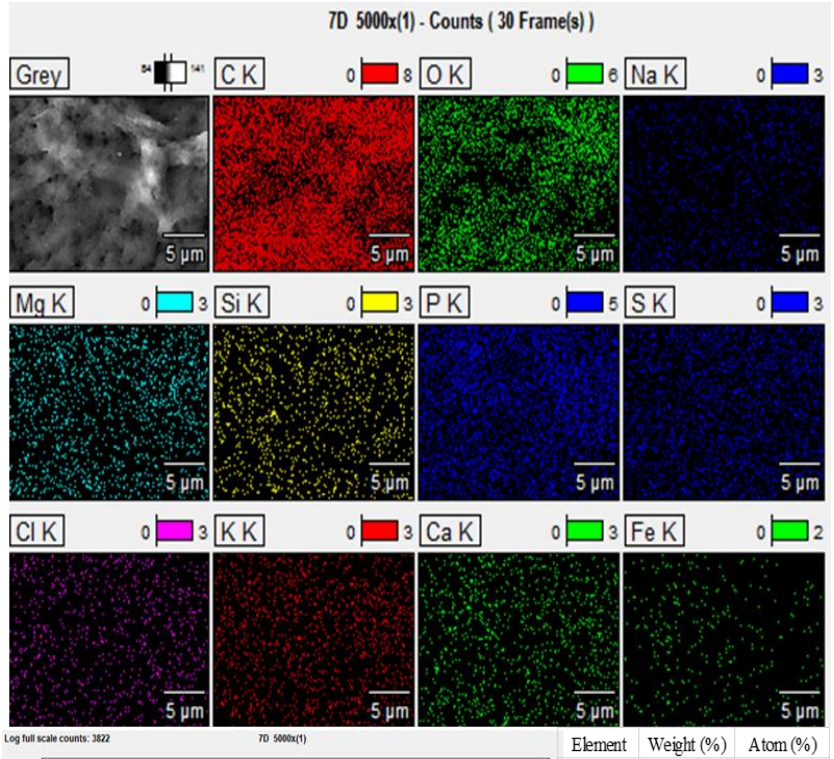


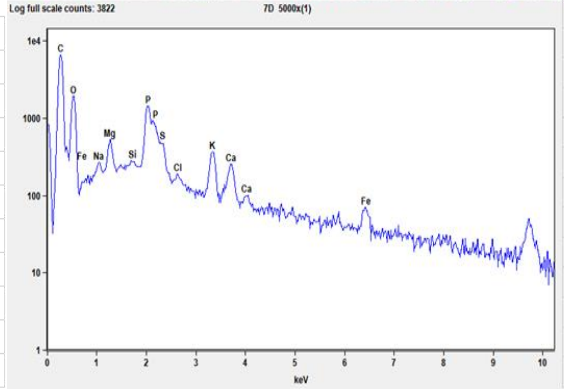
Element	Weight (%)	Atom (%)
C K	65.03	71.14
N K	13.02	12.21
O K	18.65	15.32
Na K	0.2	0.11
Mg K	0.32	0.17
Si K	0.04	0.02
P K	1.28	0.54
S K	0.11	0.04
Cl K	0.13	0.05
K K	0.6	0.2
Ca K	0.42	0.14
Fe K	0.21	0.05
Total	100	100



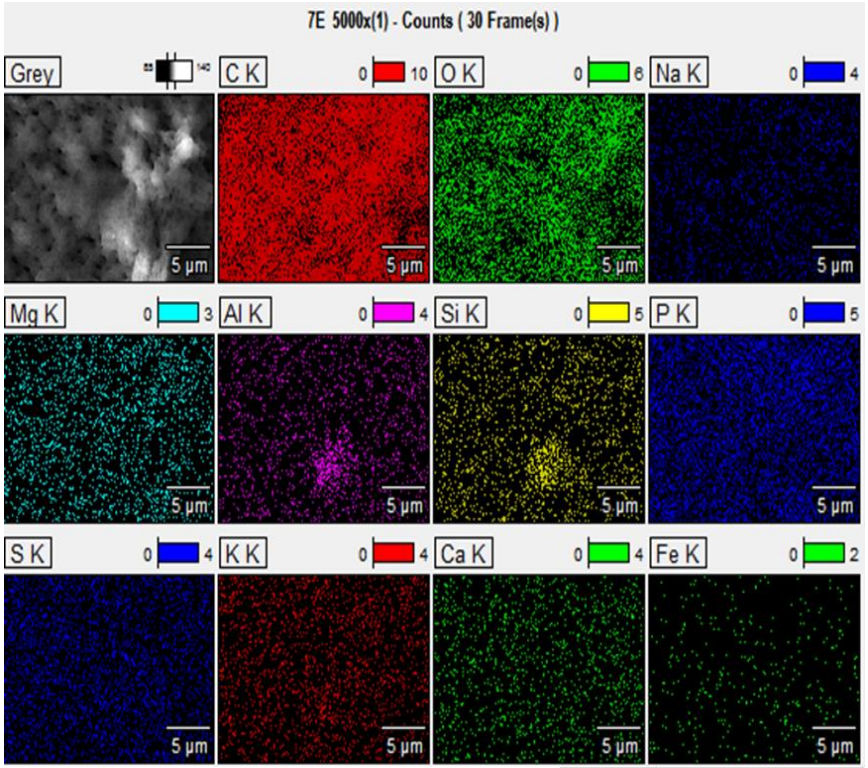


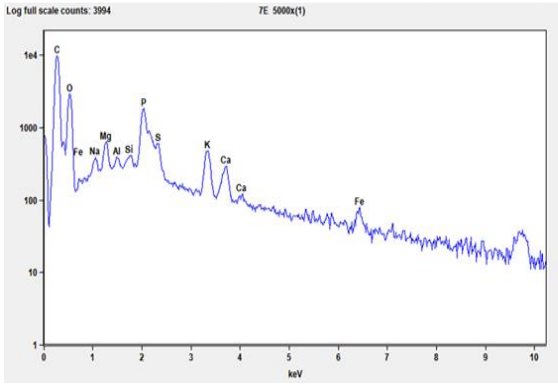
Element	Weight (%)	Atom (%)
C K	74.38	81.23
O K	20.22	16.58
Na K	0.66	0.37
Mg K	0.38	0.21
P K	1.53	0.65
Cl K	1.29	0.48
K K	0.8	0.27
Ca K	0.48	0.16
Fe K	0.25	0.06
Total	100	100





Element	Weight (%)	Atom (%)
C K	74.93	81.36
O K	20.81	16.96
Na K	0.22	0.13
Mg K	0.42	0.22
Si K	0.09	0.04
P K	1.55	0.65
S K	0.02	0.01
Cl K	0.25	0.09
K K	0.79	0.26
Ca K	0.56	0.18
Fe K	0.37	0.09
Total	100	100





Element	Weight (%)	Atom (%)
C K	74.84	81.07
O K	21.4	17.41
Na K	0.27	0.15
Mg K	0.36	0.19
Al K	0.09	0.04
Si K	0.14	0.07
P K	1.39	0.58
S K	0.17	0.07
K K	0.69	0.23
Ca K	0.43	0.14
Fe K	0.22	0.05
Total	100	100

Chapter 7

Use of near-infrared spectroscopy on predicting wastewater constituents to facilitate the operation of a membrane bioreactor

This chapter is based on:

Kim SY, Ćurko J, Kljusurić JG, Matošić M, Crnek V, Lopez-Vazquez CM, Garcia HA, Brdjanović D, Valinger D (2021) Use of near-infrared spectroscopy on predicting wastewater constituents to facilitate the operation of a membrane bioreactor. *Chemosphere* 272: 129899. https://doi.org/10.1016/j.chemosphere.2021.12989

Abstract

The implementation of near-infrared (NIR) spectroscopy in the municipal and industrial wastewater treatment has been continuously expanding. As an alternative to the conventional analytical methods for monitoring constituents in wastewater treatment processes, the use of NIR spectroscopy is considered cost-effective and less time-consuming. NIR spectroscopy does not in any way adulterate measured sample as no prior treatment is needed thus making it a waste-free technique. On the negative side, one must be very well acquainted with chemometric techniques to interpret results. In this study, filtered and centrifuged wastewater and sludge samples obtained from a laboratory-scale membrane bioreactor (MBR) wastewater treatment system were analysed. Essential wastewater constituents were determined and compared, employing two analytical methods (conventional and NIR spectroscopy). Special attention was given to the soluble microbial products (SMP) and the extracellular polymeric substances (EPS). These two parameters are critical in MBR systems since they may promote membrane fouling. The measured parameters through NIR spectroscopy were analysed and processed by conducting partial least squares regression (PLSR) and artificial neural networks (ANN) models to assess whether the evaluated wastewater constituents could be monitored by applying NIR spectroscopy. Although excellent results were obtained with PLSR models, ANN exhibited a better performance in terms of correlating NIR spectra with all the measured parameters, resulting in correlation coefficients in most cases higher than 0.97 for training, test, and validation. Based on the results achieved by this research, the combination of NIR spectra and chemometric modelling offers advantages compared to conventional analytical methods.

7.1 Introduction

Biological wastewater treatment systems based on the activated sludge concept have been widely adopted for treating wastewaters containing biodegradable pollutants. As continuous monitoring is required to maintain a stable wastewater treatment process, over the years many analytical methods (e.g., ion or gas chromatography, titrimetric or colourimetric absorption photometry, among others) have been used for the identification and quantification of different chemical compounds commonly found in raw and treated wastewater. However, the listed methods are quite time-consuming; they demand specialised laboratory equipment and require complex samples preparations. Even though the analytical time for the determination of the most relevant raw and treated wastewater chemical parameters (e.g., chemical oxygen demand (COD), and constituents (total nitrogen (TN), NH_4-N, NO_2-N, NO_3-N, total phosphorus (TP), PO_4-P, etc.) has been significantly reduced due to the development of test kits (e.g., Hach Lange Cuvette Tests), such application is much costlier than the traditional methods (e.g., titration method), thus increasing the operational costs of a wastewater treatment plant (WWTP) (Li et al. 2017).

The technology of membrane bioreactor (MBR), which incorporates membrane filtration to the activated sludge process, has become an established wastewater treatment technology. MBR systems produce a clarified and disinfected effluent with a very low biochemical oxygen demand (BOD) and free of suspended solids. MBR systems present several other advantages including handling higher mixed liquor suspended solids (MLSS) concentrations than conventional activated sludge (CAS) systems, operating at high solid retention times (SRTs), producing low amounts of sludge, handling high organic and shock loads, and satisfying the most challenging wastewater discharge standard (Henze et al. 2008; Kim et al. 2019; Pollice et al. 2008). One of the major disadvantages of MBR technology is membrane fouling and associated activities for the cleaning and replacement of membranes (Bagheri et al. 2019). Soluble microbial products (SMP) and extracellular polymeric substances (EPS) are the major causes of membrane fouling. The SMP consists of soluble organic compounds generated as a consequence of the bacterial metabolism and bacterial autolysis. These compounds can also be present in influent wastewater (Soh et al. 2020). The EPS are highly hydrated and usually characterized by a mixture of high molecular weight polymers. Proteins, polysaccharides, humic acids, lipids, and nucleic acids, include the major constituents making up the EPS (Frølund et al. 1996). The EPS can be further classified into soluble EPS (sometimes also referred to as SMP (Laspidou and Rittmann, 2002)) and bound EPS. Besides, the EPS is subdivided into the carbohydrate fraction of the EPS (EPS_c) and the protein fraction of the EPS (EPS_p). The analytical determinations of SMP and EPS are usually time-consuming, and they require both analytical skills, as well as specific analytical laboratory equipment (Nielsen and Jahn, 1999). Also, there are different methods for determining EPS which add difficulties when comparing results produced and reported using different analytical procedures (Comte et al. 2006; D'Abzac et al. 2010). Therefore, the development of alternative methods for determining

EPS and SMP is highly needed and desirable.

In such a context, the application of near-infrared (NIR) spectroscopy has enabled the development of new analytical methods for predicting results replacing conventional analytical methods. The basic principle in NIR spectroscopy is that an examined sample is irradiated with NIR radiation, usually between 750 and 2500 nm, and the reflected or transmitted radiation is recorded in the form of a spectrum (Prieto et al. 2017). Compared to the traditional analytical methods for monitoring wastewater treatment compounds, NIR spectroscopy is faster and avoids the use of toxic or corrosive chemical reagents (Pereira et al. 2019). As such, particular advantages of NIR spectroscopy include (i) non-destructive and non-invasive features of such analytical method; (ii) cost-effectiveness of the determination; and (iii) lack of residuals by-products needed to be disposed of after conducting the analytical determinations, among others (Xie et al. 2016). The NIR spectroscopy analyses can be influenced by non-linearities of experimental conditions (e.g., temperature, agitation, aeration, dispersive light, etc.); however, all these parameters can be well controlled while performing the analysis (Dias et al. 2008; Prieto et al. 2017).

The most important constraint imposed by the NIR determinations is that the results (expressed as absorbance) themselves are not directly comparable with the results generated by the conventional analytical methods. That is, to interpret the results derived from the NIR spectroscopy, chemometric techniques such as multiple linear regression analysis (MLRA), principal component analysis (PCA) and partial least squares regression (PLSR) need to be carried out followed by chemometric modelling (Xu et al. 2008). The chemometric techniques and modelling have become an integral part of the spectral data analysis along with the pre-processing of the NIR spectra (Gajdoš Kljusurić et al. 2017) which aims at removing physical interferences in the spectra to improve the subsequent multivariate regression, classification model, or exploratory analysis (Rinnan et al. 2009). The NIR spectroscopy monitors the vibrations of molecules in the NIR region producing a large set of data. The chemometric techniques and models use various tools to find the best possible connection in such large datasets relating the information contained in the spectra with the associated specific analytical parameters to be determined. If the observed correlation between the dataset and the parameters to be determined is acceptable, then a certain pattern of behaviour of a measured parameter could be established. The methodology requires calibrating and validating the model before predicting the results of the specific analytical parameters to be determined. There are different tools used in that modelling part, such as PCA, principal component regression, PLSR, and artificial neural networks (ANN), among others. The PCA and PLSR are amongst the most frequently used calibration procedures to determine linear relationships between the targeted parameter and the intensity of spectral absorption bands (Han et al. 2020). In recent years, a combination of PCA and ANN has shown great potential for high non-linearity applications.

The use of NIR spectroscopy as an alternative analytical method for the determination of

wastewater treatment constituents is relatively new. Takamura et al. (2002) has been one of the first references that introduced this concept. The authors investigated a relationship between NIR spectra and a presence and concentration of organic matter in municipal wastewater expressed as total organic carbon (TOC), COD, and BOD. Suehara et al. (2007) also assessed the use of NIR spectroscopy for determining concentrations of urea, solids, and oil of a biodiesel fuel wastewater from a biodiesel fuel production plant with satisfactory accuracy. Moreover, other researchers have been evaluating the use of NIR spectroscopy to predict the concentration of relevant municipal and industrial wastewater treatment parameters including total suspended solids, BOD, COD, TOC, TN, and TP (Dahlbacka et al. 2014; Inagaki et al. 2010; Pan et al. 2012; Pan and Chen, 2012; Pascoa et al. 2008; Yang et al. 2009). Even though some studies applied NIR spectroscopy for determining wastewater treatment-related constituents, there is no information in the literature on the application of NIR analytical methodology on the determination of wastewater parameters for MBR systems. MBR systems produce treated wastewater by filtering the wastewater through a micro/ultra-filtration membrane. Thus, MBR effluent is free of suspended solids and a suitable media for NIR spectral analyses, which need to be conducted in homogenous media. Also, there is no literature regarding the analytical determination with NIR spectroscopy of SMP and EPS constituents, which are known cause of membrane fouling in the MBR system.

This research aimed at evaluating the use of NIR spectroscopy followed by chemometric modelling (PLSR and ANN models) for the determination of MBR relevant wastewater treatment constituents including COD, TN, NH_4-N, NO_2-N, NO_3-N, PO_4-P, SMP, EPS_c, EPS_p. Also, this research evaluated the capabilities of NIR spectroscopy to notice changes in the operational performance of the MBR system by interpreting the NIR spectra from the wastewater samples.

7.2 Materials and methods

7.2.1 MBR experiment

A laboratory-scale MBR treating synthetic wastewater was continuously operated for 80 days. The MBR system was first provided with fine bubble diffusers, and later with a pressurized aeration system (PAS) to supply dissolved oxygen. The lab-scale PAS consisted of a pressurized chamber in which the mixed liquor stream was recirculated from the bioreactor by a peristaltic pump getting exposed to pure oxygen at high-pressure conditions; the pure oxygen was supplied by an oxygen cylinder providing the desired pressure in the pressurized chamber. The pressurized chamber had a total volume of 2.75 L, and it was occupied with 0.55 L of mixed liquor at an operational pressure of 689 kPa. The MBR was inoculated with fresh mixed liquor taken from a full-scale municipal WWTP. The two experimental setups of the MBR with the two different aeration systems are shown in Figure 7.1. The configuration of the MBR was the same for both systems; only the aeration systems provided to the MBR were different. The MBR was operated for 40 days with the fine bubble diffusers. Then, the diffusers were replaced

by PAS and the MBR was operated for the subsequent 16 days. Later, the MBR was operated again with fine bubble diffusers for 18 days. Finally, the PAS was introduced again, and the MBR was operated for the additional six days. The bioreactor had a total volume of 30.6 L (16 × 25.5 × 75 cm) with a working volume of 6.5 L. The MBR was equipped with a flat-sheet membrane (XJ3 module by Kubota made of chlorinated polyethylene with an effective filtration area of 0.11 m^2 and nominal pore size of 0.4 μm). The bioreactor base was fitted with a stone coarse bubble diffuser (Uxcell, model number: US-SA-AJD-231698, Hong Kong) to provide shear, thus cleaning the membrane surface.

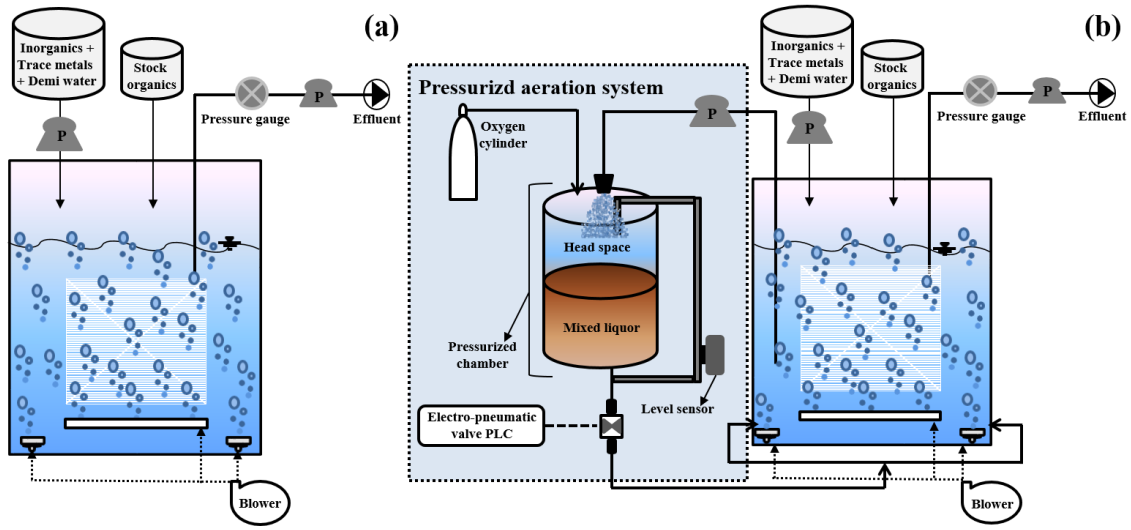


Figure 7.1 Experimental setup of the lab-scale MBR with two aerations systems: (a) bubble diffusers and (b) PAS

The MBR was fed with synthetic wastewater as described in Table 7.1. The feed has COD, TN, and TP concentrations of 1,140 mg L^{-1}, 52.3 mg L^{-1}, and 11 mg L^{-1}, respectively. Two piston pumps were provided to extract the permeate out from the bioreactor through the membrane and to add the synthetic wastewater. A hydraulic retention time of 4.0 hours was set in the MBR system and an SRT for the sludge of 10 days. The MBR system worked in steady-state.

Table 7.1 Characterization of the synthetic wastewater reaching the MBR system

Chemical compounds	Concentration (mg L^{-1})	Chemical compounds	Concentration (mg L^{-1})
$C_6H_{12}O_6$	421.88	$FeCl_3 \cdot 6H_2O$	19.36
$C_2H_3NaO_2$	571.28	$C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$	30.00
Peptone	260.00	$MnCl_2 \cdot 4H_2O$	0.74
Yeast	40.00	$ZnSO_4 \cdot 7H_2O$	2.50
NH_4Cl	65.69	$CuSO_4 \cdot 5H_2O$	0.61
KH_2PO_4	48.33	$CoCl_2 \cdot 6H_2O$	2.09
$NaHCO_3$	251.95	$Na_2MoO_4 \cdot 2H_2O$	0.26
$CaCl_2$	40.37	H_3BO_3	0.13
$MgSO_4$	65.65	$NiSO_4 \cdot 7H_2O$	0.29

During the lab-scale MBR operation, samples were regularly collected to determine the concentration of the following parameters in the treated effluent (permeate) COD, TN, NH_4-N, NO_2-N, NO_3-N, and PO_4-P, and in the filtered mixed liquor SMP and EPS. The analytical determinations were carried out both by conventional analytical techniques, as well as by NIR spectroscopy.

The samples taken from the laboratory-scale MBR included: (i) the treated effluent/permeate (referred as the effluent filtered sludge (EFS)); and (ii) the supernatant of the centrifugated sludge referred as: (a) the sludge supernatant for determining SMP (SS-SMP), and (b) the sludge supernatant for determining EPS (SS-EPS) (depending on the method of sample preparation as explained in the section 2.2.2). Thirteen samples were taken during the MBR experiment. Eight samples were taken when the MBR system was operated with the fine bubble diffuser aeration system (abbreviated MBR-DIFF), and five samples were sampled when the MBR system was operated with the PAS aeration system (abbreviated MBR-PAS). The summary of the abbreviation used for sampling purposes is presented as follows:

- MBR-DIFF: MBR system provided with fine bubble diffusers
- MBR-PAS: MBR system provided with PAS
- EFS: MBR effluent
- SS-SMP: Sludge supernatant for SMP measurement
- SS-EPS: Sludge supernatant for EPS measurement

7.2.2 Analytical determination

7.2.2.1 Chemical analyses – conventional analytical methods

Conventional analytical determinations for COD, NH_4-N, NO_2-N, NO_3-N, TN, and PO_4-P were conducted with Hach Lange Cuvette Tests (LCK 238, 303, 304, 314, 339, 341, 342, 350, 514).

7.2.2.2 SMP and EPS analyses – conventional analytical methods

The SMP and EPS analytical determinations were carried out following the method described by Le-Clech et al. (2006). Mixed liquor samples containing a volume of 60 mL were centrifuged for 5 min at 5,000g using a Rotina 35 centrifuge (Hettich, Germany). The supernatant was then filtered through a 1.2 μm Minisart® syringe filter (Sartorius, Germany). The filtrate represented the SMP solution referred to as SS-SMP. The SMP concentration was determined by analysing the TOC content using a TOC analyser (TOC-5000A, Shimadzu, Japan) and determining the UV_{254} absorbance by a spectrophotometer UNICAM Helios Beta (Thermo Fisher Scientific, USA) following the method reported by Jarusutthirak and Amy (2006).

After removing the supernatant from the sample for the SMP determination, the remaining pellet retained at the bottom of the centrifuge tube was re-suspended with demineralized water. The mixture was then heated for 10 min at a temperature of 80 ℃ in a water bath (Memmert, Germany), which was then centrifuged for 10 min at 7,000g. The supernatant was then filtered

through the 1.2 μm filter, which represented the EPS solution referred to as SS-EPS. The EPS can be further classified into carbohydrate EPS (EPS_c), and protein EPS (EPS_p). The EPS_c was determined by photometric methods performing H_2SO_4/phenol oxidation followed by a colourimeter method using a DR3900 spectrophotometer (Hach, USA) (Lowry et al. 1951). The EPS_p was determined by applying the Folin–Ciocalteu method with a bovine serum albumin solution as the standard (Dubois et al. 1956).

7.2.2.3 NIR spectroscopy

The measurements of the spectra were performed using a NIR spectrophotometer NIR128L-1.7 (Control Development, South Bend, Indiana, USA) provided with a control development software Spec32 using a halogen light source (HL-2000) for the wavelength range of λ = 904 – 1699 nm. The complete NIR instrument setup has been previously described in a previous study carried out by Bicanic et al. (2015). Ten consecutive determinations were recorded for every sample across the entire spectral range of the instrument. For all the samples no prior treatment was used and 2 mL of sample was transferred in 10 mm quartz cuvette that was placed in holder preventing any light interference during measurement. The recorded spectra, referred to as the raw spectra in the text, were not pre-processed to alleviate the entire subsequent chemometric processing. Also, no mechanical or chemical pre-treatment of the samples was needed before conducting the NIR spectroscopy measurements.

7.2.3 Data modelling

7.2.3.1 Principal Component Analysis

The PCA was used both for identifying patterns and for highlighting similarities and differences between the data of the individual set of the experiment. Furthermore, PCA was used to extract as much significant information from large data set and reduce it to a more suitable form for further calculations. Since the data table contained 896 values for each recorded spectra (considering all the evaluated wavelengths), the physico-chemical properties of the samples could be hidden within such large amount of that; therefore, it was necessary to lower as much as possible the number of variables needed for further calculation whilst not losing any essential information. Also, it is important to select the key wavelengths in the NIR spectrum; particularly, those associated with the vibration of molecules in the observed wavelength range. These wavelengths are more significantly related to the physicochemical parameters of interest and they have to be chosen before conducting the PCA analysis. Then after conducting the PCA analysis those physico-chemical parameters will be preserved in factors. The relevance of the selected number of factors that will be observed was estimated based on the percentage of the entire number of factors describing the variation in the observed dataset with the final goal to capture the highest possible percentages of the variation (Bicanic et al. 2015). The unprocessed raw spectra were used to perform the PCA by using the Unscrambler® X 10.4, software (CAMO software, Norway).

7.2.3.2 PLSR modelling

To predict the values of the measured parameters in the samples from the NIR spectra, PLSR modelling was applied. The PLSR model is one of the most popular linear calibration methods used in quantitative NIR data analysis (Alexandrino and Poppi, 2013; Huang et al. 2013). The PLSR model simultaneously reduces the amount of data (dimension reduction of the NIR spectra matrix), while performs the regression analysis. The PLSR methodology prediction is achieved by extracting from the predictors, a set of orthogonal factors called the latent variables, which have the best predictive power (Abdi, 2003). PLSR modelling was carried out on coordinates of NIR spectra factors obtained by PCA using Unscrambler® X 10.4, software (CAMO software, Norway). The model performance was assessed by evaluating the square of the correlation coefficients of calibration (R^2_C) and validation (R^2_V), the root mean square error of calibration (RMSEC), the root mean square error of prediction (RMSEP), the standard error of prediction (SEP), the residual predictive deviation (RPD), and the ratio of error range (RER). The RPD represents the ratio of the standard deviation of the original data to the SEP, while the RER represents the ratio of the range of the original data to the SEP. A good NIR calibration model is obtained when the correlation coefficient value is higher than 0.81, while the minimum values for both RPD and RER are over 2.5. In term of a model that is excellent and could be used with any application, the correlation coefficient value should be over 0.98 with RPD and RER values of above 8.1 and 41 respectively (Mangalvedhe et al. 2015).

7.2.3.3 Artificial neural network modelling

To predict the values of the measured parameters in the samples from the NIR spectra, ANN modelling was applied. Multiple layer perceptron networks were developed using Statistica 10.0 software (StatSoft, USA). Based on the results obtained from the PCA, coordinates including the first five factors from the PCA were selected and used as the input variables in terms of the percentage of the total variance. These first five factors explained 99.9 % of the total variance. The results of the analytical testing in terms of COD, TN, NH_4-N, NO_2-N, NO_3-N, PO_4-P, SMP, EPS_c and EPS_p concentrations were used as the output values. The ANN training was performed by separating the data into training, testing, and validation at 60:20:20 ratio. A back-error propagation algorithm available in Statistica 10.0 (Stat-Soft, USA) was applied for the training the model. The model performance was evaluated based on the R^2 and RMSE coefficients for the training, testing, and validation.

7.3 Results and discussion

The samples obtained from the MBR system were analysed both by conventional analytical methods and NIR spectroscopy. The output of the NIR spectroscopy is a whole spectrum rather than a single value as observed in conventional analytical methods. Therefore, the NIR results are needed to be further processed by the use of models. In this research, PLSR and ANN were selected as the processing models to investigate whether they could model the NIR spectra to predict values obtained by conventional analytical methods and to determine which model, PLSR or ANN performed more accurately. The MBR system was provided with two completely

different aeration systems, which exposed the biomass to different conditions, namely pressure and shear, which in turn could have affected the biological performance of the system. For that reason, the NIR spectra were analysed to evaluate the capacity of the developed models to predict the origin of the samples; i.e., to evaluate if the models could relate the samples to the specific aeration technology used and to notice changes on the operational performance of the MBR system.

7.3.1 Conventional analytical methods

The values of the parameters determined by conventional analytical methods are presented in Table 7.2. The minimum, maximum, average, and standard deviation values were reported for the 13 EFS, SS-SMP, and SS-EPS analysed samples. The composition of the effluent from the MBR system indicated relatively low COD, phosphate, and ammonia concentrations as expected from a state-of-the-art biological wastewater treatment system (i.e., the MBR), which utilized organic matter, nitrogen, and phosphorus for bacterial growth. The concentrations of ammonia, nitrate, and nitrite indicated that complete nitrification was achieved in the MBR system (i.e., the ammonia originally present in the influent wastewater was converted almost completely to nitrate). The centrifuged samples of the sludge from which both the EPS and SMP were determined, exhibited a relatively high concentration of such microbial by-products; this was also expected considering the relatively high sludge concentration in the MBR system, of approximately 15 g L^{-1}.

Table 7.2 The concentration range of measured parameters using conventional analytical methods

Sample	EFS						SS-SMP	SS-EPS	
Parameter	COD (mg L^{-1})	TN (mg L^{-1})	NH_4-N (mg L^{-1})	NO_2-N (mg L^{-1})	NO_3-N (mg L^{-1})	PO_4-P (mg L^{-1})	SMP (L mg^{-1}-m^{-1})	EPS_c (mg L^{-1})	EPS_p (mg L^{-1})
Minimum	17.3	12.8	0.07	0.001	2.7	0.1	0.08	340.8	539.4
Maximum	60.5	41.4	3.25	0.14	36.0	8.2	0.58	648.9	1336.6
Average	37.7	26.7	0.21	0.05	22.0	4.1	0.31	484.2	825.5
St.dev.	12.4	6.2	0.56	0.04	6.7	2.1	0.18	104.2	245.9

St.dev: standard deviation

7.3.2 Partial least squares discriminant analysis

The NIR determinations were carried out by measuring 10 spectra for each of the 13 analysed samples for EFS, SS-SMP, and SS-EPS resulting overall in 390 spectra. Since different samples often resulted in similar trends and sometimes almost identical spectra, there was the need to detect fingerprint within the spectra that could be used for distinguishing the individual parameters to be determined from the analysed samples. Figure 7.2 shows the combined NIR average raw spectra for the three types of analysed samples (EFS, SS-SMP, and SS-EPS). In the wavelength range from 928 to 1350 nm, it was not possible to distinguish major differences between the spectra. This was also confirmed by performing factor analysis (FA), so this part

of the spectra was not used for further analyses and calculations. Selecting or rejecting a particular region of wavelengths cannot simply rely on visual inspection. Even the smallest differences can sometimes hide relevant information. Therefore, to find the fingerprint for the subsequent chemometric analysis (PLSR and ANN), the average spectra for each sample (EFS, SS-SMP and SS-EPS) was obtained from all the original raw spectra recorded. On these average spectra for all the samples, FA in the observed wavelength region (λ = 904 – 1699 nm) with a weight setpoint of 0.8 was performed. This is the simplest way to obtain relevant part or parts of spectra containing significant information about the samples. As presented in Figure 7.2, three different significant wavelength regions were identified: (i) 904-928 nm which detects the third overtone C-H vibrations and the second overtone region for C-H stretches, (ii) 1350-1356 nm, and (iii) 1400-1699 nm related to the first and second overtone region for O-H and N-H, as well as the first overtone region for C-H (Eldin, 2016). For those three regions, it is visible that the highest differences accrue in the third region (1400-1699 nm) where average EFS spectra have the lowest absorbance and average SS-EPS spectra have the highest absorbance. The same is visible for the first region (904-928 nm) and the lowest distinction between different spectra of samples visible in the second region (1350-3356 nm).

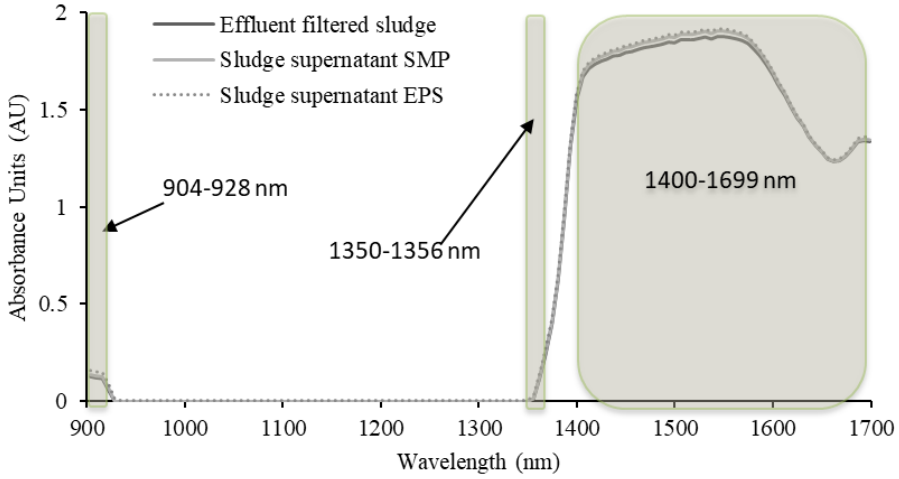


Figure 7.2 Near infrared average raw spectra of the EFS, SS-SMP and SS-EPS with the significant wavelengths

After unravelling the relevant region of the spectra that could provide significant information about the samples, a partial least squares discrimination analysis (PLS-DA) was carried out to determine if the analysed spectra could distinguish variations between the different evaluated samples (EFS, SS-SMP, and SS-EPS). Moreover, since the samples also come from the MBR system operating with different sources of aeration systems (MBR-DIFF and MBR-PAS), the PLS-DA was also carried out to evaluate the capacity of the analysed spectra and also to distinguish variations among those samples. PLS-DA has enabled the development of a non-invasive on-line monitoring method using analytical results in a way that it allows running processes to be corrected if needed. It also shortens the time used in each step and increases the

quality of the end-product (analytical result) (Alcalà et al. 2010). The PLS-DA was able to distinguish from 39 tested samples and determine which sample belonged to a different group (EFS, SS-SMP or SS-EPS). For instance, the PLS-DA could completely distinguish the EFS samples from the SS-SMP and SS-EPS samples for all the evaluated samples. Similarly, the same situation was observed for all the SS-SMP samples and all the SS-EPS samples. Furthermore, the PLS-DA was able to distinguish differences between the samples taken from the MBR system when provided with the fine bubble diffusers (24 MBR-DIFF samples out of the 39 samples analysed) from those taken with the MBR system provided with the PAS (15 MBR-PAS samples out of the 39 samples analysed) with 100% separation efficiency.

The next step was to investigate the quantitative relation between the NIR spectra and the evaluated parameters in the EFS (COD, TN, NH_4-N, NO_2-N, NO_3-N, PO_4-P), SS-SMP and SS-EPS (EPS_c, EPS_p) samples. To evaluate such quantitative relationship, PLSR models were applied. The NIR spectra of the samples were used as the inputs and the parameters measured with conventional analytical methods as the outputs. The results of the PLSR models are presented in Table 7.3. Three different PLSR models were performed for each of the evaluated samples (EFS, SS-SMP and SS-EPS). The first PLSR model was performed on all the NIR spectra including all the samples taken from the MBR system regardless of the aeration system used (indicated as Combined MBR-DIFF and MBR-PAS in Table 7.3). The second and third PLSR models were performed on samples taken from the MBR system provided with the bubble diffusers or with the PAS, respectively. The data matrix of the PLSR model consisted of 429 rows and 341 columns. Each of the EFS, SS-SMP and SS-EPS samples, represented one-third of the rows, respectively. The PLSR model was conducted in two steps as follows: first, the model needed to be trained, and later validated. Every second NIR spectra (out of the 10 spectra carried out per sample – EFS, SS-SMP, and SS-EPS) were used for training the model with the corresponding measured and evaluated parameter. The remaining NIR spectra were used for validating the model with the corresponding measured parameter. Before conducting the PLSR models, all the NIR spectra were pre-treated by applying the standard normalized variate (SNV) method.

The PLSR models were subsequently calibrated and validated. For evaluating the model, standard parameters as described by Yang et al. (2016) were used, including RMSEC, R^2c, RMSEP, SEP, R^2v, RPD, and RER. RMSEP and SEP, as the simplest and most efficient indicators, to determine the uncertainty in the NIR predictions. Good models are obtained when: (i) the RMSE and RMSEP coefficients (which represent the prediction error of the model) are as low as possible; (ii) the RPD coefficient ranges between 2.5 and 3 or higher (Nicolai et al. 2007); and (iii) the RER coefficient ranges between 2.5 and 10 or higher (AACC method 39-00). The study of Yang et al. (2016) suggested that a model with an RPD in the range of 2.5 to 3 and more than 3 provides good and excellent prediction, respectively. Based on the RPD values in our study, almost all the models showed either very good or excellent results in terms of correlating the NIR spectra with the measured parameters.

Table 7.3 Results of the PLSR models (RMSE, RMSEP, SEP, R^2_C, R^2_V) and model efficiency parameters (RPD, RER) in different samples obtained from two different aeration systems used in lab-scale MBR

Sample	Treatment	Parameter	Calibration		Validation			RPD	RER
			RMSE	R^2_C	RMSEP	SEP	R^2_V		
EFS	Combined MBR-DIFF and MBR-PAS	COD	2.774	0.962	3.015	3.022	0.926	3.785	13.136
		TN	2.119	0.924	2.410	2.418	0.854	2.740	10.257
		NH_4-N	0.007	0.904	0.008	0.008	0.818	2.416	8.645
		NO_2-N	0.008	0.960	0.010	0.010	0.922	3.785	13.813
		NO_3-N	1.431	0.949	1.644	1.644	0.900	3.267	10.052
		PO_4-P	0.379	0.932	0.443	0.442	0.869	2.904	11.998
	MBR-DIFF	COD	1.447	0.990	1.753	1.705	0.980	7.425	19.974
		TN	1.059	0.983	1.161	1.167	0.967	5.886	19.751
		NH_4-N	0.004	0.966	0.004	0.004	0.933	4.060	10.349
		NO_2-N	0.006	0.986	0.006	0.006	0.971	6.291	19.230
		NO_3-N	1.089	0.975	1.335	1.335	0.951	4.794	12.379
		PO_4-P	0.268	0.975	0.342	0.336	0.950	4.773	15.779
	MBR-PAS	COD	0.935	0.983	1.454	1.457	0.965	5.948	14.964
		TN	1.697	0.817	2.540	2.516	0.668	1.918	4.392
		NH_4-N	0.006	0.901	0.007	0.007	0.812	2.551	5.950
		NO_2-N	0.003	0.986	0.004	0.004	0.971	6.516	16.769
		NO_3-N	0.954	0.935	1.133	1.144	0.874	3.119	7.126
		PO_4-P	0.295	0.794	0.357	0.360	0.630	1.811	4.307
SS-SMP	Combined MBR-DIFF and MBR-PAS	SMP	0.067	0.896	0.008	0.076	0.803	2.338	6.589
	MBR-DIFF	SMP	0.028	0.976	0.034	0.094	0.952	1.757	4.828
	MBR-PAS	SMP	0.032	0.658	0.047	0.047	0.918	3.853	8.901
SS-EPS	Combined MBR-DIFF and MBR-PAS	EPS_c	33.040	0.916	36.610	36.608	0.839	2.582	8.415
		EPS_p	64.402	0.960	69.243	69.413	0.922	3.711	11.484
	MBR-DIFF	EPS_c	27.980	0.947	26.950	27.051	0.897	3.314	10.924
		EPS_p	52.058	0.971	60.011	59.960	0.944	4.433	10.105
	MBR-PAS	EPS_c	19.301	0.961	24.347	24.490	0.924	4.023	9.354
		EPS_p	6.369	0.994	12.826	12.745	0.988	10.213	27.585

When comparing the efficiency of the model for different aeration systems highest values of R^2 for validation of 0.933 – 0.980 and R^2 values of 0.966 – 0.990 for calibration were observed in the treated effluent/permeate (EFF) for fine bubble diffuser aeration system (MBR-DIFF) samples with RPD values ranging from 4.060 – 7.425 and RER values ranging from 10.349 – 19.974. The lowest efficiency of the model was observed for sludge supernatant for determining (SS-SMP) for combined spectra of MBR-DIFF and MBR-PAS SMP samples with R^2 value of 0.803 for validation and R^2 value of 0.896 for calibration with RPD and RER values of 2.338 and 6.589, respectively. It is also important to notice that the highest efficiency of the model was achieved for EPS_p samples for MBR-PAS aeration system of sludge supernatant for determining EPS with R^2 value of 0.988 for validation and R^2 value of 0.994 for calibration with RPD and RER values of 10.213 and 27.585, respectively. For that parameter, the model was applicable for on-line monitoring with NIR spectroscopy. Although most of the parameters had high RPD values, some parameters like NH_4-N for EFS samples (combined MBR-DIFF and MBR-PAS), TN and PO4-P for EFS samples (MBR-PAS) had values of 2.416, 1.918 and 1.811, respectively. For SS-SMP samples (both in combined MBR-DIFF and MBR-PAS and in MBR-DIFF) the SMP exhibited a lower RPD value of 2.338 and 1.757, respectively thus limiting the model for their monitoring to qualitative rather than quantitative.

Although we have not found in similar experiments to ours in the literature that would use NIR spectroscopy and PLS modelling for measurement of constituents characteristic for MBR, some studies attempted to use NIR spectroscopy in combination with PLS modelling for prediction of certain parameters in wastewater. Inagaki et al. (2010) worked with samples from a sewage treatment facility in Nagoya, Japan. They measured total phosphorus, total nitrogen, biochemical oxygen demand, total organic carbon and turbidity with correlation coefficients for cross-validation of 0.79, 0.78, 0.83, 0.79, and 0.75, respectively. Furthermore, Dahlbacka et al. (2014) tried to predict COD in wastewater from pulp and paper mill. Since the values of R^2 for validation and R^2 for validation in PLS model were 0.76 and 0.19 respectively, their model was not suitable for on-line predictions. One of the highest R^2 values for cross-validation was recorded in the work of Pascoa et al. (2010) where the wastewater treatment process was conducted in a custom-designed sequential batch reactor. Using NIR and PLS modelling for total solids, total suspended solids and COD, R^2 values were 0.92, 0.91, 0.87 with RER values of 15.6, 15.8, 9.8 and RPD values of 3.48, 3.54, 2.75 respectively.

7.3.3 Artificial neural networks

Although very good predictions were observed for PLSR models, the scope of this research was also to compare the predictions of the NIR spectra using ANN models. The first step for developing the ANN models involved the performance of PCA on all the spectra for all the samples. The NIR spectra used in this work contained 793 wavelengths. Therefore, to reduce the amount of data that later could be used for conducting the ANN models, PCA was carried out to get coordinates of factors (scores). PCA has been used in several studies to scale down NIR spectroscopy wavelengths to match the column number of output variables used for the

ANN model (Allouche et al. 2015; Candolfi et al. 1999; Dou et al. 2007; Gorry, 1990). Thus, shortening the training time of the ANN model. The first five factors obtained by PCA, which explained 99.99% of the variance, were used as the inputs for the ANN analyses; the same parameters as utilized in the PLSR models were used as the outputs including COD, TN, NH_4-N, NO_2-N, NO_3-N, PO_4-P from the EFS samples, SMP from the SS-SMP samples, and EPS_c and EPS_p from the SS-EPS samples. The development of ANN, like the human brain, requires the use of a large amount of data for training purposes. From the collected NIR spectra, the largest percentage of data needed to be used for training, while the rest of the data was split between the testing of the learned knowledge and the validation of the trained and tested knowledge.

The ANN model was then performed by splitting the experimental data. For instance, out of the 10 NIR spectra obtained per each of the evaluated samples, six of them were used for training, two of them for testing, while the remaining two for validation. One hidden layer was used for the ANN development, and the number of neurons in the hidden layer was set to a range from 3 to 11. The very same procedure as used in the PLSR models was performed regarding the use of the data from the EFS, SS-SMP and SS-EPS samples to obtain the ANN models. As described in Table 7.3, the three sets of samples (EFS, SS-SMP, and SS-EPS) were evaluated. At each of the evaluated samples, one network was selected for all the samples without considering the aeration source (Combined MBR-DIFF and MBR-PAS); a second and third network were selected when the MBR system was provided with bubble diffusers and with the PAS, respectively. Since for each step multiple ANN were tested, the performance of the ANN models was evaluated based on both the R^2 and the RMSE coefficient on the training, testing, and validation phases; the selected ANN are presented in Table 7.4.

The criteria considered for evaluating the performance of the models were as follows: R^2 values below 0.70 indicated that the model could only distinguish low-medium-high values; R^2 values between 0.70 and 0.90 indicated that the models could be considered precise, and R^2 above 0.90 indicated a good model (Liu et al. 2011; Urbano-Cuadrado et al. 2004). The results obtained for the ANN models for all the cases showed very good correlations between the NIR spectra and the investigated parameters. On the ANN modelling, different neural networks were used as can be seen from the network structure in Table 7.4. For example, under the EFS sample for MBR-DIFF treatment, the ANN model presented five inputs, 10 neurons in a hidden layer, and six outputs, which gave the best performance in terms of training test and validation with R^2 values of 0.997, 0.996 and 0.994, respectively. The five inputs refer to the first five PCA factors of the NIR spectra related to the six outputs (evaluated/measured parameters: COD, TN, NH_4-N, NO_2-N, NO_3-N, PO_4-P), through the 10 neurons.

Table 7.4 Characteristic of the ANN models developed for the prediction of parameters

Sample	Treatment	Network structure	Training perf. (R^2)	Training Error (RMSE)	Testing perf. (R^2)	Testing Error (RMSE)	Validation perf. (R^2)	Validation Error (RMSE)	Hidden activation	Output activation
EFS	Combined MBR-DIFF and MBR-PAS	5-11-6	0.955	0.018	0.959	0.017	0.942	0.026	Exponential	Logistic
	MBR-DIFF	5-10-6	0.997	0.002	0.996	0.003	0.994	0.004	Tanh	Logistic
	MBR-PAS	5-8-6	0.994	0.005	0.987	0.023	0.956	0.036	Tanh	Logistic
SS-SMP	Combined MBR-DIFF and MBR-PAS	5-9-1	0.943	0.006	0.925	0.009	0.919	0.008	Tanh	Identity
	MBR-DIFF	5-5-1	0.996	4E-1	0.994	0.001	0.997	0.001	Tanh	Logistic
	MBR-PAS	5-10-1	0.991	0.001	0.992	0.001	0.971	0.005	Tanh	Logistic
SS-EPS	Combined MBR-DIFF and MBR-PAS	5-9-2	0.984	0.003	0.949	0.010	0.958	0.007	Tanh	Logistic
	MBR-DIFF	5-6-2	0.980	0.008	0.937	0.014	0.979	0.007	Tanh	Logistic
	MBR-PAS	5-9-2	0.997	0.001	0.997	0.001	0.984	0.005	Tanh	Identity

Table 7.5 describes the correlation between the NIR spectra and the specific evaluated/measured parameter obtained by the ANN models. A very good correlation between the NIR spectra and the measured parameter was obtained for all the evaluated parameters, including both aeration systems. For instance, the ANN model for the previous example with a network structure of 5-10-6 for the EFS sample when the MBR was provided with the bubble diffuser aeration exhibited an R^2 validation performance of 0.996 for COD, 0.999 for TN, 0.997 for NH_4-N, 0.993 for NO_2-N, 0.993 for NO_3-N, and 0.989 for PO_4-P.

Table 7.5 ANN models for the prediction of the evaluated parameters

Sample	Treatment	Parameter	Training perf. (R^2)	Testing perf. (R^2)	Validation perf. (R^2)
EFS	Combined MBR-DIFF and MBR-PAS	COD	0.989	0.973	0.972
		TN	0.976	0.986	0.969
		NH_4-N	0.990	0.971	0.990
		NO_2-N	0.993	0.991	0.994
		NO_3-N	0.994	0.986	0.987
		PO_4-P	0.989	0.965	0.979
	MBR-DIFF	COD	0.998	0.995	0.996
		TN	0.997	1.000	0.999
		NH_4-N	0.997	0.996	0.997
		NO_2-N	0.995	0.996	0.993
		NO_3-N	0.998	0.995	0.993
		PO_4-P	0.996	0.995	0.989
	MBR-PAS	COD	0.979	0.984	0.989
		TN	0.997	0.972	0.981
		NH_4-N	0.991	0.997	0.988
		NO_2-N	0.994	0.999	0.998
		NO_3-N	0.969	0.957	0.946
		PO_4-P	0.978	0.983	0.969
SS-SMP	Combined MBR-DIFF and MBR-PAS	SMP	0.984	0.965	0.910
	MBR-DIFF	SMP	0.996	0.994	0.997
	MBR-PAS	SMP	0.991	0.992	0.971
SS-EPS	Combined MBR-DIFF and MBR-PAS	EPS_c	0.977	0.952	0.941
		EPS_p	0.992	0.946	0.975
	MBR-DIFF	EPS_c	0.981	0.891	0.968
		EPS_p	0.979	0.983	0.989
	MBR-PAS	EPS_c	0.995	0.996	0.973
		EPS_p	0.999	0.997	0.996

The results indicated a very good correlation between the values predicted by the ANN model and the measured water quality parameters by conventional analytical techniques for all the constituents determined in the analysed EFS, SS-SMP, and SS-EPS samples. In addition, good correlations were also obtained regardless of the aeration system placed in the MBR system. The ANN models exhibited R^2 values higher than 0.9 for the training, testing, and validation phases of the NIR spectra for all measured parameters. Only one R^2 value below 0.9, of 0.891, was observed in the testing phase for EPS_c in the SS-EPS samples when the MBR system was provided with the bubble diffusers. However, such sample exhibited training and validation R^2 values of 0.981 and 0.968, respectively.

7.3.4 Practical application

Based on the obtained results for all the evaluated parameters, modelled NIR spectra can be used as a reliable alternative for monitoring COD, TN, NH_4-N, NO_2-N, NO_3-N, PO_4-P, SMP, EPS_c, EPS_p in MBR wastewater samples for samples that do not contain suspended matter and an expert is available to model the results of NIR spectroscopy. In this regard, the NIR spectroscopy may be able to tackle the limitations imposed by conventional analytical methods for the determination of specific wastewater treatment constituents such as microbial products like SMP and EPS. In terms of operation of the MBR, a possibility to quickly and accurately measure microbial products associated with membrane fouling could lead to more sustainable operation with less chemicals for cleaning, which would reduce its environmental footprint and help its application in water reuse and resource recovery. Moreover, the ability of NIR to be employed as an on-line measurement tool enables an operator of MBR treatment to get important information on the performance of the treatment in almost real-time.

7.4 Conclusions

NIR spectroscopy of wastewater samples coupled with chemometric modelling using both PLSR and ANN was very successful in predicting several key water quality parameters in wastewater treatment. Particularly, the determination of SMP, EPS_c and EPS_p was extremely important since such compounds are highly associated with membrane fouling in MBR systems. ANN models achieved a better performance in terms of correlating NIR spectra with all the measured parameters compared to PLSR. This approach of handling a large amount of spectroscopy data through chemometric modelling resulted in a promising strategy for wastewater treatment monitoring. The models distinguished between different samples originated from the same wastewater treatment provided with different aeration systems that had affected the water quality and sludge characteristics. This feature cannot be achieved through conventional analyses, and it seems that a lot of insight can be obtained from the chemometric analysis of NIR spectra.

7.5 References

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Chapter 8

Reflection and outlook

The chapters in this thesis addressed several issues, such as: i) the oxygen transfer limitations of conventional aeration systems, ii) the suggestion of an approach to overcome the limitations imposed by conventional aeration systems, iii) the evaluation of the biological performance of a membrane bioreactor (MBR) equipped with an SDOX unit including the evaluation of the changes observed in the microbial population, and iv) the membrane filtration performance of an MBR system equipped with the SDOX unit. This final chapter presents experiences gained during my research. The chapter ends by presenting an outlook for future research.

8.1 Reflection

Oxygen supply is required for biological aerobic treatment. Aeration consumes more than 50% of the total power consumed by wastewater treatment plants (WWTPs) that use biological aerobic treatment processes (Henriques and Catarino, 2017). Conventional diffused aeration systems are still extensively used to supply dissolved oxygen to biological treatment processes in WWTPs, despite their low oxygen transfer efficiency (OTE). Despite continuous research and development, it seems difficult to develop a new diffused aeration system with a higher OTE than the OTE of the existing diffused aeration system. Note that novel technologies are applied in the wastewater treatment areas to increase process efficiency and the overall performance of WWTPs. However, despite its low OTE, it is still surprising that diffused aeration systems are still commonly used. Is it true that there are no candidates to take its place? In this context, this dissertation introduced an innovative oxygen transfer system with a high OTE in the wastewater treatment process compared to conventional aeration systems (i.e., fine and coarse bubble diffusers) to reduce the power-related expense of WWTPs and to achieve new operational conditions uncapping the limitations of conventional systems.

Chapter 1 introduces the doctoral dissertation and explains the reason for this research. Chapter 2 summarizes the literature required for this study. Chapters 3–7 described the experimental data produced from each experiment. Reflection and outlook describe the main research findings for each experiment and my viewpoints on each outcome.

The current oxygen transfer limitations imposed by conventional aeration systems

In Chapter 3, the oxygen transfer performance of a conventional fine bubble diffuser was evaluated in clean water and at MLSS concentrations ranging from 4 to 40 g L^{-1} to investigate limitations imposed by fine bubble diffusers in the context of the high-loaded MBR (HL-MBR). The HL-MBR concept requires operating the MBR system at the highest practically possible MLSS concentration and sludge activity (i.e., high loading rates and low solid retention times (SRTs)). So far, the oxygen transfer performance of conventional fine bubble diffusers in wastewater has been evaluated focusing on either the negative impact of high MLSS concentrations on the oxygen transfer, or on the positive impact of high SRTs on the oxygen

transfer. In this study, however, the detrimental effects of the SRT (i.e., short SRT < 5 days) on the oxygen transfer were assessed. As expected, the oxygen transfer performance (i.e., the alpha factor) decreased with increasing the MLSS concentration. In addition, the shorter the SRT the lower the oxygen transfer performance of the system; the short SRTs appear to have contributed to the accumulation of surfactants and related compounds in the activated sludge matrices negatively impacting the oxygen transfer processes. Poor oxygen transfer was observed at both high MLSS and short SRTs conditions; that is, the ideal conditions defining the HL-MBR concept.

Investigating oxygen transfer phenomena is a very important line of research in biological aerobic wastewater treatment. Many studies demonstrated that oxygen transfer is highly impacted by MLSS concentrations greater than 20 g L^{-1} when dissolving air/oxygen via conventional diffused aeration systems (e.g., fine and coarse bubble diffusers). However, one of the significant differences between this research and that of other studies is that the activated sludge used in the oxygen transfer experiments (particularly at high MLSS concentrations) was obtained from a WWTP working at short of approximately 5 days. The short SRT of the sludge taken from the municipal wastewater treatment plant imposed a detrimental effect on the oxygen transfer process. Among many factors influencing oxygen transfer, to our knowledge this is the first study evaluating the negative effects of the short SRT on the oxygen transfer at high MLSS concentrations. The detrimental effects of short SRTs on the oxygen transfer performance when working at relatively low (activated sludge standard MLSS concentrations) were still significant; however, it was still feasible to operate such systems. However, the oxygen transfer performance when working at short SRTs and high MLSS concentrations exhibited such a negative impact on the oxygen transfer jeopardizing the effectiveness of conventional diffuser for introducing dissolved oxygen (beyond energy efficiency considerations). Short SRTs and high MLSS concentrations are key parameters when designing the HL-MBR concept. This research demonstrated that it is almost technically impossible to operate a biological wastewater system at high MLSS concentrations at short SRTs equipped with fine bubble diffuser. Therefore, this chapter reaffirms the need for oxygenation alternatives to enhance the oxygen transfer capacity in aerobic activated sludge processes operated at high MLSS concentrations and short SRTs (i.e., at the key operational conditions of the HL-MBR concept).

Alternative aeration system (SDOX) to cope with the current oxygen transfer limitation

In Chapter 4, the oxygen transfer performance of a supersaturated oxygenation technology (i.e., the supersaturated dissolved oxygen (SDOX) system) was assessed in clean water and at MLSS concentrations ranging from 4 to 40 g L^{-1}. The evaluation aimed at demonstrating that innovative aeration technologies such as the SDOX system can cope with the current limitations imposed by conventional aeration systems. The oxygen mass transfer rate coefficient (K_La) for

the SDOX unit in clean water was lower than for the fine bubble diffusers. However, much higher oxygen transfer rates (OTR)s and alpha factors (mass transfer ratio of process-water to clean-water) as a function of the MLSS concentrations were observed. In addition, approximately 100% of standard oxygen transfer efficiency (SOTE) in clean water were observed for the SDOX system; thus, the SDOX technology could be suggested as an alternative technology to reach new operational design parameters for innovative wastewater treatment systems, while simultaneously reducing the operational costs of the WWTPs.

In this study it was demonstrated that the oxygen transfer performance of conventional aeration systems (e.g., fine bubble diffuser) was highly impacted by the high MLSS concentrations and short SRTs. The situation called for exploring alternatives for supplying dissolved oxygen; particularly, when working at high MLSS concentrations and short SRTs. The SDOX technology introduces dissolved oxygen in a completely different way compared to conventional diffused aeration systems. When using the SDOX technology dissolved oxygen can be effectively transferred at MLSS concentration higher than 20 g L^{-1}, situation that has been challenging so far for the conventional bubble diffusers. Thus, this research demonstrated for the first time that it is possible to supply oxygen in such high MLSS concentrations range operating with short SRT sludge. In addition, much higher alpha factors and oxygen transfer efficiency were reported compared to conventional aeration systems. In the case of CAS operated at low MLSS concentrations (of approximately 3 g L^{-1}) conventional aeration systems effectively operate, although still extremely inefficiently. On the other hand, conventional aeration systems limit the maximum MLSS concentration in a biological system at approximately 20 g L^{-1}. For instance, beyond 30 g L^{-1} is either not technically or not economically feasible to operate. Therefore, a promising strategy to improve the oxygen transfer in the activated sludge (in particular at high MLSS) could be the application of the SDOX technology. Chapter 4 mostly presents and discusses such findings. However, it is important to highlight that the entire evaluation was carried out in a laboratory-scale set-up. Therefore, further research is needed to still demonstrate the oxygen transfer performance advantages of the SDOX system at large/full-scale plants to validate the innovation in oxygen transfer towards overall operation of biological aerobic WWTPs.

On the application of the SDOX to biological wastewater treatment

Chapter 5 describes the operation of an MBR using the two different types of aeration systems previously discussed (i.e., conventional bubble diffusers and the SDOX system). A laboratory-scale MBR was started initially provided with a fine bubble diffuser; after operating the system for three SRTs, the aeration system was replaced by the SDOX unit. In Chapter 4, the effects of the high-pressure conditions and shear-effects introduced by SDOX were evaluated on the performance of the MBR mostly in terms of carbon removal, nitrification, and microbial population dynamics. The performance of the MBR was assessed by monitoring several parameters including the sludge MLSS and MLVSS concentrations, the sludge activity,

changes in particle size distribution (PSD), organic matter removal and nitrification performance, and changes in the microbial community within the sludge. The SDOX aeration system did not influence the active biomass fraction and the performance of the MBR. In addition, the high-pressure applied and high shear-effects introduced by the SDOX unit did not contribute to significantly alter the microbial community in the sludge.
High-pressure conditions are clearly advantageous in terms of oxygen transfer rates, while detrimental effects could be eventually expected when microorganisms are continuously exposed to such conditions. However, the study demonstrated that the biomass in the MBR system was relatively stable under such high-pressure and high-shear effect conditions. That is, the high-pressure conditions (together with the high-shear) exerted by SDOX unit were confirmed to have no negative impact on the biological wastewater treatment performance. However, in this experiment, the operation was performed in a relatively short experimental period (i.e., an experimental duration with the SDOX unit of approximately 1.5 SRT days); thus, it is desirable to evaluate the effects of the SDOX unit at longer exposure times of approximately 3 SRTs or even higher. In addition, it would be desirable to evaluate the performance of the SDOX technology in a full-scale context (either municipal or industrial) rather than in a laboratory-scale system fed synthetic wastewater. Although there may be limitations in drawing conclusions from the results of this study alone, the SDOX technology can be proposed as an alternative technology for DO supply in biological aerobic WWTPs to minimize the system's footprint while reducing operating costs without jeopardizing the biological performance of the system.

Impact of high-pressure and high-shear effects on the membrane filtration performance

Chapter 6 describes the impact of the high-pressure and high-shear effect conditions introduced by SDOX system on the membrane filtration performance. A bench-scale MBR fed synthetic wastewater was continuously operated for 80 days. Several parameters were evaluated in the system to assess the membrane filtration performance including the determination of inherent sludge parameters, visual inspections of the membrane, and permeability tests, among others. The results demonstrated that the high-pressure and high-shear effects introduced by the SDOX contributed to severe membrane fouling compared to the situation observed when the MBR was equipped with fine bubble diffusers. Biofouling seemed the principal contributor to the cake layer formation when using bubble diffusers, whereas organic fouling seemed to be the primary contributor to the cake layer formation when using SDOX technology. In addition, it is plausible that concentration of small particles could be a main parameter affecting the intensive membrane fouling (e.g., formation of a dense and thin cake layer). However, the PSD itself alone cannot unquestionably elucidate the deteriorated membrane fouling propensity. Therefore, presumably, a combination of several factors (certainly including PSD of sludge) resulted in the serious membrane fouling imposed by the high-pressure and shear effects. It is important to highlight that membrane scouring was not applied when conducting this evaluation to maximize

the fouling effects on the membranes. The use of air scouring could have alleviated the membrane fouling effects when using the SDOX unit.

Indeed, the membrane filtration performance was affected by the SDOX technology. However, it is important to state that membrane cleaning mechanism, or membrane relaxation were not applied to intentionally maximize the negative effects of the SDOX equipment on the membrane filtration performance. The SDOX system shifted the PSD of the sludge towards smaller particles eventually contributing to membrane fouling. Agglomeration of particles (i.e., the formation of larger particles) were noticed at the end of each SDOX operation phase (i.e., at the end of phases 2 and 4), which could indicate the physical adaption of the sludge to the SDOX effects. However, long-term evaluations are needed to confirm or reject such a hypothesis. In addition, the influence of the high-pressure and high-shear conditions on the membrane filtration performance needs to be evaluated feeding real wastewater as well as with different types of membranes, as discussed in Chapter 5 in this section. In addition, as have mention earlier, the provision of membrane relaxation and membrane cleaning step would be needed to optimize the stable operation of an MBR with the SDOX technology. By doing this, possibilities of extending the rapid replacement cycle of the membrane observed in this study can be expected.

Advantages of using NIR spectroscopy on predicting wastewater constituents

The Chapter 7 presents the results of NIR experiments interpreted with the help of chemometric techniques. NIR technology is characterized by being cost-effective and rapid. As an alternative to conventional analytical methods for monitoring constituents in wastewater treatment, the effluent, SMP and EPS concentrations of a wastewater treatment process could be predicted by the combination of NIR spectra and chemometric modelling.
Chapter 7 is little bit out of the main line of this dissertation; however, it was found out an easy and simple way to measure analytical parameter without conducting analytical determination as usual. Therefore, this is an interesting finding and appropriate for this dissertation. Through this study, the combination of NIR technology and chemometric modelling offers merits over conventional analytical methods. It is also expected to be applicable to monitoring WWTPs.

To summarize, researchers increasingly recently focused on exploring pressurized aeration systems in activated sludge processes to achieve higher OTE while biodegrading wastewater. The use of SDOX could be a promising strategy for improving oxygen transfer performance in the activated sludge process (in particular at high MLSS). In this context, this study could help provide guidelines for designing the next generation of biological wastewater treatment processes.

8.2 Outlook

It is obvious that the MBR market is globally expanding (Global Membranes Market Report 2020). The application of MBR systems to the municipal and industrial wastewater treatment field has been continuously expanding. As per recent research and market reports, a global market for MBRs reached a value of $3.3 billion in 2021; the report predicted the MBR market to reach $5.8 billion by 2027, i.e., an annual growth rate of 10.31% would be achieved during the 2022–2027 period (https://www.researchandmarkets.com, accessed on 14 March 2022). Furthermore, the global wastewater diffused aerators market reached a value of US$5.3 billion in 2018 according to Persistence Market Research, and it is projected to reach US$ 10.4 billion by 2029, corresponding to an annual growth rate of 6.4% during the 2018–2029 period (https://www.persistencemarketresearch.com, accessed on 14 March 2022).

For MBRs aerobically treating municipal or industrial wastewater, aeration costs can represent more than 50% of the total energy expenditure in the WWTP (Mannina et al. 2020). Moreover, conventional diffused aeration systems have been commonly used to supply dissolved oxygen into MBRs, which include coarse bubble diffusers for membrane scouring, and fine bubble diffusers for biomass growth and mixing. Although it was not scope of this research, considering the intensive energy costs of the coarse bubble aeration in MBRs just for membrane scouring, it is expected that the SDOX aeration system can also contribute to reduce the needs of aeration for membrane scouring by discharging the oxygen supersaturated mixed liquor from the SDOX pressurized chamber directly below the membranes in the MBR basin. This may introduce new possibilities for further research.

Furthermore, from the scientific standpoint, research on the MBR treating either synthetic or real wastewater operated at a short SRT below 10 days (the shorter the better for evaluating the HL-MBR concept) and at high MLSS concentration of >20 g L^{-1}, is required to confirm the concept of HL-MBR considering both a technical and economical evaluation. This study was successfully conducted in the context of using such an innovative aeration system (i.e., SDOX unit) for supplying dissolved oxygen to mixed liquor. However, research on the impact of high-pressure and high shear on the biological and membrane filtration performances is still in its early stages. For instance, it would be interesting to examine how the high-pressure and shear conditions may affect the membrane fouling when using other types of membranes such as hollow fiber membranes or ceramic membranes rather than the flat sheet membrane used in this study. Moreover, for MBR operation with SDOX conducted in this study, the system was fed with synthetic wastewater. Therefore, the situation calls for additional research in terms of the effects of high-pressure aeration systems on the MBR systems treating real municipal/industrial wastewater. It is desirable to verify whether the membrane fouling observed in this study appears similarly while treating real wastewater, which is important for biological performance and microbial population change. Furthermore, this type of research often involves scale-up research to evaluate the applicability to WWTPs.

Moreover, another interesting challenge is to examine the impact of SDOX on the CAS system for determining total operating costs in the context of energy savings. Although the SDOX aeration system is suitable for biological systems operated at high MLSS concentrations of >15 g L^{-1}, it is important to examine whether it can reduce the power cost of WWTPs compared to standard CAS systems.

Decentralized wastewater systems may be expanded in the future. Because of the potential economic benefits of SDOX compared to the conventional diffused aeration system (under certain circumstances), the use of the SDOX unit is proposed for decentralized WWTPs, since such systems usually require a much smaller footprint compared to centralized systems. Furthermore, if immediate (quick start-up) wastewater treatment is required, such as sanitation provision during natural or human-caused disasters, a containerized movable/portable WWTP combined with SDOX technology may play an important role in providing emergency sanitation. An example of such a technology is presented in Figure 8.1. In such a case, the HL-MBR concept would be one of the most suitable technology to deal with the emergency; to achieve sufficient biological performance under HL-MBR operational conditions, an SDOX system with a high OTE of ~100% and high OTRs will be required rather than conventional diffused aeration characterized by inefficient oxygen transfer at high MLSS conditions.

This study presents a potential alternative (i.e., SDOX system) for enhancing oxygen transfer performance and its potential applications in the wastewater treatment sector. The SDOX unit was presented as a new concept for oxygen supply in wastewater treatment systems. However, more research is needed to: (i) better understand the response of microorganisms exposed at the high-pressure conditions and high-shear introduced by the SDOX unit; (ii) elucidate the effect of the high-pressure and high-shear conditions on the settleability of the sludge (if secondary clarifier would be used as the main solid/liquid separation process); and (iii) better understand the application of the SDOX technology for aerobic digestion applications and its comparison with anaerobic digestion. Future studies on these topics are needed to both confirm and expand the potential use of the SDOX technology in wastewater treatment applications.

Figure 8.1 OVIVO® compact and movable MicroBlox™ membrane bioreactor (MBR) system (adapted from https://www.ovivowater.com, accessed on 27 Febraury 2020)

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Study on the effect of the high-pressure and high-shear conditions imposed by high-pressured aeration technology on the settleability of the sludge is required if secondary clarifier would be used as the main solid/liquid separation process (Photo by Sang Yeob Kim)

About the Author

Sang Yeob Kim was born in in Changwon (formerly Masan), Republic of Korea. He served at Republic of Korea Army from 2005 to 2007. In 2010, he obtained Bachelor of Science in Environmental Engineering from Pukyong National University (Busan, Republic of Korea). He continued at Pukyong National University to pursue a Master of Science degree in environmental engineering, particularly focusing on a symbiotic relationship between bacteria and microalgae on wastewater treatment. In 2012, he successfully completed his MSc. studies.

In July 2013, he started PhD research at IHE Delft Institute for Water Education and Delft University of Technology (Delft, the Netherlands). His PhD research focused on the evaluation and application of innovative aeration system on the biological wastewater treatment, particularly biological wastewater treatment plants operated at high mixed liquor suspended solids. During PhD study period, Sang Yeob joined Faculty of Food Technology and Biotechnology at University of Zagreb (Zagreb, Croatia) as a visiting researcher and conducted part of his experimental work.

Currently Sang Yeob is working at the department of Civil and Environmental Engineering, Sejong University (Seoul, Republic of Korea) as a senior researcher. His current research topic is to seek for operational and technical alternatives to comply with total organic carbon standards in effluent from industrial wastewater treatment facilities.

Sang Yeob is highly interested in wastewater treatment and would like to continue the experiments he conducted during his PhD period. He also seeks to continuously contribute to academia with new research.

List of Publications

JOURNAL ARTICLES

Kim SY, Garcia HA, Lopez-Vazquez CM., Milligan C, Livingston D, Herrera A, Matošić M, Ćurko J, Brdjanovic D (2019) Limitations imposed by conventional fine bubble diffusers on the design of a high-loaded membrane bioreactor (HL-MBR). *Environmental Science and Pollution Research* 26(33):34285–34300. https://doi.org/10.1007/s11356-019-04369-x

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Kim SY, Ćurko J, Matošić M, Lopez-Vazquez CM, Brdjanović D, Garcia HA, (*In preparation*) Effects of a sidestream concentrated oxygen supply system on the membrane filtration performance of a high-loaded membrane bioreactor

CONFERENCE PRESENTATIONS

Kim et al. (2019) Impact of sidestream pressure aeration system on the biological performance and shifts in microbial population dynamics in a submerged membrane bioreactor (poster presentation), IEEC & BWR 2019, 10-13 Dec, Busan, Korea

Kim et al. (2019) Influence of side-stream pressure aeration system on possible applications in wastewater treatment (accepted for oral presentation), IEEC & BWR 2019, 10-13 Dec, Busan, Korea

Kim et al. (2019) Influence of Side Stream Supersaturated Aeration Technology on Membrane Fouling and Azithromycin Removal in a Membrane Bioreactor (accepted for oral presentation), 11th Micropol & Ecohazard Conference 2019, 20-24 Oct, Seoul, Korea

Kim et al. (2019) Influence of side-stream pressure aeration system on the biological wastewater treatment (poster presentation), The 7th Busan global water forum, 18-19 Sep, Busan, Korea

Kim et al. (2016) Evaluation of a super-oxygenation system and a conventional aeration system on oxygen transfer capabilities. UNESCO-IHE PhD symposium, 3-4 Oct, Delft, The Netherlands (accepted for oral presentation)

Kim et al. (2015) Comparison of a super-oxygenation system and a conventional aeration system. XIX znanstveno-stručni skup Voda i javna vodoopskrba, 29 Sep-2 Oct, Trakošćan, Croatia (accepted for oral presentation)

Kim et al. (2015) Applicability of high pressure supersaturating oxygenation to MBRs wastewater treatment. UNESCO-IHE PhD symposium, 28-29 Sep, Delft, The Netherlands (accepted for oral presentation)

Kim (2015) Applicability of high pressure supersaturating oxygenation to MBRs wastewater treatment. EKC 2015, 22-24 July, Strasbourg, France (accepted for oral presentation)

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Sang Yeob
22 October, 2022 in Seoul

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Other PhD and Advanced MSc Courses

- Conventional wastewater treatment, IHE Delft (2014)
- Modelling of wastewater treatment processes and plants, IHE Delft (2014)
- Industrial Effluent Treatment - Online Course, IHE Delft (2018)

Management and Didactic Skills Training

- Member of IHE PhD Fellows' Association Board (2014-2015)
- Supervising MSc student with the thesis entitled 'Influence of supersaturated oxygen transfer technology on membrane fouling and azithromycin removal in a membrane bioreactor' (2015-2016)
- Supervising MSc student with the thesis entitled 'Influence of concentrated oxygen delivery technology in solid/liquid separation of aerobic systems' (2014-2016)

Oral Presentations

- *Applicability of high pressure supersaturating oxygenation to MBRs wastewater treatment*. EKC 2015, 22 -24 July 2015, Strasbourg, France
- *Influence of side stream supersaturated aeration technology on membrane fouling and azithromycin removal in a membrane bioreactor.* 11th Micropol & Ecohazard Conference 20-24 October 2019, Seoul, South Korea
- *Influence of sidestream pressure aeration system on possible applications in wastewater treatment*. IEEC & BWR Conference, 10 -13 December 2019, Busan, South Korea

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IHE DELFT
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under the auspices of UNESCO

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The operation of membrane bioreactors (MBRs) at high mixed liquor suspended solids (MLSS) concentrations (higher than 15 g L^{-1}) may enhance the loading rate treatment capacity, while minimizing even further the MBR system's footprint. However, oxygen transfer in wastewater treatment is significantly influenced by the MLSS concentrations. Particularly, conventional diffused aeration systems (fine and coarse bubble diffusers) exhibit a poor oxygen transfer in wastewater treatment applications; particularly, when operating at MLSS concentrations higher than 15 g L^{-1}. The oxygen transfer performance of the supersaturated dissolved oxygen (SDOX) system was evaluated in activated sludge with MLSS concentrations from 4 to 40 g L^{-1} as a promising technology for uncapping such limitation. The operational conditions exerted by the SDOX technology did not affect the concentration of active biomass. Moreover, the biological performance of the MBR was not affected by the introduction of the SDOX technology. In addition, the microbial community was relatively stable although some variations at the family and genus level were evident during each of the study phases. Indeed, the membrane filtration performance was affected by the SDOX technology. A combination of several factors (certainly including particle size distribution of sludge) resulted in the serious membrane fouling imposed by the high-pressure and shear effects. However, this could be influenced due to the scale of the laboratory-based research. More research would be needed to confirm those findings.

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