Coupling process of catalytic membrane with AOP for fouling and OMPs removal

By

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Abstract

Ceramic ultrafiltration is a promising technology for water reclamation, but issues with membrane fouling and the removal of organic micro-pollutants have limited its development. Recent research has shown that catalysis-based ultrafiltration has the potential to address these problems. In this study, catalysis-modified ($CuFe_2O_4$ and Pd) ultrafiltration was investigated for fouling mitigation and organic micro-pollutant removal. The membranes were successfully synthesized and it was found that using Fenton oxidation (a combination of $CuFe_2O_4$ membrane with H_2O_2 backwash) had a 93.9% higher cleaning efficiency than applying demi-water. Besides, it was found that the backwash flux and backwash time were crucial in determining the cleaning efficiency of Fenton oxidation, with a smaller backwash flux or longer backwash time resulting in better permeability recovery. However, the application of Fenton oxidation was also found to be limited by the instability of the $CuFe_2O_4$ catalyst in acidic environment, and the problem of catalyst leaching led to a decrease in cleaning efficiency. Additionally, it was discovered that using PMS oxidation was more effective for OMPs removal compared to Fenton oxidation, with a removal efficiency of up to 90%. Overall, this work demonstrated the potential of catalyst-coated ultrafiltration for water treatment and highlighted the benefits of combining membrane filtration with advanced oxidation processes.

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Abbreviation list

ALD	Atomic layer deposition
AOP	Advanced oxidation process
AOT	Advanced oxidation technology
BWF	Bacckwash flux
BWT	Backwash time
ICP-MS	Inductively coupled plasma-mass-spectrometry
LC-MS	Liquid chromatography–mass spectrometry
MF	Microfiltration
NOM	Natural organic matters
NF	Nanofiltration
OMP	Organic micro-pollutant
Pd	Palladium
PMS	Peroxymonosulfate
PR	Permeability recovery
RO	Reverse osmosis
SEM	Scanning electron microscopy
TMP	Transmembrane pressure
UF	Ultrafiltration
XRD	X-ray diffraction

1. Introduction

1.1. Background

Ceramic ultrafiltration (UF) has emerged as an attractive new technology for water reclamation, given its superior separation capability upon various organic molecules and small colloids [1]. Besides, several characteristics make ceramic membranes more suitable for municipal sewage: their resistance to high temperatures, pressures, and corrosion of chemicals [2]. With the breakthrough of manufacturing technology, ceramic UF membrane with good quality has been commercially available [3]. However, there are still two serious problems remaining to be solved: one is to control the organic fouling amount accumulated in the membrane body, and the other is to control the OMPs concentration in permeate water, in this case the water quality for industry or agricultural use could be guaranteed [4].

Advanced oxidation process (AOP), as an innovated technology, has been applied in water treatment, by which it would trigger active free radicals to degrade the pollutants via Fenton oxidation, persulfate oxidation, photocatalysis oxidation, and so on. The process can be achieved with the assistance of catalysts such as noble metals like palladium (Pd), and non-precious metal like $CuFe_2O_4$. However, nanocatalyst particles in practice face the problem of recycling, meaning that after the treating of targeted wastewater, it requires an extra process to separate the catalysts from the system. Also, the catalyst residuals in water body increase the risk of environment and health. Therefore, the development of protocols for catalyst reuse is essential for the application of AOP. In this case, the integration of membrane with the AOP appears to be attractive. The catalysts can be modified on the membrane surface or embedded into the pores, with which membrane exhibits the catalysis function.

Membrane fouling severely leads to a flux decline, thus deteriorating the productivity of cleaning water. Fouling in plants could account for more than 20 % of the operating cost, among which 70 % of the total cost contributes to the membrane damage caused by the fouling or during fouling removal via chemical cleaning [5]. For the cake layer formation, physical cleaning (like backwash and forward flush) would only partially restore the permeance due to the strong adherence between the fouling layer and the membrane surface. Another common cleaning method used for ceramic membrane is chemical cleaning, generally including acid, alkali, and NaClO, which can remove both reversible and irreversible fouling. However, the method requires large consumption of chemicals, which might produce a toxic waste stream. Furthermore, the low efficiency may ask for an intensive energy input [6]. Due to the shortages of traditional physical and chemical cleaning, a new advanced technology is required to treat the fouling problem of ceramic membranes.

Coupling AOP with membrane could achieve a quick removal of fouling compared with the traditional strategy, in the reason of the nonselective and highly reactive radicals, i.e. hydroxyl radicals (·OH) induced by Fenton reaction. The Fenton oxidation processes on the membrane surface could attack the anchoring sites at the catalytic membrane/foulant interface, which would result in fouling layer detachment [7]. Additionally, Fenton method is environmentally friendly and harmless to membrane integrity [8]. Thus, iron-based catalysts have recently caught much attention from researchers due to their high catalytic activity, accessibility, recyclability and low toxicity [9]. Fenton oxidation has been verified well applicable to gel-layer fouling removal. Lin et al. (2021) [10] adopted Fe_3O_4 hydrosol nanoparticles as active Fenton catalysts and found oxalic acid-aided Fenton cleaning for 15 min could achieve stable initial normalized fluxes (83.33 – 90.15%) of the iron-oxide pre-coated membrane during 5 filtration and cleaning cycles. Except for Fenton oxidation, peroxymonosulfate (PMS) activation was verified to be another promising choice for membrane fouling removal [11].

The presence of organic micro-pollutants at trace levels (ng/L to µg/L) is another considerable problem in the last decades. Membrane-based technology is regarded as a promising process to improve the present procedures of water treatment. For example, the removal efficiency of most OMPs with RO / NF proves to be higher than other advanced water treatment processes, such as adsorption on activated carbon and advanced oxidation [12] [13], in reason that membrane with small pores exists the effect of steric hindrance. While NF / RO offers great advantages for OMPs removal, it produces a high saline concentrate (brine) at the same time [14], and the produced brine makes it difficult to get permits for discharge. The molecular properties of the OMPs are generally smaller than the pore size of MF / UF membranes, hence, the MF / UF system cannot act as barriers for OMPs removal [15].

Integrating AOP with the membrane for micropollutant removal catches more attention in recent years. Under the function of the AOP, the generated radicals could degrade the micropollutants rapidly. Even if applying UF membranes with pore size of 20 nm at a permeate flux of 100 LMH, nearly 100 % of trace contaminations can be degraded [16]. On account of the properties of created radicals, they have the capacity to eliminate varieties of micropollutants. Considering the obstinate nature of some trace matter in water bodies, AOP is much more attractive due to its high oxidation rate. When employing AOP with UF, UF could provide a high flux to guarantee the water yield and pollutants removal, while AOP will be served as the process to degrade the matters with low molecular weights. Both Fenton oxidation and PMS activarion have been proved to be non-selective and effective for degradation of OMPs. For instance, Gupta et al. [17] applied Fenton oxidation for ciprofloxacin (CPX) degradation and finally obtained maximum ciprofloxacin removals about 70%. Besides, Ahn et al. (2016) demonstrated [18] noble metal catalyst palladium (Pd) supported on metal oxides (Al_2O_3 or TiO_2) could activate PMS and consequently degrade organic pollutants.

In this study, the different coupling processes of catalytic membrane with AOP will be investigated. Catalysis-based membrane such as $CuFe_2O_4$ and palladium would be coated onto the UF membrane, because such catalysts have been proved to show a better performance in AOP. The potential of catalytic UF combined with AOP in fouling mitigation and OMPs removal would be investigated to have a deep understanding of the potential application of this integrated technology.

1.2. Problem statement

Membrane fouling and organic micropollutant degradation are ongoing challenges in membrane separation. Fouling leads to permeate flux loss and increased operating costs, while traditional methods such as forward flush / backwash can be ineffective and may risk damaging the membrane. Advanced oxidation processes (AOP) are highly effective in removing organic fouling through reactions with hydroxyl radicals (HO·), but their effectiveness is often limited by weak mass transfer of pollutant molecules. For micro-pollutant degradation, the use of NF / RO membranes is common, but these membranes have low water productivity and produce high-saline concentrate (brine), which is difficult to discharge into fresh surface water. Single MF / UF processes are also inadequate for retaining most OMPs due to their large pore size. However, when combined with other chemical processes, such as AOP, MF / UF can become a viable option for OMP removal [19]. While the potential of the coupled UF-AOP process in degrading OMPs is acknowledged, there are still gaps in understanding how to improve its performance and what the limiting factors are during the process.

1.3. Research objective and question

The purpose of this study is to examine the feasibility of combining catalytic membrane technology with advanced oxidation processes (AOPs) for water treatment. The research has two specific goals: 1) to evaluate the performance of catalyst-coated ultrafiltration (UF) membranes for removing organic fouling using AOPs with hydrogen peroxide backwash, and 2) to investigate the effectiveness of catalyst-coated UF membranes for removing organic micropollutants (OMPs) using a low-dose and continuous application of hydrogen peroxide or PMS during filtration of contaminated water.

In order to achieve the objective, research questions are proposed as the following:

1) What are the potential factors affecting the membrane cleaning efficiency? (i.e. 1 backwash flux, 2 backwash time, 3 stability of coated-catalyst)

2) Whether the coupling process of catalyst-coated UF membrane with AOP is able to degrade OMPs?

2. Literature review

2.1. Ceramic membrane

In the membrane filtration process, the feed stream is separated into concentrate and permeate under the function of transmembrane pressure (TMP) driving force. Membrane technique is well applied in wastewater treatment and has good performance in water purification and reclamation.

Generally, membrane can be classified into two categories based on its fabricated material: polymeric membrane and ceramic membrane. Polymeric membranes lead the membrane separation industry market because they are very competitive in performance and economics [20]. Some common polymers in membrane synthesis consist of polysulfone(PS), polyether sulfone(PES), polyacrilonitrile (PAN), polyvinylidene fluoride (PVDF) and polyvinylchloride (PVC).

Different from polymeric membranes, ceramic membranes are made from inorganic materials (such as alumina, titania, zirconia oxides, silicon carbide or some glassy materials). In comparison to polymeric membranes, ceramic membranes have relatively fewer research studies and industry applications. However, it is because of ceramic membrane advantages of good chemical resistance and thermal stability that they can be applied in separations where aggressive media (acids, strong solvents) are present or used for high temperature membrane operations. Thus, ceramic ultrafiltration (UF) has emerged as an attractive new technology for water reclamation and attracted an increasing amount of corresponding research.

Typically, ceramic membranes consist of several sub-layers, including a support layer which is fabricated by macro-porous alumina (α-Al_2O_3), an intermediate sublayer which narrow the water path, and an active layer which is composed of micro-porous alumina (α-Al2O3) [1]. Ceramic membrane is distinguished with its characteristics of good chemical resistance, thermal stability and high mechanical strength. The exceptional advantages extend its application in harsh conditions such as aggressive chemical (strong acids and bases) and high temperature. Additionally, it is experimentally demonstrated to be less susceptible to organic fouling due to its hydrophilic property [21]. Thus, it has been mainly applied in the landfill leachate treatment, food and beverage industry, and chemical production process [3].

According to the pore size, membranes can be divided into two categories: one category is microfiltration and ultrafiltration membranes (MF and UF), the other is nanofiltration and reverse osmosis (NF and RO) membranes. MF and UF membranes are aimed at particles or colloids (microorganisms, viruses, clay particles, oil emulsion droplets) while NF and RO membranes are applied to retain micropollutants and ions. NF is originated from RO, and it is distinguished by its relatively higher water permeability, lower operating pressure and lower salt rejection [22]. Typically, ultrafiltration membranes have a pore size of ranging from 1 - 100 nm [23][24].

2.2. Catalytic membrane

With the development, advanced oxidation processes (AOPs) involved with reactive oxygen species are appealing for oxidizing organic pollutants at ambient conditions. Thus, heterogeneous AOPs based on catalytic nanomaterials now are prevalently studied, which can promote electron transfer and production of reactive oxygen species and thereby improve degradation efficiency for aqueous organic pollutants. However, the problem is that aggregation of catalysts usually impedes catalytic activity and mass transport, consequently causing performance attenuation. Besides, reutilization of micro-materials is challenging due to the inevitable washout.

Motivated by the existing challenges, AOPs was integrated with membrane filtration to form a catalytic membrane to overcome the inherent hurdles of catalysts for practice use. For example, micro/nano-catalysts (e.g. MnO, CuO and ZIF-67) could be coated onto ceramic or polypropylene membrane surface to achieve catalytic degradation of organic pollutants. Catalytic membrane has its unique advantages. On the one hand, the surface pollutants can be simultaneously oxidized to achieve self-cleaning of the fouled membrane. On the other hand, the catalyst integrated with the membrane can be facilely recycled and reused. For a catalytic membrane, the combination of the open pore path and transmembrane pressure provide easier access of the reactants to the catalyst because the catalysts exist not only on the membrane surface but also in the membrane pores. Thus, for multiphase reactions such a type of membrane configuration is often preferable [25]. Besides, Using catalytic membranes high-pressure operation could be avoided, because a better three-phase contact may be realized [26]. It is due to catalytic membrane good characteristics of high intrinsic activity of the catalytic composition, well-developed catalytic surface and minimal mass transfer limitations of the catalytic performance [27] that catalytic membrane has caught more attention in catalytic reaction for fouling or organic micro-pollutant removal.

2.3. Catalyst coating methods

Typically, catalyst coating methods could be classified into two major sections: physical surface coating and chemical surface coating techniques. Among the physical surface coating, the most commonly applied methods, such as physical vapor deposition(PVD), dip coating and filtration would be mainly discussed. As to the chemical surface coating methods, sol-gel method and chemical vapor deposition(CVD) and atomic layer deposition(ALD) would be mainly introduced.

2.3.1. Physical vapor deposition(PVD)

Physical vapor deposition (PVD) includes a variety of deposition methods in which the target material is evaporated from a condensed phase to vapor and then transmitted to an ambient substrate for condensation under a vacuum, low-pressure gas or plasma environment. PVD is a versatile technique to prepare thin films of pure metals, alloys or compounds [28]. As an atomic deposition process, PVD has found wide applications to produce functional films with improved abrasion resistance, corrosion resistance, superconductivity, light conductivity and electrical conductivity [29].

2.3.2. Dip coating

Dip coating involves the immersion of a membrane substrate into a solution containing coating substances, followed by removal and drying of the coated substrate. The technique is capable of coating both dense or porous membrane substrates with diverse shapes including flat sheet , tubular, and hollow fiber [30]. The coating layer thickness can be controlled by adjusting different process parameters such as immersion time, withdrawal speed, solution composition, dipping cycles. Its advantages include excellent versatility, facile operation, and easy scale-up.

2.3.3. Filtration

Filtration for catalyst immobilization refers to the process where a catalyst-loaded solution or suspension is filtrated through a porous membrane, during which the catalysts are attached on the membrane surface or the inner channel [31]. Either covalent bonding or non-covalent bonding (hydrophobic/hydrophilic or electrostatic interactions) exists between the catalyst and the membrane surface. Catalyst coating by the covalent bonding during filtration involves a certain reaction of active functional groups, and thus often offers better catalyst stability (i.e., less catalyst leaching) when compared to that by non-covalent bonding. However, the catalytic activity may be adversely affected by covalent bonding due to the chemical modification [32] of catalyst. Owing to its facile and straightforward operation, filtration has widely been applied to immobilize either homogeneous or heterogeneous catalysts on both inorganic and polymeric porous membranes for water treatment

2.3.4. Solution-gelation

The solution-gelation (sol-gel) technique is a well-studied technique to synthesize solid materials from small molecules, which generally starts with the hydrolysis of a liquid precursor (sol), which undergoes poly-condensation to form gel [33]. Typical sol-gel process consists of four stages: (1) hydrolysis, (2) monomers condensation to form chains and ions, (3) growth of particles, and (4) tight aggregation of the polymer [34]. Sol-gel technique has an advantage of enabling nanomaterial catalysts to be uniformly dispersed and coated on substrates with various geometries. Besides, the coated surfaces has a long durability for that the sol-gel-supported catalysts are often strongly bonded to the substrate. However, the sol-gel technique application in industrial production is always limited by its problem of long time consuming [35].

2.3.5. Chemical vapor deposition(CVD)

Chemical vapor deposition (CVD) is a popular surface coating technique for a variety of applications, during which a volatile coating precursor is vaporized in an inert atmosphere by heat, light, and/or plasma-discharge, and then reacted on a solid substrate surface to produce a desired deposit [36]. The modification process is similar to the PVD technique except that the precursors in CVD are generally in vaporized state (as a chemical compounds), while the precursors in PVD are often in elemental state (as a pure metal) without chemical reactions on the surface [37]. CVD has become one of the most promising techniques for massive production of functional materials such as semiconductor, optics, and electronics, and offer outstanding control of coating properties such as thickness and density. In addition, CVD is capable of coating functional layers down to nanoscale, and often involve no use of various toxic organic solvents (particularly useful for insoluble materials coating) [38].

2.3.6. Atomic layer deposition(ALD)

Atomic layer deposition is a subclass of CVD, which involves different precursors reacting on a substrate surface in a sequential manner for thin film deposition [39]. The most distinct difference between ALD with other CVD techniques is that ALD proceeds layer by layer with alternatively pulsing the source gases, while CVD is a continuous process with all the reactants supplied at the same time for film growth [40]. Accordingly, the ALD enables superior thickness and uniformity control for the film deposition than other CVD techniques. For example, Zhang, et al. coated TiO_2/ZnO composite on a microfiltration PVDF membrane at atomic scale with superior uniformity using ALD technique [41]. The ALD process is widely used as it provides ultra-thin nano-layers in an extremely precise manner on a variety of substrates, including micron to sub-micron size particles.

2.4. Fouling of ceramic membrane

Membrane fouling is a process by which the particles, colloidal particles, or solute macromolecules are deposited or adsorbed onto the membrane pores or onto a membrane surface by physical and chemical interactions or mechanical action, which results in smaller or blocked membrane pores. Membrane fouling can cause severe flux drops and affects the quality of the water production. Severe fouling may require intense chemical cleaning or even membrane replacement, which increases the operating costs of a treatment plant. Membrane fouling has traditionally been thought to occur through three mechanisms—pore blocking, pore constriction, and cake formation. Pore blocking occurs when the particulates or solutes with small size distribution are introduced to membrane's body. Pore constriction happens when pollutants are absorbed into the internal pore, pore plugging occurs when pollutants plug pores, and finally cake formation occurs when pollutants pile up onto the membrane surface. Membrane fouling categories could be classified into inorganic fouling, organic fouling, colloidal fouling and biofouling, among which organic fouling is the most serious fouling type [42]. To date, the main cause of ceramic membrane fouling was the colloidal or dissolved organic matter [43].

2.4.1. Organic fouling

Among the commonly encountered foulants in water reclamation, organic fouling is a major category which includes humic acids, proteins, polysaccharides, etc. Humic acids refer to the fraction of humic substances that are not soluble in water under acidic conditions ($pH<2$) but is soluble at higher pH. They are formed by the decomposition of heterogeneous and refractory polymeric organic compounds [44]. Humic acids are a heterogeneous mixture having both aromatic and aliphatic components and containing three main functional groups: carboxylic acids (COOH), phenolic alcohols (OH), and methoxy carbonyls (C=O) [45]. As to the proteins fouling, its formation can be attributed to the aggregation of proteins in solution, which is resulted from electrostatic repulsion reduction [46]. Thus, the proteins aggregation on the membrane surface would cause fouling. Compared to other common organic substances such as proteins and humic acids, polysaccharides existing widely in distinct water environments would cause more serious fouling problems. The high fouling propensity of polysaccharides can be attributed to their intrinsic gelling property, which contributes a lot to the gel layer formation in membrane filtration process. In spite of the high porosity and thinness, gel layer shows extraordinarily high filtration resistance, which reaches almost one hundred times higher than that of cake layer [47].

2.4.2. Factors affecting organic fouling

As to factors affecting organic fouling, past studies on ceramic membranes suggest a series of factors which might influence the natural organic matters(NOM) fouling, including solution chemistry, membrane surface properties, and hydrodynamic conditions [48].

It is indicated that the increase of foulant concentration in the feed water would enhance concentration polarization and foulant deposition at the membrane surface [49]. A high concentration of salt compresses electrical double layer (EDL) and decays the stability of the colloids, thus increasing the collision frequency and attachment of foulants to the membrane. Calcium ion has a stronger interaction with alginate than other multivalent cations. Therefore, an increased concentration of calcium ion in the feed water enhances calcium bridging [50]. Besides, pH and foulant type would influence membrane fouling as well.

Membrane surface properties such as the functional groups of the membrane, the morphology of membrane (i.e. surface roughness) and hydrophobicity would also contribute to membrane fouling. The surface charge (zeta potential) influences membrane fouling by affecting the interaction energy with charged foulant [50]. Besides, it is proposed that an increase of surface roughness decreased the adhesion of alginate to the membrane [51]. Moreover, it is noteworthy that the adhesive foulants might alter surface charge and hydrophobicity, and accordingly changes the separation mechanism of the membrane. Moreover, it is stated that foulants were retained by size exclusion, whereasthe retention of large solute by a pre-fouled membrane was mainly caused by adsorption [52].

Meanwhile, hydrodynamic condition is another factor contributing to membrane fouling. Typically, permeate flux plays a crucial role in membrane fouling in two aspects. On the one side, the increase of permeate flux increases the probability and frequency of collision between foulants and membrane. On the other side, an enhanced permeate flux introduces a greater hydrodynamic drag force to the solute, which increases membrane fouling. Besides, a higher TMP increases permeate flux, and an increase of cross-flow velocity decreases the propensity of foulant deposition. Additionally, temperature, recovery factors, membrane modules and the design of spacer would affect membrane fouling as well [50].

2.4.3. Membrane fouling mitigation methods

Assuming that membrane fouling could cause a serious of negative effects to the wastewater treatment process, fouling mitigation is necessary for the practical application of the membrane process. Generally, based on if fouling can be removed by physical cleaning (forward and backward flush), fouling can be categorized into reversible fouling and irreversible fouling [6]. Physical cleaning is aimed at removing the loosely attached foulants, which is known as reversible foulant. However, as to the fouling attributed to colloidal organic matters, which is more tenacious and hydraulically irreversible, is mainly mitigated by chemical cleaning [3]. Besides, pre-coat engineering is also a good fouling control method. In this method, a suspension is dosed on the membrane (the precoat layer) to form an easily removable and permeable layer on the membrane [2]. Moreover, one of the advanced oxidation processes (AOP) technique, Fenton oxidation, has also been widely used in water and wastewater treatment [53].

2.4.3.1. Direct forward flush and backwash

When forward flush is applied, the feed or permeate flows through the system more rapidly than during the production phase. Because of the more rapid flow resulting turbulence, particles absorbed to the membrane are released and discharged. However, as to the particles that are absorbed in the membrane pores, they can only be removed through backwash. During the backwash progress, permeate is flushed through the feed water side of the system under pressure, applying much higher the flux that is used during filtration. Although forward flush and backwash are efficient in preventing membrane fouling by the removal of hydraulically reversible fouling from the membrane surface, these methods are not effective in removing gel layer fouling and inorganic layers caused by inorganic salts such as calcium and iron salts.

2.4.3.2. Chemical cleaning

Compared with physical cleaning, chemical cleaning provides excellent performance for the removal of gel layer fouling and pore blocking. For example, alkaline (sodium hydroxide (NaOH)) and oxidizing (sodium hypochlorite (NaClO) and potassium permanganate ($KMnO_4$)) agents are efficient in removing organic foulants and microbial contaminants. Acid reagents (hydrochloric acid (HCl), ethylenediamine tetra acetic acid (EDTA), ascorbate and citrate) were effective in desorbing inorganic salts [54]. However, chemical cleaning agents, such as NaOH or citric acid, are incapable of fully eliminating the foulants even if the flux was entirely recovered, leading to a progressive flux decrease with successive filtration cycles. Besides, secondary pollution from the chemical cleaning solution and the easily formed disinfection by-products represent secondary pollution sources in treated waters, which require additional treatment [55].

2.4.3.3. Enhanced precoating engineering

Enhanced precoat engineering (EPCE) is another fouling control method widely used for polymeric UF and MF [56]. In this method, a suspension is dosed on the membrane (the precoat layer) to form an easily removable and permeable layer on the membrane. During filtration the fouling attaches or adsorbs onto the precoat layer instead of on the membrane. When the threshold pressure is reached, the membrane will be hydraulic backwashed. Then, during backwash the cake layer detaches easily from the membrane. Alternatively, precoating using coagulants has also been found to have the function of enabling UF membranes to remove natural organic matter.

2.4.3.4. Advanced oxidation process

The advanced oxidation process(AOP) is also a great technique to remove membrane fouling when combined with different catalysts. In this method, hydrogen peroxide (H_2O_2) is used as a powerful oxidant for it can break down high molecular weight organic pollutants and even mineralize them while generating no secondary by-products [53]. With regard to H_2O_2, the Fenton or Fenton-like reactions have been widely used in water and wastewater treatment [53]. The hydroxyl radicals (HO·) generated in the Fenton or Fenton-like reaction systems are non-selective oxidants and significantly stronger than H_2O_2. Therefore, organic foulants including readily biodegradable organic compounds (proteins polysaccharides, humic acid, and fluorescent substances) and bio-refractory organic compounds could be efficiently oxidized and removed by ·OH [57]. As such, Fenton or Fentonlike reactions could theoretically achieve high membrane cleaning efficiencies. For instance, polymeric membranes coated with photocatalysts (e.g., β-FeOOH and $CuFe_2O_4$) demonstrated the much better performance of antifouling and catalytic self-cleaning in the presence of H_2O_2 [42].

2.5. Organic micro-pollutants removal

2.5.1. Organic micro-pollutants

Organic micro-pollutants are synthetic chemicals found in water sources and treated wastewater at concentrations in the range of micrograms per liter or lower. Micro-pollutants tend to be resistant to biodegradation and many are bioactive. Sources of micro-pollutants include pesticides, solvents, detergents, pharmaceuticals, and personal care products and the major part comes from several sources like domestic or industrial wastewater, hospital effluents, or agricultural run-off. The primary characteristics of these substances are high toxicity, very low biodegradability and resistance to degradation and to conventional biological treatments Thus, the pollutants may cause long-term consequences, such as bioaccumulation in the environment and carcinogenicity. It is noticed that the presence of organic micro-pollutants in water bodies, streams and groundwater has become a subject of major concern throughout the world [58].

2.5.2. Micro-pollutants removal method

Because of the micro-pollutants threat and harm mentioned above, a supplementary treatment is essentially required for the effective removal of micro-pollutants from wastewater streams. As to the available treatment methods removing OMPs from water, the most widely applied techniques include membrane filtration, advanced oxidation processes and activated carbon adsorption [59].

2.5.2.1. Membrane filtration

Membrane filtration is a method of separating particles in liquid solutions. The semi-permeable membrane acts as a barrier which retains larger particles but allows smaller molecules to pass through the membrane into the permeate. Some membrane-based processes, such as nanofiltration (NF) and reverse osmosis (RO), have become an attractive option to remove OMPs in water [60]. The operational principle of these membrane-based processes is similar: a pressure gradient as the main driving force and a semi-permeable membrane as the barrier for contaminants. Compared to RO, NF employs membranes with bigger pores, resulting in a lower rejection of solutes, but NF has the advantage that it can be operated at lower pressure. However, although relatively high rejection values are observed for most organic micropollutants, several pollutants can still be found in the permeate of NF/RO installations.

2.5.2.2. Adsorption

Adsorption is a surface phenomenon by which molecules attach to an adsorbent solid using various processes that vary in intensity (physical or chemical adsorption). Among different kinds of materials used for micro-pollutants adsorption, activated carbon has the most widely application. The characteristic of activated carbon is an adsorbent with large porous surface area, controllable pore structure, thermostability and low acid/base reactivity [61]. Besides, activated carbon has a superior ability for removal of a wide variety of organic and inorganic pollutants dissolved in aqueous media. Generally, the application of this material is usually in granular form inside a filter or in powder form, generally in an activated carbon contactor/separator [62].

2.5.2.3. Advanced oxidation technologies

Innovative advanced oxidation technologies (AOTs), including chemical oxidation technologies (COTs) and advanced oxidation processes (AOPs), are designed to enhance the degradation and mineralization of micro-pollutants (MPs) or to transform them into less toxic compounds. AOTs are widely studied technologies for the oxidation of organic MPs via reactions with the highly reactive radicals. Hydroxyl radical mediated AOTs utilize hydroxyl radicals (HO·), the most powerful oxidizing species after fluorine. These unselective radicals might mineralize the parent compounds with no generation of secondary waste, yielding CO_2, H_2O and inorganic ions as final products. Depending on the number of phases involved during the transport and reaction of the species, AOTs can be divided into homogeneous and heterogeneous processes. Homogeneous AOTs include processes that utilize UV, H_2O_2, the Fenton reagent, dissolved O_3, wet oxidation (WO) and wet peroxide oxidation (WPO); whereas heterogeneous AOTs comprise of heterogeneous photocatalysis, heterogeneous Fenton-like processes, catalytic and photocatalytic ozonation, catalytic wet oxidation [63].

2.6. Advanced oxidation process

Advanced oxidation processes (AOPs), in a broad sense, are a set of chemical treatment procedures designed to remove organic (and sometimes inorganic) materials in water and wastewater by oxidation through reactions with hydroxyl radicals (·OH) [64]. In comparison to traditional membrane techniques, one of their advantages is that they effectively degrade recalcitrant components without generating a secondary waste stream. Moreover, in most cases the formation of hazardous species in the effluent is limited, which is a specifically important benefit over competing technologies.

2.6.1. Fenton oxidation

Among these AOP techniques, the Fenton process is a widely studied and used catalytic method based on the generation of hydroxyl radicals (HO·) from hydrogen peroxide with iron ions acting as homogeneous catalyst at acidic pH and ambient conditions. The HO· radical has a high standard oxidation potential and reacts with most organic and many inorganic solutes with high-rate constants. In a Fenton reaction iron works as a catalyst for hydrogen peroxide, resulting in an advanced oxidation reaction. Free radicals are formed being able to degrade organic matter (OM). During the Fenton reaction process, both iron forms, iron(II) and iron(III), react with hydrogen peroxide which are known as a Fenton and a Fenton-like reaction [65]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^{\cdot} + H^{+} \qquad [1]$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^{-} \qquad [2]$$

$$HO^{\cdot} + OM \rightarrow OM_{oxid} \qquad [3]$$

2.6.2. Peroxymonosulfate oxidation

Activated peroxymonosulfate (HSO_5^-, PMS) is an emerging advanced oxidation process that can degrade both natural organic matter and recalcitrant micropollutants. PMS is stable at room temperature, but can be activated by various agents such as transition metals (e.g., iron, palladium), heat, and ultraviolet (UV) light to form sulphate radicals ($SO_4^{-\cdot}$), which are highly reactive. During the oxidation progress, the sulphate radicals can react with inorganic ions (e.g., Cl^- and CO_3^{2-}), generating secondary reactive species ($Cl^{\cdot}$ /$CO_3^{-\cdot}$) owning relatively high reactivity with OMPs [66]. It is due to its inexpensive price, high stability, and good solubility in water [67] that PMS has been widely applied for membrane fouling mitigation and OMPs removal.

2.7. Couple membrane-AOP process

Over the past few decades, various technologies have been explored for the treatment of organic wastewater. However, such conventional processes are not very effective for complete removal of organic pollutants. These technologies usually need complicated equipment, with a high energy consumption and high operating costs, and some of them also require large amounts of chemicals, resulting in byproduct wastes and sludge [68].

As to the conventional processes, membrane technology has its advantages of high separation selectivity, low energy consumption and no requirements for additional chemicals [69]. However, the technique is suffering from membrane fouling and incomplete decontamination problem. Advanced oxidation process(AOP) could well decompose the organic compounds to less refractory products, and even mineralize them to CO_2, H_2O, and other inorganic specie [70]. However, their efficiencies are often limited by the weak mass transfer of the pollutant molecules. Besides, their energy consumption is still at a relative high level for commercial uses.

However, although membrane technology and advanced oxidation process have their own limitations, it is encouraging that the combination of membrane technology with AOPs can effectively mitigate the membrane fouling problems, thereby improving the overall separation performance [71]. As expected, a synergistic design of such coupling processes can further improve the process performance and reduce the energy consumption. According to Ganiyu et al.(2015) [71] research, it presented a general overview on the coupling of membrane filtration and advanced oxidation process (membrane-AOPs) for removal of pharmaceutical residues. The coupled membrane-AOP processes were considered to be promising for effective removal of hazardous substances as compared to the individual process component alone.

3. Experiment 1: alginate fouling removal

The alginate fouling removal experiment aimed to evaluate the effectiveness of Fenton oxidation for alginate fouling removal and to investigate the influence of various factors, such as backwash flux, backwash time, and catalyst stability, on the membrane cleaning efficiency. The study first compared Fenton oxidation with other common cleaning methods, such as physical and chemical cleaning, to assess the improvement in membrane permeability recovery provided by Fenton oxidation (Section 3.3.1). Then it investigated the effect of backwash flux (Section 3.3.2) and backwash time (Section 3.3.3) on membrane cleaning efficiency. Finally, it examined the stability of the catalyst-coated membrane by applying different chemical agents (Section 3.3.4), and analyzed the catalyst stability impact on membrane cleaning efficiency (Section 3.3.5).

3.1. Materials

Among the applied experiment materials, copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$; >= 98% purity; solid), Iron(III) nitrate ($Fe(NO_3)_3 \cdot 6H_2O$; >= 96% purity; solid), sodium alginate (≥ 99.0%), sodium chloride ($NaCl$) and sodium bicarbonate ($NaHCO_3$) and citric acid ($C_6H_8O_7$, ≥ 99.0%) were purchased from Sigma-Aldrich(Germany). Hydrogen peroxide (H_2O_2, 30%), calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$, ≥ 99.0%) were purchased from Merck (Germany). All chemicals were used as received. Copper iron oxide ($CuFe_2O_4$) catalyst applied in this research was synthesized in the lab. Na-alginate was the model organic foulant that represented model pollutant in organically loaded wastewater. The chemical composition of Na-alginate was $(C_6H_7NaO_6)_n$. In addition, the 0.2 µm disposable syringe filters (CHROMAFIL® Xtra PE-20/25) were purchased from MACHEREY-NAGEL (Germany).

In the research, commercially available UF membranes (CoorsTek Netherlands) with mean pore size of 100 nm were used in this study. The membranes have a single channel and a tubular configuration with dimensions of 10 mm in outer diameter, 7 mm in channel diameter and 100 mm in length. The effective filtration area of each membrane is 0.00163 m^2. The membranes were sealed with epoxy glue on the membranes edges to avoid feed water passing through the edges from the feed to the permeate during filtration. The membranes were operated in an inside-out mode during filtration.

3.2. Method

3.2.1. Synthesis of $CuFe_2O_4$ membrane

Regarding Zhang et al. 2019 [72] publication, we took use of the sol-gel combustion method to synthesize $CuFe_2O_4$ catalyst on ceramic membrane, according to citrate complexation. At first, cupric nitrate, ferric nitrate and citric acid were added successively into demi-water with a molar ratio of 1 : 2 : 3.6. Here we measured 7.25g $Cu(NO_3)_2{\cdot}3H_2O$, 24.24g $Fe(NO_3)_3{\cdot}9H_2O$ and 20.75g critic acid with the electrical balance and dissolved the powders in 150ml demi-water. Afterwards, the prepared homogeneous solution was applied for 3 cycles of coating processes with the coating system (Figure 1). For each coating cycle, we filtrated 50ml precursor solution through the ceramic membrane and immediately dried the wetted membrane in the oven for 10 minutes after each coating cycle. By this way more synthetic ingredients could be retained in the membrane body. Besides, the coating solution was filtrated through the ceramic membrane with a very slow permeate flux under 0.1 bar transmembrane pressure (TMP) to ensure the membrane surface and body have sufficient contact with the coating solution.

After the coating process, the coated membrane was then heated in a muffle furnace at a rate of 10 °C per minute and kept at a temperature of 400°C for 2 hours to eliminate the citric acid retained in the ceramic membrane [72]. The synthesized catalyst-coated membrane was allowed to naturally cool down to room temperature. To determine if the $CuFe_2O_4$ catalyst was successfully formed on the ceramic membrane, samples were cut from the catalyst-coated membrane for further analysis. The composition of catalyst-coated membrane samples was characterized by X-ray diffraction (XRD) (X-ray facilities group, Faculty of 3ME, TU Delft), and the element distribution of the catalyst-coated membrane samples was determined by scanning electron microscopy (SEM) analysis (Faculty of Applied Science, TU Delft). The results of the XRD and SEM analysis can be found in Appendix A and B respectively.

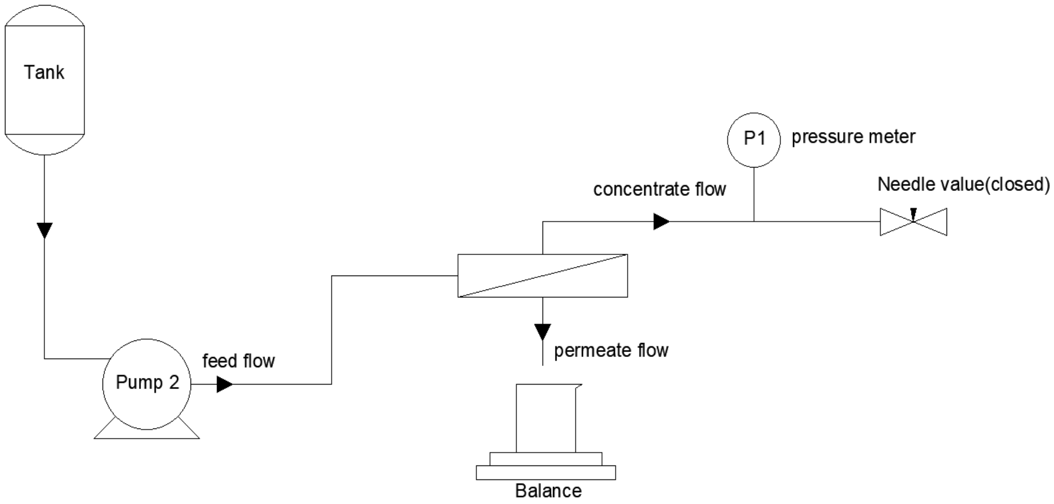


Figure 1. Set up of the coating system

The applied equipments of the coating system include: 1) coating solution tank 2) feed pump 3) crossflow membrane module 4) permeate collection vessel weighed by a scale 5) needle valve. During the coating process, the concentrate side of the membrane module was closed with a needle valve.

3.2.2. Alginate fouling removal system

Prior to the alginate fouling removal experiment, a demi-water permeability assessment of applied membranes was applied to measure the initial permeability, and then the alginate fouling removal experiment was carried out with 4 cycles to evaluate the membrane's permeability recovery over an extended period of performance. Each experiment cycle mainly consisted of 3 phases (Table 1). In the process of demi-water permeability assessment, alginate fouling and forward flush, the applied demi-water / alginate solution entered in the membrane module from its feed side and came out from its permeate side (Figure 2 (a)). However, during the backwash process, the applied 30mM H_2O_2 solution was passed through the membrane module from the permeate side to the feed side (Figure 2 (b)). In the alginate fouling removal experiment, all of the applied membranes were cleaned prior to the experiment and the filtration processes were performed at a constant transmembrane pressure (TMP) and room temperature.

Prior to the fouling removal experiment, a demi-water permeability assessment of pristine / catalyst-coated membranes was firstly conducted. During the process, the feed water was controlled with a flow rate of 1.5 L/min (cross flow velocity = 0.65 m/s) and a transmembrane pressure (TMP) of 0.3 bar. The applied membranes were stabilized with demi-water for 15 minutes to determine the initial permeability ($P_{initial}$).

After demi-water permeability assessment, the alginate fouling removal experiment would be conducted. Phase 1 was the alginate fouling process, in which a synthetic foulant, sodium alginate, was used to mimic extracellular polymeric substrate (EPS) found in municipal sewage. Besides, NaCl (5 mM), $CaCl_2$ (3 mM) and $NaHCO_3$ (1 mM) were added into sodium alginate solution (50 mg/L) to simulate the solution chemistry of natural waters. The pH of alginate solution was controlled around 7.0 , modulated by 1 mM HCl and 1 mM NaOH. In this phase, the retentate was recycled to the feed tank (5 L) and the permeate was continuously collected for measuring the membrane permeability.. The alginate filtration was executed with a constant TMP of 0.3 bar and a constant feed flow rate of 1.5 L/min. In this case, a constant cross-flow velocity of 0.65 m/s was adopted during the fouling process (for 75 min). At the end of the fouling process, the stabilized permeability with alginate solution was applied to demtermine the permeability after fouling process ($P_{fouling}$).

After the alginate fouling process, phase 2 was the backwash process. In this phase 30 mM H_2O_2 solution (pH = 2.5) was used to clean the membrane. The H_2O_2 backwash was executed with a constant TMP and a constant feed flow rate of 0.4 L/min for a certain time interval. Besides, the potential factors which might affect the membrane cleaning efficiency, such as backwash flux or backwash time, would have further discussion in Section 3.3.2 and 3.3.3 .

The final phase was a one-minute forward flush to remove any remaining loose alginate fouling material on the membrane. The forward flush was applied with a higher feed flow rate of 2.5 L/min (cross flow velocity = 1.08 m/s). During this process, the needle valve on the membrane concentrate side was kept open to maintain a high-speed feed flow rate, resulting in a TMP of 0 for the membrane during the forward flush process.

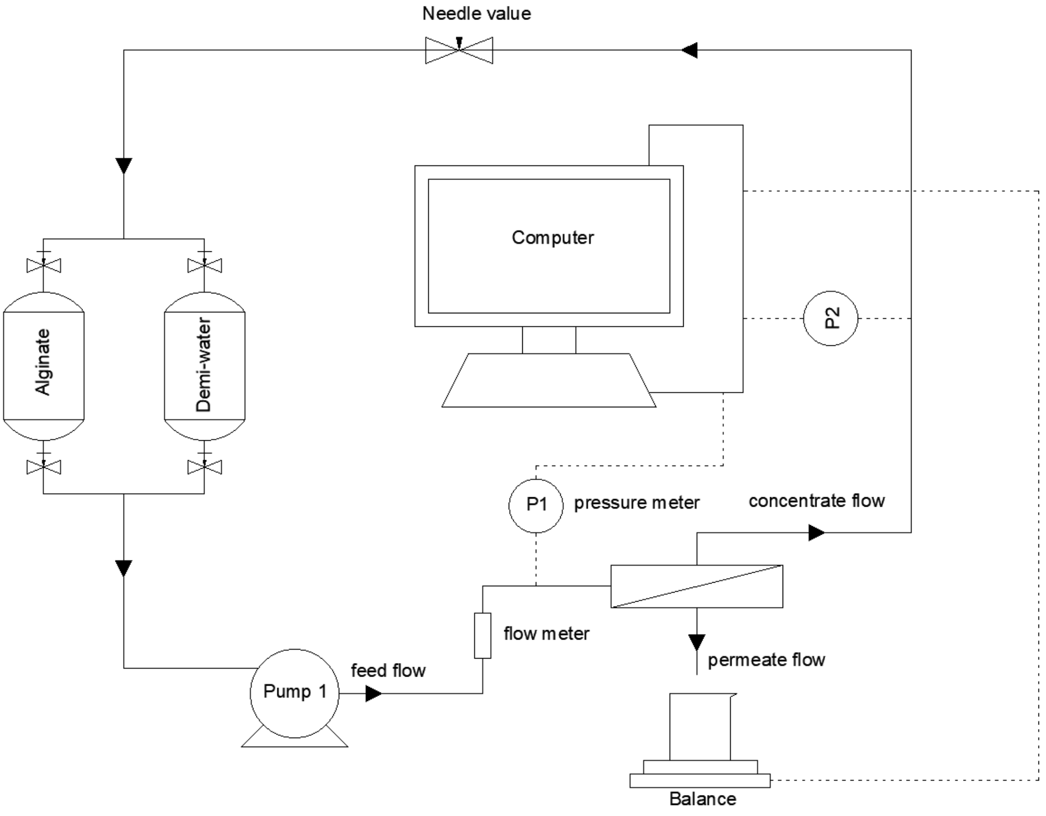
After finishing one cycle of alginate fouling removal experiment, the next cycle would start with the alginate fouling process again. Importantly, the initial permeability of the next cycle with alginate solution would be assumed as the permeability of the previous cycle after cleaning process ($P_{cleaned}$). Hence, for each cylcle, the permeability recovery ratios after cleaning could be calculated using Eq [4]:

$$PR = \frac{P_{cleaned} - P_{fouiing}}{P_{initial} - P_{fouling}} \times 100\% \qquad [4]$$

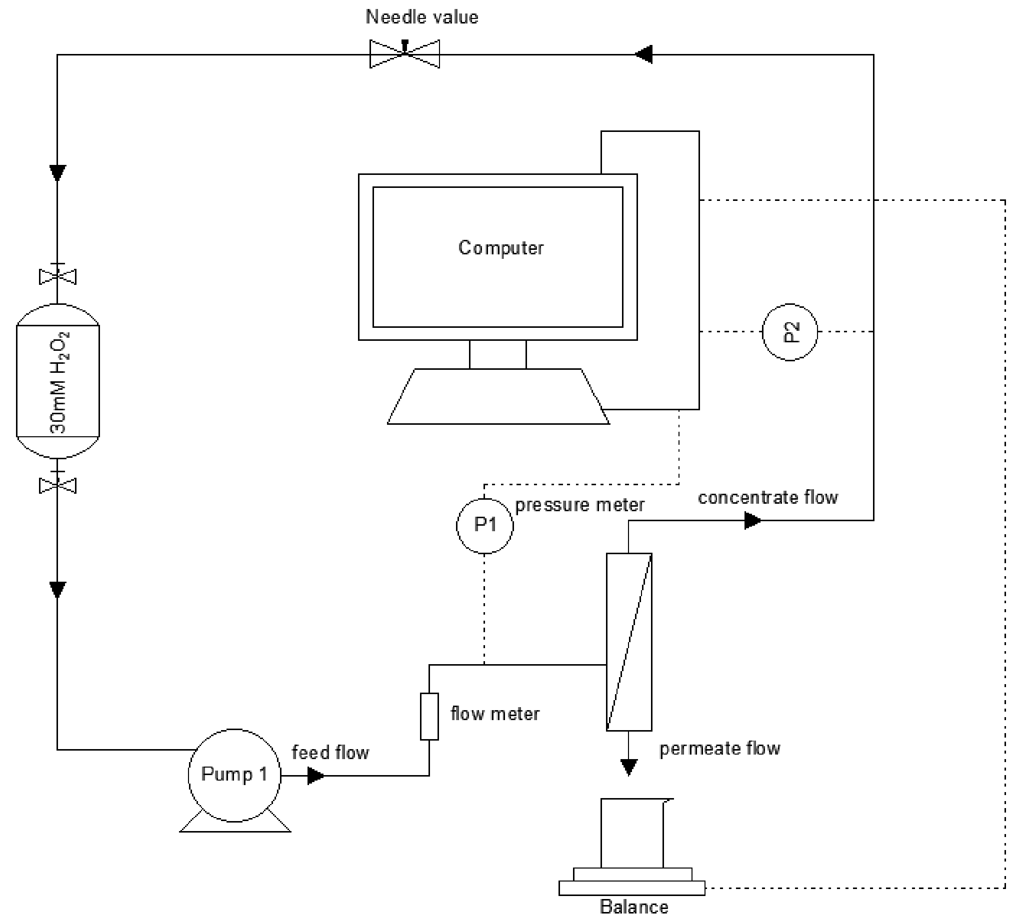
where PR refered to the permeability recovery, meaning to which extent membrane permeability could regain after the cleaning process. Besides, $P_{initial}$ denoted the initial demi-water permeability prior to the fouling removal experiment, and $P_{fouling}$ denoted the permeability at the end of the fouling stage respectively. After cleaning process, the initial permeability of the next fouling cycle was regarded as $P_{cleaned}$.

Phase	Feed flow rate (L/min)	TMP (bar)	Temperature(°C)	pH	Time(min)
Alginate fouling (50PPM)	1.5	0.3	room	7	75
Backwash (30mM H_2O_2)	0.4	0.3/0.5/1	room	2.5	6/18/36
Forward flush	2.5	/	room	-	1

Table 1. An overview of fouling removal experiment phases



(a)



(b)

Figure 2. Equipment set up for alginate fouling removal experiment
(a). Set up for water permeability assessment, alginate fouling process and forward flush (b). Set up for backwash process. Applied equipments: (1) alginate solution tank (2) Demi-water tank (3) 30mM H_2O_2 tank (4) feed pump (5) crossflow membrane module (6) permeate collection vessel weighed by a scale (7) computer that recorded the balance weight and TMP values (8) needle valve used to modulate the TMP of the membrane module.

3.2.3. Examination of catalyst stability

The stability of the $CuFe_2O_4$ catalyst was heavily dependent on the leaching of Cu / Fe elements in the applied chemical agents. To gain a better understanding of the catalyst leaching, the dissolution of Cu / Fe from the $CuFe_2O_4$-coated membrane was studied. In the alginate fouling removal experiment, 30 mM H_2O_2 (pH = 2.5) was combined with $CuFe_2O_4$-coated membrane to generate Fenton oxidation for membrane cleaning. Except for the applied cleaning agent H_2O_2, NaClO and NaOH were also commonly used as chemical cleaning agents for algae-fouled membranes. In this study, H_2O_2, NaClO and NaOH, were applied to examine the stability of $CuFe_2O_4$-coated membrane in acidic and alkaline environment.

The stability of the $CuFe_2O_4$ catalyst on the membrane was evaluated by measuring the amount of Cu and Fe that leached out of the membrane when exposed to different cleaning agents. In particular, the $CuFe_2O_4$-coated membrane was soaked in 30mM H_2O_2 (pH = 2.5), 0.1% NaClO, and 10mM NaOH solutions for 8 hours, and samples were collected every hour to measure the concentration of Cu and Fe that leached out of the membrane. This experiment was conducted to determine if significant leaching occurred during the soaking period.

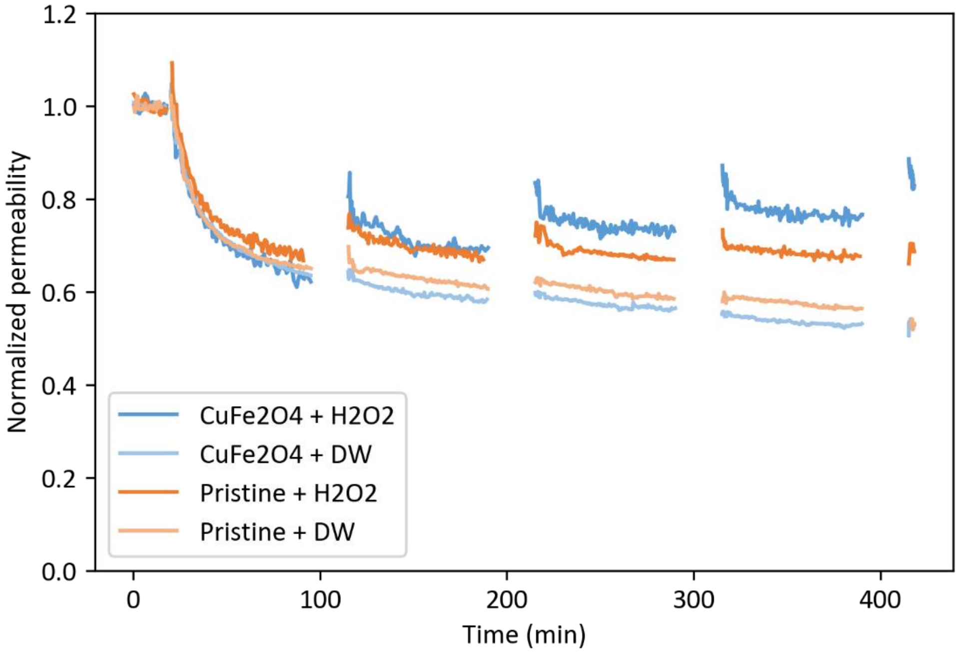
3.3. Results and discussion

3.3.1. Cleaning efficiency of Fenton oxidation

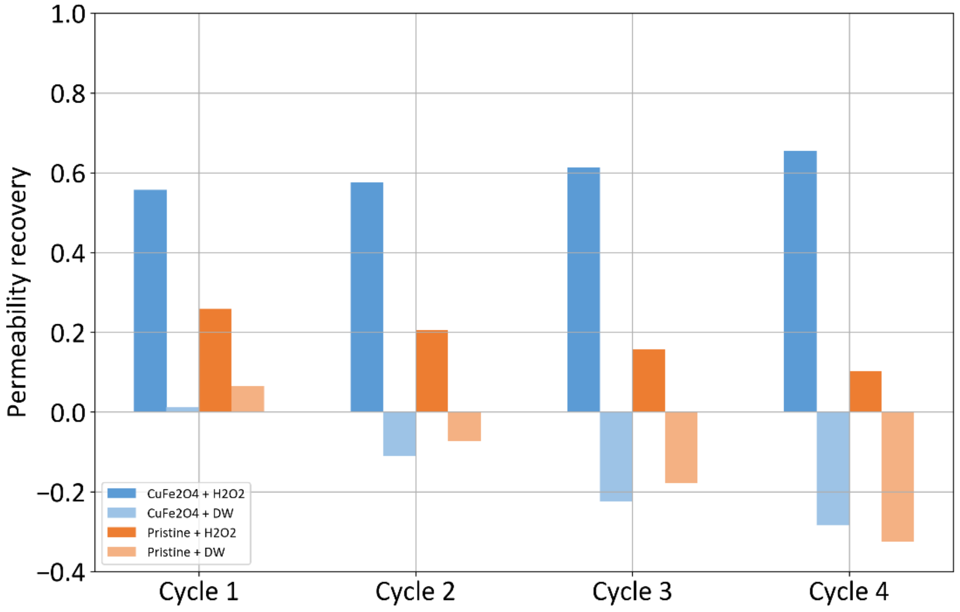
The results of Figure 3 revealed that the Fenton oxidation method, which utilized $CuFe_2O_4$-coated membrane in combination to H_2O_2 backwash, had the highest permeability recovery in comparison to physical cleaning (using demi-water backwash) and chemical cleaning (pristine membrane in combination to H_2O_2 backwash). The permeability recovery of Fenton oxidation was 55.7% for the first cycle, and it increased to 65.5% for the final cycle.

The results of the comparison also showed that physical cleaning methods, such as demi-water backwash, were not effective in removing alginate fouling. As the number of cycles increased, the permeability recovery of the two controlled trails with demi-water backwash both showed a decline tendency and even became negative in later cycles. This indicated that the alginate fouling on the membrane became more severe over time. The poor cleaning efficiency of demi-water backwash can be attributed to the strong bridging effect between carboxylic groups of polysaccharide molecules and divalent or multivalent metal ions, as reported in Xin et al. 2015 research [73], which made the gel-like fouling have strong adherence to the membrane and increased the difficulty of fouling removal.

The chemical cleaning had a better cleaning efficiency than physical cleaning, but less effective than Fenton-based oxidation. As an oxidizing agent, the applied H_2O_2 had the capability to oxidize some organic compounds directly [74]. However, without the existence of certain catalyst, the H_2O_2 itself could not generate highly reactive hydroxyl radicals (·OH) induced by Fenton oxidation for alginate fouling removal. Thus, the chemical cleaning could only partially mitigate alginate fouling and led to a small-scale permeability recovery. For example, the permeability recovery of chemical cleaning reached 25.9% in the first cycle, but gradually decreased to 10.2% in the final cycle.



(a)



(b)

Figure 3. Cleaning efficiency of Fenton oxidation compared with other cleaning methods (a) Permeability behavior and (b) Permeability recovery during the alginate fouling removal experiment. Experiment conditions: backwash flux = 90 LMH, backwash time = 18 min, applied Ca concentration = 3 mM.

3.3.2. Impact of backwash flux

The results in Figure 4 demonstrated that the cleaning efficiency of Fenton oxidation could be influenced by the backwash flux. The best performance was observed with a backwash flux of 60 LMH, resulting in permeability recovery of 69.4% in the first cycle and 87.0% in the final cycle. On the other hand, a backwash flux of 140 LMH had the worst performance, showing a decline of permeability recovery with the increase of experiment cycles, from initial permeability recovery of 52.6% in the first cycle to 15.8% in the final cycle. This suggested that smaller backwash flux was more effective in removing gel-like fouling, while larger backwash flux might decrease the cleaning efficiency and even strengthen the severity of alginate fouling on the membrane over time. The reason why a smaller backwash flux performed better cleaning efficiency while a larger backwash flux did not is because a smaller backwash flux provides the hydroxyl radicals with a longer retention time, and thus giving them more time to oxidize and remove the alginate fouling. However, a larger backwash flux might shorten the retention time, and even directly flush away the hydroxyl radicals before they have a chance to react with the alginate fouling.

Compared with Fenton oxidation, employing demi-water for backwash had no improvement of permeability recovery, even increasing the backwash flux from 60 to 140 LMH. Also, with the increase of experiment cycles, negetive permeability recovery was observed as well. As to the phenomenon, Resosudarmo et al. [75] revealed that demi-water backwash for alginate removal would disperse the alginate structure, and if the formed fouling was severe, the strong chelation between calcium and alginate would inhibite the alginate dispersion form membrane into feed. Hence, with more cycles, more gel-like alginate fouling would be attached to the membrane, thus leading to the negative permeability recovery. Furthermore, unlike Fenton oxidation, a larger backwash flux was found to be more effective for demi-water cleaning as the larger backwash flux was able to loosen and flush away the alginate fouling [76].

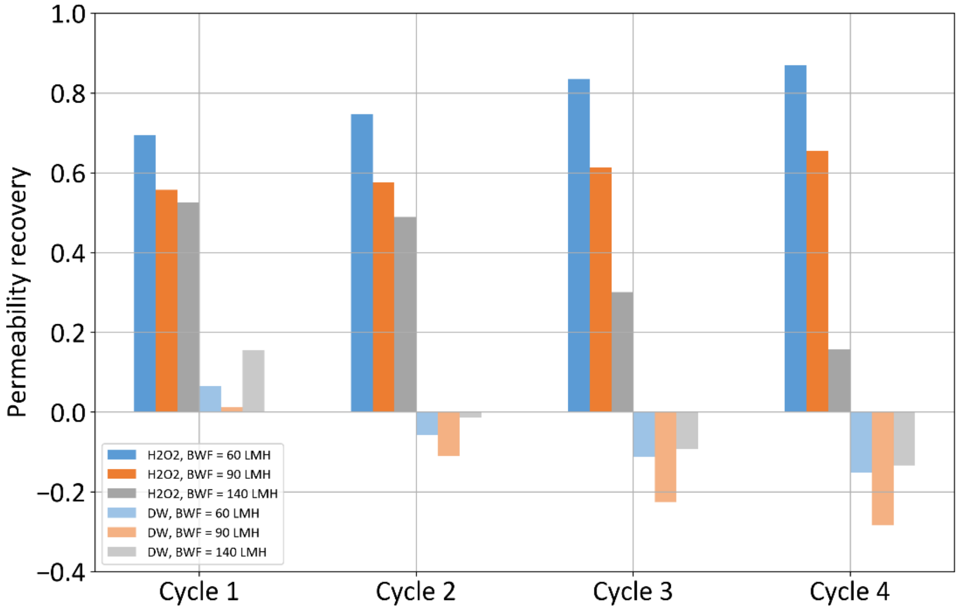


Figure 4. Effect of backwash flux: permeability recovery of Fenton oxidation and demi-water cleaning. Experiment conditions: backwash flux = 60 / 90 / 140 LMH, backwash time = 18 min, applied Ca concentration = 3 mM.

3.3.3. Impact of backwash time

Figure 5 illustratesd that the cleaning efficiency of Fenton oxidation could also be impacted by the backwash time. It was observed that as the H_2O_2 backwash duration increased, the permeability recovery of Fenton oxidation improved. For example, 6-minute Fenton oxidation had a permeability recovery of 35.6% for the first cycle and 51.0% for the final cycle, whereas 36-minute Fenton oxidation had a permeability recovery of 60.9% for the first cycle and 80.3% for the final cycle. Therefore, it was obvious that that a longer backwash time led to better cleaning efficiency in Fenton oxidation. The reason could be attributed to that the extension of backwash duration increased the contact time between H_2O_2 and the $CuFe_2O_4$ membrane, which led to a higher generation of hydroxyl radicals that effectively oxidize and remove the alginate fouling on the membrane.

Extending the duration of demi-water backwash from 6 to 36 minutes did not improve the cleaning efficiency, similar to increasing the demi-water backwash flux from 60 to 140 LMH. The permeability recovery of demi-water backwash remained unchanged and even showed negative values in later cycles. In comparison, Fenton oxidation showed a much higher cleaning efficiency, as seen when applying backwash flux of 90 LMH and backwash time of 18 min, Fenton oxidation performed a permeability recovery of 49.5% in cycle 1, which was 5.7 times higher than the permeability recovery of 7.4% for demi-water cleaning.

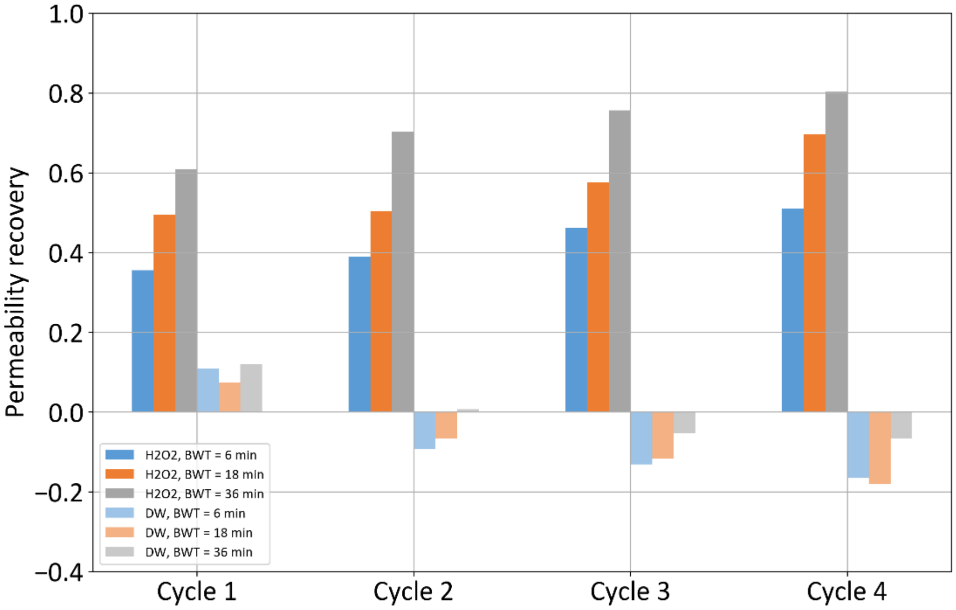


Figure 5. Effect of backwash time: Permeability recovery of Fenton oxidation and demi-water cleaning. Experiment conditions: backwash flux = 90 LMH, backwash time = 6 / 18 / 36 min, applied Ca concentration = 3 mM.

3.3.4. Stability of synthesized catalyst

The synthesized $CuFe_2O_4$ catalyst performed good stability in 0.1% NaClO and 10 mM NaOH solution (Figure H.1 , Figure H.2), while showed unstability when soaking in 30 mM H_2O_2. As shown in Figure 6, after immersing $CuFe_2O_4$ membrane in 30mM H_2O_2 for 8 hours, an obvious Cu leaching was found, which increased from initial 0 to final 6.07 mg/L. The obvious Cu leaching illustrated that the $CuFe_2O_4$ membrane was untable when exposed to acidic environment. However, when exposed to alkaline envionrment, the $CuFe_2O_4$ membrane appeared to be very stable, as almost no Cu / Fe element leaching was found during the soaking process, where the $CuFe_2O_4$ membrane was immersed in 0.1% NaClO or 10mM NaOH for 8 hours

On the basis of X-Ray analysis for catalyst component (Figure A.3), there were two compunds might be the potential source of leaching Cu, which were CuO and $CuFe_2O_4$. As metal oxide, CuO could react with acid (see Equation [5]). Besides, according to Boyanov et al. 2015 research [77], $CuFe_2O_4$ was also verified to have solubility in HCl, thus leading to Cu leaching when soaking in HCl solution. However, for Fenton oxidation, its environment should be controlled with a pH of 2.5 for best effect [78]. Thus, the limited acidic environment for Fenton oxidation might be a disadvantage for $CuFe_2O_4$-coated membrane application.

$$CuO + 2H^+ = Cu^{2+} + H_2O \qquad [5]$$

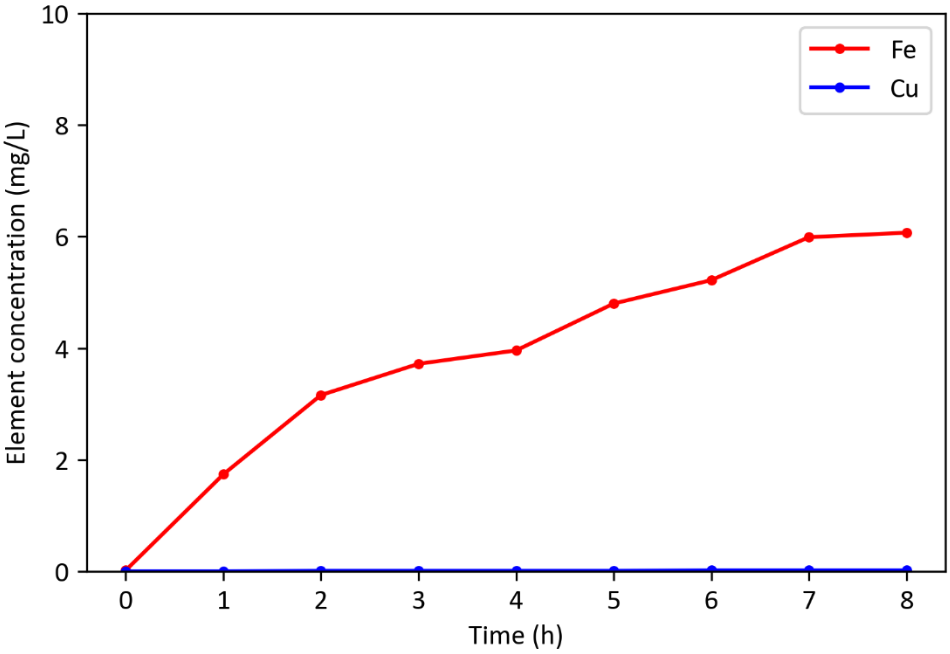


Figure 6. Element concentration change with 30mM H_2O_2 soaking solution

3.3.5. Impact of catalyst leaching

Figure 7 illustrated the effect of catalyst leaching on the cleaning efficiency of Fenton oxidation by comparing the permeability recovery of a newly synthesized $CuFe_2O_4$ membrane with a $CuFe_2O_4$ membrane that was soaked in 30 mM H_2O_2 for 96 hours. The results showed that the newly synthesized membrane without catalyst leaching had a higher permeability recovery of 49.5% for the first cycle and 69.6% for the final cycle, while the membrane with catalyst leaching had a lower permeability recovery of 30.1% for the first cycle and 45.9% for the final cycle. This difference in permeability recovery demonstrated that catalyst leaching significantly reduced the cleaning efficiency of Fenton oxidation, with a decline in permeability recovery ranging from 16.8% to 23.7%.

The $CuFe_2O_4$ membrane was verified to be unstable in acidic environment and the catalyst leaching problem resulted in an obvious decline of permeability recovery. However, for Fenton oxidation, it should be exposed to acidic environment (pH = 2.5) for best cleaning effect. Hence, the catalyst leaching problem was difficult to be avoided, and thus remaining to be a limitation for the application of Fenton oxidation technique in wastewater / industry practice.

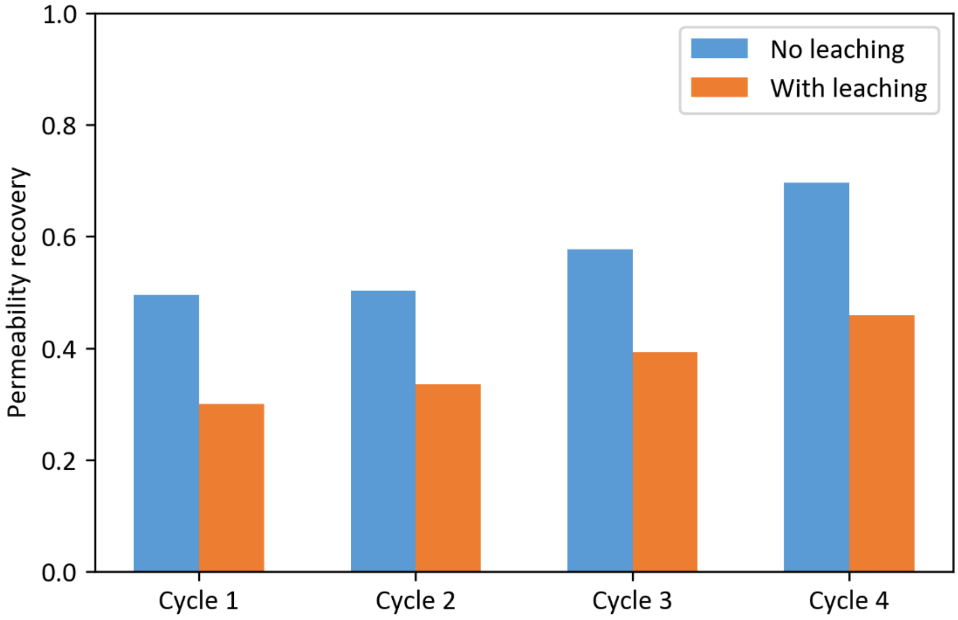


Figure 7. Permeability recovery of $CuFe_2O_4$ membrane with/without catalyst leaching. Experiment conditions: backwash flux = 90 LMH, backwash time = 18 min, applied Ca concentration = 3 mM.

4. Experiment 2: OMPs degradation

The aim of the OMPs degradation experiment was to explore if the combination of catalyst-coated membrane with AOP was able to degrade OMPs. Here we applied three different combination processes: OMPs dosed with H_2O_2 for filtration through $CuFe_2O_4$ membrane, OMPs dosed with PMS for filtration through $CuFe_2O_4$ membrane [79], and OMPs dosed with PMS for filtration through Pd membrane [16]. By comparing the OMPs degradation efficiency of different applied methods, we aimed to determine which combination process was most effective in degrading OMPs.

4.1. Materials

In the experiment, a total number of 7 kinds of OMPs with good solubility in high pure water [80] were selected as the targeted pollutants to be removed. All the selected OMPs were purchased from Sigma-Aldrich (Germany). Their physicochemical and structural properties are listed in Table 2.

Besides, the peroxymonosulfate (> 4.0% active oxygen basis) and the sodium thiosulfate ($Na_2S_2O_3$, >= 99%) were purchased from Sigma-Aldrich (Germany). The hydrogen peroxide (H_2O_2, 30%) was were purchased from Merck (Germany). The applied catalyst copper iron oxide ($CuFe_2O_4$) and palladium (Pd) were both synthesized in the lab. The 0.2 µm glass fiber filters were purchased from ADVANTEC* (Japan).

In this research , the applied ceramic UF membranes had the same size as the alginate fouling removal experiment (Section 3.1).

Name	Molecular formula	Molecular weight (g/mol)	pKa	Antibiotic
Sotalol(SOT)	$C_{12}H_{20}N_2O_3S$	272	9.43	Antibiotic
Metoprolol(MP)	$C_{15}H_{25}NO_3$	267	9.67	
Trimethooprim (TMP)	$C_{14}H_{18}N_4O_3$	290	7.16	Antibiotic
Propranolol(PPL)	$C_{16}H_{21}NO_2$	259	9.53	
Benzotraiazole(BT)	$C_6H_5N_3$	119	9.04	Corrosion inhibitors
Carbamzepine(CBZ)	$C_{15}H_{12}N_2O$	236	15.96	Anti-epilleptic
Diclofenac(DIC)	$C_{14}H_{11}Cl_2NO_2$	296	4	Analgestics/Anti-inflammatories

Table 2. Physicochemical and structural properties of the selected OMPs

4.2. Method

4.2.1. Sythesis of Pd membrane

In the OMPs degradation experiment, two kinds of catalyst-coated membranes were put into application: $CuFe_2O_4$ membrane and Pd membrane. The concrete synthesis method of $CuFe_2O_4$ membrane had already been mentioned in Section 3.2.1.

Taking reference from Li et al. (2022) [81] research, the atomic layer deposition (ALD) method was applied for synthesis of Pd membrane. Hence, the Pd membrane was synthesized in a flat substrate reactor operating at atmospheric pressure. 1 – 3 ceramic membranes were put in the reactor for each synthesis. The ALD precursor ($Pd(hfac)_2$)) was kept at 70 °C and the co-reactants was kept at room temperature during the experiments. N_2 (99.999 vol%) was used as both carrier and purging gas. The reactor was heated and maintained at 200 °C for all ALD process. 0.5 L/min flow rate of $Pd(hfac)_2$ plus 0.5 L/min compensation N_2 gas was used for precursor doing procedure for 30s, followed by 1 L/min N_2 dosing for 30 s as purging procedure. 0.7 L/min formalin dosing combined with 0.3 L/min N_2 doing for 40 s was used as co-reactant dosing procedure and after that, 30 s of 1 L/min N_2 doing was used as purging procedure. The detailed information on Pd ALD operation conditions can be found in Table 3. By repeating the above mentioned procedure for required times, the different ALD cycled samples were prepared.

Material	Precursor (T, °C)	Coreactant (T, °C)	$T_{reaction}$ (°C)	Exposure Time (s) Precursor-N_2-Co-reactant-N_2
Pd	$Pd(hfac)_2$ (70)	Formalin (RT)	200	30-30-40-30

Table 3. Detailed information of Pd ALD operation conditions

4.2.2. OMPs degradation system

Prior to the OMPs degradation experiment, we performed a water flux assessment on the applied membrane. The revolutions per minute (RPM) of the feed pump was kept at a constant value of 150, while the needle valve was adjusted to maintain a constant permeate flux of approximately 30 LMH.

After the water flux assessment, 2 liter of OMPs solution with a concentration of approximately 5 µg/L for each type of OMPs was prepared. An initial sample of the OMPs solution, designated as F0, was taken from the 2 liter feed OMPs solution in the volumetric flask. After obtaining the initial OMPs sample, a specific amount of H_2O_2 / PMS chemicals was added into 2 L OMPs solution to achieve a concentration of 40 µM H_2O_2 / PMS. The mixed solution was stirred for a certain time, and then the pH was adjusted to a suitable value (pH 2.5 [78] for mixed OMP-H_2O_2 soluton, pH 7 [82] for mixed OMP-PMS solution), modulated by 1mM HClO and 1 mM NaOH. In this case, the best optimal condition of pH for Fenton oxidation could be achieved.

Figure 8 illustrated the setup for the OMPs degradation experiment, where the OMPs solution mixed with an oxidizing agent (H_2O_2 or PMS) was fed into the membrane module and flowed out through the permeate and concentrate sides, with a constant permeate flux of 30 LMH. The experiment lasted for 60 minutes. Samples of the permeate were collected at various time intervals (Table 4) to observe the change in OMPs concentration over time. The concentrate solution was collected in a waste tank, preventing any recirculation during the OMPs filtration process.

During the filtration process, the oxidizing agent was mixed with the OMPs solution, which then passed through the membrane and entered into the permeate solution. However, it was important to note that the remaining oxidizing agent in the permeate solution could continue to react with the OMPs. To prevent this, 50 µL of a 40 mM $Na_2S_2O_3$ stock solution was added into each collected permeate sample (5 mL) to halt the Fenton reaction. Afterwards, the samples were filtered through fiber filters produced by ADVANTEC* to remove any suspended solids or leaching catalyst.

After glass fiber filter filtration, all the collected samples were sent for LC-MS test (Waters, ACQUITY UPLC I-Class, Xevo TQ-S micro fitted with the ESI) to measure OMPs concentration. The OMPs removal efficiency could be calculated using formula 6:

$$OMPs\ removal\ efficiency = \frac{C_{initial} - C_{permeate}}{C_{initial}} \quad [6]$$

where OMPs removal efficiency (%) denoted the decrease in OMPs concentration due to oxidation through AOP. In the formula, $C_{initial}$ denoted the OMPs concentration of initial OMPs sample (F0), while $C_{permeate}$ denoted the OMPs concentration of the collected permeate samples after filtration with AOP, respectively (µg/L).

Sample name	F0	P1	P2	P3	P4	P5
Collected time interval	/	0-5 min	10-15 min	20-25 min	40-45 min	55-60 min

Table 4. Collected OMPs samples at different time intervals

Sample F0 was taken from the orginal prepared OMPs solution, containing 5 µg/L for each type of selected OMPs. Sample P1, P2, P3, P4, P5 were permeate samples collected at different time intervals of the OMPs filtration process. The duration of OMPs filtration was 60 minutes.

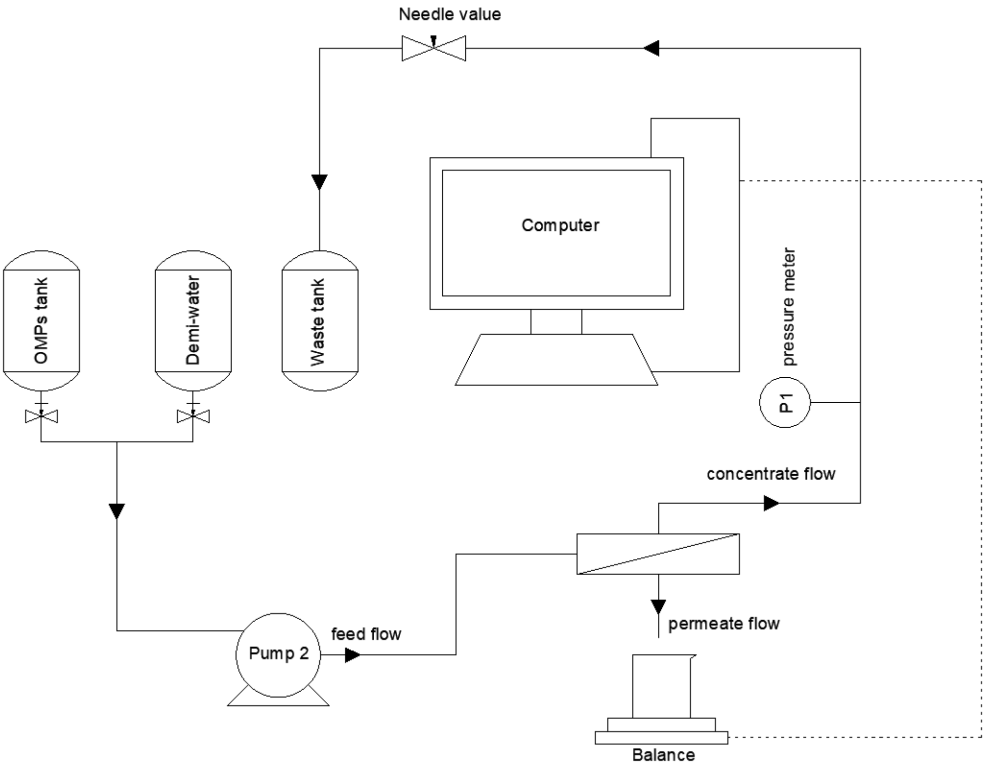
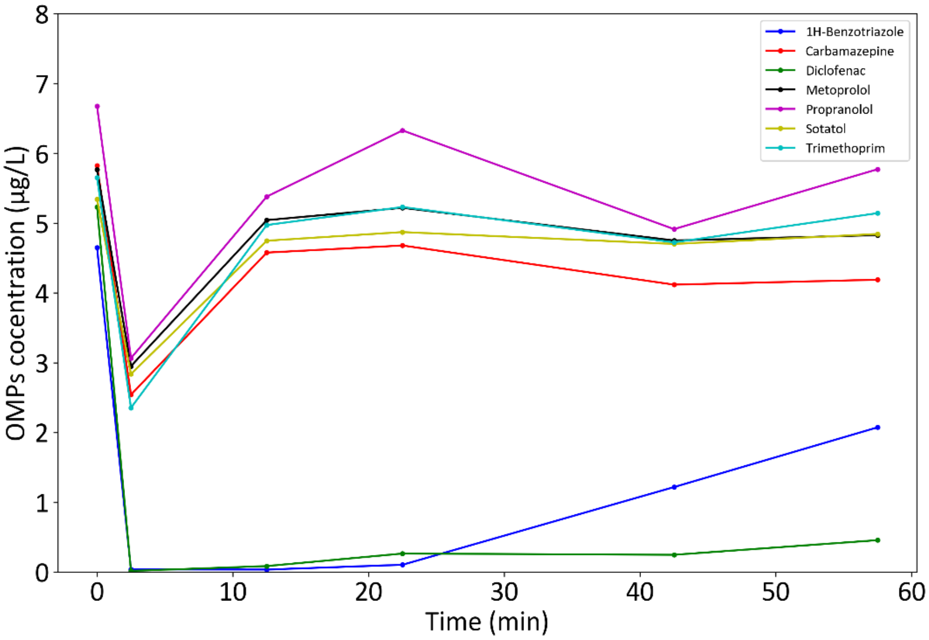


Figure 8. Equipment set up for OMPs degradation experiment

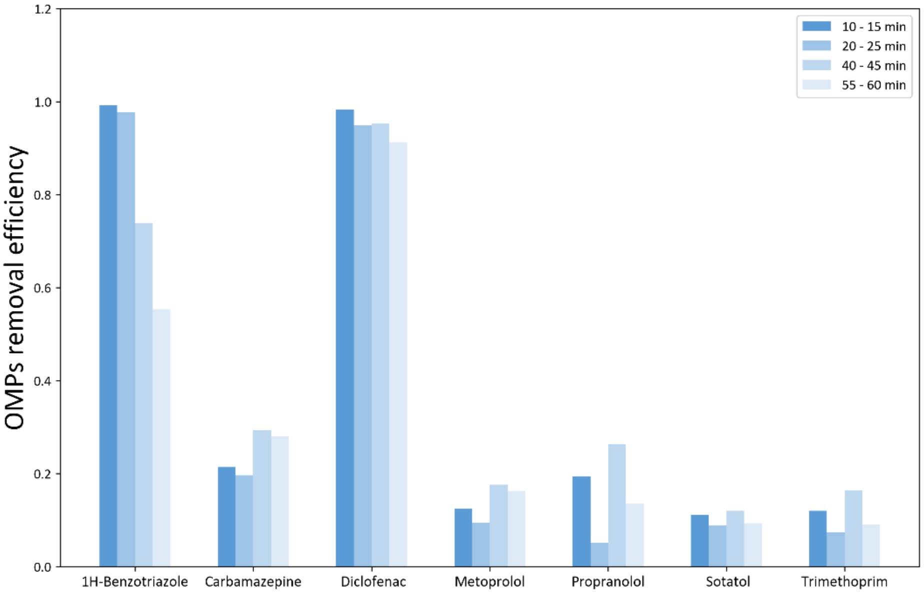
Applied equipments: 1) OMPs solution tank 2) Demi-water tank 3) Waste tank 4) feed pump 5) membrane module 6) permeate collection vessel weighed by a scale 7) computer recorded the balance weight and TMP values 8) needle value to adjust the TMP of the membrane.

4.3. Results and discussion

Figure 9 (a) showed the change in concentration of OMPs during a 60-minute duration of Fenton oxidation. It was observed that there was a sudden drop in OMPs concentration at sample P1 (0-5 min), which was determined to be an inaccurate result. This inaccuracy might have been caused by an issue with dilution of demi-water. As previously discussed in section 4.2.2, a water flux assessment was conducted on the applied membrane before the OMPs degradation experiment, which resulted in some demi-water being retained in the membrane module. During the initial stage of the OMPs degradation experiment, this retained demi-water, along with the inlet OMPs solution, entered into the permeate and ultimately affected the OMPs concentration in the permeate sample. Therefore, the inaccurate result of sample P1 (0-5 min) was not considered in the subsequent analysis. Figure 9 (b) illustrated the OMPs removal efficiency of Fenton oxidation. Out of the 7 selected OMPs, only the concentration of Diclofenac decreased significantly by more than 90%. However, the concentration of the remaining 6 OMPs did not decrease to the desired low level. Therefore, Fenton oxidation was not found to be effective for OMPs removal.



(a)



(b)

Figure 9. OMPs removal efficiency of Fenton oxidation

(a) OMPs concentration change (b) OMPs removal efficiency. Experiment conditions: constant permeate flux = 30 LMH, applied OMPs solution: H_2O_2 concentration = 40 μmol/L , pH = 2.5

Figure 10 demonstrated the results of an experiment that aimed to evaluate the OMPs removal efficiency of PMS oxidation activated by $CuFe_2O_4$. The results indicated that PMS oxidation activated by $CuFe_2O_4$ had high degradation rates for 3 kinds of the selected OMPs (1H-Benzotriazole, Diclofenac and Sotatol), with removal rates of more than 99%. However, when PMS oxidation activated by $CuFe_2O_4$ was applied, it had a removal rate of only about 20% for Carbamazepine, Meteprolol and Trimethoprim. Hence, despite PMS oxidation activated by $CuFe_2O_4$ showing improved performance for OMPs removal compared to Fenton oxidation, it did not perform significant improvement for certain types of OMPs.

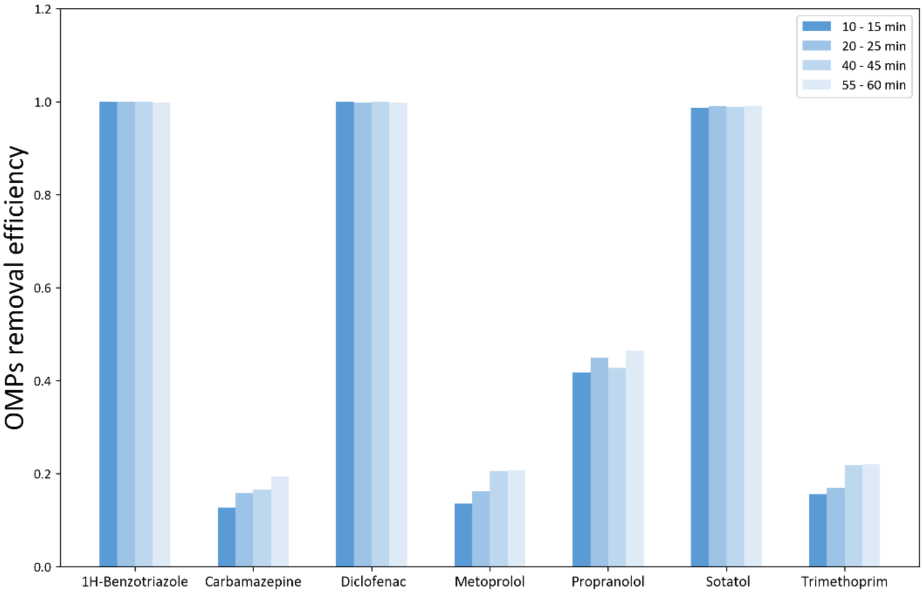


Figure 10. OMPs removal efficiency of PMS oxidation activated by $CuFe_2O_4$

Experiment conditions: constant permeate flux = 30 LMH, applied OMPs solution: PMS concentration = 40 μmol/L , pH = 7

Figure 11 illustrated the results of an experiment that aimed to evaluate the OMPs removal efficiency of PMS oxidation activated by Pd. The results showed that under the influence of this advanced oxidation process (AOP), 5 kinds of the selected OMPs achieved a high removal efficiency of more than 95%. Additionally, for OMPs that are relatively difficult to degrade, such as Carbamazepine and Metoprolol, PMS oxidation activated by Pd also showed significant improvement. For example, Carbamazepine achieved a removal rate of 55.8% and Metoprolol had a degradation rate of 70.2%. Therefore, in comparison to Fenton oxidation and PMS oxidation activated by $CuFe_2O_4$, PMS oxidation activated by Pd had the best performance for OMPs removal.

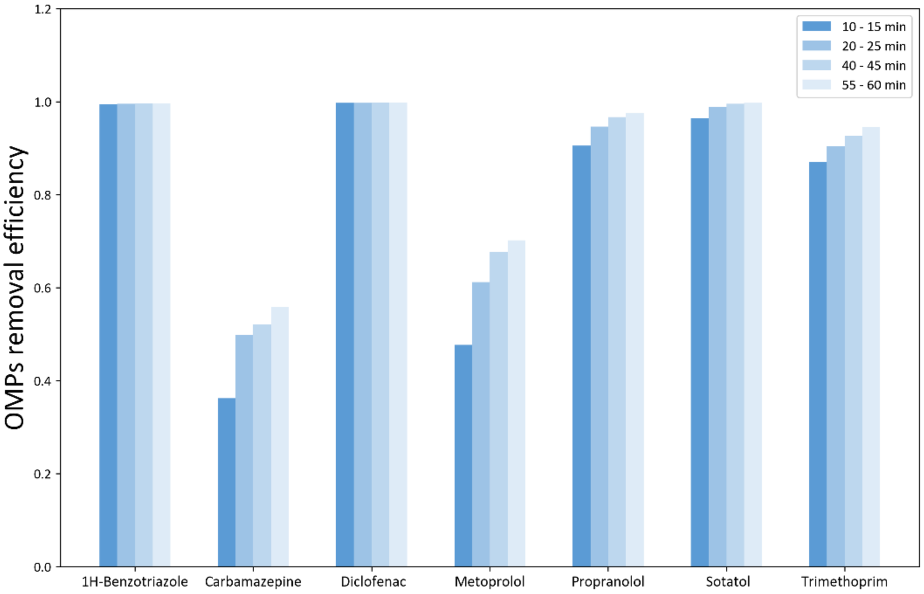


Figure 11. OMPs removal efficiency of PMS oxidation activated by Pd

Experiment conditions: constant permeate flux = 30 LMH, applied OMPs solution: PMS concentration = 40 µmol/L , pH = 7

Figure 12 exhibited the performance of PMS oxidation without catalyst activation (OMP-PMS mixed solution in combination to pristine membrane). This experiment was set as a blank trial to reflect the PMS oxidation effect without catalyst activation. As observed, PMS alone was still able to oxidize certain types of OMPs to some extent, even without the presence of catalyst for activation. For example, the OMP Diclofenac was removed 93%, which may be attributed to PMS's strong oxidizing properties [83].

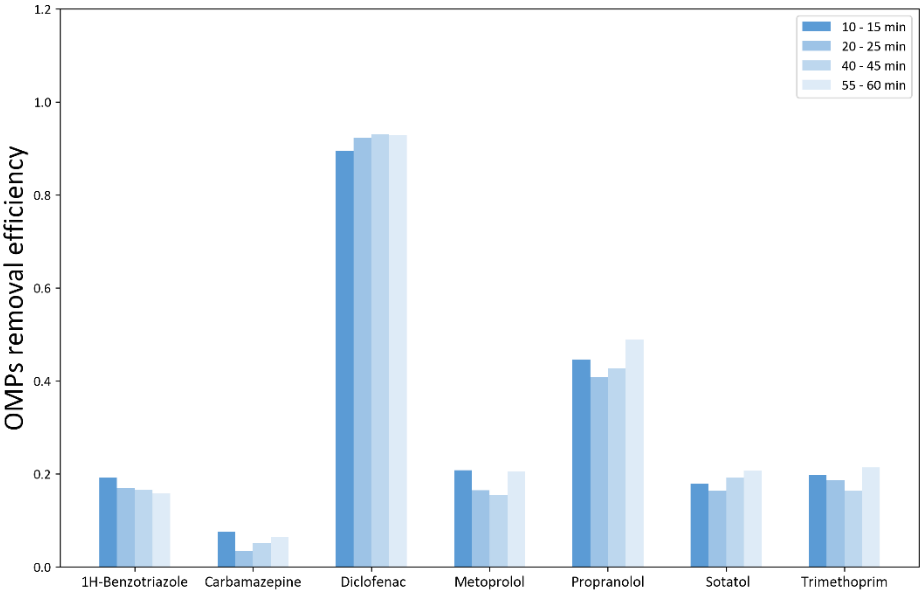


Figure 12. OMPs removal efficiency of PMS oxidation without activation

Experiment conditions: constant permeate flux = 30 LMH, applied OMPs solution: PMS concentration = 40 µmol/L , pH = 7.

Figure 13 presented the results of four OMP degradation experiments in one figure. As to the quantification of OMPs removal efficiency, $C_{permeate}$ was applied with the average OMPs concentration of permeate samples collected at different time intervals (samples P3 (20 – 25min), P4 (40 – 45min) and P5 (55 – 60min)). The results showed that PMS oxidation activated by Pd had the highest removal efficiency for all of the selected OMPs. However, the capability of Fenton oxidation for OMPs degradation was less effective in comparison to activated PMS oxidation. This might be attributed to the difference in reduction potential of the reactive radicals generated by each process. Typically, Fenton oxidation generated highly reactive hydroxyl radicals (·OH), which had strong oxidizing potential with a standard reduction potential of 1.7 – 2.5 V [84]. Compared to hydroxyl radicals (·OH), the sulphate radicals ($SO_4^{\cdot-}$) produced by PMS activation had a higher reduction potential of 2.5 – 3.1 V [85], which made them more efficient for degrading organic matters in comparison to ·OH.

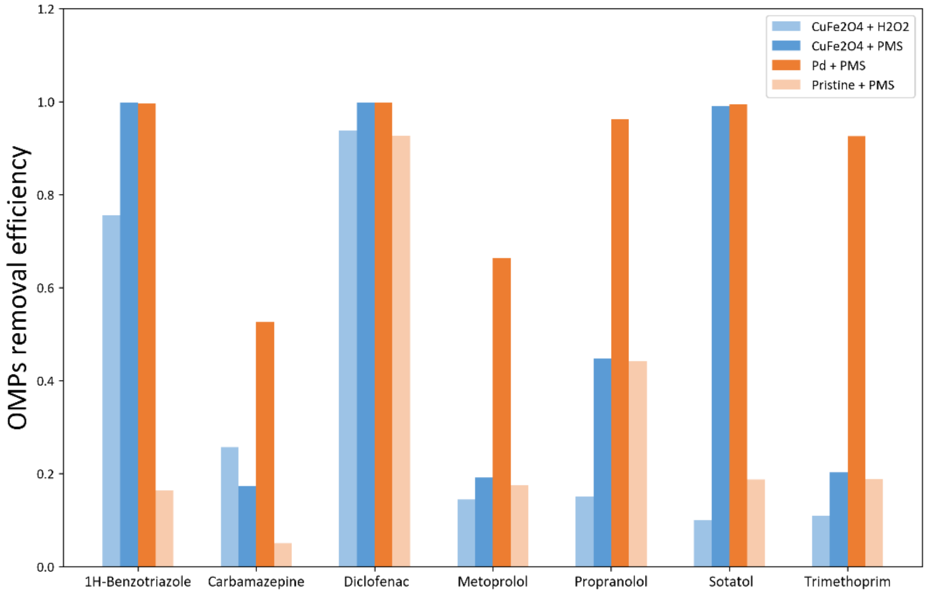


Figure 13. OMPs removal efficiency of 4 parallel experiments
($C_{permeate}$ takes the average OMPs concentration of sample P3, P4 and P5)

5. Uncertainty and limitation

According to the above discussion and analysis, several limitations of this research would be summarized in this section. Besides, the corresponding recommendations would also be proposed for improvement of further experiments.

5.1. Instability of catalyst

On the basis of Section 3.3.4, an obvious Cu leaching happnened during the Fenton oxidation process, which illustrated the synthesized $CuFe_2O_4$ membrane was unstable in acidic environment. The unstability of catalyst $CuFe_2O_4$ might result in a series of disadvantages. On the one side, the leaching compounds would contaminate the produced permeate water. On the other side, part of catalyst leaching would lead to a lower cleaning efficiency of Fenton oxidation. Hence, although acidic environment (pH = 2.5) provided Fenton oxidation with the best condition for alginate fouling removal, it was hard to avoid the problem of catalyst leaching, which would be a limitation of Fenton oxidation application.

5.2. Inaccurate measurement of OMPs concentration

As observed from Figure 9 (a), there was a sudden drop of the OMPs concentration at sample P1 (0 - 5 min), which illustrated the inaccurancy of measuring result. According to analysis of section 4.3, it was known that the inaccurate result of sample P1 might have been caused by the issue of demi-water dilution. To mitigate the impact of demi-water dilution, it would be advisable to firstly place the wetted membrane module in an oven to evaporate any remaining demi-water for a specific time period before the start of OMPs degradation experiment.

6. Conclusion

On the basis of discussion results, the following conclusions could be drawned from this research:

1) The $CuFe_2O_4$ membrane worked well for the membrane permeability recovery when backwashed with H_2O_2. The smaller backwash flux and longer backwash time resulted in higher permeability recovery.

2) The $CuFe_2O_4$ catalyst was unstable and dissolved slowly when exposed to acidic environment, which negatively impacted the cleaning efficiency of Fenton oxidation. Additionally, Fenton oxidation was ineffective for OMPs degradation.

3) PMS oxidation performed a higher OMP removal efficiency than Fenton oxidation. Thus, the Pd membranes were more promising than $CuFe_2O_4$ membranes.

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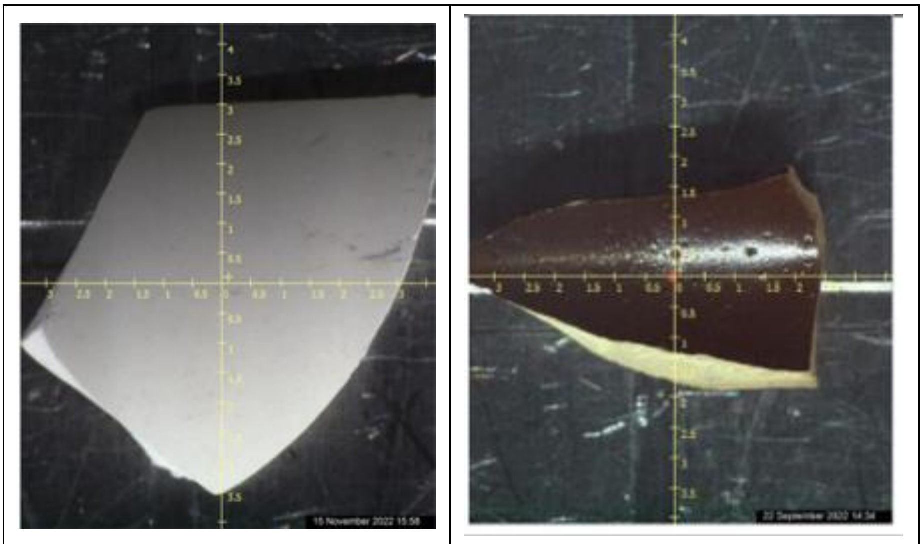
Appendix A: XRD pattern of synthesized catalyst

In this section, we applied X-Ray analysis for synthesized catalyst-coated membrane. As a comparison, the XRD pattern of pristine membrane was also analyzed. Figure A.2 illustrated the main component of pristine ceramic membrane was aluminum oxide (Al_2O_3). Figure A.3 indicated that $CuFe_2O_4$ was successfully formed on the catalyst-coated membrane. However, some by-products, such as cupric oxide (CuO) and ferric oxide (Fe_2O_3), were formed on the catalyst-coated membrane at the same time.



Pristine membrane

Coated membrane

Figure A.1. Coated membrane and pristine membrane sample for X-Ray test

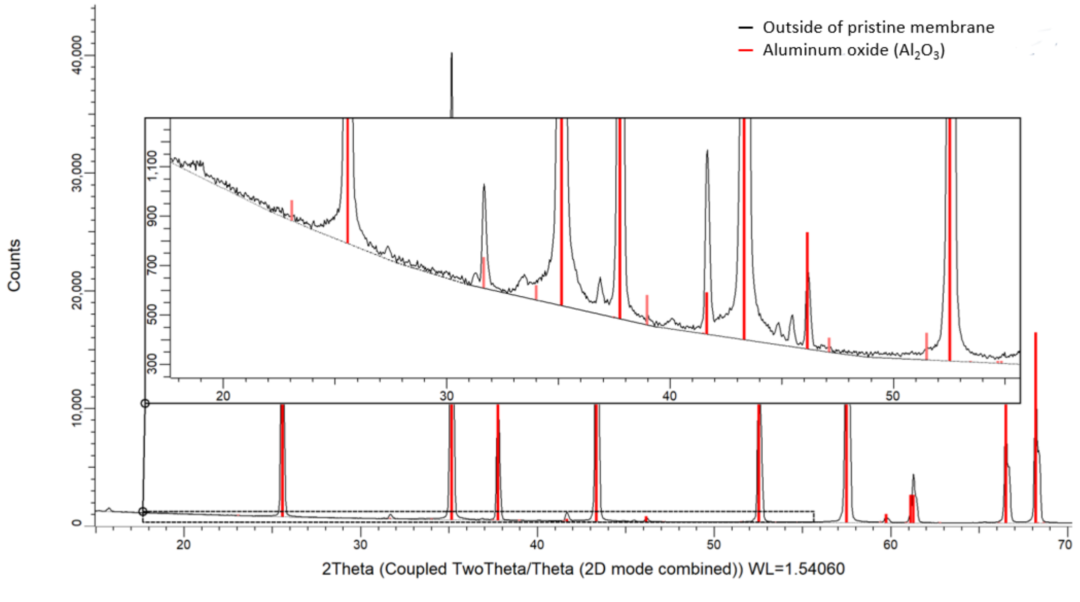


Figure A.2. Pristine membrane XRD pattern with matching phases

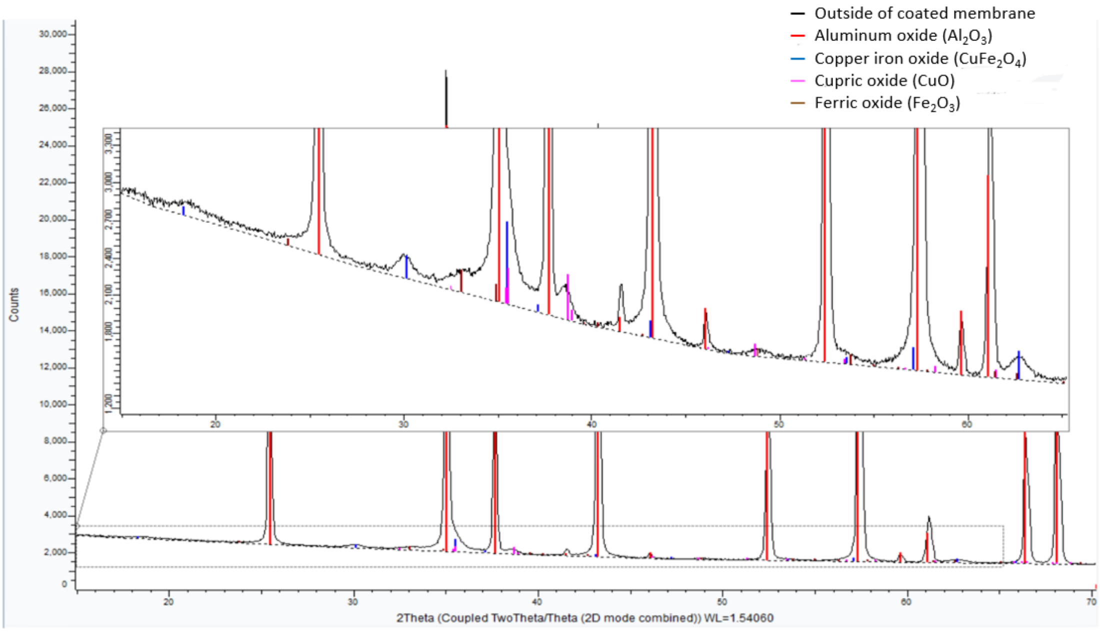


Figure A.3. Catalyst-coated membrane XRD pattern with matching phases

Note: For X-Ray analysis, all the samples were analyzed between coupled θ and 2θ, with a scan step size of 0.04 º 2θ and a counting time per step of 2s, operating at 50 kV and 1000 mA using Ca Kα radiation.

Appendix B: SEM test for element distribution

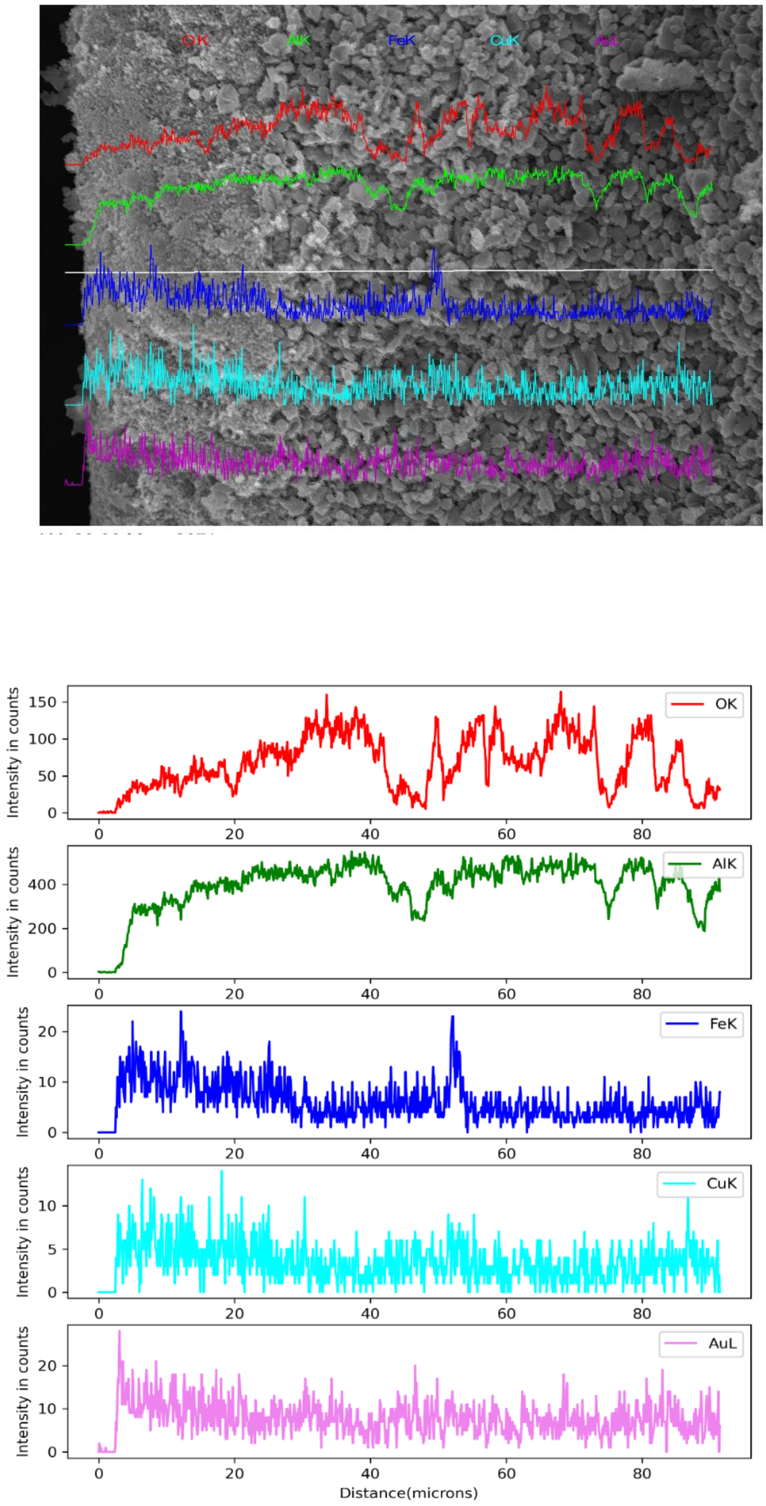


Figure B.1. Element distribution in catalyst-coated membrane cross section

Appendix C: Estimation of catalyst amount

In this section, we were aimed at estimating the actual amount of catalyst formation on the membrane. Here we applied 50 mL of 4 mol/L hydrochloric acid (HCl) to dissolve the total catalyst synthesized on the coated membrane. The coated membrane was soaked in the prepared hydrochloric acid for 96 hours to ensure all the coating catalyst deprived from the membrane and finally dissolved in the soaking solution. After 96 hours of immersion, the original sample was collected with 5 ml and diluted three-fold, ICP technique was applied for Cu and Fe concentration measurement, and Table C.1 showed the measuring result for Cu and Fe element.

Sample name	Cu	Fe
WL-C0	115.09	174.74
All concentration in ppm(mg/kg)		

Table C.1. ICP-MS measurement for Cu and Fe concentration

On the basis of measuring result, the actual Cu and Fe coating amount on the membrane was then calculated:

$$Cu = 115.09 \times 3 \times 0.05 = 17.26mg = 0.27mmol$$

$$Fe = 174.74 \times 3 \times 0.05 = 26.211mg = 0.47mmol$$

$$Cu : Fe = 1 : 1.74 > 1 : 2$$

According to the calculation result, it could be found the actual molar ratio of Cu : Fe was larger than the theoretical value of 0.5, which indicated part of Cu elemnt might exist in the formation of CuO on the membrane instead of $CuFe_2O_4$. Hence, taking Fe amount as the accurate value, and the total amount of synthesized $CuFe_2O_4$ catalyst was estimated to be 56.143 mg

Appendix D: Backwash flux impact

In order to investigate the backwash flux impact on the cleaning efficiency, we took use of 30 mM H_2O_2 solution / demi-water for membrane cleaning with different backwash flux (60 / 90 / 140 LMH). The corresponding experiments were applied with the same alginate solution with a dosage of 3 mM calcium, and controlled with the same backwash time of 18 min

Figure D.1 reflected the $CuFe_2O_4$ membrane permeability behavior when backwashed with 30 mM H_2O_2 solution, which illustrated that lower backwash flux resulted in higher permeability recovery for Fenton oxidation. Figure D.2 reflected the $CuFe_2O_4$ membrane permeability behavior when applied with demi-water backwash, and it indicated demi-water cleaning was unable to recovery the membrane permeability.

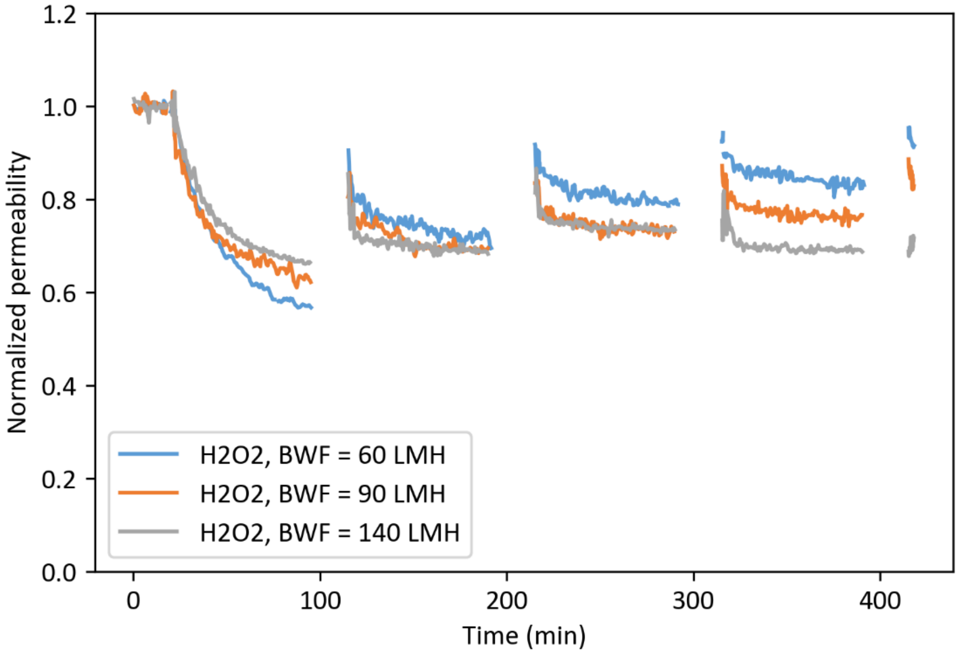


Figure D.1. Effect of backwash flux: permeability behavior of Fenton oxidation

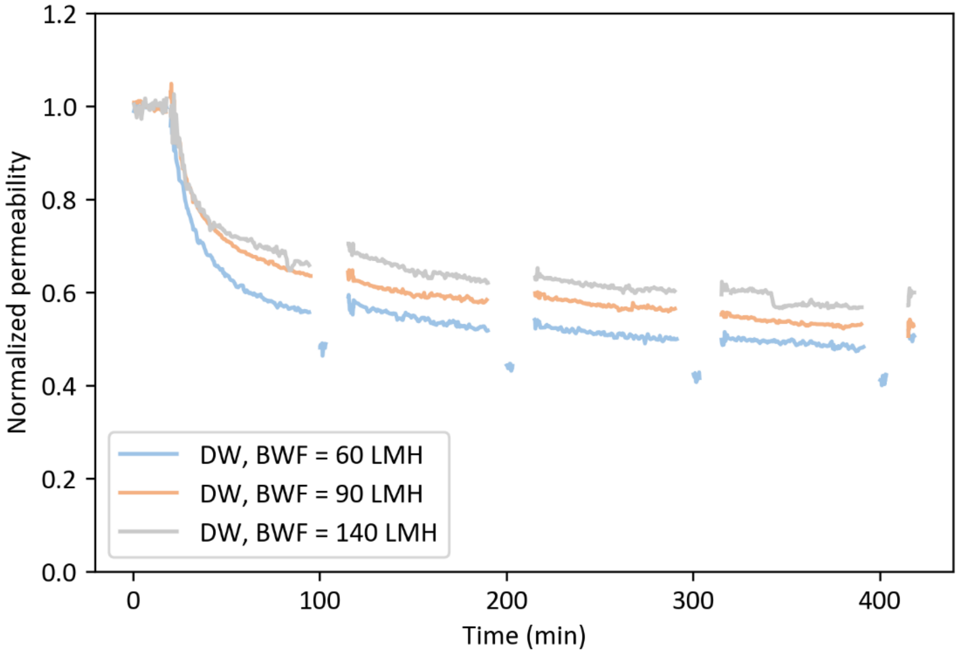


Figure D.2. Effect of backwash flux: permeability behavior of demi-water cleaning

Appendix E: Backwash time impact

We also applied 30 mM H_2O_2 solution / demi-water for membrane cleaning with different backwash duration (6 / 18 / 36 min), aiming at knowing the impact of backwash time on the cleaning efficiency. The corresponding experiments were applied with the same alginate solution with a dosage of 3 mM calcium, and controlled the same backwash flux of 90 LMH.

Figure E.1 reflected the $CuFe_2O_4$ membrane permeability behavior when backwashed with 30 mM H_2O_2 solution, which illustrated that longer backwash time resulted in higher permeability recovery for Fenton oxidation. Figure E.2 reflected the $CuFe_2O_4$ membrane permeability behavior when applied with demi-water backwash, and also indicated the membrane permeability was difficult to recover during demi-water cleaning.

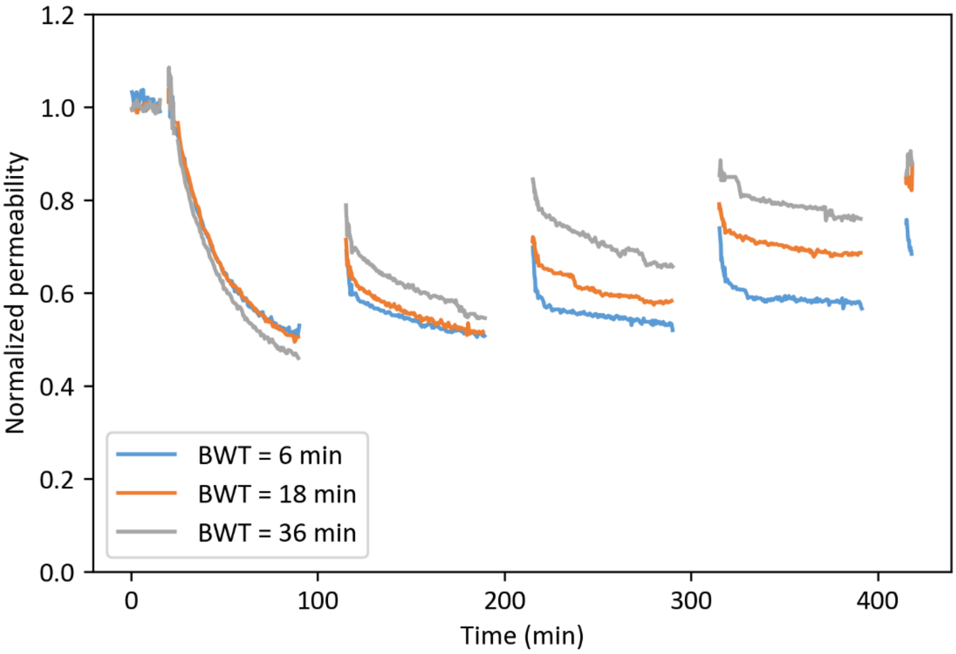


Figure E.1. Effect of backwash time: flux behavior of Fenton oxidation cleaning

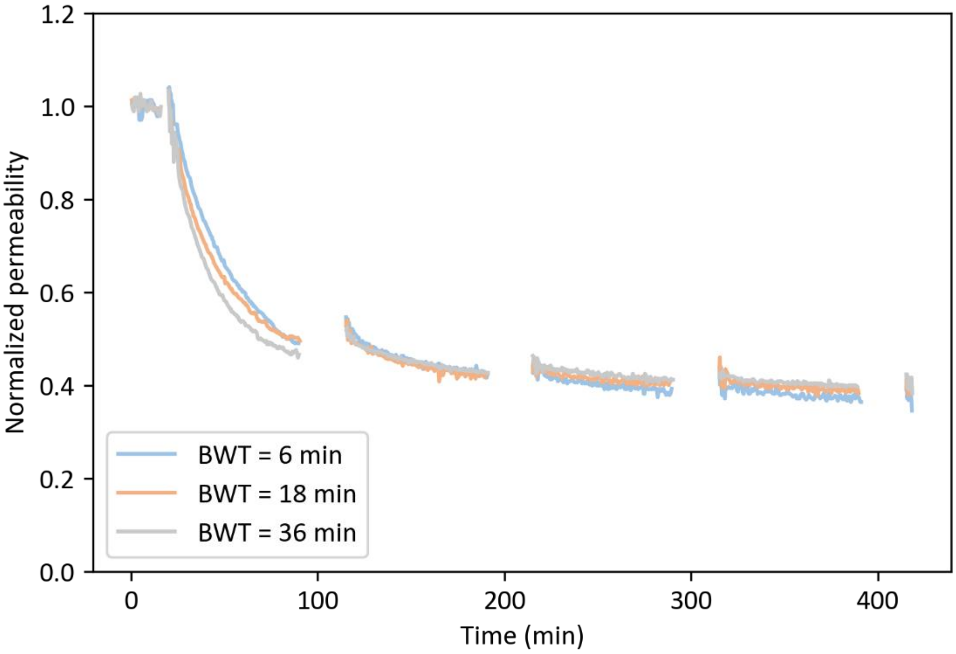


Figure E.2. Effect of backwash time: flux behavior of demi-water cleaning

Appendix F: Calcium concentration impact

We also performed an initial explorement of calcium concentration impact on the cleaning efficiency. Here we applied alginate solution with different calcium dosage (1 / 3 / 5 mM). The corresponding experiments were controlled with the same backwash flux (90 LMH) and backwash time (18 min).

Both Figure F.1 and Figure F.2 showed that when alginate solution with different calcium concentration were applied for membrane fouling process, the relevant permeabilities after the fouling process were totally different. It was found alginate solution with 1 mM Ca dosage resulted in lower membrane permeability, while alginate solution with 5 mM Ca dosage caused higher membrane permeability. In this case, we assumed that alginate solution with lower Ca concentration might generate more severe membrane fouling, but alginate solution with higher Ca concentration might mitigate the membrane fouling.

Figure F.3 reflected the permeability recovery of Fenton oxidation and demi-water cleaning, and no findings could be drawn because the fouling curves of applied Ca concentrations were totally different. Hence, there was no necessity for further discussion about the calcium concentration impact.

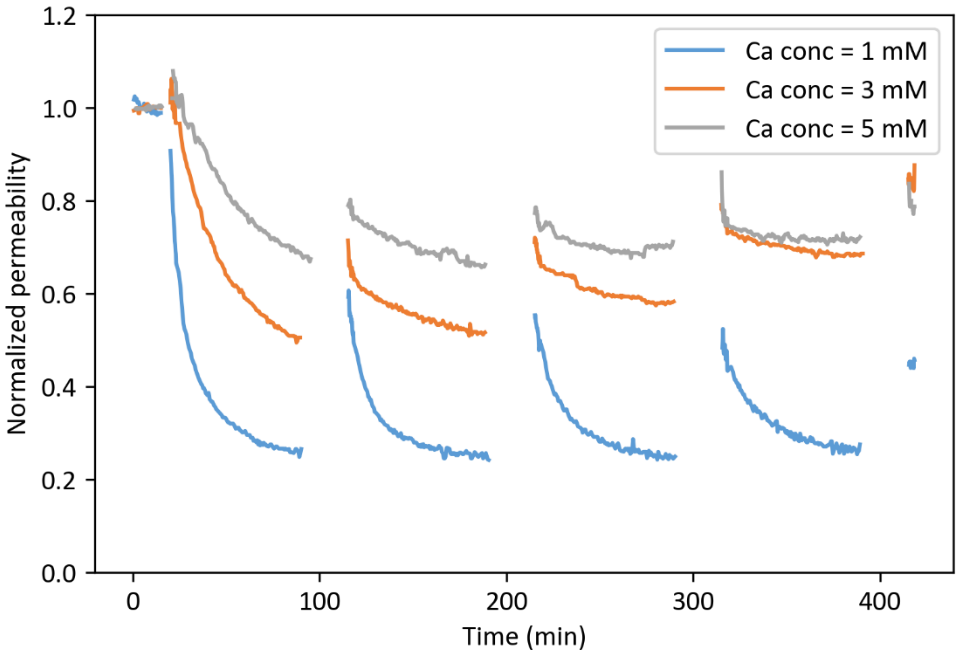


Figure F.1. Effect of Ca concentration: permeability behavior of Fenton oxidation

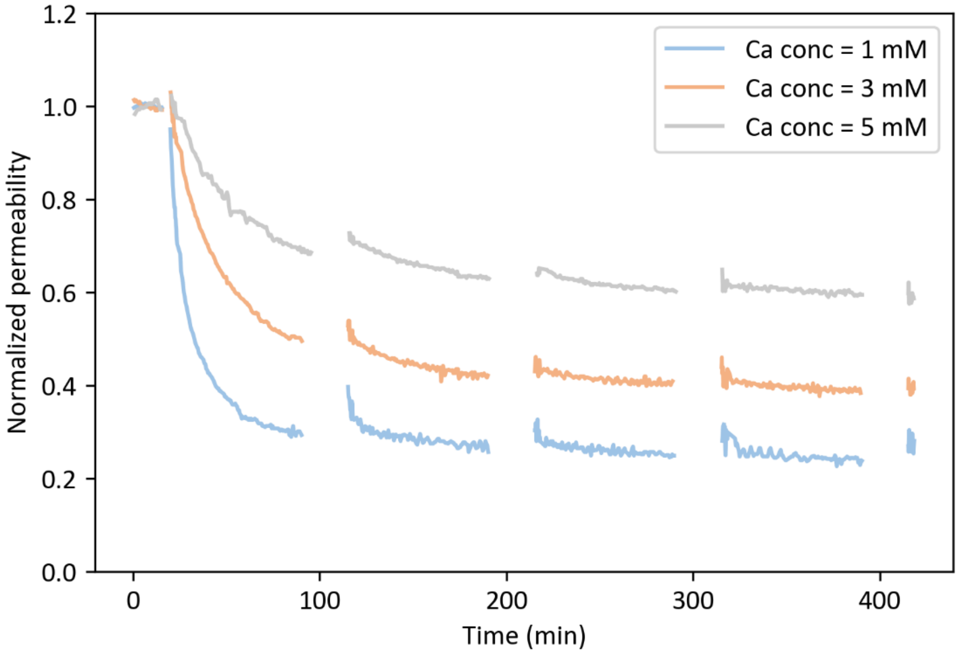


Figure F.2. Effect of Ca concentration: permeability behavior of demi-water cleaning

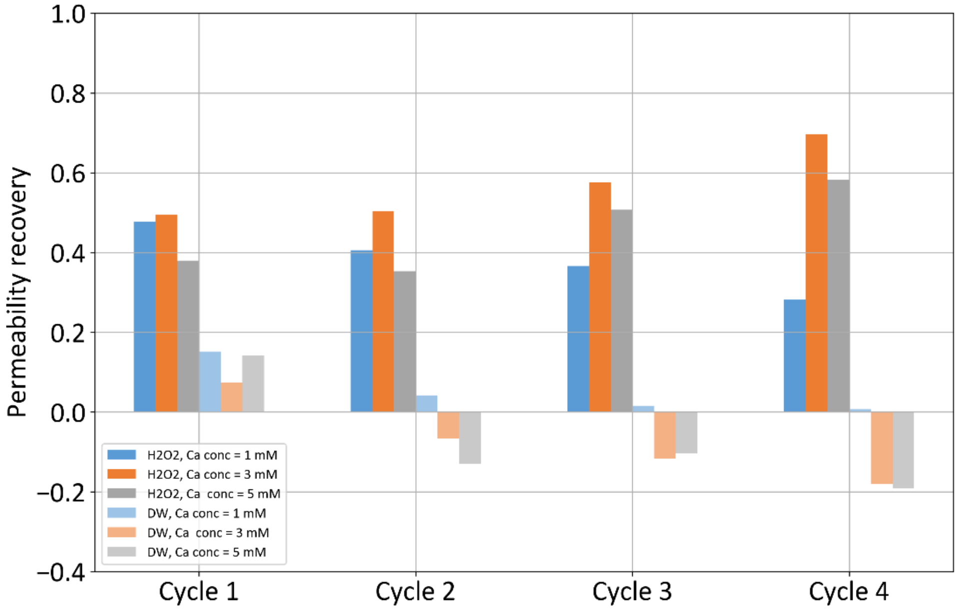


Figure F.3. Effect of Ca concentration: permeability recovery of Fenton oxidation and demi-water cleaning. Experiment conditions: backwash flux = 90 LMH, backwash time = 18min, applied Ca concentration = 1 / 3 / 5 mM.

Appendix G: Particle size measurement

This section we measured the particle size of alginate solution with different Ca concentrtaions. The figure results indicated that alginate solution with lower Ca concentration generated smaller-size particles.

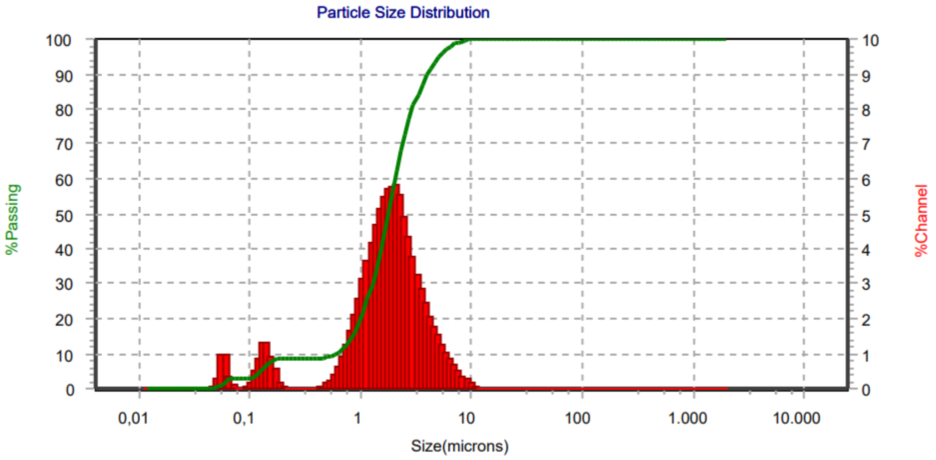


Figure G.1. Particle size of alginate solution with 1 mM Ca

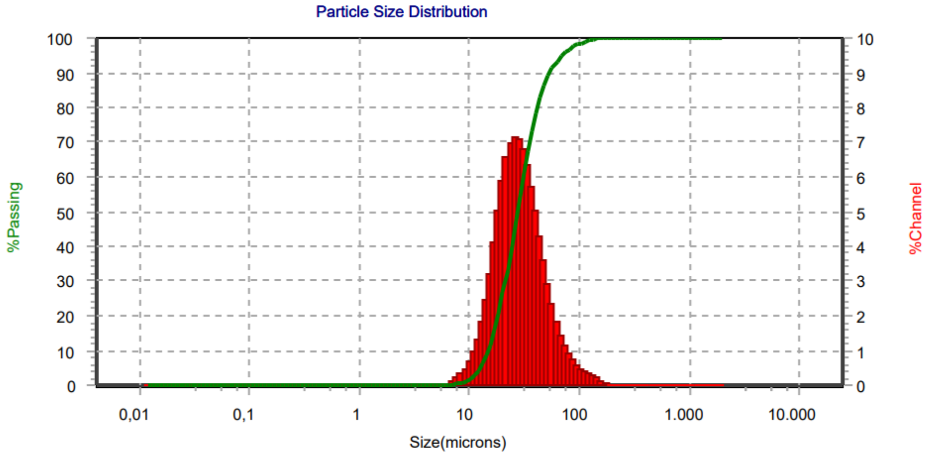


Figure G.2. Particle size of alginate solution with 3 mM Ca

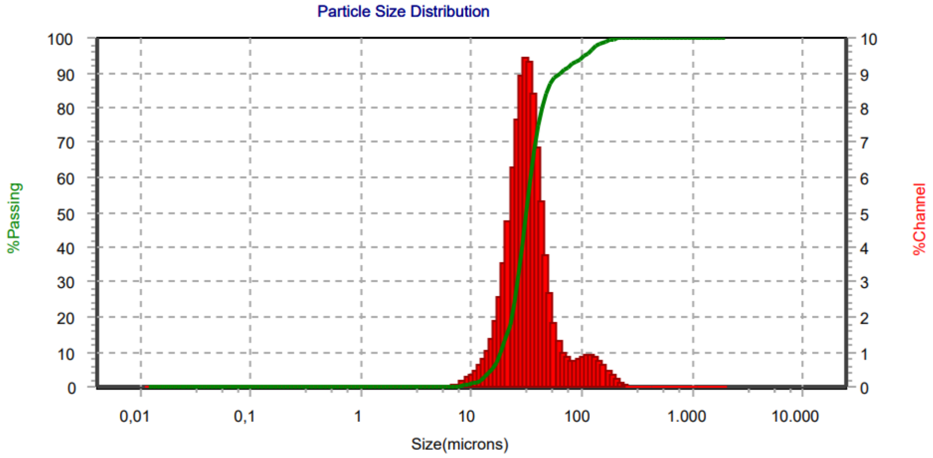


Figure G.3. Particle size of alginate solution with 5 mM Ca

Appendix H: Catalyst leaching in soaking solution

Figure H.1 reflected the catalyst leaching of $CuFe_2O_4$ membrane when soaking in 0.1 % NaCl, and it illustrated that only a small amount of Fe leaching happened. Figure H.2 reflected the catalyst leaching of $CuFe_2O_4$ membrane when soaking in 10 mM NaOH, and it was found no Fe or Cu leaching happned. Thus, the $CuFe_2O_4$ membrane showed good stability in 0.1% NaClO or 10 mM NaOH solution

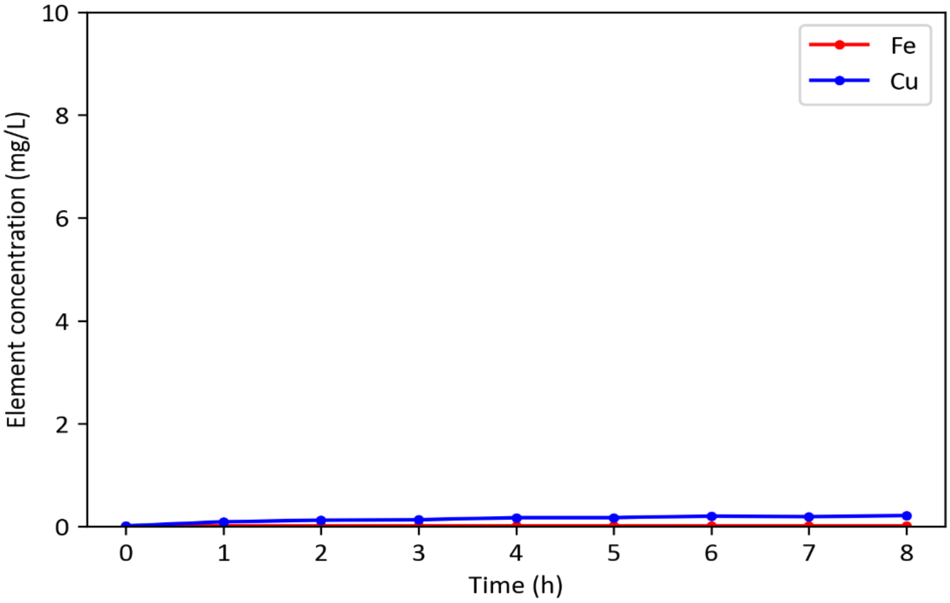


Figure H.1. Element concentration change for 0.1% NaClO soaking solution

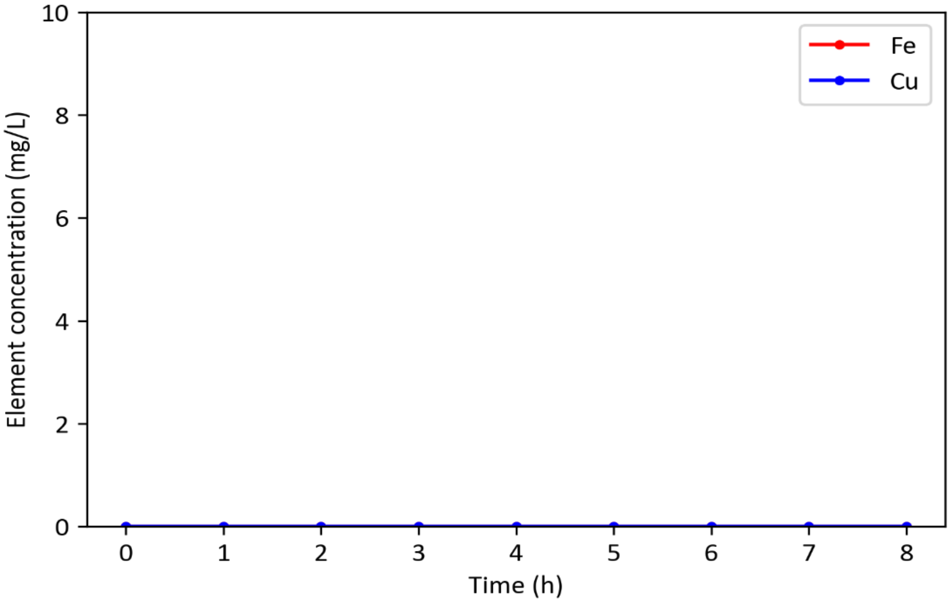


Figure H.2. Element concentration change for 10mM NaOH soaking solution

Appendix I: Catalyst leaching impact

In order to investigate the impact of catalyst leaching on the cleaning efficiency of Fenton oxidation, we compared the permeability recovery difference between the newly synthesized $CuFe_2O_4$ membrane (No leaching) and the $CuFe_2O_4$ membrane soaking in 30 mM H_2O_2 solution (With leaching). The soaking duration was set with 96 hours to ensure all the unstable catalyst deprive from the membrane body.

From Figure I.1, it was found the the cataylst leaching resulted in a decline of $CuFe_2O_4$ membrane permeability recovery, which illustrated that the catalyst leaching could decrease the cleaning efficiency of Fenton oxidation

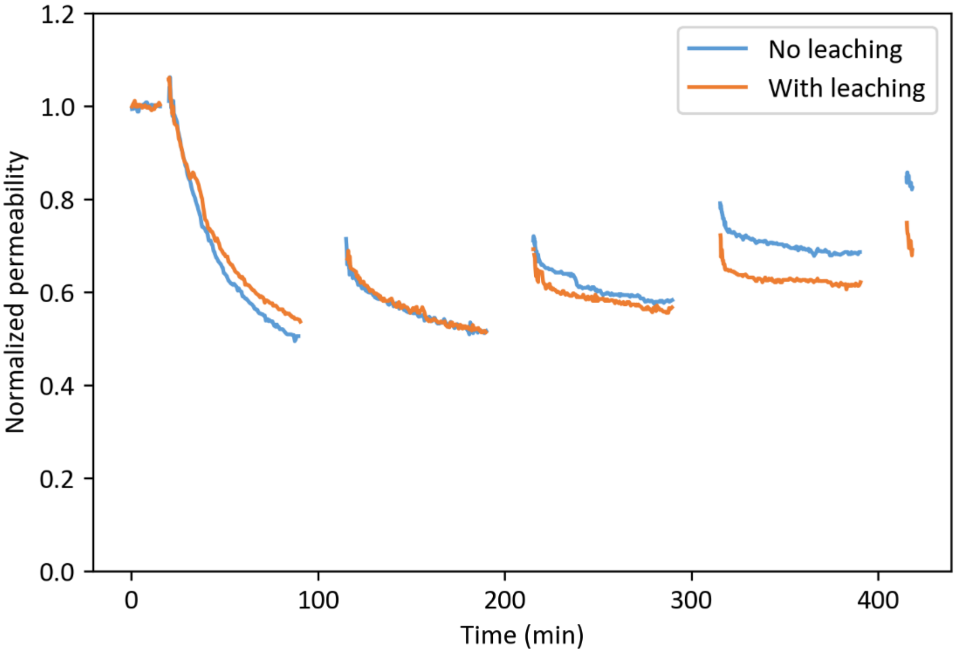


Figure I.1. Permeability behavior of $CuFe_2O_4$ membrane with / without catalyst leaching

Appendix J: OMPs removal efficiency

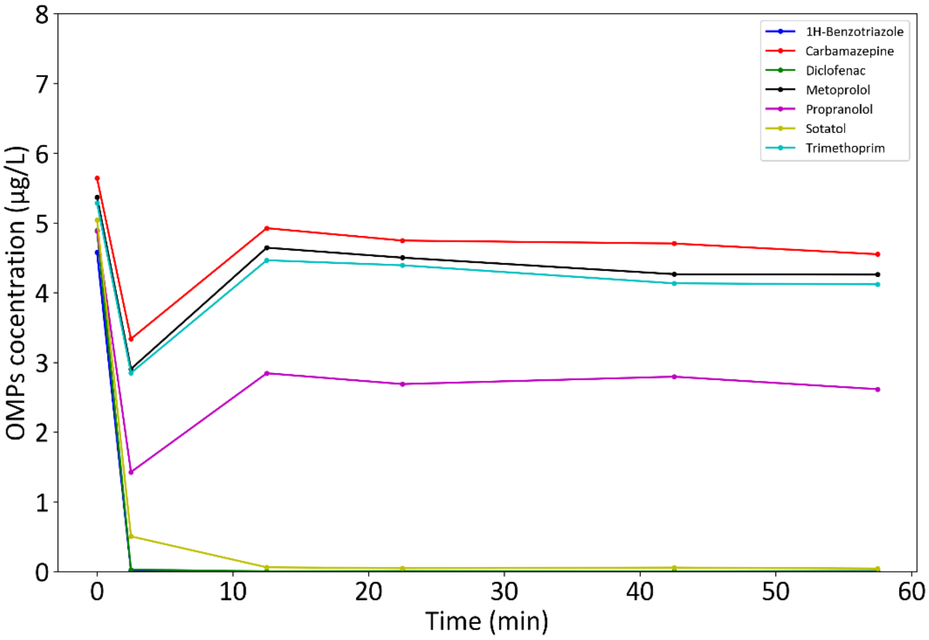


Figure J.1. OMPs concentration change of PMS oxidation activated by $CuFe_2O_4$
(The Figure is arranged in the same way as Figure 10)

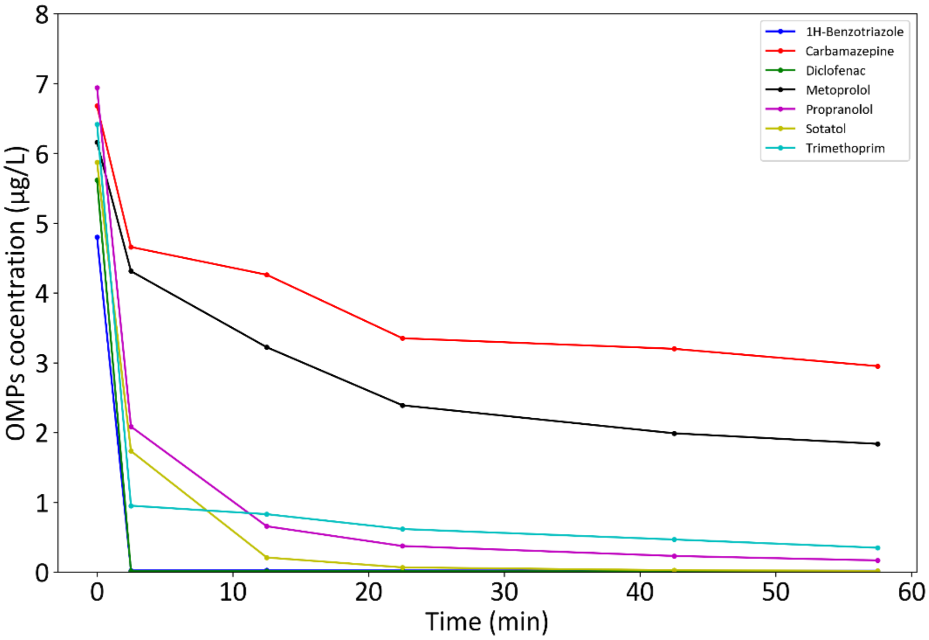


Figure J.2. OMPs concentration change of PMS oxidation activated by Pd
(The Figure is arranged in the same way as Figure 11)

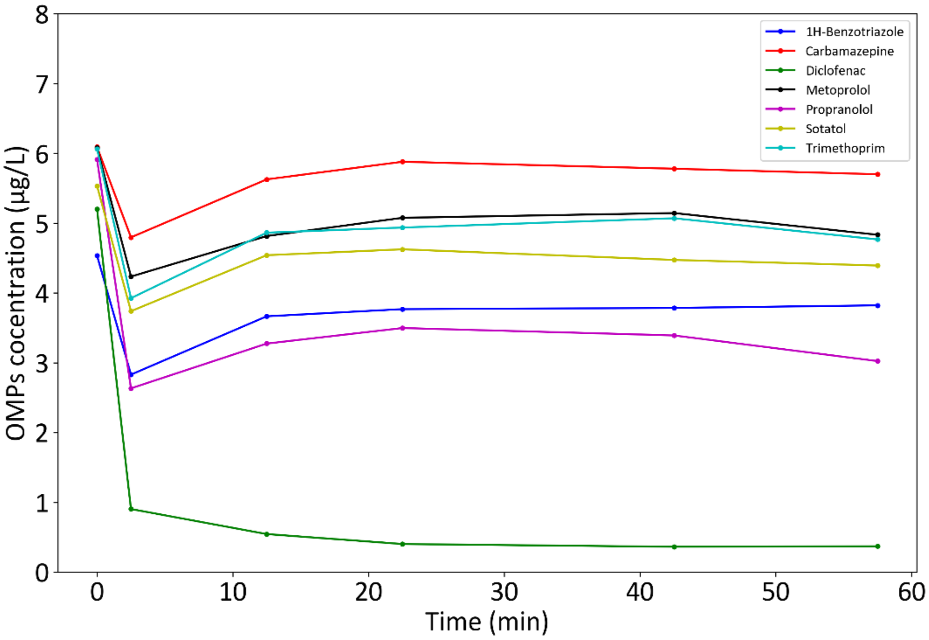


Figure J.3. OMPs concentration change of PMS oxidation without activation (The figure is configured in the same way as Figure 12)