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PLANT-WIDE MODELLING OF THE UPM PULP MILL WASTEWATER TREATMENT PLANT IN URUGUAY

Silvia María Bentancur Caballero

PLANT-WIDE MODELLING OF THE UPM PULP MILL WASTEWATER TREATMENT PLANT IN URUGUAY

DISSERTATION

for the purpose of obtaining the degree of doctor
at Delft University of Technology
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and
in fulfilment of the requirement of the Rector of IHE Delft
Institute for Water Education, Prof.dr. E.J. Moors,
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by

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This dissertation has been approved by the (co)promotors.

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To my family

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SUMMARY

The main objective of this research was to assess the performance of the UPM wastewater treatment plant (WWTP) by applying standard wastewater treatment modelling tools and experimental methods. Different operational and configuration alternatives to enhance UPM's WWTP performance were investigated. The main focus was phosphorus (P) removal.

Modelling of activated sludge systems in municipal WWTP has become a useful tool and well-established practice despite that over the years the complexity of the models has increased. However, modelling of industrial WWTP (specifically pulp and paper mill industries) still exhibits some challenges.

This research has been conducted at the UPM pulp mill facilities in Fray Bentos, Uruguay. The UPM pulp mill in Uruguay is one of the most modern pulp mills in the world. The mill uses the chemical Kraft process, which is worldwide the most used pulping process in the pulp and paper industry. It has an annual production capacity of 1.3 million tons of fully bleached eucalyptus pulp. The WWTP consists of a conventional aerobic activate sludge system designed for an influent flow of approximately 73,000 m^3/day.

The pulp mill conventional activated sludge treatment has shown to have a high effectiveness to remove chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solids (TSS), total nitrogen (TN) and total phosphorus (TP) meeting the standards set for the discharge of effluent into the Uruguay River. Even though the removal efficiency of TP is relatively high (above 80 %), the TP concentration in the effluent exhibited values extremely close to the discharge standard, and on some occasions the company exceeded the permitted limit in the discharge of TP to the river. The company is restricted to both monthly and annual discharge limits. The company can never exceed the average monthly limit of 74 kgTP/d, and the annual limit corresponds to an average of 60 kgTP/d. To meet the annual permit limit TP discharge value to the river of 60 kg/d, the company set an internal monthly target TP discharge of 60 kg/d. The WWTP was not designed for nutrient removal; at many other paper mill WWTPs the influent to the treatment plant is low in nutrients and the addition of nutrients is necessary to properly achieve the biological treatment of organic matter. At the pulp mill WWTP of study, due to the high concentrations of biodegradable organic matter, 2,500 kg of urea are dosed daily to cover the N requirements for biomass growth. However, the addition of P is not necessary since the hardwood that is used for the pulp production, eucalyptus, has a high content of P.

The simulations of the biological wastewater treatment were carried out using the software BioWin v. 3.0 (EnviroSim Associates Ltd., Canada). BioWin developed its own integrated activated sludge/anaerobic digestion (AS/AD) model which is applied in the software. This model is a combination of the international models ASM1, ASM2d, and ASM3 proposed by the International Water Association (IWA) incorporating the anaerobic digestion model (ADM) as well. A sampling program and measuring campaign was carried out at the pulp mill WWTP to characterize the wastewater according to the STOWA protocol. The model calibration was obtained by adjusting some wastewater fractions, and kinetic and stoichiometric parameters as follows: (i) kinetic parameters including aerobic decay rate and aerobic denitrification DO half saturation; and (ii) stoichiometric parameters including N and P in biomass, and endogenous residue. In addition to the wastewater characterization, an aerobic batch evaluation was carried out at the laboratory facilities of the pulp mill WWTP aiming at obtaining the necessary information to calibrate the model. Once the model was calibrated, the performance of the WWTP was properly predicted. Wastewater data from different periods of time was used aiming at validating the model.

A good model that describes the performance of the WWTP was obtained. The model describes well both the current operation of the plant, as well as the historical performance. The following key effluent parameters were used to validate the model: COD, TSS, TN and TP. Modelling the plant allows the prediction of different future scenarios. Different potential scenarios were evaluated to reduce the TP concentration in the effluent. Including an anaerobic phase prior to the aerobic process may reduce the TP concentration in the effluent. In addition, chemical P removal (CPR) at the sweep coagulation range showed that the P concentrations can be further reduces to concentrations below 0.1 mg/L.

Using a mathematical model of the pulp mill WWTP, a resource recovery assessment was carried out. Through the evaluation of different scenarios, the potential production of methane from secondary sludge, with its inherent energy savings, and the recovery of P as struvite were estimated. Considering the current WWTP configuration with a sludge retention time (SRT) of 32 days, and according to the model, which is a simplification of reality, the assessment indicates that the implementation of an anaerobic digester (AD) to treat the excess sludge can lead to a methane production of approximately 1736 m^3 CH_4/d, being a promising alternative to increase the WWTP treatment performance. Furthermore, the model predictions suggest that by shortening the SRT from 32 to 5 days, the methane production could increase by up to 5568 m^3 CH_4/d. If the methane produced is used to generate electrical energy to operate the WWTP, energy savings of about 88 % can be achieved. Regarding the potential recovery of P as struvite, the addition of a struvite reactor could be an efficient option to recover approximately 1611 mg/L of struvite (corresponding to a load of about 433 kg/d). By optimizing the process performance, these findings highlight the potential recovery of resources in pulp mill WWTP, while complying with stringent effluent discharge standards. In addition, further research activities such as pilot-test or detailed laboratory studies may be needed to validate the previous recommendations for industrial-scale application.

The CPR process in pulp mill WWTP was studied to understand how the following key operational factors: chemical additives dosage and type, pH, temperature, mixing intensity and different doses of polymer impact on the TP removal efficiency. Tests were carried out at laboratory scale. The effect of three precipitating agents were analysed at different temperatures (30, 45 and 60 ^oC), pH (from default, about 4.0 to 10.5) and mixing intensity (100, 200 and 300 rpm). The higher P removal efficiency was obtained at 60 ^oC and pH 10.5 for all types of precipitating agents. The pH showed a great influence on P removal, with an optimal pH of 10.5 for the best TP removal. Only by raising the pH to 10.5, without using any precipitating agent, the soluble P was removed. The precipitation of P occurred, but the P was not able to settle. As the pH raised, the precipitation of P occurred with the metals Ca and Mg present in the wastewater. The optimal chemical additives dosage was found to be 600 mg$Ca(OH)_2$/L, 200 mg$Al_2(SO_4)_3\cdot14.3H_2O$/L and 50 mg$FeCl_3\cdot6H_2O$/L. The highest TP removal efficiency was 95 % with $Ca(OH)_2$, 98% with $Al_2(SO_4)_3$ and 93 % with $FeCl_3$. The high temperature of the wastewater from the cellulose pulp process, approximately 60 ^oC, showed favouring the P removal process compared to lower temperatures such as 30 and 45 ^oC. The variation of mixing intensity in the coagulation process and the addition of different doses of polymer in the flocculation stage did not have a significant effect on the removal of P.

In addition, the potential biological removal of P was evaluated in a lab-scale SBR under fully aerobic conditions for merely biomass synthesis. The CPR process was studied following a co-precipitation (through the addition of coagulants to the lab-scale SBR) and a post-precipitation approach (conducting different jar-tests with the effluent from the SBR). Three coagulants ($FeCl_3$, $Al_2(SO_4)_3$, and $Ca(OH)_2$) were tested at different concentrations. The treatment of the pulp mill effluent by merely biological means was unable to contribute to a considerable P-removal due to the low P growth requirements of the biomass. The co-precipitation CPR approach showed to be highly effective independently of the coagulant used (at doses of 300 mg$FeCl_3\cdot6H_2O$/L, 300 mg $Al_2(SO_4)_3\cdot14.3H_2O$/L or 400 mg$Ca(OH)_2$/L) resulting in removal efficiencies of between 79 and 82% and achieving final soluble P wastewater concentrations in the range of 0.28 to 0.34 mgP/L. However, it struggled to comply with the discharge standard permit limit (annual) of 60 kg TP/d. On the other hand, the post-precipitation approach (with the addition of $Al_2(SO_4)_3$ at a PO_4^{3-}/metal salt ratio (mol-to-mol) of 1:10 or when dosing 400 mg$Ca(OH)_2$/L) allowed to achieve the lowest observed TP and soluble P concentrations (lower than 0.5 and 0.2 mgP/L, respectively). Thus, the most suitable CPR approach to treat the pulp mill industrial effluent was post-precipitation since it was able to consistently comply with the maximum discharge standard of 60 kg TP/d.

The WWTP at UPM was properly modelled and the model allows the prediction of actual and future plant scenarios. The model shows that alternatives to the current WWTP configurations can be proposed to improve the plant performance. In addition, CPR exhibit great opportunities to reduce P concentrations in the effluent even further.

SAMENVATTING

Het hoofddoel van dit onderzoek was het beoordelen van de prestaties van de UPM-afvalwaterzuiveringsinstallatie (AWZI) door gebruik te maken van standaard tools voor het modelleren van waterzuivering en experimentele methoden. Verschillende operationele en configuratie-alternatieven werden onderzocht om de prestaties van de UPM- AWZI te verbeteren, met nadruk op de verwijdering van fosfor (P).

Modellering van geactiveerde slibsystemen in gemeentelijke AWZI's is een nuttig en welomschreven instrument geworden, ondanks dat de complexiteit van de modellen in de loop der jaren is toegenomen. Het modelleren van industriële AWZI's (specifiek in de pulp- en papierindustrie) vertoont echter nog steeds enkele uitdagingen.

Dit onderzoek werd uitgevoerd bij de UPM-papierfabriek in Fray Bentos, Uruguay. De UPM-papierfabriek in Uruguay is een van de modernste papierfabrieken ter wereld. De fabriek gebruikt het chemische Kraft-proces; wereldwijd het meest gebruikte pulpproces in de pulp- en papierindustrie. Het heeft een jaarlijkse productiecapaciteit van 1,3 miljoen ton volledig gebleekte eucalyptusvezel. De AWZI bestaat uit een conventioneel aerobe actiefslibinstallatie ontworpen voor een influentstroom van ongeveer 73.000 m^3/dag.

De conventionele actiefslibbehandeling van de papierfabriek heeft aangetoond een hoge doeltreffendheid te hebben bij het verwijderen van chemische zuurstofvraag (COD), biologische zuurstofvraag (BZV), totaal zwevende stoffen (TSS), totaal stikstof (TN) en totaal fosfor (TP), waarbij wordt voldaan aan de gestelde normen voor de lozing van effluent in de Uruguay-rivier. Hoewel de verwijderingsefficiëntie van TP relatief hoog is (boven 80 %), vertoonde de TP-concentratie, in het effluent, waarden die extreem dicht bij de lozingsnorm lagen, en op sommige momenten overschreed het bedrijf de toegestane limiet voor de lozing van TP naar de rivier. Het bedrijf is beperkt tot zowel maandelijkse als jaarlijkse lozingslimieten. Het bedrijf mag nooit het gemiddelde maandelijkse limiet van 74 kg TP/dag overschrijden, en het jaarlijkse limiet komt overeen met een gemiddelde van 60 kg TP/dag. Om aan het jaarlijkse vergunningslimiet voor TP-lozing naar de rivier van 60 kg/dag te voldoen, stelde het bedrijf intern een maandelijks streefdoel voor TP-lozing van 60 kg/dag in. De AWZI was niet ontworpen voor de verwijdering van voedingsstoffen; bij veel andere AWZI's voor papierfabrieken is het influent naar de zuiveringsinstallatie laag in voedingsstoffen en is de toevoeging van voedingsstoffen noodzakelijk voor een goede biologische behandeling van organisch materiaal. In de AWZI van de papierfabriek van deze studie, vanwege de hoge concentraties biologisch afbreekbare organische stof, worden dagelijks 2.500 kg ureum gedoseerd om te voorzien in de N-behoeften voor de groei van biomassa. De toevoeging van P is echter niet nodig

omdat het hardhout dat wordt gebruikt voor de pulpproductie, eucalyptus, een hoog P-gehalte heeft.

De simulaties van de biologische waterzuivering werden uitgevoerd met behulp van de software BioWin v. 3.0 (EnviroSim Associates Ltd., Canada). BioWin heeft zijn eigen geïntegreerde model van actiefslib/anaërobe spijsvertering (AS/AD) ontwikkeld dat wordt toegepast in de software. Dit model is een combinatie van de internationale modellen ASM1, ASM2d en ASM3, voorgesteld door de International Water Association (IWA), en omvat ook het anaërobe spijsverteringsmodel (ADM). Een bemonsteringsprogramma en meetcampagne werden uitgevoerd bij de AWZI van de papierfabriek om het afvalwater te karakteriseren volgens het STOWA-protocol. De modelkalibratie werd verkregen door enkele afvalwaterfracties en kinetische en stoichiometrische parameters aan te passen, waaronder (i) kinetische parameters zoals de aerobe afbraaksnelheid en de halfverzadiging van DO voor aerobe denitrificatie; en (ii) stoichiometrische parameters zoals N en P in biomassa en endogeen residu. Naast de karakterisering van afvalwater werd een aerobe batchevaluatie uitgevoerd in de laboratoriumfaciliteiten van de AWZI van de papierfabriek met als doel de benodigde informatie te verkrijgen voor de kalibratie van het model. Nadat het model was gekalibreerd, werd de prestatie van de AWZI adequaat voorspeld. Afvalwatergegevens uit verschillende tijdsperioden werden gebruikt om het model te valideren.

Er werd een goed model verkregen dat de prestaties van de AWZI beschrijft. Het model beschrijft zowel de huidige werking van de installatie als de historische prestaties op een goede manier. De volgende belangrijke effluentparameters werden gebruikt om het model te valideren: COD, TSS, TN en TP. Het modelleren van de installatie maakt de voorspelling van verschillende toekomstscenario's mogelijk. Verschillende potentiële scenario's werden geëvalueerd om de TP-concentratie in het effluent te verminderen. Het opnemen van een anaërobe fase vóór het aerobe proces kan de TP-concentratie in het effluent verminderen. Bovendien toonde het chemische P-verwijderingsproces (CPR) in het bereik van vlokkingsvloeiing aan dat de P-concentraties verder kunnen worden verlaagd.

Gebruikmakend van een wiskundig model van de afvalwaterzuiveringsinstallatie van de papierfabriek, werd een beoordeling van hulpbronnenherstel uitgevoerd. Door de evaluatie van verschillende scenario's werd de potentiële productie van methaan uit secundair slib, met bijbehorende energiebesparingen, en de terugwinning van fosfor als struviet geschat. Gezien de huidige configuratie van de afvalwaterzuiveringsinstallatie met een slibretentietijd (SRT) van 32 dagen, en volgens het model, dat een vereenvoudiging van de realiteit is, geeft de beoordeling aan dat de implementatie van een anaërobe vergister (AD) voor de behandeling van overtollig slib kan leiden tot een methaanproductie van ongeveer 1736 m^3 CH_4/d, wat een veelbelovend alternatief is om de prestaties van de afvalwaterzuiveringsinstallatie te verbeteren. Bovendien suggereren de modelvoorspellingen dat, door de SRT te verkorten van 32 naar 5 dagen, de methaanproductie tot 5568 m^3 CH_4/d zou kunnen toenemen. Als het geproduceerde methaan wordt gebruikt om elektrische energie op te wekken voor de werking van de afvalwaterzuiveringsinstallatie, kan een energiebesparing van ongeveer 88 % worden bereikt. Wat betreft het potentieel voor de terugwinning van fosfor als struviet zou de toevoeging van een struvietreactor een efficiënte optie kunnen zijn om ongeveer 1611 mg/L struviet terug te winnen (wat overeenkomt met een lading van ongeveer 433 kg/d). Door de procesprestaties te optimaliseren, benadrukken deze bevindingen het potentieel voor het terugwinnen van hulpbronnen in de afvalwaterzuiveringsinstallatie van papierfabrieken, terwijl wordt voldaan aan strenge lozingsnormen. Bovendien zijn verdere onderzoeksactiviteiten zoals pilot-tests of gedetailleerde laboratoriumstudies wellicht nodig om de eerdere aanbevelingen te valideren voor industriële toepassing op grote schaal.

Het CPR-proces in de afvalwaterzuiveringsinstallatie van papierfabrieken werd bestudeerd om inzicht te krijgen in hoe de volgende cruciale operationele factoren van invloed zijn op de efficiëntie van fosforverwijdering: dosering en type chemische additieven, pH, temperatuur, mengintensiteit en verschillende doses polymeer. Tests werden uitgevoerd op laboratoriumschaal. Het effect van drie neerslagmiddelen werd geanalyseerd bij verschillende temperaturen (30, 45 en 60 °C), pH (van standaard, ongeveer 4.0 tot 10.5) en mengintensiteit (100, 200 en 300 rpm). De hoogste P-verwijderingsefficiëntie werd bereikt bij 60 °C en pH 10.5 voor alle soorten neerslagmiddelen. De pH had een grote invloed op P-verwijdering, met een optimale pH van 10.5 voor de beste TP-verwijdering. Alleen door de pH te verhogen tot 10.5, zonder enig neerslagmiddel te gebruiken, werd het opgeloste P verwijderd. De neerslag van P vond plaats, maar het P kon niet bezinken. Naarmate de pH steeg, vond de neerslag van P plaats met de metalen Ca en Mg aanwezig in het afvalwater. De optimale dosering van chemische additieven bleek 600 mg$Ca(OH)_2$/L, 200 mg$Al_2(SO_4)_3 \cdot 14.3H_2O$/L en 50 mg$FeCl_3 \cdot 6H_2O$/L te zijn. De hoogste TP-verwijderingsefficiëntie was 95 % met Ca(OH)2, 98 % met $Al_2(SO_4)_3$ en 93 % met $FeCl_3$. De hoge temperatuur van het afvalwater uit het cellulosepulp-proces, ongeveer 60 °C, bleek gunstig te zijn voor het P-verwijderingsproces in vergelijking met lagere temperaturen zoals 30 en 45 °C. De variatie van mengintensiteit in het stollingsproces en de toevoeging van verschillende doses polymeer in het flocculatie-stadium hadden geen significant effect op de verwijdering van P.

Bovendien werd de potentiële biologische verwijdering van P geëvalueerd in een laboratorium-SBR onder volledig aerobe omstandigheden en uitsluitend voor biomassasynthese. Het CPR-proces werd bestudeerd volgens een co-precipitatie (door toevoeging van coagulantia aan de laboratorium-SBR) en een post-precipitatiebenadering (uitvoeren van verschillende jar-tests met het effluent van de SBR). Drie coagulantia ($FeCl_3$, $Al_2(SO_4)_3$ en $Ca(OH)_2$) werden getest bij verschillende concentraties. De behandeling van het effluent van de papierfabriek door louter biologische middelen kon niet bijdragen aan een aanzienlijke P-verwijdering vanwege de lage P-groeibehoeften van de biomassa. De co-precipitatie CPR-benadering bleek zeer effectief te zijn ongeacht het gebruikte coagulans (bij doses van 300 mg$FeCl_3 \cdot 6H_2O$/L, 300 mg$Al_2(SO_4)_3 \cdot 14.3H_2O$/L of 400 mg$Ca(OH)_2$/L), resulterend in verwijderingsefficiënties tussen 79 % en 82 % en het bereiken van uiteindelijke oplosbare P-waarden in het afvalwater in het bereik van 0.28 tot 0.34 mgP/L. Het voldeed echter moeilijk aan de toegestane lozingsnorm (jaarlijks) van 60 kg TP/d. Aan de andere kant liet de post-precipitatiebenadering (met de toevoeging van $Al_2(SO_4)_3$ bij een PO_4^{3-}/metaalzoutverhouding (mol-tot-mol) van 1:10, of bij dosering van 400 mg $Ca(OH)_2$/L), toe om de laagste waargenomen TP- en oplosbare P-concentraties te bereiken (minder dan 0.5 en 0.2 mgP/L respectievelijk). Daarom was de meest geschikte CPR-benadering voor de behandeling van het industriële effluent van de papierfabriek de post-precipitatie, aangezien deze consistent voldeed aan de maximale lozingsnorm van 60 kg TP/d.

De afvalwaterzuiveringsinstallatie van UPM werd adequaat gemodelleerd en het model maakt de voorspelling van huidige-en toekomstige installatiescenario's mogelijk. Het model toont aan dat er alternatieven voor de huidige configuraties van de afvalwaterzuiveringsinstallatie kunnen worden voorgesteld om de prestaties van de installatie te verbeteren. Bovendien biedt CPR grote kansen om de P-concentraties in het effluent nog verder te verminderen.

CONTENTS

1

INTRODUCTION

1.1 GENERAL INTRODUCTION

Uruguay is a stable country, both economically and politically, and it is among the best ranked countries in the world in environmental sustainability (Uruguay natural, 2023). The forestry sector began its steady growth in the late 1980s, as a result of favourable government policies. In 1987 a new forestry law was approved, and in June 1990 the government established an ambitious goal of planting 200,000 trees in a period of 5 years (Rosario Pou & Asociados, 2013). Twenty years after of the approval of the Forestry Law, Uruguay is considered an important certified wood supplier. It has soils and climatic conditions that allow optimum growth of rapid growing species such as Eucalyptus and Pinus (Rosario Pou & Asociados, 2013).

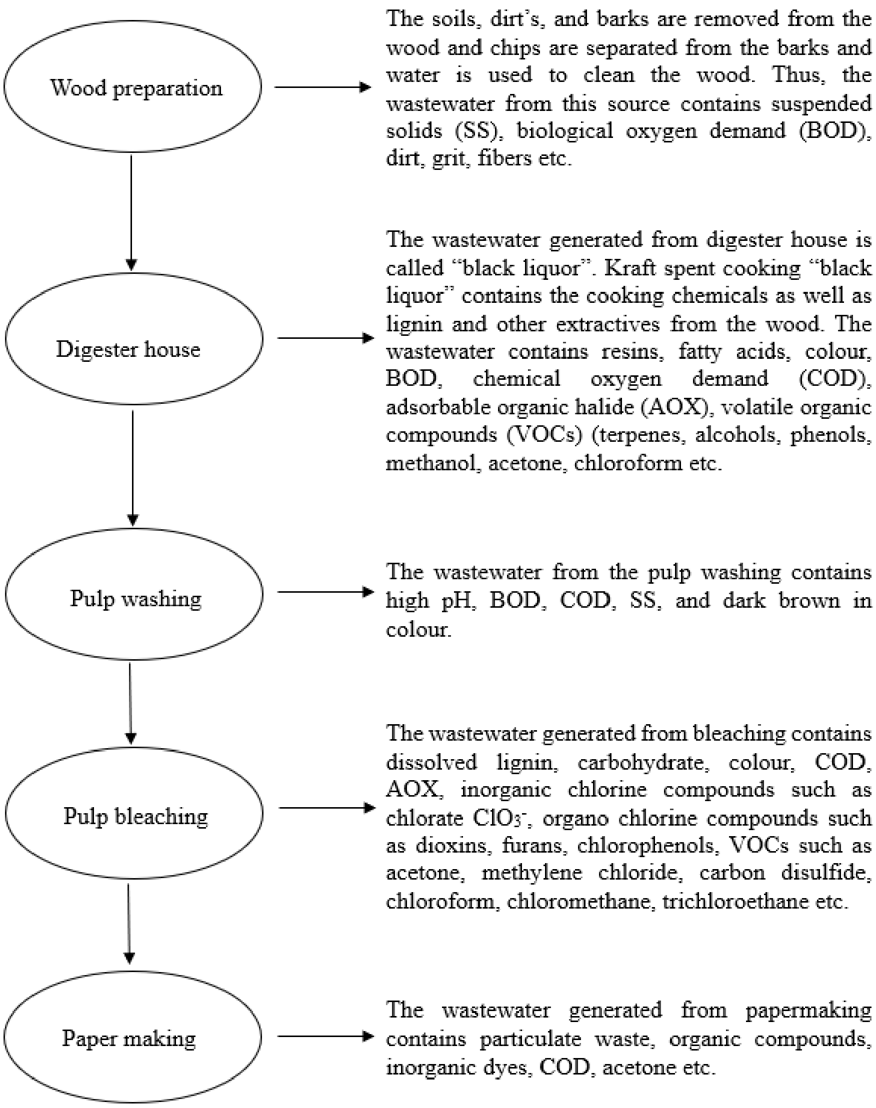
The forest area has been increased during the last 20 years, reaching 920,000 hectares in 1990, 1,412,000 in 2000, 1,520,000 in 2005, 1,744,000 in 2010, and 1,845,000 in 2015. The total forest area in Uruguay is only 10.5 % of the total area. The highest concentration of forest area is in Rivera, Tacuarembó, Paysandú, Río Negro and Lavalleja Departments, with a range from 100,000 to 200,000 hectares. The most important plantations in Uruguay are based on the genus eucalyptus (70 %) and followed by the genus pinus with 28 % of the area (Uruguay XXI, 2011).

The pulp production in Uruguay in 2015 reached a value of 2,361 thousand tons, using the total chemical method of production; Uruguay is the third country in South America regarding pulp production after Brazil and Chile. The wood pulp production over the years was only of 34,000 tons until the year 2006; however, from 2008 the amount of pulp produced has increased on more than 1,000 thousand tons reaching 2,361 thousand tons in 2015. This remarkable change was due to the installation of a cellulose pulp production plant by the Finnish company Metsä-Botnia (currently UPM) in the city of Fray Bentos, Department of Río Negro and STORA ENSO-ARAUCO in the city of Conchillas, Department of Colonia.

The present research was carried out at the UPM pulp mill wastewater treatment plant (WWTP) in Fray Bentos, Uruguay. The pulp mill in Uruguay, South America, was designed and built by the Finnish company, which operates three additional plants in Finland. UPM is a global company with presence in 45 countries and with 54 production plants in 12 countries. The company has six business areas: Biorefining, Energy, Paper, Specialty paper, Label, Plywood; and additional business in Biocomposites and Biochemicals. The plant started its operation in Uruguay in November 2007. It is located 5.2 km away from the city of Fray Bentos (Río Negro Department), next to the Uruguay River, and 1.2 km from the international bridge "Libertador General José de San Martin", which connects Uruguay and Argentina. The initial pulp production capacity expressed in air dry ton (ADT) per year was 1 million. After two years of operation, in 2009, the pulp mill was taken over by UPM. In 2014, the pulp mill increases the pulp production capacity to 1.3 million of ADT per year. The fully loaded factory can process up to 4.5 million m^3 of eucalyptus per year.

1.2 TYPICAL PULP AND PAPER MILL WASTEWATER COMPOSITION

According to (Pokhrel and Viraraghavan 2004) each pulping process utilizes large amount of water, which makes up a large part of the factory's effluent. The most significant sources of pollution are wood preparation, pulping, pulp washing, screening, washing, and bleaching; the generated pollutants are presented in Figure 1.1.



The soils, dirt's, and barks are removed from the wood and chips are separated from the barks and water is used to clean the wood. Thus, the wastewater from this source contains suspended solids (SS), biological oxygen demand (BOD), dirt, grit, fibers etc.

The wastewater generated from digester house is called "black liquor". Kraft spent cooking "black liquor" contains the cooking chemicals as well as lignin and other extractives from the wood. The wastewater contains resins, fatty acids, colour, BOD, chemical oxygen demand (COD), adsorbable organic halide (AOX), volatile organic compounds (VOCs) (terpenes, alcohols, phenols, methanol, acetone, chloroform etc.

The wastewater from the pulp washing contains high pH, BOD, COD, SS, and dark brown in colour.

The wastewater generated from bleaching contains dissolved lignin, carbohydrate, colour, COD, AOX, inorganic chlorine compounds such as chlorate ClO_3^-, organo chlorine compounds such as dioxins, furans, chlorophenols, VOCs such as acetone, methylene chloride, carbon disulfide, chloroform, chloromethane, trichloroethane etc.

The wastewater generated from papermaking contains particulate waste, organic compounds, inorganic dyes, COD, acetone etc.

Figure 1.1 Pollutants from various sources of pulping and papermaking (Pokhrel and Viraraghavan, 2004)

The characteristics of the pulp-processing wastewater depend on various factors such as the type of the process, type of the raw materials, process technologies applied, recovery methods applied, the amount of water used, etc. (Pokhrel and Viraraghavan 2004). The general characteristics of the wastewater produced at various pulp processes and typical composition of raw municipal wastewater with minor contribution of industrial wastewater are show in Table 1.1.

Table 1.1 Characteristics of wastewater at various pulp processes (Adopted from (Pokhrel and Viraraghavan 2004)) and typical composition of raw municipal wastewater with minor contributions of industrial wastewater (Henze et al., 2008)

		Parameters			
Process	pH	TS (mg/L)	SS (mg/L)	BOD_5 (mg/L)	COD (mg/L)
Digester house	12	51,589	23,319	13,088	38,588
Kraft mill	8	8,260	3,620	-	4,112
Pulping	10	1,810	256	360	-
Bleached pulp mill	8	-	1,133	1,566	2,572
Pulp and paper	8	4,200	1,400	1,050	4,870
Raw municipal wastewater with minor contributions of industrial wastewater (medium)	7.5	-	400	350	750

In addition to the characteristics of the wastewater generated at various pulp processes presented in Table 1.1, several authors have reported the presence of other types of contaminants in the wastewater from pulp and paper processes, such as: lignin or other wood components (extractives or carbohydrates) and wood-derived components (resin acids, fatty acids, phytosterols and retene, among others) (Latorre et al., 2006; Ashrafi et al., 2015; Kamali and Khodaparast, 2015; Lindholm-Lehto et al., 2015; Cabrera, 2017; Ramos et al., 2022). In the bleach kraft mill wastewater, AOX concentrations of 12.5 mg/L and resin concentrations of 69 µg/L were reported by Pokhrel and Viraraghavan, (2004).

According to the information shown in Table 1.1 the highest load of contaminants occurs in the digester house, with extremely high concentrations of 51,589 mgTS/L, 23,319 mgSS/L, BOD_5 of 13,088 mg/L and COD of 38,588 mg/L. On the other hand, if we compare these parameters with the pulp mill bleaching process, which is the one used at UPM, it is possible to see that we have much lower concentrations: 1133 mgSS/L, BOD_5 of 1566 mg/L and COD of 2572 mg/L. However, the concentrations of suspended solids and organic load in pulp mill bleaching are significantly higher (almost three times more) than the concentrations of these contaminants in municipal wastewater. With respect to pH, it is very similar between a raw municipal wastewater and that produced in the pulp mill bleaching process. These findings provide a comprehensive overview of the varied environmental parameters within each process, highlighting potential implications for wastewater treatment.

1.3 TREATMENT OF EFFLUENTS FROM PULP AND PAPER PRODUCTION

Pulp and paper mill production effluents are complex mixtures; it contents high content of organic matter, suspended solids, and other types of contaminants such as mentioned in the previous section: lignin or other wood components (extractives or carbohydrates), wood-derived components (resin acids, fatty acids, phytosterols and retene, among others) and chlorinated organic matter. However, the characteristic of wastewater depends on numerous factors including raw material (wood) type and composition, and the chosen wood-processing technology.

To reduce the organic matter and chlorinated organic matter in the effluent, pulp and paper mill can modify the production process and apply different cleaner production technologies. The main objectives are to reduce the amount of residual lignin entering the bleach plant, and ideally to eliminate the use of chlorine in the bleaching process (Servos, et al. 1996).

According to (Saarela, et al. 2008) the main streams that need to be treated are coming from bleaching process but there are also other streams from e.g. wood handling, pulp drying, evaporating and causticizing processes.

With the aim to protect the water quality, different industrial effluent treatment processes are need. The environmental legislation is becoming increasingly stricter and is the obligation of the industry to meet the effluent quality standards. According to Sumathi and Hung (2006) the most common processes employed by the pulp and paper mills during preliminary, primary, secondary, and tertiary stages of effluent treatment are presented in Figure 1.2.

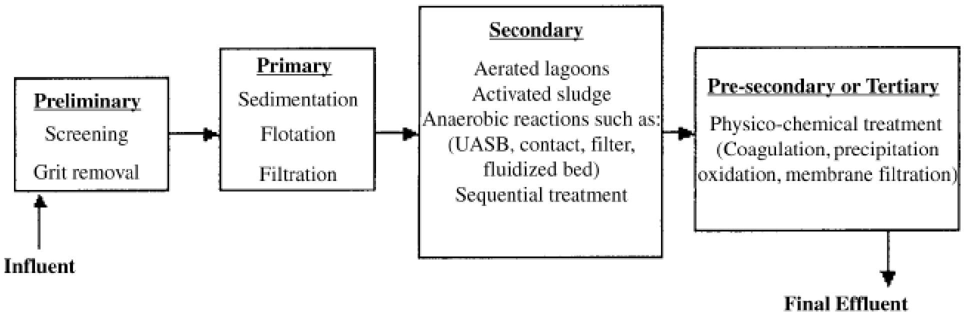


Figure 1.2 The unit processes employed by pulp and paper mills for effluent treatment (Sumathi and Hung 2006)

The wastewater treatment technologies can be separated in physico-chemical and biological process. Treatment such as membrane separation, chemical coagulation and precipitation and advance oxidation processes are physico-chemical methods, whereas the most commonly used biological treatment systems for the pulp and paper mill discharges are activated sludge, aerated lagoons, and anaerobic treatment.

1.3.1 Membrane separation techniques

Membrane separation processes operate based on the following mechanisms: pressure driven, which include reverse osmosis (RO), ultrafiltration (UF), and nanofiltration (NF); concentration driven, which include diffusion dialysis, vapour permeation, and gas separation; electrically driven, which include electrodialysis; and temperature difference driven, including membrane distillation (Strathmann, 1981; Fonseca Couto et al., 2018; Li et al., 2021; El Batouti et al., 2022). Membrane filtration (UF, RO, and NF) is a potential technology for removing colour, COD, AOX, salts, heavy metals, and total dissolved solids (TDS) from pulp and paper effluents (Nuortila-jokinen et al., 2003; Kallioinen et al., 2006; Mänttäri et al., 2008; Zhang et al., 2009; Valderrama et al., 2021), resulting in the generation of high-quality effluent for water recycling and final discharges. In addition, membrane bioreactor (MBR) with is the association of microfiltration (MF) or UF with biological treatment can be applied in order to obtain high water quality (Fonseca Couto et al., 2018). However, the main disadvantages are high capital and maintenance costs, membrane fouling, and requirements for the pre-treatments of discharges (Sumathi and Hung 2006).

1.3.2 Chemical coagulation and precipitation

These methods consist in the addition of metal salts to cause agglomeration of small particles into larger flocks that can be easily removed by settling. According to (Sumathi and Hung 2006) almost all the toxic compounds presents in pulping and bleaching effluent, which have a biodegradable fraction of polar and hydrophobic compounds, resin acids, long-chain fatty acids, aromatic acids and phenols, lignin and terpenes, can be effectively removed through coagulation using chloride and sulphate salts of iron (Fe^{3+}) and aluminium (Al^{3+}). Nevertheless, these methods have also disadvantages such as the generation of chemical sludge which should be treated to eliminate the adsorbable toxic pollutants prior to sludge disposal.

1.3.3 Advanced oxidation processes

There are various advanced oxidation processes such as photocatalysis, photo-oxidation using hydrogen peroxide (H_2O_2)/UV or ozone (O_3)/UV systems, Fenton-type reactions, wet oxidation, and by employing strong oxidants such as ozone that can be applied to destruct chromophoric and nonchromophoric pollutants in pulp and paper effluents.

- Photocatalysis: It has a good performance regarding near total oxidation and elimination of organic compounds.
- Photo-oxidation: Using (H_2O_2)/UV or (O_3)/UV combinations generate hydroxyl radicals that are short lived but extremely powerful oxidizing organics through hydrogen abstraction. The result is the total destruction of refractory organics without generation of sludge or residues.
- Fenton-type reactions are a good option for effluent treatment, involving hydrogen peroxide (H_2O_2) and ferrous ion as the solution catalyst. A slightly acidic pH is required and results in the formation of highly reactive hydroxyl radicals ($^{\cdot}OH$), which can degrade many organic pollutants.
- Wet oxidation: is a process where organic contaminants reacted with an oxidant at high temperature (220–290 °C) and pressures (100–250 bar) to promote rapid destruction.
- Strong oxidants: Oxidants such as chlorine, oxygen, ozone, and peroxide have been proposed for the treatment of pulp bleach effluents. Ozonation has been reported to reduce the toxicity of bleached Kraft mill effluents at low dosages.

Some of advantages of various oxidation processes are non-selective and rapid destruction of pollutants, absence of residues, and improved biodegradability of the effluents. On the other hand, they have some disadvantages as extremely short half-life of the oxidants and high expense of their generation (Sumathi and Hung 2006).

1.3.4 Activated sludge treatment

The activated sludge treatment is one of the most used for effluent of pulp and paper mill treatment (Srinivasan, 1994; Thompson et al., 2001; Karlsson et al., 2011; Cabrera, 2017). Activated sludge treatment is a conventional aerobic biological treatment which consists in the following three basic components: 1) a reactor in which the microorganisms responsible for treatment are kept in suspension and aerated; 2) liquid-solids separation, usually a sedimentation tank; and 3) a recycle system for returning solids removed from the liquid-solids separation unit back to the reactor (Metcalf and Eddy, 2003a; Sumathi and Hung, 2006; Henze et al., 2008). This process is used for the reduction of COD, BOD, TSS, and AOX in waste effluents (Leiviska et al., 2008; Leiviska, 2009). Different factors such as nutrients control, aeration, low loading rates, introduction of equalization and buffer basins seemed to be the key process control parameters for successful treatment (Henze et al., 2008).

Worldwide there are a high number of full-scale activated sludge plants to treat pulp and paper mill effluents (Ashrafi et al., 2015; Kamali and Khodaparast, 2015; Elsergany et al., 2015; Toczyłowska-Mamińska, 2017), most of them in Unites States, Canada, and Finland (Sumathi and Hung, 2006). It is generally known that this treatment has a good performance to pollutants reduction, mainly COD, BOD and TSS. However, the two common operational problems with the application of aerobic conventional activated sludge (CAS) treatment are the often limiting concentrations of nitrogen (N) and phosphorous (P) in the plant influent that are vital for the maintenance of active microbial population in an activated sludge plant (especially the case when industrial effluents are of concern) (Mobius, 1991; Kenny, 2009; Kang et al., 2011; Vashi et al., 2019a), and sometimes an excessive growth of filamentous organisms that influence the sludge settling properties and consequently affect the effluent quality.

1.3.5 Aerated lagoons

Aerated lagoons are a simple form of (often land-based) biological treatment. They have some advantages over other technologies such as lower energy requirements for operation and a lower quantity of pre-stabilized sludge. In developed countries, aerated stabilization basins were the earliest choice for secondary treatment of pulp and paper effluents. In contrast, developing countries still commonly rely on this method as the most popular alternative.

According to Sumathi and Hung (2006), aerated lagoons are classified on the basis of the extent of mixing. A completely mixed lagoon is similar to an activated sludge process where efficient mixing is provided to supply adequate concentrations of oxygen to microorganisms and to keep the biomass in suspension. Nonetheless, the system does not include a mechanism for recycling biomass or solids. Aerobic bacteria oxidize a portion of the biodegradable organics into carbon dioxide and water, and the rest is utilized to generate biomass components. Several completely mixed aerated lagoons may be linked in series to facilitate the stabilization of synthesized biomass and organic solids under aerobic conditions. On the other hand, in a partially mixed aerated lagoon, also known as facultative lagoon, the power input adequately satisfies the system’s oxygen requirements but is insufficient for keeping the solids in suspension. This allows for settlement of biosolids by gravity sedimentation and subsequent stabilization through anaerobic processes. Thus, the biological activity in facultative lagoons is partially aerobic and anaerobic.

1.3.6 High-rate anaerobic treatment

With the high-rate anaerobic reactor development the use of anaerobic treatment for pulp and paper effluents has been implemented (Habets and De Vegt, 1991; Driessen and Wasenius, 1994; Driessen et al., 1999; Meyer and Edwards, 2014). High-rate reactors typically achieve 80-90 % reduction in BOD_5, with biogas and methane production of 0.5 m^3/kg COD and 0.35 m^3/kg COD, respectively (Sumathi and Hung, 2006). There are different types of bioreactor configurations used for industrial wastewater such as upflow anaerobic sludge blanket (UASB), anaerobic contact (AC), anaerobic filter (AF), hybrid UASB with filter (UASB/AF), expanded granular sludge blanket (EGSB), fluidized bed (FB), down-flow stationary fixed film (DSFF), and anaerobic lagoons (Sumathi and Hung, 2006; Henze et al., 2008; van Lier et al., 2016). UASB and EGSB reactors are most widely implemented for the anaerobic treatment of industrial wastewater (van Lier et al., 2016).

As the pulp and paper industries generate a high strength wastewater with the potential to recovery energy in the form of biogas anaerobic degradation treatment is mostly used (Meyer and Edwards, 2014). According to van Lier et al. (2016) worldwide pulp and paper industry has installed a 11 % of the total of anaerobic technology for industrial wastewater treatment. Moreover, anaerobic microorganisms have shown to be more efficiently in dehalogenating and degrading chlorinated organic compared to aerobic microorganisms (Sumathi and Hung, 2006). In addition, anaerobic treatments have lower capital investment and the small required land areas are advantages that convert this treatment in a cost-effective option (Henze et al., 2008; Chernicharo, 2015). On the other hand, some key issues with the anaerobic treatment application can occur such as the inhibition of the methanogenic population by the some wastewater components such as lignin derivates, resin and fatty acids (Meyer and Edwards, 2014; Ashrafi et al., 2015).

1.4 UPM MANUFACTURING PROCESSES

The UPM pulp mill is one of the most modern of such type in the world. The capacity of the mill is 1,300,000 ADT per year of fully bleached eucalyptus pulp. The mill uses the chemical Kraft process, which is worldwide the most used pulping process in the pulp and paper industry. The robustness of the Kraft pulp, the ability of the process to handle almost all species of soft and hard wood, and the favourable economics due to a high chemical recovery efficiency (of about 97 %), give the Kraft process a considerable advantage over other pulping processes (Tran & Vakkilainnen, 2008). The pulp is bleached without elementary chlorine (ECF) according to the recommendations of the Best Available Techniques (BAT) (Saarela et al., 2008).

The complete fiber line and chemical recovery processes are presented in Figure 1.3. The wood, once arrived at the plant as debarked logs, goes to the woodyard where it is stored according to the different species of eucalyptus; later on, it is sent to two parallel chipping lines. After this step, the wood chips are digested at elevated temperature (it starts at 155 ^oC, then in the middle of the process it is 150 ^oC and at the end it is 137 ^oC) and pressure between 4 and 9 bar in a water solution of sodium sulphide (Na_2S) and sodium hydroxide (NaOH) (better known as the white liquor). This is the beginning of the Kraft pulping process. The white liquor chemically dissolves the lignin that binds the cellulose fibres together. Then, black liquor is separated from the pulp by washing and it is sent to the Kraft recovery system. The inorganic pulping chemicals are recovered for reuse, while the dissolved organics are used as fuel to produce steam and power. For every ton of pulp produced, the Kraft pulping process generates about 10 tons of weak black liquor that needs to be processed through the chemical recovery process (Tran & Vakkilainnen, 2008).

Once the pulp is cooked and washed, it passes through the oxygen delignification and knotting and through the screening processes. The separated and washed knots are returned back to the chip feeding system to be re-cooked, while the final reject comprising mostly impurities, like sand, is removed from the system as a solid waste and sent to the landfill (Saarela et al., 2008).

One of the most critical processes is the pulp bleaching which usually employs bleaching sequences consisting of four or more alternating bleaching stages to eliminate the residual lignin and chromophores (Isaza Ferro et al., 2021). In this process, the required pulp quality in terms of brightness and cleanliness should be reached. Each bleaching stage uses elevated temperature for a long period of time, making the overall duration of the bleaching sequences several hours (Isaza Ferro et al., 2021). The selected bleaching sequence in the UPM mill is (A/D)-Eop-D-P (Saarela et al., 2008). With the aim to improve delignification a pre-treatment with hot acid hydrolysis stage (A-stage) is carried out preceding bleaching (Juvonen, 2020). The pulp mill uses ECF bleaching technology, and chlorine dioxide (ClO_2) is the main oxidant added, which include 2 chlorine dioxide (D) bleaching stages. D stage oxidizes lignin structures, which are later solubilized during alkaline extraction (E) (Isaza Ferro et al., 2021). The residual chromophores are removed by a final peroxide bleaching stage (P) giving the pulp good brightness stability. Hydrogen peroxide and oxygen gas (E_{op}) are used to intensify the alkaline extraction (Isaza Ferro et al., 2021).

The bleaching plant is the only open process. The pulp mill discharges an average annual below 20 m^3/ADT about of 70,000 m^3/day of liquid effluent. They are generated in different processes of the plant and the main flow is from the bleach plant which is directly sent to the wastewater treatment plant (WWTP). Besides, minor flows from chip washing, wood chip digestion, spent pulping liquor evaporator condensates, pulp screening, thickening and cleaning operations also are treated in the WWTP.

The main characteristics of the wastewater entering the WWTP align with those outlined in Table 1.1 for wastewater originating from the bleached pulp mill process. The wastewater introduced to the WWTP exhibits a similar concentration in terms of SS and COD. Additionally, it contains AOX, although at reduced levels due to the use of the ECF process in pulp bleaching. Furthermore, it comprises nutrients such as N and P, though in significantly lower concentrations compared to municipal wastewater. Although this specific data is not provided in Table 1.1, a typical composition of raw municipal wastewater, with minor contributions from industrial wastewater (medium concentrate wastewater) presents concentration of approximately 60 mgN/L for total nitrogen (TN) and 15 mgP/L for total phosphorus (TP).

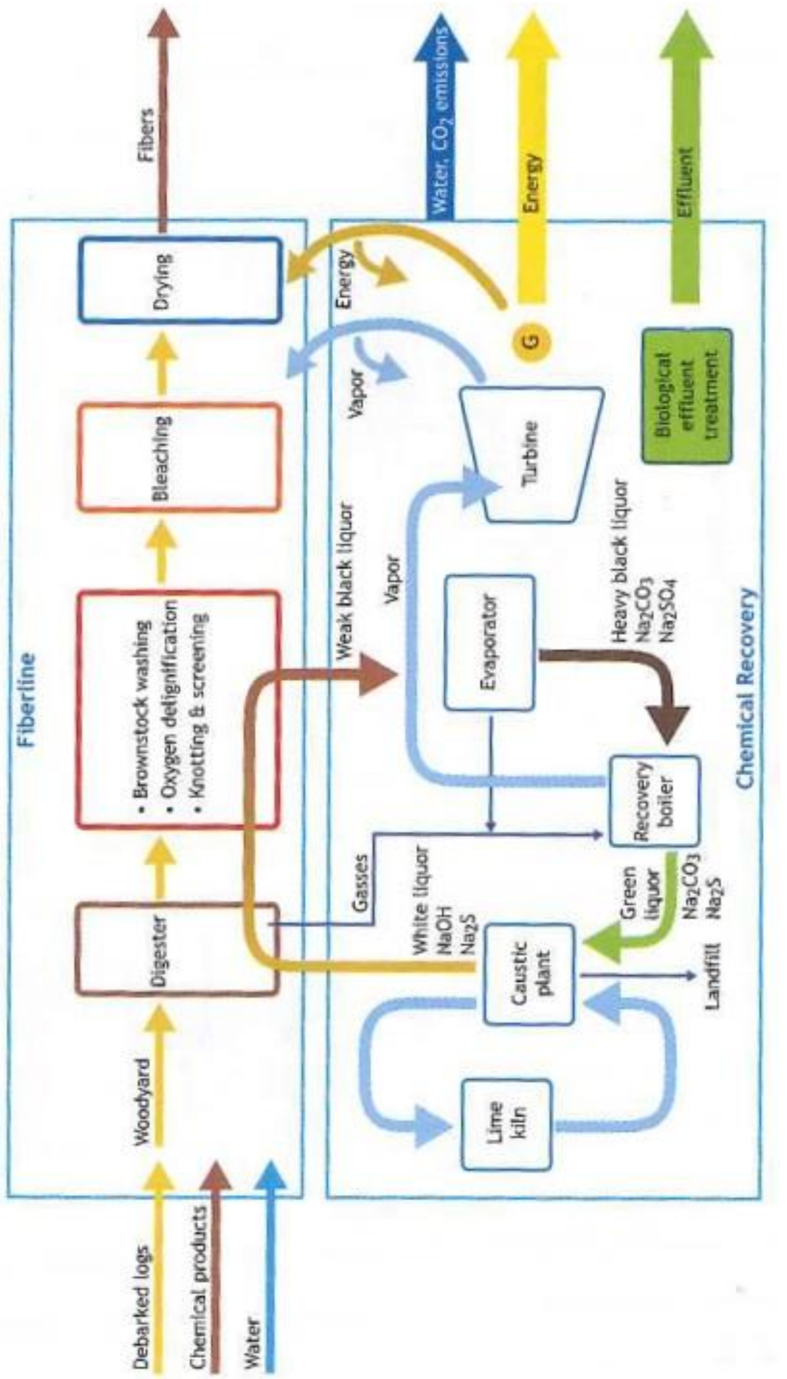


Figure 1.3 The Kraft pulping process (Faroppa and Annala, 2004)

1.5 PROBLEM STATEMENT

As describes previously in section 1.4, the mainstream sent to the biological WWTP plant originates from the bleaching process and is composed of a considerable amount of SS, organic matter, and in minor proportion AOX, and nutrients such as N y P. The UPM pulp mill wastewater treatment was evaluated in 2014. The influent to the biological (secondary) treatment and final effluent to Uruguay river characterization is presented in Table 1.2 (Bentancur, 2014).

Table 1.2 Wastewater characterization, measured values during sampling campaign carried out from October 21st to 28, 2013

Measurements				
Description	**Symbol**	**Influent**	**Effluent**	**Units**
Total influent COD	COD_{total}	1588	268	$gCOD/m^3$
Influent COD soluble *	COD_{filt}	1243	260	$gCOD/m^3$
Influent BOD_{10}	BOD_{10}	911	6.9	$gBOD/m^3$
Influent BOD_{10} soluble *	$BOD_{10, filt}$	749		$gBOD/m^3$
Influent Volatile fatty acids	VFA	217		gAcetic Acid/m3
Total Nitrogen **	TN	15.8	1.28	gN/m^3
Total Kjehldahl Nitrogen	TKN	15.8	1.17	gN/m^3
Ammonium	NH_4	0.23	0.04	gN/m^3
Nitrite	NO_2	ND	ND	gN/m^3
Nitrate	NO_3	0.03	0.10	gN/m^3
Total Phosphorus	TP	3.67	0.58	gP/m^3
Total Phosphorus soluble *	TP_{filt}	2.35	0.54	gP/m^3
Orto-phosphate	PO_4	2.15	0.47	gP/m^3
Total Suspended Solid	TSS	220.2	4.08	$gTSS/m^3$
Inorganic Suspended Solid	ISS	45.4	ND	$gISS/m^3$
Volatile Suspended Solid	VSS	174.8		$gVSS/m^3$
Temperature	T	30		ºC

* 0.45 μm membrane filtered

** TN after urea addition

The COD concentration in the UPM wastewater characterization exhibits a value lower than that indicated in Table 1.1 for bleached pulp mill process. Nevertheless, it is important to highlight that the characterization presented in Table 1.2 refers to the wastewater before it enters the biological (secondary) treatment, signifying that it has undergone a pre-treatment phase where a portion of the organic matter was already removed. A parallel observation can be made for the concentration of SS, as they are effectively eliminated during the primary treatment process.

The regulation and standards for the WWTP effluents are established by the Uruguayan environmental authorities, Ministry of Environment, (MVOTMA, 1979). The Ministry of Environment established specific limits for UPM because it is a mega industrial plant and due to the large amount of water used in the process and converted into wastewater. Regarding TP, UPM is restricted to both monthly and annual discharge limits. The company can never exceed the average monthly limit of 74 kgTP/d, and the annual limit corresponds to an average of 60 kgTP/d. In Figure 1.4, the graph shown TP discharge to the Uruguay River with respect to the aforementioned limits. In order to meet the annual permit limit TP discharge value to the river of 60 kg/d, UPM set an internal monthly target TP discharge of 60 kg/ADT. This parameter can be seen in Figure 1.4 mentioned as Monthly Target 2018: 0.060 ton/d.

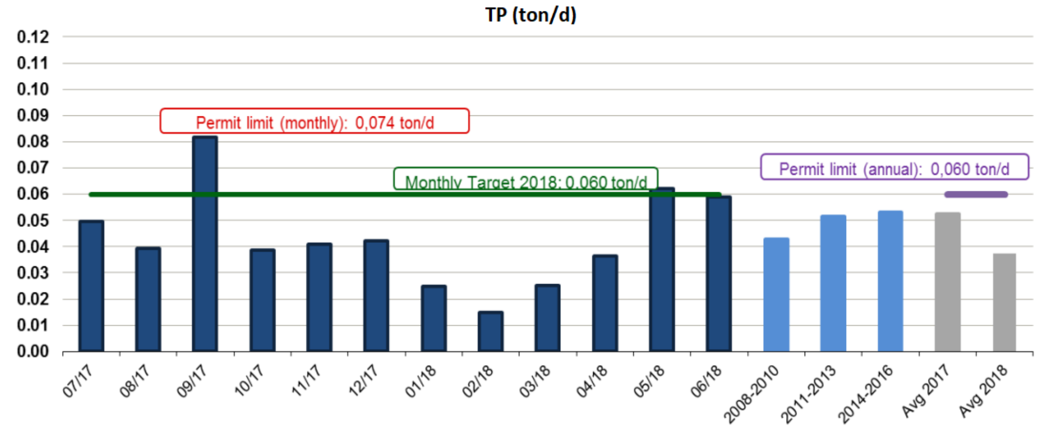


Figure 1.4 Average monthly phosphorus discharge – UPM (2017-2018) (UPM, 2018)

The current UPM pulp mill CAS treatment has shown to have a high effectiveness to treat COD, BOD, TSS, TN and TP meeting the standards set for the discharge of effluent into the Uruguay River. Even though the removal efficiency of TP is relatively high (above 80 %), the TP concentration in the effluent exhibited values close to the discharge standard. As shown in Figure 1.4, in September 2017, the company exceeded the permitted limit in the discharge of TP to the river.

The current UPM WWTP is not designed for nutrients (N and P) removal; at many other paper mill WWTPs the influent to the treatment plant is low in nutrients and even the addition of nutrients to the influent is necessary to achieve the desired degree of biological removal of organic matter. Table 1.3 shows a comparison between the characteristics of the pulp mill WWTP influent wastewater to biological treatment (based on data collected from May to August 2013) and typical wastewater characteristics from a raw municipal wastewater and two other pulp mill WWTPs.

Table 1.3 Comparison between the wastewater characteristics of the pulp mill WWTP, typical raw municipal wastewater, and from two other pulp mill WWTPs (Bentancur, 2014)

	Raw Municipal WW (Netherlands) Meijer and Brdjanovic (2012)	**Pinus radiata Kraft Pulp Mill** (Chile) Diez et al. (2002)	**Stora Enso Fine Paper Oulu kraft Pulp mill** (Finland) Keskitalo and Leiviska (2010)	**Bleached Kraft Pulp Mill** (Uruguay) May to August 2013
Parameter	**Average**	**Average**	**Average**	**Average**
COD total	750	1208	1167	**1588**
COD soluble	300	-	-	1243
BOD_5	350	319	255	911
VFA (as acetate)	30	-		217
N total	60	6.1	6.6	**6.5**
Ammonia-N	45	-	0.2	0.2
P total	15	1.1	1.7	**3.7**
Ortho-P	10	-	2.4	2.2
TSS	400	147	-	220
VSS	320	-	-	175

The pulp mill wastewater of study (in Uruguay) had higher organic matter concentrations (including the biodegradable organic fraction) than a typical raw municipal wastewater. For instance, the COD/BOD ratio of the pulp mill influent was lower than 2, indicating a considerable presence of biodegradable components in the influent (Rodrigues et al., 2008) and (Zaher and Hammam, 2014). When comparing the nutrient composition between the municipal wastewater and the pulp mill wastewater an opposite trend was observed. TN and TP concentrations of 60 mgN/L and 15 mgP/L, respectively (Metcalf and Eddy, 2003a; von Sperling, 2008; Henze et al., 2008; Chen et al., 2020) where reported for municipal wastewater, whereas TN and TP concentrations of 6.5 mgN/L and 3.7 mgP/L, respectively were reported for the pulp mill wastewater in Uruguay.

The pulp mill wastewater at the UPM plant had similar characteristics (in terms of total COD, TN, TSS and ammonia) like those reported from other pulp and paper mill wastewaters (Lindblom et al., 2004), (Barañao and Hall, 2004), and (Keskitalo and Leiviskä, 2010). However, the BOD_5 and TP concentrations were considerably higher compared with other pulp mill. This may be attributed to the composition of the wood used as raw material which has a higher P content. At the UPM pulp mill WWTP, due to the high concentrations of biodegradable organic matter, 2,500 kg of urea is dosed daily to cover the nitrogen requirements for biomass growth (approximately 16 mgN/L). As is shown in Table 1.3 the TN concentration in the influent to the biological treatment is 6.5 mgN/L, and Table 1.2 presents the influent TN concentration after urea addition, about 15.8 mgN/L. The addition of P is not necessary since the hardwood that is used for the pulp production, eucalyptus, has a high content of phosphorus.

In the last years, the TP concentration in the eucalyptus hardwood used as inlet at the pulp mill has been increased, due to a higher concentration of this nutrient in the soil, so the TP concentration in the influent to the UPM WWTP has also increased. The WWTP receives two flows of wastewater from the industrial plant, a stream with high solids content, named WAL, and another stream with low solids content, identified as WAB. In Figure 1.5, two graphs are shown in which the increase in TP concentration over the years were measured in each of the two streams.

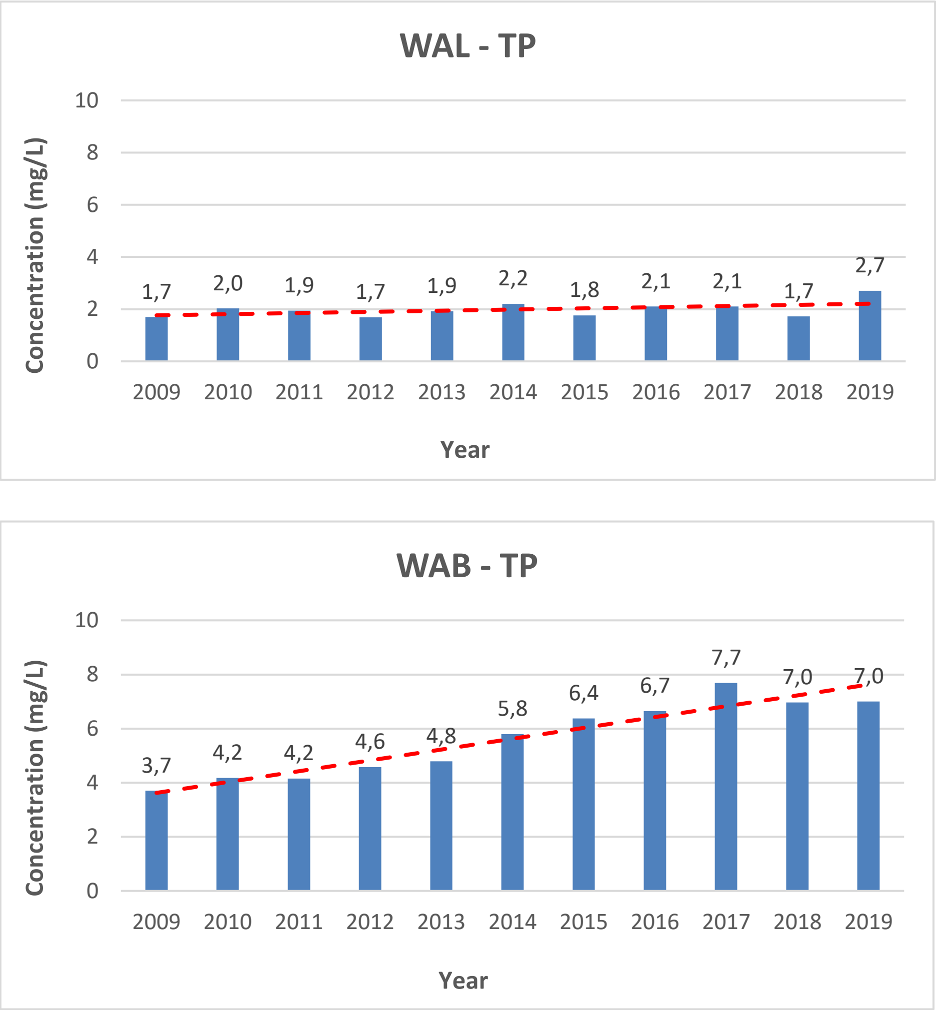


Figure 1.5 TP concentration over the years in WAL and WAB streams to the WWTP

After WAL and WAB streams are pre and primary treated both are mixing in an equalization basin, and then the total stream is sent to the biological treatment. As the

WWTP was not designed for nutrient removal, P concentrations in the effluent close to the discharge limit imposed by Ministry of Environment were observed. To control the situation regarding TP concentration in the effluent, a new pre-treatment process has been implemented in the WAB stream. The new chemical pre-treatment consists of a tank where lime is added to the influent; the influent pH is increased, and the phosphate is precipitated and removed in a clarifier. The decision of how much flow from the WAB line passes through the new precipitation plant depends on the P concentration in the influent. The higher the P concentration in the influent, the larger the influent flow directed to the chemical precipitation plant; otherwise, the flow goes directly to the neutralization and equalization basins. The decision on the blending flow is taken by the plant engineer on a daily basis. Therefore, it is of a great importance to consider the entire wastewater treatment plant, (including pre-treatment, primary and secondary treatment processes) to better understand the entire operation of the WWTP; of particular interest, the chemical P-removal processes, and its main impact on the plant-wide processes, including the subsequent equalization, activated sludge, and waste activated sludge (WAS) treatment processes.

Once the WWTP operation is well understood, the operation of the plant can be further improved and optimized (such as the dosage of metals, metal type, mixing, reaction time, age of flocs, among others) for a better performance of the WWTP including the achievement of lower P concentrations in the effluent.

1.6 PHOSPHOROUS IN AQUATIC ENVIRONMENT

Phosphorus is an essential element for all living organisms and plays a major role in many physiological processes (Metcalf and Eddy, 2003; Lopez-Vazquez, 2009; Peng et al., 2018). However, in recent years, excessive amounts of P discharged into aquatic environments due to anthropogenic activity have become one of the main causes of water eutrophication, which has negative effects on water quality (Clark et al., 1997; De-Bashan and Bashan, 2004; Bunce et al., 2018). Therefore, it is desirable to implement technologies to removal P and reduce the level of P entering surface waters.

In Uruguay, the main sources of P entering rivers are to various human activities, mainly with fertilizers and soil erosion. And in certain areas of high livestock density, with their excretions (Ministerio de Ambiente, 2020). Of the TP values recorded between 2016 and 2019 in the country's watercourses, reservoirs and lagoons, 84 % were unacceptable. Non-acceptable concentrations according to reference values proposed by the Technical Water Board (2017) correspond to concentrations greater than 70 μgP/L for lotic systems and greater than 50 μgP/L for lentic systems (Ministerio de Ambiente, 2020). Considering the average for the 2016-2019 period, unacceptable high levels are observed in all watercourses and lentic systems of the country, probably due to the anthropogenic activities carried out in the basins (Ministerio de Ambiente, 2020).

Phosphorus can be found in different forms in natural waters and in wastewaters. These forms can be divided into dissolved, colloidal, and particulate phosphorus. The separation between dissolved and particulate fractions is achieved by filtration through 0.45 µm membrane filters (Spivakov et al., 1999). The particle size of colloidal phosphorous can vary and depends of the methods of its determination; typically can be found in the range from 0.01 to 1.0 µm (Ekama and Wentzel, 2008).

According to the Standard Methods for the Examination of Water and Wastewater (APHA et al., 2012) phosphorus occurs in water merely as phosphates. These are classified as orthophosphates, condensed phosphates (pyro-, meta-, and other polyphosphate), and organically bound phosphate (APHA et al., 2012). At the same time, it is possible to find chemically bond phosphorus (Gu et al., 2014).

Orthophosphates are phosphates that respond to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample and are called reactive phosphorus (APHA et al., 2012). The reactive phosphorus is largely a measure of orthophosphate, but also includes a small fraction of any condensed phosphate which usually is hydrolysed unavoidably in the procedure. Reactive phosphorus occurs in both dissolved and suspended forms. Orthophosphates such as: PO_4^{3-}, HPO_4^{2-}, H_2PO^{4-} , H_3PO_4 are in dissolved form. However, from chemical precipitation with divalent or trivalent metals, orthophosphates will become particulate (Scherrenberg, 2011).

The conversion of different dissolved and particulate condensed phosphates into orthophosphates is achieved by acid hydrolysis at 100 °C and the respective fraction of the total phosphorus is called acid-hydrolysable phosphorus (Spivakov et al., 1999). Acid-hydrolysable phosphorus can be divided into four components: polyphosphorus, pyrophosphorus, metaphosphorus, and lower oxidation states (Scherrenberg, 2011).

1.7 BACKGROUND OF UPM WASTEWATER TREATMENT PLANT

The UPM WWTP was designed for an influent flow of 25 m^3/ADT (approximately 0.8 m^3/s). The first configuration of the WWTP consisted of a mechanical pre-treatment followed by an extended biological activated sludge treatment for the removal of COD, TSS, and AOX compounds. The first process configuration of the UPM WWTP is presented in Figure 1.6.

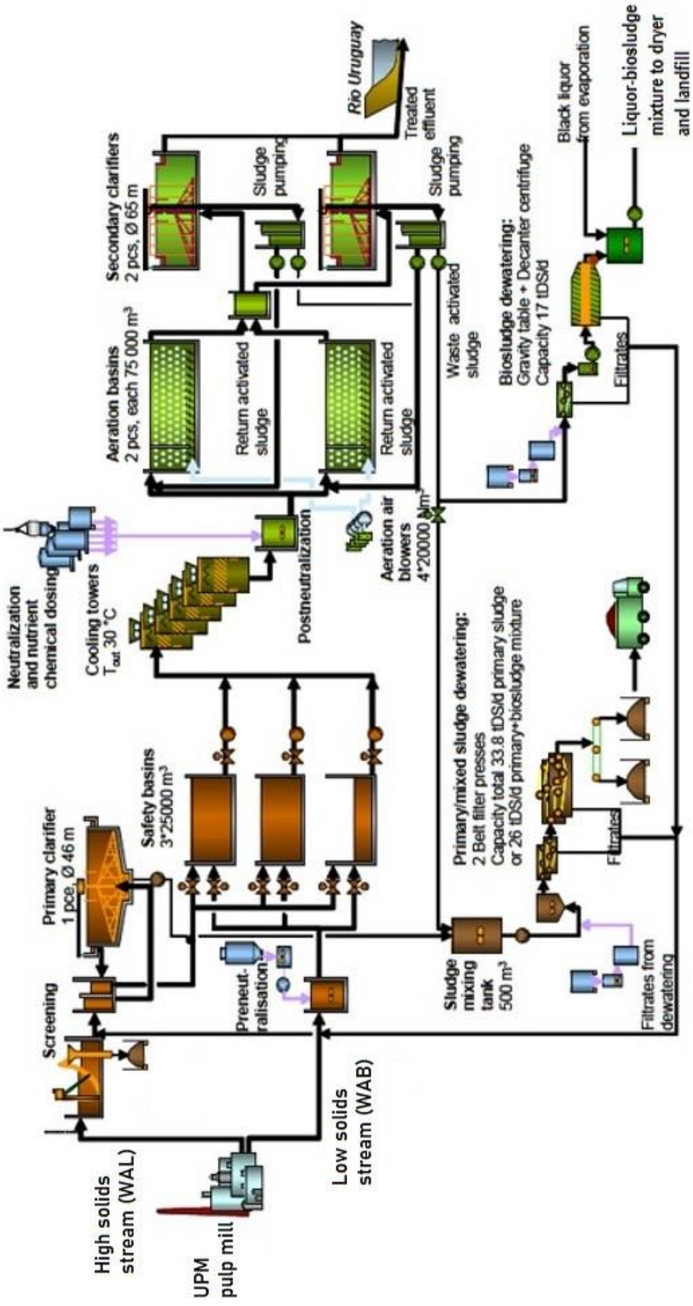


Figure 1.6 UPM WWTP process flow diagram (Saarela, et al. *2008)*

The industrial wastewater treated at the WWTP consists of two streams: WAL, with a TSS concentration about 1000 mg TSS/L, and WAB, with a TSS about 196 mg TSS/L. The WAL stream is composed of wastewater generated from the white liquor plant, evaporation plant, recovery boiler, drying process, wood handling, water treatment, and fiberline. This stream is approximately one third of the entire influent flowrate to the evaluated pulp mill WWTP (0.27 m^3/s). As shown in Figure 1.6, the incoming WAL stream is sent through a coarse screen to remove larger solids and later on through a primary clarifier (1 unit, D = 46 m) to remove settleable solids (primarily fibres). Then, this stream is sent to the three safety and equalization basins (of 25,000 m^3 each one). The equalization basins with a hydraulic retention time (HRT) of 16 hours. The WAB stream represents about two thirds of the influent flow to the WWTP (0.53 m^3/s) and is mostly generated in the acid and alkaline bleaching processes and to a lesser extent at the chemical and white liquor plants. The WAL stream is discharged directly in the pre-neutralization tank (to adjust the pH from about 4.3 to 7). Thereafter, the neutralized stream is stored in the safety and equalization basins where it gets mixed with the high solids stream (of pH 8.4).

Once the two flows are mixed in the safety and equalization basins (where the variations in flows and concentrations are balanced) the equalized flow is directed to the cooling towers to decrease the wastewater temperature from 55 to approximately 30 °C, to prevent the inhibition of the biological treatment by high influent temperature. Thereafter, the cooled influent is post-neutralized for pH adjustment (to obtain pH about 7), urea is added as additional nitrogen source, and the wastewater enters the biological activated sludge treatment consisting of two aerobic reactors in parallel (each one of 75,000 m^3), with a HRT of 48 hrs and sludge retention time (SRT) of 32 d. The oxygen for both aeration basins is supplied by four air blowers (with an installed capacity of 20,000 Nm^3/d each). The mixed liquor from the aerobic reactors is sent to the secondary clarifiers (two units in parallel, each one with a D = 65 m), with a HRT of 10 hrs. Finally, the final effluent is discharged into the Uruguay River.

After the secondary clarifiers, the settled sludge is separated into the return of activated sludge (RAS) and WAS. The RAS flow is returned to the aeration basin, whereas the WAS flow is directed to the dewatering process. The primary sludge treatment line begins at the sludge mixing tank (with a storage capacity of 500 m^3). Then, the sludge is treated in a primary dewatering unit with two screw presses with a total capacity of 33.8 TDS per day. After dewatering, the filtrate is returned to the screening section and the wet solids are transported to the final disposal and reuse site (forest plantations). The WAS that is directly sent to a separate section for WAS dewatering, a gravity filter followed by a centrifuge with a capacity of 17 TDS/d. Likewise, the filtrate from the primary sludge dewatering process is sent back to the screening unit, and the black liquor - sludge cake mixture is sent to dryer and then the dried sludge is transported to the landfill.

Based on the information about the performance of the plant, it can be concluded that the WWTP effluent complies with the standards regarding COD, BOD, TSS, AOX and TN, since concentrations of these parameters in the effluent are below the allowable standard values established by the local environmental regulations (MVOTMA, 1979). The TP, even though the removal efficiency is high, is the only observed parameter in which the WWTP operates at level just below the acceptable limit. As said before, the WWTP was not designed for nutrients removal. Usually pulp mill wastewater is deficient in nutrients (Mobius, 1991), (Kenny, 2009), (Kang et al., 2011), (Vashi et al., 2019b); therefore, in most of the occasions, nutrients need to be dosed to get an efficient biological removal of organic matter. However, at the evaluated pulp mill, in our study, the TP influent concentration is too high compared to others pulp mill in the world; due to the hardwood used to pulp production in Uruguay (Bentancur et al., 2020) and (Bentancur et al., 2021). Thus, even N is still needed to be added, P needs to be removed, rather than added.

Removal of TP has been very good in terms of the BAT for preventing and controlling industrial pollution, in an order of 40~66 % of maximal range prescribed by the BAT (range 0.01-0.04 kg/ADT). The TP discharge permit on a yearly basis was 0.02 kg/ADT until 2015, then to authorize the increased in the pulp production capacity (from 1.1 to 1.3 million tons) a new standard was set by the Uruguayan government to the UPM pulp mill with a new restriction in the TP permit limit for discharging into the Uruguay River; the new limit was set to 0.016 kg/ADT. The UPM WWTP long term average in 2022 was 0.012 kg/ADT (The Biofore Company UPM, 2023).

1.7.1 Recent developments at the UPM WWTP

In order to improve the WWTP performance in respect to TP removal, some changes were applied in 2015 in the treatment process such as the phosphorus precipitation process with lime treatment as shown in Figure 1.7.

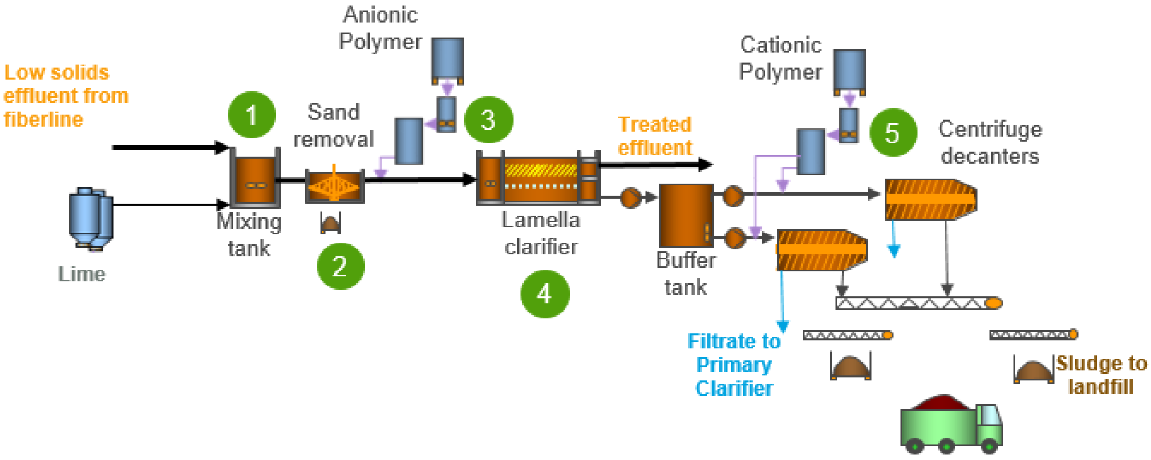


Figure 1.7 Phosphorous precipitation with lime process flow diagram

Where:

1. = rapid mixing of effluent from fibreline (acidic + alkaline) with hydrated lime
2. = sand removal
3. = anionic polymer addition followed by flocculation (slow mixing)
4. = laminar sedimentation
5. = water removal at decanter centrifuges with cationic polymer aid

The new process flow diagram of the WWTP is shown in Figure 1.8.

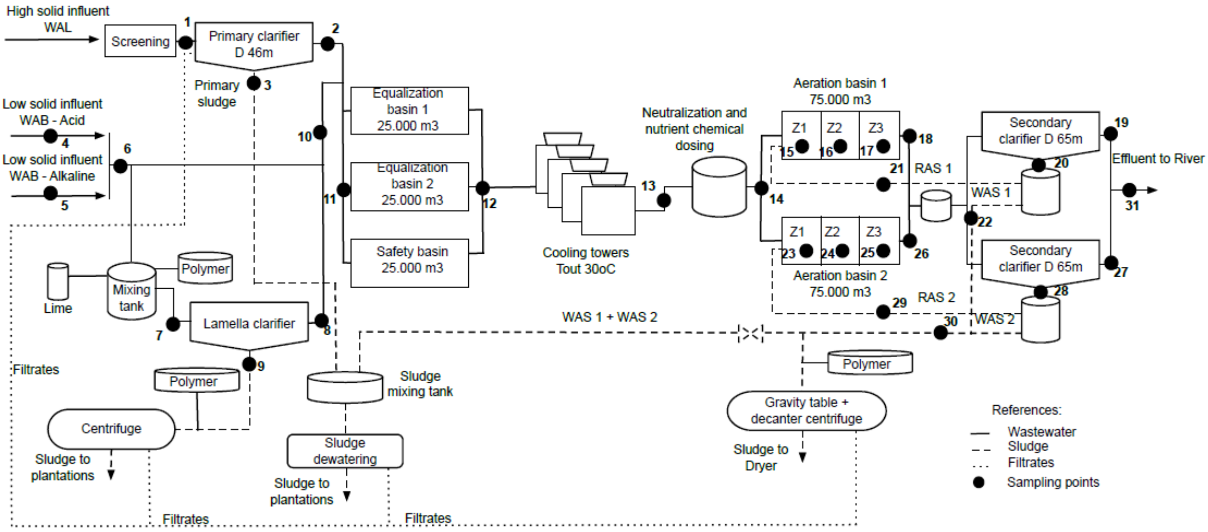


Figure 1.8 New process flow diagram of the UPM WWTP

The main difference with the previous process configuration diagram is the new part of chemical precipitation as pre-treatment in the WAB stream. This treatment is applied only to the low solids content line since it is the one with a higher concentration of TP (approximately 11 to 14 mg/L). The WAL line has an average TP concentration of 1.9 mg/L.

The WAB stream consists in two different streams:

1) Acid filtrate from A/D1 stage (acid stage + chlorine dioxide) with a flow of 30,240 m^3/d and a TP concentration of approximately 8 to 9 mgP/L.
2) Alkaline filtrate from peroxide and sodium hydroxide (Eop) with a flow of 12,960 m^3/d and a TP concentration of approximately 3 to 5 mgP/L.

The total stream is approximately 43,200 m^3/d (about two thirds of the influent flow to WWTP); however, the new pre-treatment system allows to treat the total or part of the stream depending on the TP needed to be removed.

The chemical pre-treatment (shown in Figure 1.8) includes a tank where lime is added; the influent pH is increased to about 10, and the phosphate is precipitated are removed in a clarifier. In addition to phosphate, part of organic matter, and other solids may also precipitate. This leads to a lower concentration of organic matter in the inlet to the aerobic reactor. The solids are transported to the final disposal site (landfill).

1.8 ALTERNATIVES TO IMPROVE PHOSPHORUS REMOVAL AT UPM WWTP

Development of technologies for phosphorus removal started in the 1970s in response to the issue of eutrophication and the need to reduce the levels of phosphorus affecting water bodies (Henze et al., 2008). Eutrophication has been one of the main environment concerns reported in recent decades (Clark et al., 1997; De-Bashan and Bashan, 2004; Bunce et al., 2018). The consequence of the eutrophication includes the following aspects: a diminution in the depth of water bodies, due to the progressive sedimentation; a green to brown colour in the water; a decrease in transparency; a decrease of the level of oxygen in the deeper zone; a greater amount of biomass, with the appearance of species that indicate the eutrophication such as Cyanophyceae or blue-green algae (Jiang and Graham, 1998; Lopez-Vazquez, 2009). The degree of eutrophication, and the several water quality problems, is largely dependent on the supply of nutrients, such as inorganic nitrogen and phosphorous (Albertson and Sherwood, 2011; Beretta-Blanco and Carrasco-Letelier, 2021).

In order to improve the TP removal at UPM WWTP some strategies need to be evaluated for meeting the environmental discharge standards. P removal can be achieved through biological, chemical or a combination of both techniques. Due to the popularity and worldwide application of the activated sludge systems, biological phosphorus removal is generally incorporated in those systems (Lopez-Vazquez, 2009). The advantages of biological over chemical P removal (high removal efficiency, economy, environmentally friendly operation, and potential phosphorus recovery (Lopez-Vazquez, 2009)) aroused the interest of scientists who continued studying and investigating about the enhanced biological phosphorus removal (EBPR) metabolic mechanisms, optimization process configurations, among other researches.

1.8.1 Enhanced biological phosphorus removal

The EBPR is the biological uptake and removal by activated sludge systems in excess of the amount of P required for growth of activated sludge (Metcalf and Eddy, 2003; Henze et al., 2008; van Loosdrecht et al., 2016; Chen et al., 2020). In the completely aerobic activated sludge system, the amount of P typically incorporated in the sludge mass is about 0.02 mgP/mgVSS. This can give a P removal of about 15-25 % of the P in many municipal wastewaters (Henze et al., 2008).

EBPR process can be implemented by incorporating an anaerobic stage at the beginning of the activated sludge system (van Loosdrecht et al., 2016). In this process, ordinary heterotrophic organisms (OHOs) and polyphosphate-accumulating organisms (PAOs) coexist (Henze et al., 2008). However, P removal is performed largely by PAOs that can incorporate higher amounts of phosphorus compared to OHOs (Henze et al., 2008). Therefore, PAO-enriched sludge will lead to greater P removal which can be reached by recirculating activated sludge from the secondary clarifier to the beginning of the anaerobic reactor (Inario, 2020). EBPR process can be achieved not only with an anaerobic followed by an aerobic but also with an anoxic stage (instead of the aerobic). This is possible due to the capacity of some PAOs, called denitrifying PAOs, to use nitrite or nitrate as an electron acceptor while under aerobic conditions they use oxygen (Oehmen et al., 2007).

In an EBPR activated sludge system, the amount of P incorporated in the sludge mass is increased from the normal value of 0.02 mgP/mgVSS to values around 0.06-0.15 mgP/mgVSS. This is achieved by system design or operational modifications that stimulate, in addition to the “ordinary” heterotrophic organisms present in activated sludge, the growth of organisms that can take up large quantities of P and store them internally in long chains called polyphosphates (polyP); generically these organisms are called phosphorus accumulating organisms (PAOs; sometimes also called polyphosphate accumulating organisms). PAOs can incorporate up to 0.38 mgP/mgVSS (Henze et al., 2008).

In the EBPR system both the OHOs and the PAOs coexist; the larger the proportion of PAOs that can be stimulated to grow in the system, the greater the percentage P content of the activated sludge and, accordingly, the larger the amount of P that can be removed from the influent. Thus, the challenge in design is to increase the amount of the PAOs relative to the OHOs present in the activated sludge as this will increase the capacity for P accumulation and thereby the P removal efficiency (Henze et al., 2008). The relative proportion of the two organism groups depends, to a large degree, on the fraction of the influent wastewater biodegradable COD that each organism group obtains (Henze et al., 2008).

The processes are described assuming that the influent entering the anaerobic stage contains volatile fatty acids (VFA) or that these are produced by fermentation (Lopez-Vazquez, 2009) (Chen et al., 2020). The metabolism of PAOs, is described below. The first stage in an EBPR process takes place in the anaerobic reactor. Under anaerobic conditions, PAOs use rapidly biodegradable chemical oxygen demand (RBCOD) as carbon source mainly volatile fatty acids (VFA) such as acetate and propionate that come with the influent or are synthesised by fermentative microorganisms and store them as poly-β-hydroxy-alkanoates (PHA) (Lopez-Vazquez, 2009). PHAs are carbon polymers usually poly-β-hydroxybutyrate (PHB), poly-hydroxyvalerate (PHV) or poly-β-hydroxy-2-methylvalerate (PH2MV) and the amount of each one will depend on the composition of the VFAs (van Loosdrecht et al., 2016). In addition, larger amounts of acetate lead favours PHB while propionate favours PHV and PH2VM (Oehmen et al., 2005b).

To achieve the biotransformation from VFA to PHA, PAOs use glycogen and poly- P that have stored intracellularly. Glycogen is used as reducing power (and also provides energy) and Poly-P is hydrolysed in order to produce energy as ATP. As a result of the hydrolysis orthophosphate (PO_4^{3-}) is released into the bulk liquid (van Loosdrecht et al., 2016).

The RAS recirculation in the activated sludge system from the settling stage to the anaerobic reactor enriches the anaerobic stage with PAOs and therefore the P removal will be better performed.

As mentioned at the beginning of this section the anaerobic stage may be preceded by either an aerobic or anoxic stage. In an anoxic stage denitrifying polyphosphate-accumulating organisms (DPAOs) are capable to uptake orthophosphate using nitrite or nitrate instead of oxygen as an electron acceptor (van Loosdrecht et al., 2016). In the aerobic stage, PAOs uptake and store the PO4. Oxygen is utilized as the electron acceptor and the carbon and energy source comes from PHA and the energy released will be used for PO_4^{3-} uptake and storage (van Loosdrecht et al., 2016). The PHA is also used for the growth of new biomass, glycogen replenishment and to supply PAOs with the energy needed for maintenance in the aerobic stage (van Loosdrecht et al., 2016).

In the final stage of the activated sludge system, the PAOs (with stored polyphosphate) are removed from the system by the WAS (Chen et al., 2020). A conceptual scheme of the EBPR process in an activated sludge system can be seen in Figure 1.9.

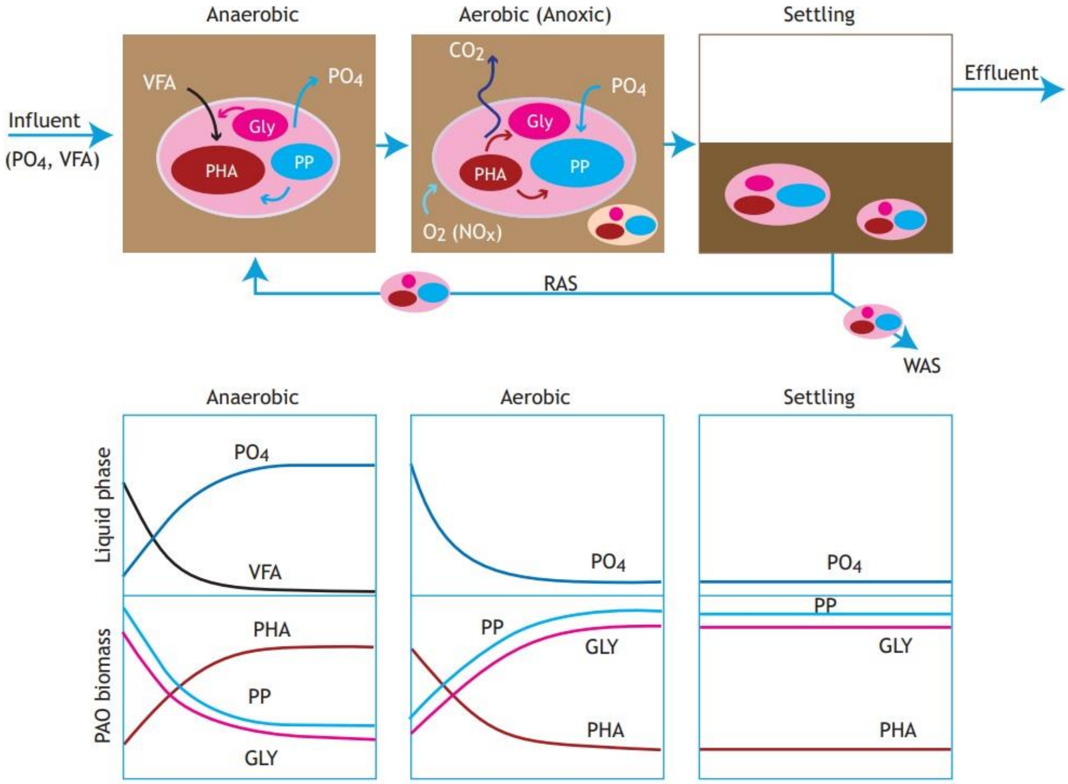
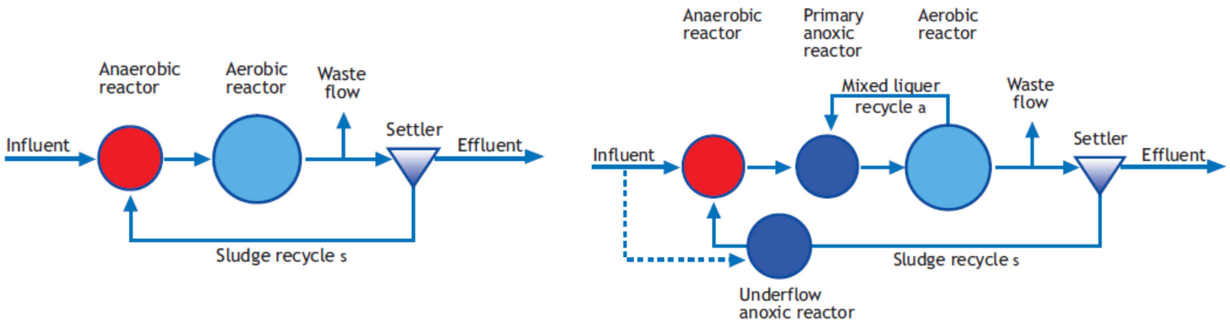


Figure 1.9 Activity of PAOs in an EBPR process (van Loosdrecht et al., 2016)

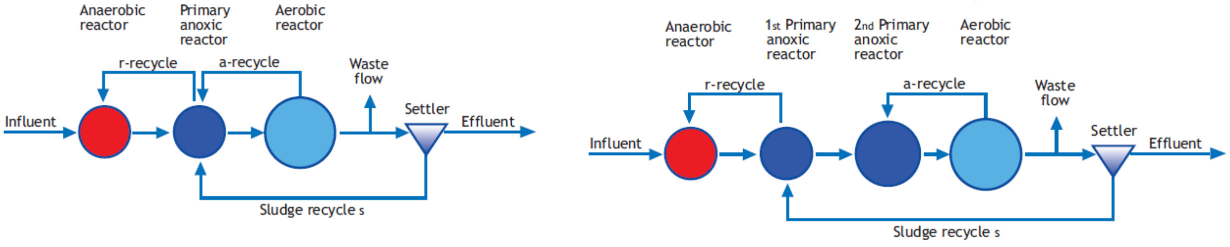
There are several EBPR configurations that have been developed over the years in order to optimize and improve the process. The main principles applied are (Henze et al., 2008):

- minimization of oxygen in the anaerobic reactor as well as nitrate or nitrite;
- maximization of the uptake of VFA by PAOs;
- minimization of the presence of particulate P in the effluent; and
- maximization of P uptake for the synthesis of biomass.

Considering that nitrogen removal is not required for the aim of this research, configurations with anoxic zones are not taken into account for denitrification. However, denitrification can be considered in order to avoid the recirculation of nitrates through the underflow sludge recycle. Figure 1.10 shows potential configurations that could be applied to a pulp mill WWTP. The basic configuration for an EBPR process consists of an anaerobic stage at the beginning of the activated sludge system, as mentioned in previous sections. To minimise the nitrate (and nitrite) entrainment in the anaerobic reactor different configurations were developed. To this end, an anaerobic-aerobic configuration (Phorodex (A/O)) can be improved by inserting an anoxic reactor in which aerobic sludge is recirculated for denitrification (e.g. Johannesburg (JHB)), or via an anoxic reactor located downstream of the anaerobic zone from where another internal recirculation to the anaerobic reactor is located (e.g. UCT configuration) (Henze et al., 2008). Also, this anoxic reactor can be divided in two to provide return sludge denitrification in the first one and aerobic sludge denitrification in the downstream anoxic reactor (e.g. MUCT configuration) (Henze et al., 2008).



(A) Phorodex (A/O) **(B) Johannesburg (JHB)**



(C) UCT (VIP) **(D) Modified UCT (MUCT)**

Figure 1.10 Configurations for biological P removal, (A) Phoredox, (B)Johannesburg, (C) UCT (VIP) and (D) MUCT. Adopted from (Henze et al., 2008)

The main microorganisms that are associated with P removal system are:

OHOs: that do not have the capability to accumulate intracellular polyphosphate as PAOs do, and therefore the low contribution to P removal in an EBPR process. OHOs are not able to uptake VFAs in the anaerobic phase due to the lack of an electron acceptor (oxygen or nitrate) in this stage (Henze et al.,2008).

PAOs: that in addition to Accumulibacter, another genus of PAO can be observed in full-scale EBPR systems: Tetrasphaera. The presence of Tetrasphaera has been studied over the recent years but with special emphasis on the carbon source that it is able to utilize, the intracellular compounds it can store, among others (Liu et al., 2019). Fernando et al. (2019) studied the presence of PAOs and glycogen-accumulating organisms (GAOs) in full-scale systems in 18 Danish WWTP and found that Tetrasphaera was the most abundant genus regarding PAOs. In addition, a number of studies have been carried out in order to evaluate the abundance of Tetrasphaera in full-scale WWTPs, including domestic as well as industrial wastewater, corroborating the importance of this genus (Liu et al., 2019).

Another type of organisms that can exist in EBPR systems are the GAOs. It was Fukase et al. (1985) who first reported the presence of these organisms which have similarities in their metabolism with PAOs. Crocetti et al. (2002) identified GAOs using sequencing batch reactor (SBR) and named them as “Candidatus Competibacter Phosphatis” usually referred to as Competibacter. These organisms compete with PAOs for the uptake of volatile fatty acids under anaerobic conditions (Oehmen et al., 2005a) using glycogen as energy and carbon source and store VFAs as PHAs (Oehmen et al., 2007). Under aerobic conditions, GAOs can oxidise PHA leading to biomass growth and replenishment of glycogen. However, the accumulation of polyphosphate was not observed in the aerobic stage. Therefore, the presence of GAOs in EBPR systems is a disadvantage since they are not capable to remove P (Oehmen et al., 2007). Studies were carried out in full-scale EBPR systems where it was reported the presence of GAOs (Oehmen et al., 2007). In addition, it was found that the VFA requirements in the anaerobic stage are higher if GAOs are present (Oehmen et al., 2007). In conclusion, GAOs are not favourable in EBPR systems since they compete with PAOs for the carbon substrate and do not contribute to P removal, is that is important to develop favourable conditions for the growth of PAOs over GAOs.

By controlling the competition and minimizing the growth of GAOs over PAOs the P effluent concentrations will be minimised. Some of the factors that affect these organisms are the carbon source, temperature, pH, dissolved oxygen, toxic compounds, among others.

The biological removal of P, through certain processes such as the EBPR, is the most studied and applied in the world, being able to achieve discharge values lower than 1 mg/L (De Haas et al., 2000; Lopez-Vazquez et al., 2008; Lopez-Vazquez, 2009). EBPR can be very effective, but there are still some disadvantages, mostly the higher construction and operating costs, and the highly sophisticated operation required (Zhen-hua and Kai, 2011). For industrial applications, and particularly in the pulp and paper industry, its implementation is still a challenge since the effluents contain complex and diverse harmful compounds, such as resin acids and sterols (Lindholm-Lehto et al., 2015b). Besides, the temperatures higher than 30 °C that may jeopardize the performance of the EBPR process (Lopez-Vazquez et al., 2008; Kazadi Mbamba et al., 2019).

1.8.2 Chemical phosphorus removal

Sometimes, chemical phosphorus removal is supplementing the EBPR (or completely replacing the EBPR) in cases where the influent phosphorus concentration is too high, or the influent characteristics are not supporting the sufficient EBPR (e.g. due to low concentration of readily biodegradable organic substrate such as volatile fatty acids in the influent). Added chemicals convert soluble and colloidal phosphorous into insoluble precipitable material (Albertson and Sherwood, 2011).

Chemical coagulation and chemical precipitation are the two main chemical processes applied in wastewater treatment for chemical phosphorus removal. However, the organic environment of the wastewater is complex and a combination of reactions can occur; likely, consisting of coagulants and phosphate complexation through an oxygen atom, precipitation of hydroxides, co-precipitation, adsorption, diffusion, and coagulation and flocculation processes (Takács, 2008; Szabó et al., 2008). Coagulation is an established process which consists of the destabilization of colloidal particles so that particle growth can occur as a result of particle collisions (Jiang and Graham, 1998). Chemical precipitation involves the addition of chemicals to alter the physical state of dissolved and suspended solids and facilitate their removal by sedimentation (Metcalf and Eddy, 2003).

The chemical precipitation of phosphorus involves the addition of the salts of multivalent metal ions to modify the physical state of dissolved and suspended solids, causing precipitation of an insoluble metal phosphate in a certain pH range that is settled out by sedimentation (Morse et al., 1998). The precipitation of phosphorous can be applied in several different locations during wastewater treatment as follows: (i) pre-precipitation is where the chemical is dosed before primary sedimentation and the phosphorus is removed with the primary sludge; (ii) co-precipitation is where the chemical is dosed directly to the biological tank of an activated sludge process and phosphate removed with secondary excess sludge; (iii) post-precipitation is where dosing follows secondary treatment; although a high-quality effluent can be produced, this third option is not generally favored because of high chemical costs and the creation of an additional, chemical, tertiary sludge, and the need for the additional settling tank for chemical sludge (Morse et al., 1998).

1.9 ACTIVATED SLUDGE MODELS

Modelling of AS processes has been developed with the intention to generate a platform with a common language that can be used in different ways to (i) get to assess the actual wastewater treatment plant performance, (ii) evaluate possible scenarios for upgrading, (iii) design a new plant, (iv) develop new control strategies, (v) provide training and (vi) provide inputs for management decisions (Henze et al., 2008).

In 1982 a task group on mathematical modelling for design and operation of activated sludge process was established by the International Association on Water Pollution Research and Control (IAWPRC) (Henze et al., 2000). In 1987, the ASM1 model was published, which is a simple model that describes carbon oxidation and nitrogen removal. This model has been widely used in several modelling studies of full-scale wastewater treatment plants and is the base for further model development (Henze et al., 2000). A matrix notation was introduced with the ASM1 model that facilitates the communication of complex models and allows the discussion about important aspects as biokinetic modelling (Henze et al., 2000).

From the mid-1980s to the mid-1990s, the biological phosphorus removal process was widely used in a full-scale wastewater treatment plant. This led to the need to include additional components and processes to describe the biological phosphorus removal (Henze et al., 2000) and in 1995 the ASM2 model was published. This model includes nitrogen and biological phosphorus removal. However, as denitrification in relation to biological phosphorus removal was not clear, it was not included in the ASM2 model. In 1999, the ASM2 model was extended and rebranded as ASM2d and the denitrifying PAOs were included.

With the recent developments and understanding of the AS process the task group in 1998 decided to develop an ASM3 model (Henze et al., 2000), which was established in order to correct defects recognized in ASM1. The main differences between the two models are the role of storage polymers and the change of the growth- decay-growth model to growth-endogenous respiration model in the ASM3 (Keskitalo and Leiviskä, 2010).

Over the last years, modelling of activated sludge systems has become a usual practice for design, control, teaching and research (Henze et al., 2000). It was designed for municipal wastewater treatment plants and has been widely and successfully used also for industrial wastewater treatment (Keskitalo and Leiviskä, 2010).

1.9.1 Activated sludge models' applications in pulp and paper mills WWTP

As described by Lindblom et al. (2004), a new model for nutrient deficit aerobic COD removal was developed and applied to the Stora Enso Hylte mill in Sweden. The model was based in ASM1 and extended to add the role of phosphorus in the biological aerobic growth and role of higher-order organisms. Nutrient limitations were included using

Monod functions. Autotrophic organisms were omitted. A measurement campaign was carried out in the WWTP for model calibration and validation. The model was used to achieve an optimal dosage of nutrient and found appropriate operating conditions regarding SRT. As a conclusion, the experience in the WWTP with the ASM1 model was successful.

According to Barañao & Hall, (2004) the treatment of effluent from a mechanical pulp and paper mill located in Port Alberni, Canada, was modelled by ASM3. The high COD concentration and the high content of readily biodegradable substrates of the wastewater from pulp and paper mill make the ASM3 model appropriate for this system. Using fresh wastewater and sludge from the mill, a series of respirometric test and analytical measurements of COD, TSS and volatile suspended solids (VSS) were carried out and the ASM3 model was calibrated. As explained in (Barañao and Hall, 2004), ASM3 was selected mainly because it includes the accumulation of storage products inside the cell. Accordingly, ASM3 has been recommended for wastewater treatment plants treating industrial wastewater with a high concentration of COD, where the storage of readily biodegradable organics is a dominant process. Based on the model, it was found that the content of readily biodegradable substrates was an important factor that made ASM3 suitable for modelling the effluent from pulp and paper mills (Barañao and Hall, 2004).

A modelling case study of Stora Enso Fine Paper Oulu bleached Kraft pulp mill wastewater treatment plant with a modified ASM1 was presented by Keskitalo and Leiviskä, (2010). The applied model was a modified ASM1 introduced by Lindblom et al., (2004) and the objective was the calibration and validation of the model by means of the long-term simulation of full-scale WWTP. The model was simplified omitting the biological nitrogen removal by the process of nitrification and denitrification. Due to the nutrient deficient wastewater, growth limiting effects on heterotrophic bacteria from N and P were included in the model. The model was able to describe the treatment plant behaviour in terms of some of the key effluent parameters, COD, N and P, when influent measurements from the process data were used as inputs to the model (Keskitalo and Leiviskä, 2010).

In this research a steady-state model was carried out (Ekama and Wentzel, 2008) to calculate both the aerobic degradation of organic matter, as well as the nutrients (P and N) requirements. This steady-state model was performed before setting up the hydraulic model of the plant built and structured using the BioWin software/simulator. BioWin developed its own integrated activated sludge/anaerobic digestion (AS/AD) model which is applied in the software (EnviroSim Associates Ltd.). This model is a combination of the models ASM1, ASM2d, and ASM3 published by the International Water Association (IWA) incorporating the anaerobic digestion model (ADM) as well (Elawwad et al., 2019).

1.10 PHOSPHORUS RECOVERY

An increasing interest for the recovery and reuse of resources from sludge waste has been seen in recent years, largely due to environmental and political considerations (Stark, 2004). Several pilot-plant studies and lab-scale experiments are performed around Europe (Stark, 2004). The Netherlands, where the environment regulations are the most stringent in Europe, is among the pioneer countries in the field of phosphorus recovery from sludge with experiments performed in full-scale plants at municipal WWTPs (Stark, 2004).

According to Shu et al., (2006) phosphorus can be recovered from wastewater through crystallization of struvite, $MgNH_4PO_4.6H_2O$. Struvite precipitates spontaneously in wastewater treatment environments when high concentrations of soluble phosphorus and ammonium are present (De-Bashan and Bashan, 2004). Other essential conditions needed are a low concentration of suspended solids and a pH higher than 7.5 (De-Bashan and Bashan, 2004). The precipitation of struvite requires that the reactants are simultaneously available in the wastewater in a molecular ratio of $1(Mg^{2+}):1(NH_4^+):1(PO_4^{3-})$ (De-Bashan and Bashan, 2004). Often, municipal wastewaters and others tend to be rich in ammonium, but deficient in magnesium. So, the addition of magnesium is required, contributing to increase the pH of the solution (De-Bashan and Bashan, 2004). The struvite production rate, a very important parameter for reactor design and efficiency estimation, increases with the concentration of struvite and mixing intensity in the reactor (Yoshino et al., 2003).

Approximately, 1 kg of struvite can be crystallized from 100 m^3 of wastewater (Shu et al., 2006). The struvite produced annually from a wastewater treatment plant that treats 100 m^3/d would be sufficient to apply on 2.6 has of arable land at an application rate of 40 kg phosphorus as P_2O_5/ha/yr as fertilizer (Shu et al., 2006).

1.11 RESEARCH QUESTION

The main research question of the present study is:

What operational conditions and alternative(s) can be modified or implemented to enhance the performance and efficiency of UPM WWTP regarding phosphorus discharges to reduce the amount of P entering surface waters?

1.12 RESEARCH OBJECTIVES

The main objective of this research is to investigate and assess the performance of the most relevant physico-chemical and biological processes at the WWTP UPM, and to evaluate different operational and configuration alternatives to enhance the overall plant performance with emphasis on the chemical phosphorus removal process.

The specific objectives include:

1. To apply steady-state mathematical modelling to describe the current performance of the UPM wastewater treatment plant.
2. Through the application of mathematical modelling, to evaluate the current operational parameters of the plant and verify their optimal values to enhance (chemical) phosphorus removal.
3. To evaluate different configuration alternatives to enhance the phosphorus removal efficiency of the plant (using mathematical modelling) and to evaluate resource recovery potential such as biogas and struvite.
4. To evaluate the chemical P removal process proposed by UPM and understand how other operational factors (like the dosage and type of chemicals, pH, time and mixing intensity) affect the chemical P removal process.
5. To evaluate different alternatives for chemical P removal, such as a co- and post-precipitation using $Ca(OH)_2$, $Al_2(SO_4)_3$ and $FeCl_3$, in a lab-scale biological reactor operated at similar conditions to those applied at the full-scale WWTP.

1.13 HYPOTESES

The UPM WWTP performance regarding the effluent quality can be improved to comply with the discharge standards by means of the following operational parameters and/or configuration modifications:

- Reducing the sludge retention time (more active biomass may be produced; therefore, incorporating more P into the cells and reducing the P concentration in the effluent).
- Changing the biological reactor zones, implementing one anaerobic zone before the aerobic zone to promote enhanced biological phosphorus removal.
- Implementing chemical phosphorus removal and filtration as post-treatment.

The efficiency of the chemical P removal process using $Ca(OH)_2$ as coagulant can be improved changing the pH, time and mixing intensity. At the same time, the use of $FeCl_3$ as coagulant will be a good alternative for P removal because iron reacts to form $FePO_4$ which is insoluble under specific pH conditions. Furthermore, the use of $FeCl_3$ will not generate incrustations in the facilities of the WWTP as it happens currently with $Ca(OH)_2$.

1.14 RESEARCH APPROACH

To achieve the research objectives presented above different research phases were carried out. The main general phases are shown in Figure 1.11 and a brief description of the approach is presented below.

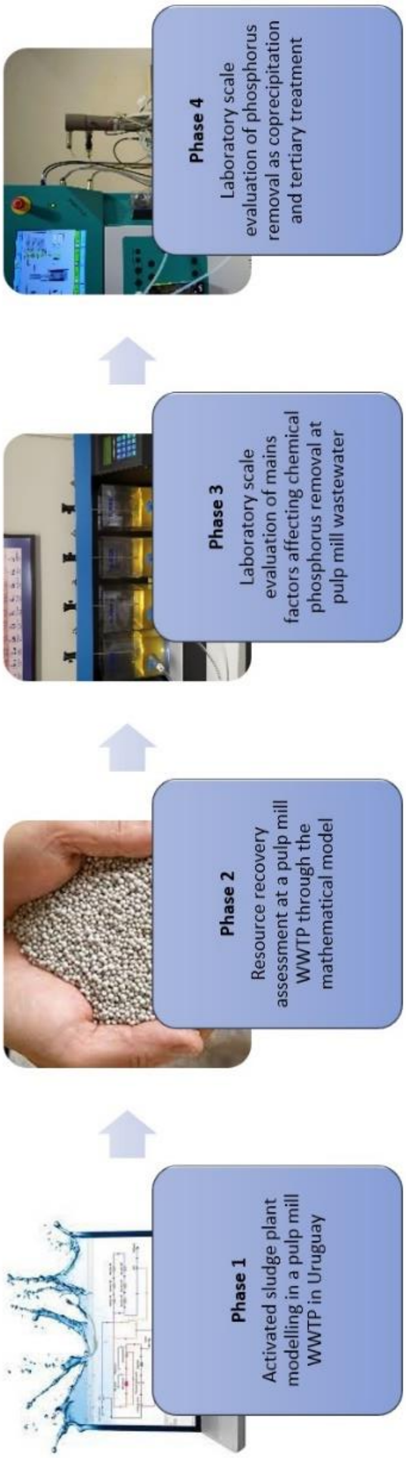


Figure 1.11. Research approach flow diagram

The phase 1 consists in activated sludge plant modelling, to address specific objectives 1 and 2. This stage involves several activities to obtain a model that is representative of the UPM WWTP and in this way to enable the evaluation of different options for improving the performance of the plant. The following parts are considered: project definition, data collection and evaluation, model structure, wastewater characterization, steady-state model, model calibration, model validation and modelling scenario study (Meijer and Brdjanovic, 2012).

In phase 2, the focus was on specific objective 3, once the activated sludge model of the WWTP is ready, the recovery of resources is evaluated, such as energy generation (biogas) through an anaerobic sludge digester and generation of struvite as a potential fertilizer.

To assess the chemical P-removal processes in the third phase, addressing specific objective 4, a jar tests was carried out in order to evaluate how operational factors (like the dosage and type of chemical, pH, time and mixing intensity) affect the chemical P removal process.

In the last phase, the attention was on specific objective 5, at laboratory scale, the removal of phosphorus from pulp mill wastewater was evaluated as co-precipitation and such as post-treatment with three different precipitating agents: $Ca(OH)_2$, $Al_2(SO_4)_3$ and $FeCl_3$.

This approach contributes to an enhanced understanding of the UPM WWTP's performance and provides valuable insights for optimizing phosphorus removal processes and overall plant efficiency.

1.15 OUTLINE OF THE THESIS

This thesis is divided into six chapters. The graphical representation of the thesis structure is shown in Figure 1.12.

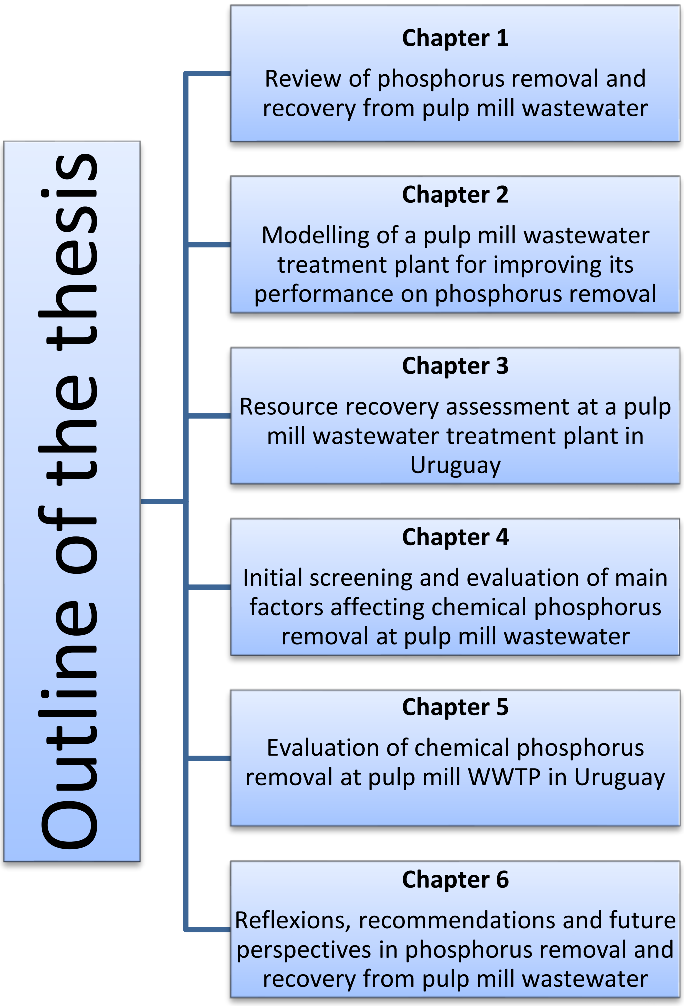


Figure 1.12. Structure of the thesis

The first chapter provides a general introduction to the research topic. It includes a briefly description of UPM manufacturing processes, phosphorus in aquatic environment, main chemical treatments for P removal from wastewater, background, and problem statement in the UPM WWTP, research objectives, hypothesis, and research approach.

The second chapter present the modelling of a pulp mill wastewater treatment plant for improving its performance on phosphorus removal using the software BioWin. While the third chapter present the resource recovery assessment at a pulp mill wastewater treatment plant in Uruguay based on the mathematical model.

Chapter four consist of screening and evaluation of main factors affecting chemical phosphorus removal at pulp mill wastewater; and chapter five describe the evaluation of chemical phosphorus removal from pulp mill wastewater at laboratory scale biological reactor.

The final chapter concludes and summarizes the findings of this research and provides further recommendations and perspectives on the subject.

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2

MODELLING OF A PULP MILL WASTEWATER TREATMENT PLANT FOR IMPROVING ITS PERFORMANCE ON PHOSPHORUS REMOVAL

This chapter is based on: Bentancur, S., López-Vázquez, C. M., García, H. A., Duarte, M., Travers, D., & Brdjanovic, D. Modelling of a pulp mill wastewater treatment plant for improving its performance on phosphorus removal. Process Safety Environmental. Protection, 146, 208–219 (2021).

ABSTRACT

The performance of a pulp mill wastewater treatment plant (WWTP) was assessed using the software BioWin aiming at providing alternatives for reducing even further the phosphorus (P) concentration in the effluent. The WWTP was designed without nutrient removal capacities, since pulp and paper wastewater are usually deficient in nutrients. However, the hard wood (eucalyptus) which is processed in such plant has a higher P content compared to other types of woods, and part of that P ended up in the raw wastewater to be treated. The wastewater was characterized following the Dutch STOWA protocol. Once the model was calibrated, historical data from different periods of time was used to validate the model. The model was able to describe the current plant operation, as well as its historical performance. Moreover, the model was used to evaluate different potential upgrading scenarios for the treatment plant aiming at increasing the plant performance on P removal. According to the model, the implementation of an anaerobic phase prior to the aerobic process showed to be a feasible scenario contributing to decrease the total phosphorus (TP) concentration in the effluent by approximately 58 %. In addition, applying chemical precipitation can further decrease the TP concentration below 0.1mg/L. However, further research activities such as pilot-testing may be needed to validate the previous recommendations of applying enhance biological and chemical P removal at such pulp mill wastewater treatment plant.

2.1 INTRODUCTION

A pulp mill located in Uruguay uses the chemical Kraft process to produce 1.1 million tons of fully bleached eucalyptus market pulp per year. The effluents generated in the pulp mill (mostly from the bleaching process) are treated in a WWTP composed of a conventional activated sludge (CAS) system with an installed capacity to treat approximately 73,000 m3/day. Originally, the CAS system was designed only to remove suspended solids and organic matter. Despite this, it operates reaching removal efficiencies of 81, 80, 86, and 97 % with regard to chemical oxygen demand (COD), TP, total nitrogen (TN), and total suspended solids (TSS), respectively. Occasionally, the P concentrations in the effluent reached values close to the discharge limit of 74 kg TP/d as a monthly load average. This deserves paying particular attention due to the strict discharge limits imposed to such industry. The CAS process is widely used around the world to treat pulp and paper mill effluents (Ashrafi et al., 2015a; Kamali and Khodaparast, 2015; Elsergany et al., 2015; Toczyłowska-Maminska, 2017). Nonetheless, nutrients such as nitrogen (N) and P need to be dosed for sustaining the wastewater treatment biological processes (Mobius, 1991; Kenny, 2009; Kang et al., 2011; Vashi et al., 2019). However, at the pulp mill WWTP of study, the hard wood used as raw material has a different P composition compared to other hard woods processed elsewhere (in terms of chemical structure and content), and some of that Pends up in the produced wastewater. Consequently, rather than dosing P as in most pulp and paper mill WWTPs, additional strategies need to be implemented to achieve P-removal and meeting the discharge standards. The presence of P in the produced wastewater introduces changes in the biological P-assimilation processes at this specific pulp mill WWTP compared to other CAS plants from the same industrial sector. Municipal CAS systems modelling has become a useful tool and well-established practice supported by several robust models developed over the years (e.g., for plant-wide modelling applications). Despite the broad application of mathematical models, there is still a limited number of studies regarding mathematical modelling of pulp and paper mill WWTPs; particularly, with respect to models that can describe the performance of pulp mill WWTPs with different P-assimilation and P-removal performances as observed in conventional WWTPs. Either the results on existent models are confidential (being only available for the industries themselves), or not enough research has been carried out on this field. The few modelling studies of pulp and paper mill WWTPs available in the literature have focused on (i) the development of a modified Activated Sludge Model No 1 (ASM1) with P- and N-limited heterotrophic growth for nutrient deficient aerobic COD removal(Lindblom et al., 2004); (ii) the use of Activated Sludge Model No3 (ASM3) on a mechanical pulp and paper mill to model an activated sludge system treating effluents with high COD concentration and high content of readily biodegradable substrates (Barañao and Hall, 2004); and (iii) a case-study with a modified ASM1 of a Stora Enso Fine Paper Oulu bleached Kraft pulp mill WWTP. The primary interest in carrying out the previously described models for the pulp mill WWTPs was to achieve an accurate prediction of the COD and nutrient removal processes. Since the wastewater at the evaluated plants were known to be nutrient deficient, growth limiting effects on heterotrophic bacteria cause by the lower N and P concentrations available in the influent were included in such models (Keskitalo and Leiviskä, 2010). In those plants, mostly soft woods were processed and consequently the P and N content in the effluents were rather low, requiring dosing urea and phosphoric acid to cover the nutrient biological growth requirements. In the pulp mill WWTP of study located in Uruguay, urea was also needed to be dosed due to the lack of N. However, the hard wood used as raw material (mainly eucalyptus grandis) had a higher P content that exceeds the biomass growth requirements and which excess needed to be removed to meet the effluent discharge standards. Instead of dosing P in such pulp mill WWTP in Uruguay, P needs to be removed. Therefore, additional strategies for P-removal are needed to be implemented and evaluated for meeting the environmental discharge standards. A mathematical model that can describe the actual performance of such pulp mill WWTP (considering the different P-assimilation and P-removal mechanisms) can be later used to predict the performance of the proposed additional strategies for P-removal. Additional strategies for P-removal include the implementation of either biological or chemical P-removal processes. When considering biological P removal, the environmental conditions in the biological reactor are designed in such a way that a specific group of heterotrophic organisms (known as poly-phosphate accumulating organisms, PAOs) can grow in the activated sludge reactor. Due to the capacity of PAOs to accumulate polyphosphates, these organisms have a much higher P content than the ordinary heterotrophic organisms (OHOs). Therefore, wasting a fraction of such sludge rich in PAOs at the wastewater treatment plant contributes to reduce the P content in the effluent. Regarding the chemical P removal, the chemical precipitation of P involves the addition of salts of multivalent metal ions causing the precipitation of insoluble metal phosphates in a certain pH range subsequent settled out by sedimentation (Morse et al.,1998). Iron chloride, aluminium chloride, or sulphates are usually used as the multivalent metal ions salts; they are dosed either to the influent (pre-precipitation), the activated sludge reactor (simultaneous precipitation), or to the final effluent (post-precipitation) to achieve the chemical precipitation of P (Henze et al., 2008). The multivalent metal ions salts commonly used for chemical P removal are also widely used in water and wastewater treatment processes for the removal of particles by a chemical coagulation/flocculation process. Coagulation/flocculation is the process of destabilizing colloidal particles, so that particle growth can occur as a result of particle collisions (Metcalf & Eddy, 2014). Particularly, at a specific combination/range of pH and concentration of the multivalent metal ions salt, a process known as sweep coagulation may occur. Sweep coagulation involves the precipitation of salts that entrained or swept down other colloidal particles as they settle in the suspension. For instance, such range of conditions with iron occurs in a pH range between 6.0 and 10.0 and with a very high iron dose of between 2.7–270 mg/L (Metcalf & Eddy, 2014). Therefore, the chemical P-removal process may occur simultaneously with other processes such as coagulation/flocculation (and particularly sweep coagulation) enhancing P-removal from the treated wastewater. The different type of eucalyptus processed at the evaluated pulp mill generates a wastewater with different characteristic compared to other paper and pulp mills worldwide; particularly, regarding the TP content on such wastewater. Some modelling attempts have been carried out on paper and pulp wastewater; however, none of such models include the characteristics of pulp mill wastewater with a higher than usual P content. Usually, P is dosed at conventional pulp and paper WWTPs to satisfy the nutrient needs for a healthy biological wastewater treatment process. In this study, P needs to be removed rather than dose. That completely modified the structure of the existent mathematical models as well as their calibration and validation processes. Without a validated model, it is not possible to predict future scenarios for evaluating additional alternatives for P removal such as the implementation of biological and/or chemical P removal. This research addressed those needs directly. This study aimed at describing the operation and performance of a pulp mill WWTP with different P-assimilation and P-removal performance. The final goal of this research was to obtain a model of such WWTP by the aid of the software BioWin with the main purpose of demonstrating and securing the satisfactory compliance of the effluent produced at the local WWTP with the effluent standards set by the local authorities, and to assess different upgrading scenarios to optimize the P-removal process.

2.2 MATERIALS AND METHODS

2.2.1 WWTP configuration

A WWTP schematic is shown in Figure 2.1. The configuration of the WWTP was determined by conducting several visits at the site and by evaluating the WWTP designed documents provided by the company. The details of such evaluations are presented in the results and discussion Section 2.3.1 WWTP configuration.

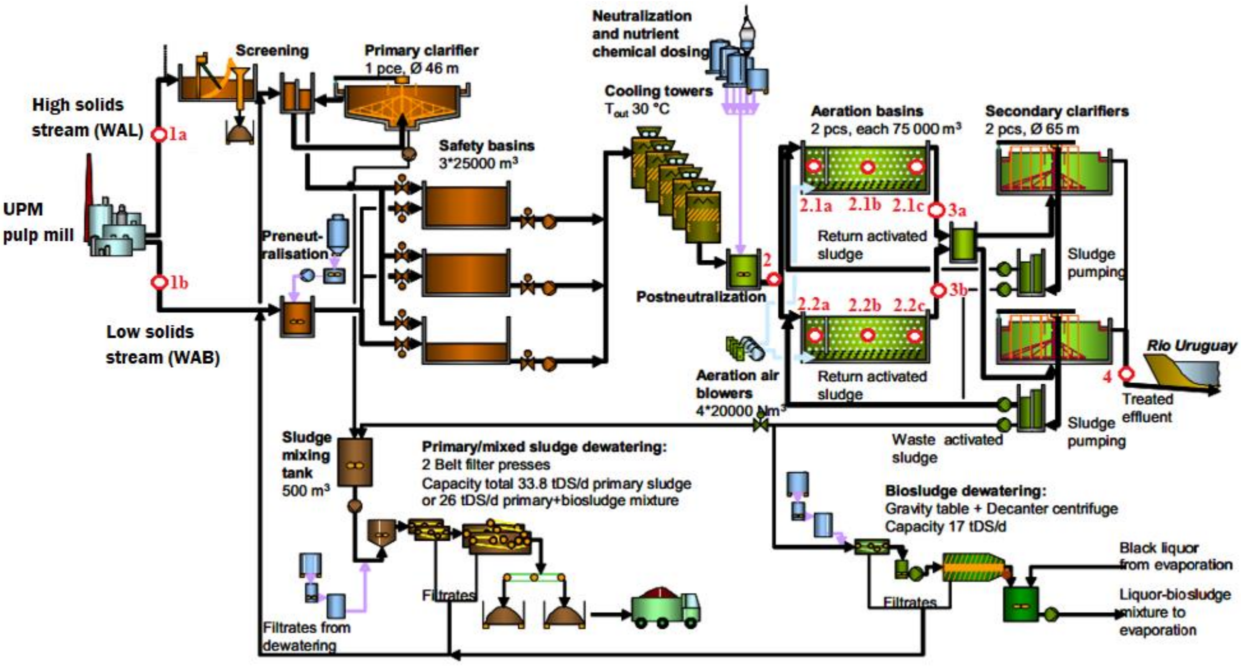

Figure 2.1 Process flow diagram of the pulp mill WWTP. The location of the sampling points carried out for the sampling campaign are indicated in the figure

2.2.2 Data collection, preliminary characterization, and WWTP evaluation

The operation and performance of each component of the WWTP were analysed using historical data considering the period from May to December 2013. The historical data was used to make a preliminary model of the plant. With the aim of evaluating the historical data obtained at the WWTP, different mass balances were executed on the following parameters: water flow, suspended solids, COD, TN and TP.

2.2.3 Wastewater fractionation and characterization

A sampling campaign was designed and implemented. The sampling campaign was carried out from October 21st to 28th, 2013.The wastewater characterizations, as well as the COD fractionation were conducted following the protocol for wastewater characterization of the Dutch Foundation for Applied Water Research (STOWA) (Roeleveld and Van Loosdrecht, 2002). Moreover, the determination of the influent and effluent flowrates was carried out simultaneously with the sampling campaign. To characterize the raw and treated wastewater, 24 h representative composite samples were collected during five consecutive days. The location of the sampling points is shown in Figure 2.1. The sampling locations were as follows: (i) the high solids content stream before screening (sampling point 1a) and the low solids content stream before pre-neutralization (sampling point 1b); (ii) after the cooling towers and just before the aeration basins (sampling point 2); (iii) along the aeration basins (sampling points 2.1a, 2.1b, and 2.1c); (iv) after the aeration basins (sampling points 3a and 3b); and (v) at the final point where the effluent from the WWTP go to the Uruguay River (sampling point 4). Parameters such as total COD, TN, TP, TSS, volatile suspended solids (VSS) and inorganic suspended solids (ISS) were determined at the laboratory facilities at the pulp mill. The analytical procedures for the determination of parameters were performed following standardized and commonly applied analytical protocols described in the Standard Methods (American Public Health Association (APHA) et al., 2012) as follows: COD (Standard Methods5220 D), TN (Standard Methods 4500-N C), TP (Standard Methods4500-P E), TSS (Standard Methods 2540 D), VSS (Standard Methods APHA 2540-E), and ISS (Standard Methods APHA 4500-E).The rest of the parameters (including nitrite (NO_2^-), nitrate(NO_3^-), ammonia (NH_4^+), biochemical oxygen demand (BOD_{10}) and orthophosphate (PO_4^{3-}) were outsourced to the Technological Laboratory of Uruguay (LATU, Uruguay). The influent BOD_{10} was also determined to estimate the total BOD using the equation and BOD-curve detailed in Roeleveld and Van Loosdrecht (2002). Typical fractions and conversion factors presented in (Roeleveld and Van Loosdrecht 2002) were used for N and P characterization.

2.2.4 Steady-state model and aerobic batch activity tests

A steady-state model was carried out (Ekama and Wentzel,2008) to calculate both the aerobic degradation of organic matter, as well as the nutrient (P and N) requirements. This steady-state model was performed before setting up the model using the software BioWin. In parallel, an aerobic batch activity test was executed in the laboratory to assess the nutrient requirements of the activated sludge biomass of such particular pulp mill WWTP. For this purpose, a laboratory set-up was assembled at the pulp mill laboratory facilities. Mixed liquor activated sludge collected at the end of the aeration basin was aerated for six hours prior to the execution of the activity test. Thereafter, the sludge was poured into the activity test reactor. The pH was adjusted to 7.5 by manually adding hydrochloric acid (HCl) 0.1 M and sodium hydroxide (NaOH) 0.1 M solutions. Allyl-N-thiourea was added as a nitrification inhibitor. In addition, 10.3 mg of urea and 53.0 mg of sodium triphosphate were added as N and P sources, respectively. At the start of the test, the influent wastewater was added into the batch reactor, and different samples were collected within the first 120 min. of the experiment, as well as after 24 and 48 h.

2.2.5 Model calibration and validation

The model was built and structured using the software BioWin. After the model was structured, it was calibrated following a stepwise approach adjusting both key wastewater fractions, as well as kinetic and stoichiometric model parameters. The calibration was carried out until the model provided a satisfactory description with less than 10 %

difference regarding the average values of the parameters periodically measured at the WWTP. For the model validation, two sets of previously collected data were used. The first set of data corresponded to the winter conditions (obtained historically from May to August 2013) and the second to summer conditions (from September to December 2013).

2.2.6 Scenarios assessment

Once the model was calibrated and validated, different simulations were executed to evaluate the potential to achieve an improved effluent quality with regard to the P-effluent concentrations with minimum modifications to the WWTP. Moreover, the capacity and robustness of the WWTP under different operational conditions were assessed. Also, the potential for reducing the operational costs of the WWTP and for implementing strategies to cope with operational and maintenance contingencies were explored. Furthermore, the evaluation of the effects of increasing the organic loading reaching the WWTP was evaluated. The following scenarios were studied:

(i) Implementation of the chemical phosphorus removal (CPR) process: CPR with iron chloride ($FeCl_3$) was evaluated, since it seems to be a cost-effective coagulant. With the objective of determining the optimal $FeCl_3$ dosage for CPR, different jar tests were carried out. The experiments were divided in two sets, as shown in Table 2.1. In the first set of experiments (E1), different coagulant dosages were added at the metal ion/PO_4^{3-} molar ratio of 1, 2.5, 5 and 10. In the second set (E2), the coagulant dosage was determined based on the iron destabilization diagram for sweep coagulation (Benjamin and Lawler, 2013). The experiments were executed both in mixed liquor activated sludge (collected at the end of the aerobic reactor in sampling points 3a and 3b), and in effluent (after the secondary clarifier, sampling point 4). The experiments were conducted at the default wastewater pH (7.2–7.9) as well as at pH 5.5 and 6.0, in accordance with (Metcalf & Eddy, 2014; Benjamin and Lawler, 2013; Jiang and Graham, 1998). A cost analysis was performed to estimate the annual costs for chemicals. For this purpose, the total coagulant requirements were quantified considering the coagulant characteristics (a commercial 40 % ferric chloride solution); a commercial price of € 100 per ton was considered (Paul et al., 2001).

(ii) Implementation of the enhanced biological phosphorus removal process (EBPR): The main goal was to explore whether the WWTP had required capacity to introduce such EBPR process. Thus, the first 25 % volume segment of the aerobic tank (corresponding to a volume of approximately 35,000 m^3) was converted into a non-aerated zone to make it anaerobic.

(iii) Assessment of higher influent flowrates: Due to a potential increase in production capacity foreseen for the coming years, the impact of higher influent flowrates generated at the pulp mill plant was evaluated. Different increases in the influent flowrates ranging from 20 to 100 % were evaluated in addition to the average influent flowrates currently treated at the WWTP.

(iv) Co-treatment of municipal wastewater: This scenario was evaluated to determine whether the pulp mill WWTP had the capacity to co-treat the municipal wastewater from a nearby city. This evaluation was considered because domestic wastewater has a high nutrients concentration; therefore, it could be a good source of N and P for the activated sludge biological treatment. For this purpose, a wastewater flowrate generated by 70 % of the 24,406 p.e. of the city was considered. Relevant municipal wastewater characteristics and concentrations were taken from typical raw municipal wastewater compositions as reported by (Meijer and Brdjanovic, 2012).

(v) Effects of shorter sludge retention time (SRT) on plant performance: Shorter SRT could lead to higher fractions of active biomass and less generation and accumulation of inert or non-degradable matter. Furthermore, it could decrease the oxygen requirements and consequently reduce the aeration costs. Shorter SRT could lead to a higher uptake of nutrients for biomass growth purposes. Also, to the generation of a less stabilized sludge which, if anaerobically treated, could lead toa higher biogas production. Thus, the effects of shortening the SRT were simulated and assessed. The SRT of the pulp mill WWTP was sequentially shortened from 32 to 25, 20, 15 and 10 days by increasing the waste of activated sludge (WAS) with-drawn per day to assess its impact on the plant performance and effluent quality.

(vi) Operation of the plant with only one treatment line: This scenario was carried out to assess the WWTP response during a potential maintenance period when only one treatment line could be in operation.

Table 2.1 Jar test experiments carried out both in mixed liquor activated sludge (AS) and in effluent for chemical phosphorus removal. E1 experiments were carried out at molar ratios of 1, 2.5, 5, and 10, while E2 experiments were carried out in the sweep coagulation coagulant dosage

E1 A	**E1B**
Mixed liquor AS	
Default pH: 7.4	pH adjusted: 5.5
E1C	**E1D**
Effluent	
Default pH: 7.7	pH adjusted: 5.5
Experiment 1 **Chemical Precipitation**	
Beaker	Coagulant dosage (mg $FeCl_3.6H_20$/L)
1	1.5
2	3.8
3	7.5
4	15.1

E2 A	**E2B**
Mixed liquor AS	
Default pH: 7.2	pH adjusted: 6.0
E2C	**E2D**
Effluent	
Default pH: 7.9	pH adjusted: 6.0
Experiment 2 **Sweep coagulation**	
Beaker	Coagulant dosage (mg $FeCl_3.6H_20$/L)
1	20
2	100
3	180
4	270

2.3 RESULTS AND DISCUSSION

2.3.1 WWTP configuration

The WWTP shown in Figure 2.1 was built in the year 2007. According to (Saarela et al., 2007) the pulp mill WWTP was designed to treat an effluent flow of 25 m^3/air dry ton (ADT) (approximately 0.8 m^3/s) mostly generated in the bleaching process. The plant had a mechanical pre-treatment followed by the CAS process for organic matter removal. The effluent to be treated at the WWTP was composed of two different streams that originate from different processing lines: (i) a high solids concentration stream, and (ii) a low solids concentration stream. Firstly, the high solids effluent came from several internal industrial processes/sections including the white liquor plant, the evaporation plant, the recovery boiler, the drying process, the wood handling process, the water treatment process, and the fibre line process. This effluent comprised up to one third of the entire wastewater. The effluent passed through a coarse screening to remove large solids, and later, through a primary clarifier (a single unit with a diameter of 46 m) for the removal of settleable solids (primarily fibres). Then, the effluent was conveyed to the safety and equalization basins (three units with a maximum capacity of 25,000 m^3 each). The low solids effluent stream made up to two thirds of the entire wastewater. The low solids stream was generated mainly at the acid and alkaline bleaching processes but also contained, to a lesser extent, effluents from the chemical and white liquor plants. This effluent stream was treated directly in the pre-neutralization tank (to adjust the pH and to make it suitable for the biological treatment). Thereafter, the neutralized effluent was mixed in the safety and equalization basins together with the high solids effluent. Once the two flows were combined, the equalized and homogeneous effluent was directed to the cooling towers to decrease the wastewater temperature from 55 ˚C to approximately 30 ˚C to prevent any deleterious temperature effect on the biological performance of the CAS system. After the temperature adjustment, the effluent was post-neutralized to adjust the pH, urea is added, and the effluent flows to the CAS system. The CAS process consisted of two aerobic reactors which were operated in parallel (each with a maximum working capacity of 75,000 m^3). The aeration tanks dimensions were 190 m length, 42 m width and 9.5 m height. For both aeration basins, the air was supplied by four air blowers (each one with a capacity of 20,000 Nm^3/h). The aeration tanks did not have compartments, yet there were three different zones, namely: a selector, zone 2, and zone 3 (Figure 2.2). In the aeration tank 1, average dissolved oxygen (DO) concentrations of 1.07 mgO_2/L, 0.77 mgO_2/L, and 2.57 mgO_2/L were reported for the selector, zone 2, and zone 3, respectively. In the aeration tank 2, average DO concentrations of 0.77 mO_2/L, 1.99 mgO_2/L and 3.38 mgO_2/L were reported for the selector, zone 2, and zone 3, respectively. The different DO concentrations observed were mainly caused by the organic matter degradation along the reactor. Nevertheless, the submerged air bubble diffusers provided satisfactory dissolved oxygen and mixing conditions. The SRT of the CAS system was set at 32 days, so the WWTP was operated as an extended aeration process to minimize the sludge production. The effluent treated in the aerobic reactors was clarified in the secondary clarifiers (two units operated in parallel, each one with a diameter of 65 m). Finally, the treated and clarified effluent was discharged into the Uruguay River. A fraction of the sludge settled in the secondary settling tank was returned to the aeration basins (recirculation of activated sludge, RAS) and the other fraction was sent to the sludge handling facilities for sludge treatment (as the WAS). There were two WAS extraction lines that direct the bio-sludge to the side-stream sludge treatment line at a flowrate of approximately 5 % of the influent flowrate. The average flowrate of the RAS observed during the sampling campaign was 115 % with respect to the influent flowrate. However, it could vary between 110 and 150 %. A biomass concentration of approximately 5.3 g mixed liquor suspended solids (MLSS)/L was maintained in the aeration basins. The sludge settled out in the primary sedimentation tank was dewatered in two belt filter presses with a total capacity of 33.8 total dry solids (t DS)/d. After dewatering, the solids were transported to their final disposal site (forest plantations). In a similar manner, the WAS was treated in a gravity table and a decanter centrifuge with a capacity of 17 t DS/d. Likewise, all the filtrates from the primary and WAS dewatering processes were returned to the headworks of the WWTP.

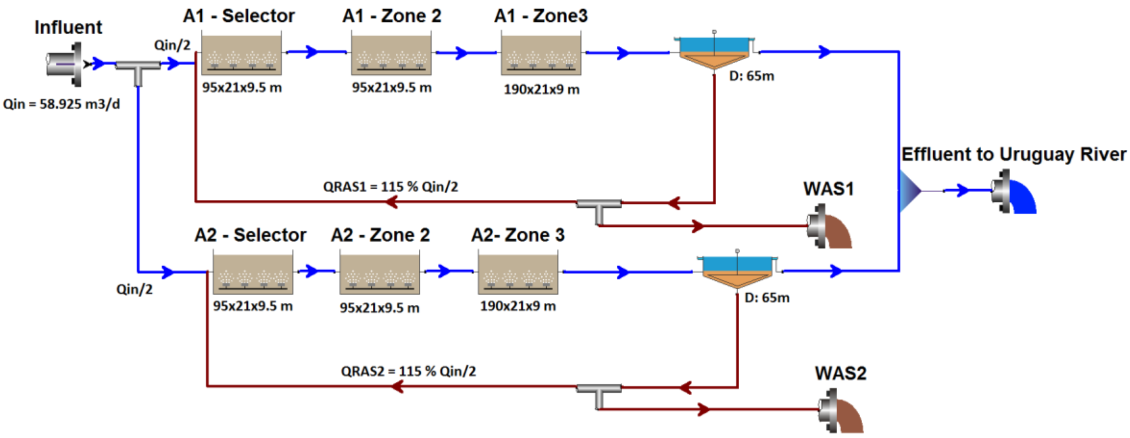

Figure 2.2 Model structure of the pulp mill WWTP: hydraulic flow diagram

2.3.2 Data collection, preliminary characterization, and WWTP evaluation

The influent flowrate to the WWTP was evaluated considering the historical data from May to August 2013; relatively stable flowrates were observed with an average influent flowrate for the reporting period of 68,488 ± 9,762 m^3/d, with minimum and maximum values of 51,567 ± 2335 and 74,726 ± 564 m^3/d, respectively. The pulp mill wastewater composition of the plant in Uruguay is presented in Table 2.2, (obtained by processing the historical data collected from May to August 2013), and it is compared both to a municipal wastewater in the Netherlands, as well as to two other pulp mill wastewaters. The pulp mill wastewater of study (in Uruguay) had higher organic matter concentrations (including the biodegradable organic fraction) than a typical raw municipal wastewater. For instance, the COD/BOD ratio of the pulp mill wastewater in Uruguay was lower than two, indicating a considerable presence of biodegradable components in the influent (Rodrigues et al., 2008; Zaher and Hammam, 2014). When comparing the nutrient composition between the municipal wastewater and the pulp mill wastewater opposite trends were observed. TN and TP concentrations of 60 mg N/L and 15 mgP/L, respectively (Henze et al., 2008) were reported for municipal wastewater, whereas TN and TP concentrations of 6.5 mg N/L and 3.7 mg/L, respectively were reported for the pulp mill wastewater in Uruguay. The pulp mill wastewater at the plant in Uruguay had similar characteristics (in terms of total COD, TN, TSS and NH_4^+) to those reported from other pulp and paper mill wastewaters (Lindblomet al., 2004; Barañao and Hall, 2004;

Keskitalo and Leiviskä, 2010). However, the BOD_5 and TP were considerably higher. This could be attributed to the composition of the wood used as raw material which had a higher P content. Table 2.3 indicates the performance of the pulp mill WWTP located in Uruguay obtained by processing the historical data collected from May to December 2013. It could be observed that the WWTP utilized the best available technologies at the time when this evaluation was carried out. The WWTP exhibited a good performance in terms of the evaluated parameters. The effluent met the local standards established by the local Environmental Regulatory Authority, DINAMA (Decree 253/79).

Table 2.2 Comparison between the wastewater (WW) characteristics of the studied pulp mill WWTP, typical raw municipal WW, and from two other pulp mill WWTPs. The data obtained from the plant in Uruguay was processed from historical data existent at the plant from May to August 2013

	Raw Municipal WW (Netherlands) Meijer and Brdjanovic (2012)	**Pinus radiata Kraft Pulp Mill** (Chile) Diez et al. (2002)	**Stora Enso Fine Paper Oulu kraft Pulp mill** (Finland) Keskitalo and Leiviska (2010)	**Bleached Kraft Pulp Mill** (Uruguay) May to August (2013)
Parameter	**Average**	**Average**	**Average**	**Average**
COD total	750	1208	1167	**1588**
COD soluble*	300	-	-	1243
BOD_5	350	319	255	911
VFA	30	-		217
N total	60	6.1	6.6	**6.5**
Ammonia-N	45	-	0.2	0.2
P total	15	1.1	1.7	**3.7**
Ortho-P	10	-	2.4	2.2
TSS	400	147	-	220
VSS	320	-	-	175

VFA: Volatile fatty acids as acetate, * 0.45 µm membrane filtered

Table 2.3 Performance of pulp mill WWTP located in Uruguay. The removal efficiencies were observed from May to December 2013 at an average flowrate of 65,639 m^3/d

Sampling point/parameter	**Total COD** [mg/L]	**BOD$_5$** [mg/L]	**Total N** [mg/L]	**Total P** [mg/L]	**TSS** [mg/L]
Influent to AS system	1499.3	811.0	16.3	3.0	249.8
Effluent to Uruguay River	284.6	6.7	2.3	0.6	8.0
Removal efficiency [%]	**81.0**	**99.2**	**85.9**	**80.0**	**96.8**
DINAMA regulations (**Discharge limit (mg/L)**)	-	60.0	-	5.0[a]	150.0

[a] Currently this parameter is limited to a monthly average load of 74Kg/d.

DINAMA: Uruguayan Environmental Agency

Table 2.4 Summary of the pulp mill WWTP COD influent fractions based on sampling campaign from October 21st to 28th, 2013, and their comparison against the COD fractions from municipal (Morse et al., 1998) and pulp and paper mill industrial wastewaters

Influent fractions	**Pulp and paper mill (Canada)** Barañao and Hall (2004)	**Stora Enso Fine Paper Oulu pulp mill (Finland)** Keskitalo and Leiviska (2010)	**Municipal wastewater** (ASM3 default) Gujer et al., (1999)	**Pulp mill (Uruguay)** STOWA protocol (1996)
Total soluble readily biodegradable COD **(S_S)**	0.49	0.31	0.43	**0.64**
Soluble inert COD (S_I)	0.14	0.26	0.13	0.14
Particulate and slowly biodegradable COD **(X_S)**	0.30	0.35	0.33	**0.19**
Particulate inert COD (X_I)	0.07	0.08	0.11	0.03

2.3.3 Wastewater fractionation and characterization

Table 2.4 shows the influent wastewater COD fractions for the pulp mill in Uruguay based on the sampling campaign carried out from October 21st to 28th, 2013. The COD fractionation is compared with COD fractionation obtained from a typical municipal wastewater (Meijer and Brdjanovic, 2012) and from two other pulp and paper mill wastewaters (Keskitalo and Leiviskä, 2010; Diez et al., 2002). The influent and effluent wastewater characteristics of the pulp mill WWTP in Uruguay were also determined from the samples obtained from the sampling campaign carried out from October 21st to 28th, 2013. The characterization is presented in Table 2.5.

As observed in Table 2.4, the COD fractionation of the pulp mill WWTP in Uruguay differed considerably with respect to those from a municipal wastewater. The pulp mill wastewater had higher concentrations of readily biodegradable COD (S_S: 64 %) than a typical municipal wastewater (S_S: 43 %). The slowly biodegradable substrates (X_S) together with the particulate inert organic material (X_I) account for 22 % of the pulp mill wastewater influent COD. For a typical municipal wastewater, the particulate fraction is much higher (approximately 44 % of the influent COD). In addition, the readily biodegradable COD (RBCOD) (S_S) of 0.64 is higher than the SS observed for other pulp mill WWTP from Canada (0.49) (Barañao and Hall, 2004), and Stora Enso Fine Paper Oulu pulp mill in Finland (0.31) (Keskitalo and Leiviskä, 2010), whereas the slowly biodegradable COD (X_S) and the particulate non-biodegradable (X_I) are lower (0.19 and 0.03, respectively). Table 2.5 shows the wastewater characterization of the pulp mill in Uruguay following the Dutch STOWA guidelines. On the left side of the table, the results for the influent and effluent wastewater characterization are presented. On the right side of the table, the wastewater fractions to be utilized in the BioWin model are presented.

2.3.4 Steady-state model and aerobic batch activity test

The performance of the pulp mill WWTP was firstly assessed by applying a steady-state model. The wastewater characterization and fractionation obtained in the previous section were used to evaluate such steady-state model. The model was evaluated at a temperature of 30 ˚C and at an SRT of 32 d. The stoichiometric and kinetic parameters were considered in accordance with Henze et al. (2008). The average annual temperature of the influent wastewater reaching the biological activated sludge process was 30 ˚C, so the model was evaluated using that temperature. Also, the kinetic endogenous respiration rate (bH) coefficient on the steady state organic material degradation model for fully aerobic systems was corrected by the temperature (Henze et al., 2008). The EBPR performance may be negatively affected under high temperature conditions (Whang and Park, 2002, 2006; Wang et al., 2020). This is because high temperature (30 ˚C) favor the growth of glycogen accumulating organisms (GAOs) over PAOs (López-Vázquez et al., 2008). According to findings reported by Brdjanovic et al. (1997,1998) the temperature could have a strong influence on the kinetics of the EBPR process both under anaerobic as well as under aerobic conditions (Brdjanovic et al., 1997, 1998). Results drawn from the steady-state model indicated that the nutrient concentrations in the influent pulp mill wastewater (TP of 3.7 mg P/L and TN of 15.8 mg N/L as described in Table 5) were insufficient to cover the growth requirements of the ordinary heterotrophic biomass involved in the organic matter removal process. Thus, suggesting that the plant could suffer from nutrient limitations. However, in practice, the pulp mill WWTP operates satisfactorily as indicated by the removal efficiencies and effluent characteristics presented in Table 2.3. To assess the actual nutrient requirements, an aerobic batch activity test was executed, and the nutrient requirements were estimated based on the organic matter removal (as COD) and on the P and N consumption. The P removed by the sludge for biomass growth (fP) was estimated at approximately 0.012 mgP/mgVSS. This value is approximately half of the value reported for municipal wastewaters (0.025 mg P/mgVSS) (Henze et al., 2008). Applying a similar approach, the biomass N requirements were estimated (fN). The fN calculated was approximately 0.037 mgN/mgVSS, lower than the value usually reported for municipal wastewater treatment plants at 0.1 mg N/mgVSS (Henze et al.,2008).

2.3.5 Model calibration and validation

Model calibration

The pulp mill WWTP layout was introduced in BioWin as shown in Figure 2.2. A preliminary simulation was carried out with the influent data from the wastewater characterization and fractionations obtained from the sampling campaign (Table 5). Initially, BioWin's default values for the kinetic and stoichiometric parameters were used. Thereafter, a stepwise calibration procedure was performed in accordance with Meijer and Brdjanovic (2012) and Hulsbeek et al. (2002), and the following parameters were modified. The COD biodegradable and non-biodegradable particulate fractions (X_S and X_I, respectively) were adjusted to 0.18 and 0.03, respectively, to match the plant MLSS concentration of 5.3 gTSS/L. The aerobic decay rates of OHOs and ammonia oxidizing bacteria (AOB) were decreased to 0.24 d^{-1} and 0.04 d^{-1}, respectively, to describe the mixed liquor volatile suspended solids (MLVSS) and NH_4^+ concentrations in the aerobic reactors. The NO_3^- concentration was calibrated by adjusting the half-saturation constant of DO of OHO (K_{OH}) to 0.35. The nutrient content of the biomass, endogenous residues, and other particulate compounds were decreased. The fP was adjusted to 0.004 and the fN to 0.025 to describe both the low nutrient assimilation observed in the sludge of the pulp mill WWTP, as well as the low effluent NH_4^+ and PO_4^{3-} concentrations. A summary of the values adjusted during the model calibration is presented in the Table 2.1 in the supplementary material section. After concluding with the calibration phase, the effluent COD, TSS, TN, TP, NH_4^+ and NO_3^-concentrations were satisfactorily described by the model. Only three kinetic parameters were adjusted (the aerobic decay rates of OHO and AOB, and the half-saturation coefficient for DO of OHO). The main difference with regard to the default values from BioWin (for conventional municipal wastewaters) were the extremely low values of the stoichiometric parameters fP and fN. The default values used by BioWin were 0.07 mg N/mgCOD and 0.022 mg P/mgCOD, respectively, whereas the calibrated values were 0.025 mg N/mgCOD and 0.004mg P/mgCOD, respectively. To verify such low nutrient assimilation, a mass balance (including the analytical determination of N and P on the primary and secondary sludges) was conducted. The mass balance results supported and confirmed such low nutrient assimilation requirements. This suggests that the extremely low N/COD and P/COD ratios observed in the pulp mill wastewater could have possibly lead to the development and proliferation of microbial populations with low nutrient requirements. Previous studies about pulp and paper mill wastewater treatment by activated sludge have also reported low nutrient concentration on this type of effluents (Diez et al.,2002; Bashaar, 2004; Bhathena et al., 2006; Ashrafi et al., 2015b; Cabrera, 2017). Cabrera (2017) observed that effluents from the wood processing industry generally exhibit a BOD:N:P ratio of 100:(1–2):(0.15−0.3); the authors reported that the addition of supplementary nutrients is commonly required (Cabrera, 2017). Davis (2005) reported that effluents from pulp and paper industries are deficient in N and P, so these nutrients need to be added to achieve the correct ratio for microbial growth. Bashaar (2004) evaluated the nutrient requirements in biological pulp and paper mill wastewaters. The authors reported that the nutrient requirements for this industrial wastewaters were lower than what is usually reported in the literature (e.g. a C:N:P ratio of 100:5:1). Similar low COD:N:P and BOD:N:P ratios were reported in the present study of 100:1.0:0.2 and 100:1.7:0.4, respectively. However, the N requirements at the evaluated pulp mill wastewater (in Uruguay) were lower than the reported values from others pulp mill wastewater.

Model validation

The predictions of the calibrated model were validated with data from two different operational periods of the pulp mill WWTP as follows: May–August 2013 and September–December 2013. The effluent model predictions were compared against the average values from the two aforementioned periods. Overall, the model was able to provide a satisfactory description of the plant performance as observed by the good match between the model predictions and the average measured values. Apparently, certain parameters, such as TSS and NO_3^-, differed considerably. However, it must be noticed that these concentrations are extremely low (and sometimes close to zero), that even a minimal increase of 0.1 mg/L can lead to an apparently high deviation between the predicted and measured value. Thus, such low differences were considered acceptable, and it was assumed that the model was adequately validated. The measured and predicted values are presented in the Table 2 in the supplementary material section.

Table 2.5 Influent and effluent wastewater characterization according to the Dutch STOWA guidelines for wastewater characterization during sampling campaign from October 21st to 28th, 2013

Influent and effluent wastewater characteristics: Measurements

Description	Symbol	Influent	Effluent	Units
Total influent COD	COD_{total}	1588	268	gCOD/m^3
Influent COD soluble *	COD_{filt}	1243	260	gCOD/m^3
Influent BOD_{10}	BOD_{10}	911	6.9	gBOD/m^3
Influent BOD_{10} soluble *	$BOD_{10,\ filt}$	749	ND	gBOD/m^3
Total Nitrogen **	TN	15.8	1.28	gN/m^3
Total Kjehldahl Nitrogen	TKN	15.8	1.17	gN/m^3
Ammonium	NH_4	0.23	0.04	gN/m^3
Nitrite	NO_2	ND	ND	gN/m^3
Nitrate	NO_3	0.03	0.10	gN/m^3
Total Posphorus	TP	3.67	0.58	gP/m^3
Total Posphorus soluble *	TP_{filt}	2.35	0.54	gP/m^3
Orto-phosphate	PO_4	2.15	0.47	gP/m^3
Total Suspended Solid	TSS	220.2	4.08	gTSS/m^3
Inorganic Suspended Solid	ISS	45.4	ND	gISS/m^3
Volatile Suspended Solid	VSS	174.8	ND	gVSS/m^3
Temperature	T	30	ND	^{o}C

* 0.45 µm membrane filtered

** TN after urea addition

*** One important assumption in the fractionation of the influent COD is the negligence of biomass fractions in the influent

Model influent composition

Description	Symbol	Value	Units
Soluble compounds			
Oxygen (negative COD)	S_{O2}	0.0	gO_2/m^3
Readily biodegradable organics	S_F	866.5	gCOD/m^3
Volatile fatty acids	S_A	153.0	gCOD/m^3
Ammonium & ammonia nitrogen	S_{NH4}	0.2	gN/m^3
Nitrate & Nitrite nitrogen	S_{NO3}	0.0	gN/m^3
Di-nitrogen gas	S_{N2}	0.0	gN/m^3
Inorganic soluble phosphorus (ortho-phosphate)	S_{PO4}	2.1	gP/m^3
Soluble inert organic matter	S_I	223.3	gCOD/m^3
Alkalinity	S_{ALK}	6.0	mol HCO/l
Solid compounds ***			
Particulate inert organic matter	X_I	246.9	gCOD/m^3
Slowly biodegradable substrate	X_S	98.3	gCOD/m^3
Active heterotrophic biomass	X_H	0.0	gCOD/m^3
Phosphate accumulating organisms	X_{PAO}	0.1	gCOD/m^3
Poly-phosphate	X_{PP}	0.0	gP/m^3
Poly-hydroxy-alkanoates	X_{PHA}	0.0	gCOD/m^3
Glycogen	X_{GLY}	0.0	gCOD/m^3
Active autotrophic biomass	X_{AUT}	0.1	gCOD/m^3

2.3.6 Scenarios assessment

Six different configurations and operational alternatives were assessed to evaluate potential improvement, upgrading scenarios, and the robustness of the plant. In this section, each scenario is presented and discussed. (i) Implementation of the CPR process: A jar test evaluation was carried out at the pulp mill laboratory facilities to define an adequate coagulant dosage. Table 2.6 displays the results of the jar test experiments. A soluble phosphorus concentration of 0.26 mg P/L was achieved with 100 mg$FeCl_3 \cdot 6H_2O$/L (experiment E2A, beaker No. 2). An even lower concentration was reached if 270 mg$FeCl_3 \cdot 6H_2O$/L were dosed (experiment E2A, beaker No.4) resulting in a P concentration of 0.11 mg P/L. However, the coagulant requirements are considerably higher (270 mg/L versus 100 mg/L) for a relatively marginal improvement in the soluble P concentrations (from 0.26 to 0.11 mg P/L). Thus, the addition of 100 mg$FeCl_3 \cdot 6H_2O$/L (experiment E2A, beaker No. 2) was selected as the optimum dosage. This also suggested that the coagulant addition could take place at the end or after the aerobic tank, following a sweep coagulation mechanism, at the regular pH observed at the plant (pH 7.2) without requiring any pH adjustment. The coagulant concentration and dosage point were included in the Biowin model (Figure 2.3), leading to a similar outcome of 0.1 mg P/L in the effluent of the WWTP. Assuming an average effluent TP concentration of 0.62 mg P/L (this value was predicted by the calibrated and validated BioWin model without applying any additional strategy for P-removal) and an effluent flowrate of 58,925 m^3/d, the estimated P load is 36.5 kg P/d. Then, if CPR is applied and an effluent TP concentration of 0.1 mg P/L is achieved, the effluent P load will be reduced to 6.5 kg P/d, which is far lower than the discharge limit of 74 kg P/d imposed by the environmental authorities to the plant. However, the WAS volumes produced per day will increase from 321 tonTSS/d to 326 tonTSS/d. This means an increase of 9.8 tonTSS/d if the two treatment lines are considered. This major amount of WAS sent to the evaporation process of the pulp mill could generate some issues in the daily operation of the mill and this point requires further evaluation. Based on the results from the jar tests (Table 2.6, E2A), the operational conditions, and the actual coagulant dosages required, the associated costs of implementing CPR were estimated. Figure 2.4 shows the effluent P soluble concentrations as a function of the coagulant dosage and the associated costs per year. As observed, the addition of 100 mg $FeCl_3$/L appears to be a satisfactory option to decrease and secure a low P concentration in the plant at an estimated annual cost of 1.2 million of euros. No sludge disposal costs were considered since the WAS is returned to evaporation process at the pulp mill.

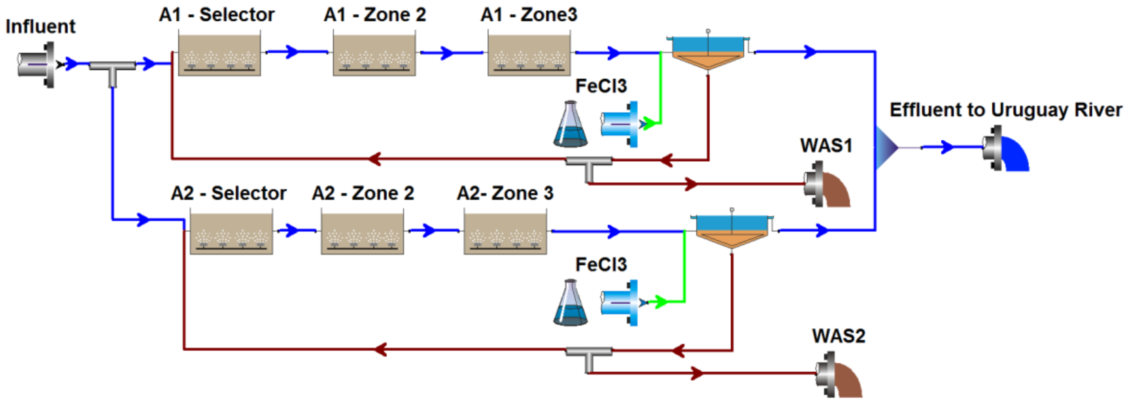

Figure 2.3 Modified layout of WWTP with chemical P removal

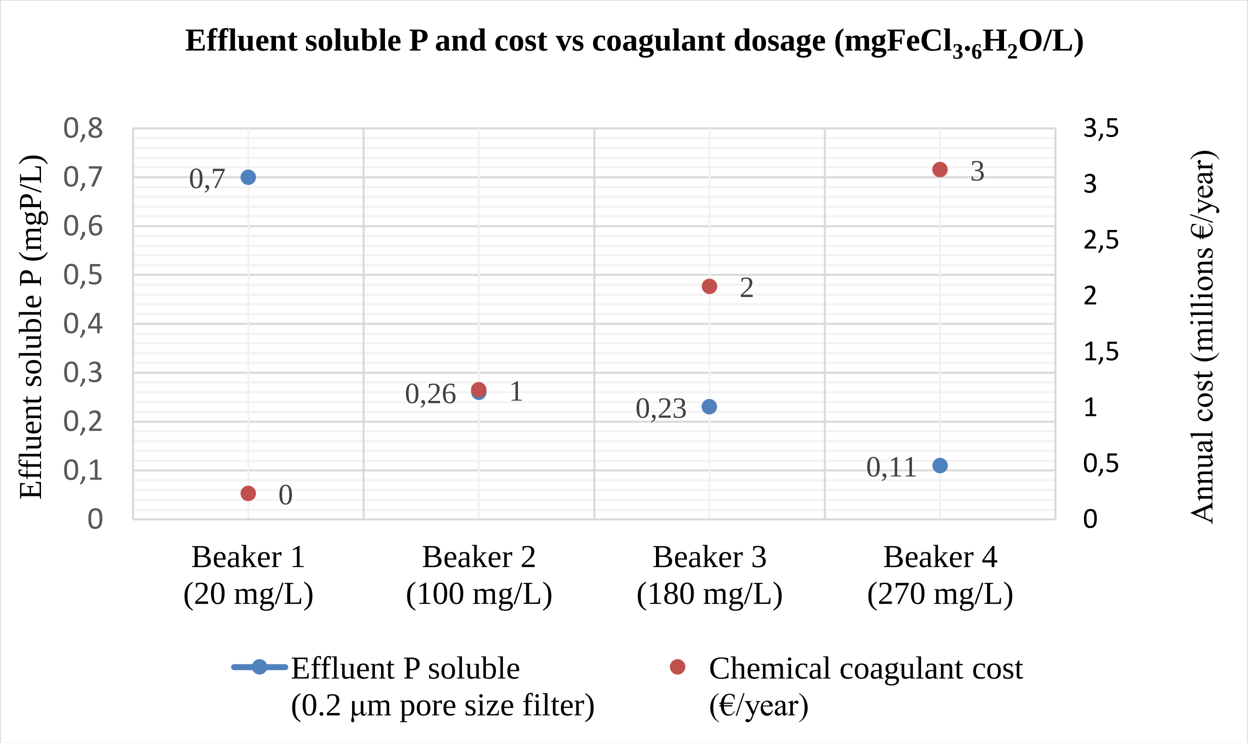

Figure 2.4 Soluble phosphorus concentrations in the effluent of the plant as a function of the coagulant dosage and costs of coagulant per year

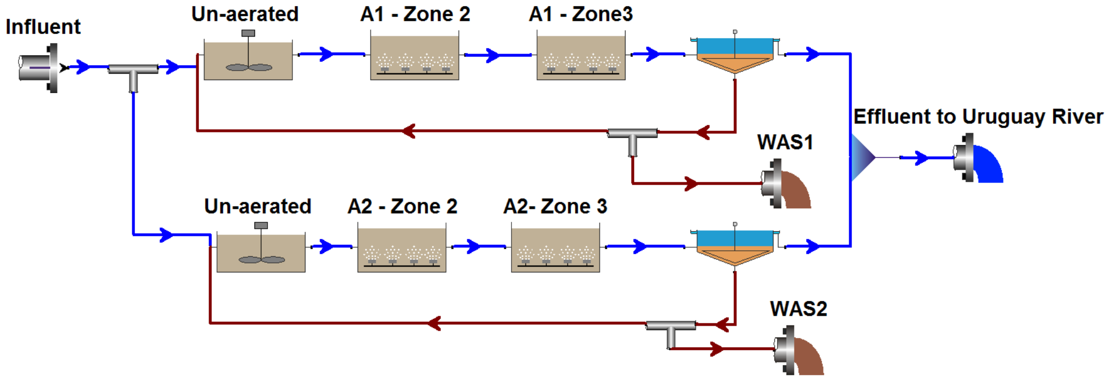

Figure 2.5 Modified layout of WWTP with un-aerated reactor zone

(ii) Implementation of the EBPR process: The EBPR process can be eventually achieved by converting a former selector (35,000 m^3) located in the beginning of the aeration basin into an unaerated zone. The modelling results predict that the TP concentration in the effluent can be decreased from 0.62 to 0.26 mgP/L. The schematic of the model is presented in Figure 2.5. For the EBPR process to develop, anaerobic conditions must be created, and a different group of heterotrophic microorganisms (known as PAOs) shall proliferate to enhance the biological P-uptake (Henze et al., 2008; López-Vázquez et al., 2008). The proposed configuration may be a good option to further remove P during the biological treatment. Only the former selector needs to be converted into an anaerobic selector by switching off the aeration in that zone. However, further research activities such as piloting-test or detailed studies may be needed to validate this configuration. The wastewater exhibited an average temperature of 30 ˚C, and these conditions may have a negative influence over the PAO's activity (Whang and Park, 2002; Lopez-Vazquez et al., 2009; Ong et al., 2014). In addition, the recommended SRT for implementing EBPR processes ranges between 10 –25 days and the nominal hydraulic retention time (HRT) from 10 to 24 h (Henze et al., 2008). In the currently evaluated pulp mill WWTP the SRT was set to 32 days and the HRT to 48 h. Therefore, further research is needed to validate this alternative.

(iii) Assessment of higher influent flowrates: The impact of higher influent flowrates caused by a potential increase in the production of the pulp mill industry was evaluated. The pulp mill WWTP was able to cope with influent flows from 20 up to 100 % higher; mostly, because the WWTP is overdesigned. Nevertheless, to keep a MLSS concentration between 4,215 and 4,750 mg/L, the SRT needs to be proportionally reduced from 32 to 26, 23, 20, 18 and 16 days as the influent flow increases from 0 to 20, 40, 60, 80 and 100 %. Also, the sludge production increases, and the sludge is less stable (the VSS and active fractions increase). However, although the WWTP would still meet the discharge limits, the effluent TP concentration would increase from 0.62 mg P/L to 0.87 mg P/L. This option needs to be carefully addressed and perhaps combined with another alternative (such as CPR and EBPR implementation) to secure the compliance with the discharge standards if higher flows need to be treated. (iv) Co-treatment of municipal wastewater: This evaluation was considered since the domestic wastewater has a high nutrients concentration (Meijer and Brdjanovic, 2012) and it could be a good source of N and P for activated sludge biological treatment. If the municipal wastewater from a near city (estimated in approximately 3,416 m^3/d) is treated at the pulp mill WWTP, the modelling studies indicate the total P concentrations in the effluent would considerably increase (up to approximately 0.8 mgTP/L). However, if EBPR is implemented (by introducing a non-aerated or anaerobic zone, as described previously) the pulp mill WWTP could have the capacity to satisfactorily treat both effluents while still achieving a final total P concentration in the effluent of approximately 0.11 mg P/L.

(v) Effects of shorter SRT on plant performance: According to model predictions, decreasing the SRT from 32 d to 25, 20, 15and 10 d would lead to an increase in the effluent P concentrations from 0.6 mg P/L to 0.7, 0.9, 1.0 and 1.2 mg P/L, respectively. This goes against what is known about P-removal, where shorter SRT help to increase P removal efficiency (Metcalf &Eddy, 2014). Taru et al. (2014) applied a mathematical model for biological P removal in CAS systems and observed that at low SRT (15 days), about 55 % of the VSS are in the active stage compared to only a 22 % at high SRT of 45 days. The active VSS mass in the reactor is the live OHO organisms performing the biodegradation processes of the organic material (Henze et al., 2008). The active fraction gives an indication of the stability of the sludge, which is related to the remaining biodegradable organics in the sludge mass (Henze et al., 2008). At low SRT the active fraction is higher than at high SRT, where the higher percentage of VSS is in the endogenous and inert fraction (Taru et al., 2014). VSS in AS systems have a variable P content mass per mg of VSS. The active PAO fraction is estimated to accumulate 0.38 mg P/mgVSS (Henze et al., 2008), whereas endogenous and inert PAO fractions accumulate on average 0.03 mg P/mgVSS (Henze et al., 2008). Therefore, if a higher percentage of VSS is in the endogenous and inert fraction, there would be a reduction on P content in the VSS, resulting in low P removal efficiency (Taru et al., 2014). Perhaps the BioWin model prediction in this study has a limitation with regard to the nutrient requirements. This alternative requires further research, and it could be implemented in combination with another operating strategy (such as CPR or EBPR). Thus, to shorten the SRT could contribute to reduce the aeration costs, but a higher sludge generation will be observed, which can increase the operational costs of the plant depending on the sludge treatment process.

(vi) Operation of the plant with only one treatment line: If, due to maintenance purposes, the plant needs to operate with only one wastewater treatment line, the model-based results indicate that this will increase the effluent TP concentration to 0.8 mg P/L. This will be close to the discharge limit. It can be explained as in the studied scenario #5, in which the impact of SRT decrement was analysed. A decrease on the SRT, may decrease the concentration of TSS in the reactor; therefore, both less active biomass would be present in the reactor decreasing the P assimilation rate, and the adsorption of colloidal P to particulate organic P would also decrease. That is, the effluent TP concentration would increase. Thus, in principle, this practice could be applied, but it is not recommendable for long periods, only for maintenance purposes and in case of contingencies.

To sum up, the performance of the pulp mill WWTP in Uruguay could be well described by a BioWin model. The model was able to describe the current operation of the WWTP, as well as the historical performance allowing also the prediction of different future scenarios. Out of the six evaluated potential scenarios for reducing the TP concentration in the effluent, two of them exhibited high chances of being employed: (i) the implementation of the CPR process, and (ii) the implementation of EBPR. The model results indicated that either applying the CPR process at the sweep coagulation range or including an anaerobic phase prior to the aerobic process (EBPR configuration) could reduce the TP concentration in the effluent near to zero. Other four scenarios were analysed to get insight on the WWTP response to eventual changes in its operation including: (iii) the assessment of higher influent flowrates, (iv) the co-treatment of municipal wastewater, (v) the effects of shorter SRTs, and (vi) the operation of the WWTP with only one treatment line. The most prominent advantages of the use of pulp mill WWTP modelling include getting better insight regarding the WWTP performance, evaluate changes in the plant layout, and support management decisions.

Table 2.6 Results of the jar-test

Initial Mixed liquor AS: Psoluble – 0.88mgP/L	**E 1 A** Mixed liquor activated sludge (AS) collected at the end of aeration basins Default pH: 7.4				**E 1 B** pH adjusted to 5.5			
	Beaker 1	Beaker 2	Beaker 3	Beaker 4	Beaker 1	Beaker 2	Beaker 3	Beaker 4
P soluble [mg/L] (0.2 µm pore size filter)	0.85	0.85	0.78	0.7	1.49	1.5	1.46	1.53
Initial effluent: Ptotal–0.72mgP/L, Psoluble–0.68mgP/L	**E 1 C** Effluent from the secondary clarifier Default pH: 7.7				**E 1 D** pH adjusted to 5.5			
	Beaker 1	Beaker 2	Beaker 3	Beaker 4	Beaker 1	Beaker 2	Beaker 3	Beaker 4
P total [mg/L]	0.76	0.72	0.74	0.7	0.69	0.67	0.68	0.69
P soluble [mg/L] (0.2 µm pore size filter)	0.62	0.61	0.64	0.51	0.63	0.63	0.65	0.61
Initial Mixed liquor AS: Psoluble–0.88mgP/L	**E 2 A** Mixed liquor AS collected at the end of aeration basins Default pH: 7.2				**E 2 B** pH adjusted to 6			
	Beaker 1	Beaker 2	Beaker 3	Beaker 4	Beaker 1	Beaker 2	Beaker 3	Beaker 4
P soluble [mg/L] (0.2 µm pore size filter)	0.7	0.26	**0.23**	**0.11**	0.96	0.35	**0.16**	**0.17**
Initial effluent: Ptotal–0.72mgP/L, Psoluble–0.68mgP/L	**E 2 C** Effluent from the secondary clarifier Default pH: 7.9				**E 2 D** pH adjusted to 6			
	Beaker 1	Beaker 2	Beaker 3	Beaker 4	Beaker 1	Beaker 2	Beaker 3	Beaker 4
P total [mg/L]	0.66	0.68	0.66	0.66	0.67	0.69	0.68	0.67
P soluble [mg/L] (0.2 µm pore size filter)	0.40	**0.23**	**0.18**	**0.16**	0.44	**0.22**	**0.19**	**0.12**

2.4 CONCLUSIONS

A pulp mill WWTP receiving wastewater with a higher than usual P-content could be properly modelled by the aid of the software BioWin. Having the WWPT modelled (calibrated and validated) could aid at securing the satisfactory compliance of the effluent with the local environmental standards, as well as to assess alternatives procedures for optimizing the WWTP performance. The STOWA protocol for wastewater characterization and the application of the software BioWin, which were mostly developed and applied for municipal wastewater treatment plants, were satisfactorily applied in this research. Minor modifications were introduced to such protocols (including certain modifications to some certain kinetic and stoichiometric parameters - such as the OHOs and AOB aerobic decay rates, and the N and P fractions in the biomass as an endogenous residue) allowing to model an industrial pulp mill WWTP operated at 30 °C and with a SRT of 32 days. While most of the pulp mill WWTPs are nutrient deficient (and urea and phosphoric acid need be added as N and P sources), the pulp mill WWTP of study located in Uruguay is N deficient but has a high P concentration since the hardwood used as raw mate-rial has a high P content. Still, an extremely low nutrient uptake was observed during the aerobic batch activity test compared to municipal WWTP. Two specific scenarios were evaluated using the calibrated and validated Biowin model to reduce the TP concentration in the effluent: CPR and EBPR. According to the model, which is a simplification of reality, including an anaerobic phase prior to the aerobic process may reduce the TP concentration in the effluent by approximately 58 %. In addition, CPR at the sweep coagulation range showed that the P concentrations can be further reduce to concentrations below 0.1 mg/L. However, further research activities such as pilot-testing or detailed studies maybe needed to validate the EBPR or chemical P removal for industrial-scale application. In addition, the industrial applicability of pulp mill anaerobic treatment should be indeed studied considering that lignin compounds from pulp mill wastewater could be inhibitors for this biological treatment. Likewise, it is necessary to evaluate other consequences regarding chemical addition for TP removal. Finally, four other scenarios were assessed to know the WWTP respond to eventual changes in its operation. This model is advantageous because allows plant technicians to evaluate possible changes in plant control or operating strategy.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.psep.2020.08.029.

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3

RESOURCE RECOVERY ASSESSMENT AT A PULP MILL WASTEWATER TREATMENT PLANT IN URUGUAY

This chapter is based on: Bentancur, S., López-Vázquez, C. M., García, H. A., Duarte, M., Travers, D., & Brdjanovic, D. Resource recovery assessment at a pulp mill wastewater treatment plant in Uruguay. Journal of Environmental Management, 255 (2020).

ABSTRACT

Using a mathematical model, a resource recovery assessment was carried out at a pulp mill activated sludge wastewater treatment plant (WWTP) located in Uruguay. Through the evaluation of different scenarios, the potential production of methane from secondary sludge, with its inherent energy savings, and the recovery of phosphorus (P) as struvite were estimated. Considering the current WWTP configuration with a sludge retention time (SRT) of 32 days, and according to the model, which is a simplification of reality, the assessment indicates that the implementation of an anaerobic digester (AD) to treat the excess sludge can lead to a methane production of approximately 1736 m^3 CH_4/d, being a promising alternative to increase the WWTP treatment performance. Furthermore, the model predictions suggest that by shortening the SRT from 32 to 5 days, the methane production could increase by up to 5568 m^3 CH_4/d. If the methane produced is used to generate electrical energy to operate the WWTP, energy savings of about 88 % can be achieved. Regarding the potential recovery of P as struvite, the addition of a struvite reactor could be an efficient option to recover approximately 1611 mg/Lof struvite (corresponding to a load of about 433 kg/d). By optimizing the process performance, these findings highlight the potential recovery of resources in pulp mill WWTP, while complying with stringent effluent discharge standards. In addition, further research activities such as pilot-test or detailed laboratory studies may be needed to validate the previous recommendations for industrial-scale application.

3.1 INTRODUCTION

The discharge of industrial effluents is one of the most important sources of pollution, affecting water courses and ecosystems. Pulp and paper mill industrial processes are energy intensive processes and, furthermore, they require large volumes and quantities of fresh water and chemicals (Thompson et al., 2001; Veluchamy and Kalamdhad, 2017). Those demands are reflected in the generation of large volumes of pulp mill wastewater containing diverse pollutants of different nature and characteristics (Singh and Chandra, 2019). The large amounts of solid waste generated in pulp and paper mill industrial processes usually contain bark, reject fibres, sludge waste from WWTP, scrubber sludge, lime mud, green liquor dregs, and boiler, and furnace ash. Regarding the sludge production, sludge disposal is a severe environmental issue due to the presence of toxic compounds (Sumathi and Hung, 2006) such as dioxins and furans (Thompson et al., 2001; Savant et al., 2006), and polychlorinated compounds and chloroform (Savant et al., 2006; Cabrera et al., 2010).

Most of the pulp and paper industries worldwide have established strict discharge standards in accordance with local legislation, that usually comprise parameters like biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solids (TSS). Pulp and paper mills can reduce the pollution load by applying a combination of cleaner technologies and end-of-pipe treatment approaches. Wastewater treatment technologies are essential to meeting the required discharge limits by applying physicochemical and biological treatments. Additionally, anaerobic digestion technologies can be applied to decrease the generation of pulp mill activated sludge (AS) waste via the anaerobic stabilization of sludge (Puhakka et al., 1992; Eikelboom et al., 2018).

While pulp mill wastewater is satisfactorily treated in WWTP with conventional activated sludge (CAS) systems (Thompson et al., 2001; Mahmood and Elliott, 2006; Nurmesniemi et al., 2007; Buyukkamaci and Koken, 2010; Bentancur, 2014; Bentancur et al., 2015; and Bentancur et al., in preparation), the implementation of resource recovery practices is still rather limited in this sector (Puhakka et al., 1992; Stoica et al., 2009; Likon and Trebse, 2012; Meyer and Edwards, 2014; Simao et al., 2018; Lopes et al., 2018) and are mostly applied in North America and Europe (Puyol et al., 2017; Solon et al., 2019). Being a resource and energy intensive sector with high (fresh) water requirements, it becomes of major importance and interest to explore potential resource recovery practices to improve the environmental footprint of these WWTP (Fernández-Arévalo et al., 2017; Venkatesh, 2018; Eikelboom et al., 2018). Such an interest has been largely reinforced in recent years by environmental and political considerations that have promoted and encouraged the recovery and reuse of resources from sludge waste (Stark, 2004; Rolamo et al., 2017). The Netherlands, which has some of the most stringent environmental regulations in Europe, is one of the pioneering countries in the field of P recovery from sludge in municipal WWTPs (Stark, 2004; van Leeuwen et al., 2018). Phosphorus can be recovered from wastewater, either combined in the sludge, chemically precipitated and crystallized mostly as struvite ($MgNH_4PO_4.6H_2O$) (Shu et al., 2006; Westerman et al., 2009; Jones et al., 2011; Rolamo et al., 2017) or as vivianite ($Fe_2(PO_4)_3{\cdot}_8H_2O$) if iron dosing is used for chemical P-removal (Wilfert et al., 2018; Solon et al., 2019). The precipitation of struvite requires that the reactants are simultaneously available in the wastewater in a molecular ratio of 1(Mg^{2+}):1(NH_4^+):1 (PO_4^{3-}) (De-Bashan and Bashan, 2004) and it is influenced by pH, temperature, mixing rate, as well as other ion concentrations that affect the saturation of the solution (Sharp et al., 2013; Rolamo et al., 2017). Often, magnesium is the limiting compound and needs to be dosed, which leads to a pH increase (De-Bashan and Bashan, 2004; Britton et al., 2005). Approximately, 1 kg of struvite can be crystallized from 100 m^3 of municipal wastewater treated daily, which would be enough to cover the P requirements of 2.6 ha of arable land at an application rate of 40 kg P as P_2O_5/ha/year as fertilizer (Shu et al., 2006). Alternatively, if iron is dosed, the ferrous iron phosphate mineral vivianite ($Fe_2(PO_4)_3{\cdot}_8H_2O$) can be formed in anaerobic systems at relatively low sulphide concentrations and a pH of about 7.0 (Wilfert et al., 2018).

Considering the major importance and increasing growth of the pulp sector in Uruguay, its high energy consumption, that the sludge generated does not offer any considerable added value (being treated and disposed of in forest plantations on landfills) and the associated environmental concerns, it is of upmost importance to study potential alternatives for the recovery of resources from the sludge waste. To this end, the anaerobic digestion of secondary sludge (to estimate the potential production of methane) and the implementation of a reactor to precipitate struvite were assessed in a pulp mill WWTP located in Uruguay (with an estimated equivalent treatment capacity of 73,000 m^3/d). Both of these applications may contribute to the generation of a circular economy around the pulp mill (Puyol et al., 2017; Sena and Hicks, 2018) by transforming (sludge) waste into valuable revalorized products. Similar principles are already applied in other projects carried out in the region (Fernández-Arévalo et al., 2017; van Leeuwen et al., 2018). Currently, there are do not exist cases of circular economy projects around the pulp industry in Uruguay, but emerging biorefinery projects do exist in Brazil (Centro de Gestao e Estudos Estratégicos, 2016; Oliveira and Navia, 2017; Simao et al., 2018). The WWTP was modelled with BioWin (Envirosim, Canada). The calibrated and validated model was applied to assess different scenarios addressing different plant configurations and operating conditions towards the development of environmentally friendly resource recovery practices.

3.2 MATERIALS AND METHODS

3.2.1 Wastewater treatment plant configuration

The WWTP was built in 2007. The plant configuration is shown in Figure 3.1. The pulp mill WWTP was designed to treat an effluent flowrate of 25 m^3/ADT (approximately 0.8 m^3/s) (Saarela et al., 2007). The plant has a mechanical pre-treatment followed by a conventional activated sludge (CAS) system for the removal of organic matter (measured in terms of COD). Two main effluent streams are received and treated at the plant, one with a high solids content (sampling point 1a) and another with a low solids content (sampling point 1 b). Sampling points 1a and 1 b are located at the beginning of the preliminary treatment stage. The preliminary treatment is composed of: screening followed by primary sedimentation (for the high solids content effluent); Ph pre-neutralization (for the low solids content effluent); 3 tank equalizers (each one with a working volume of 25,000 m^3) where the high and low solid content effluents get combined; a pH neutralization and nutrient addition stage; cooling towers (to decrease the effluent temperature to 30 °C); and, a post-neutralization step (sampling point 2).

After the preliminary treatment, the combined effluent is conveyed to the CAS system. The CAS system has two parallel treatment lines. Each line has an aeration basin of 75,000 m^3 (sampling points 2.1a, 2.1b and 2.1c for the first treatment line, and 2.2a, 2.2b and 2.2c for the second treatment line), a secondary clarifier, and a recirculation of activated sludge (RAS) from the secondary clarifier to the aeration tank. Sampling points 3a and 3b are located just after the aeration basins 1 and 2, respectively, while sampling point 4 is used to assess the water quality of the effluent prior to discharge into the Uruguay River.

The primary sludge (presumed to have a high content of inorganic suspended solids) alone or sometimes combined with a small fraction of secondary sludge (assumed to have a higher organic content) is directed to a sludge mixing tank (with a working volume of 500 m^3) and afterwards dewatered in two filter presses with a total capacity of 33.8 ton dry solids (tDS)/d primary sludge or 26 ton DS/d primary + biosludge mixture. The rest of the secondary sludge is dewatered in a gravity table and a centrifuge with a capacity of 17 ton DS/d. The filtrates from the two sludge dewatering units and from the gravity table and the centrifuge are recirculated to the preliminary treatment stage (just before the primary clarifier and the pre-neutralization stages); meanwhile, the primary dewatered sludge is disposed of in forest plantations, and the liquor-bio-sludge mixture sent to an evaporation process at the mill.

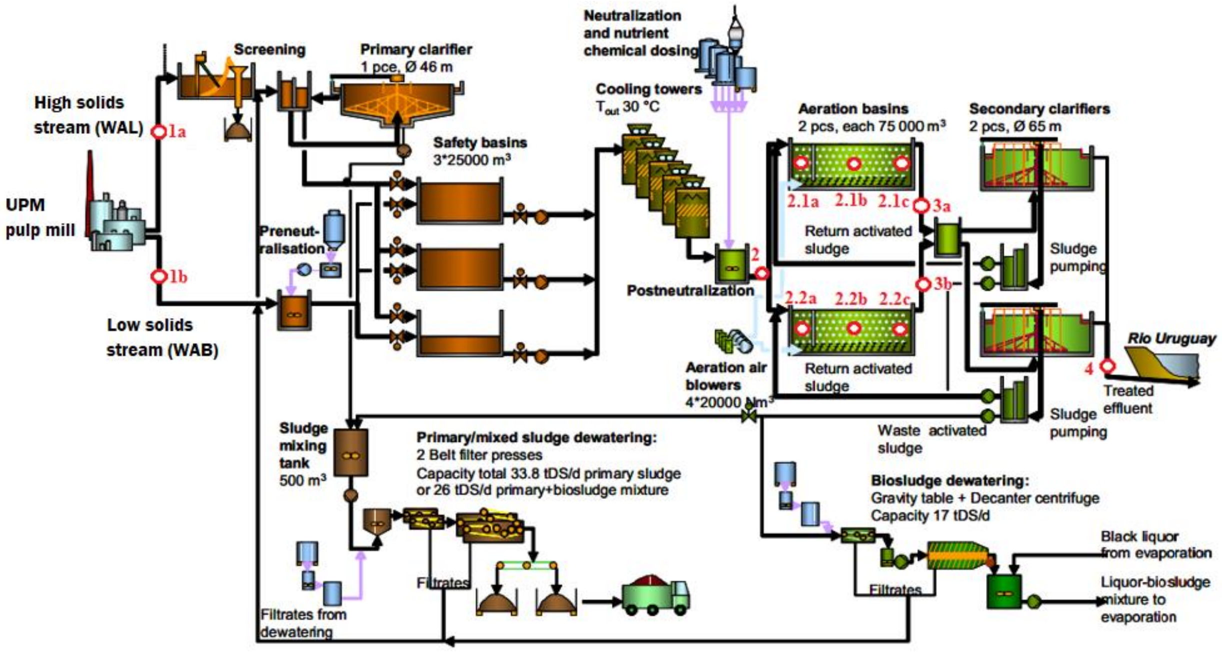


Figure 3.1 Process flow diagram of the pulp mill wastewater treatment plant (WWTP). The circles and numbers indicate the location of the sampling points used for the conduction of the sampling campaign

3.2.2 Experimental procedures

Characterization of flows

In order to obtain a general overview of the WWTP, data regarding the operation and performance of the components of the treatment system units were collected and analysed for the period comprised from May to August 2013. The historical data was used to make a preliminary model of the plant. In addition, a sampling campaign was designed and implemented to complete the required information. The sampling program and measuring campaign was carried out from October 21st to 28th, 2013, at the pulp mill WWTP to characterize the wastewater in accordance with the guidelines from the protocol for wastewater characterization of the Dutch Foundation for Applied Water Research (STOWA) protocol (Hulsbeek et al., 2002; Roeleveld and Van Loosdrecht, 2002). For this purpose, 24 h representative composite samples were collected during five consecutive days to characterize the influent and the effluent. The influent flow characterization was carried out just before the aeration basins at sampling point 2 (Fig. 3.1) and the effluent characterization at sampling point 4 (Fig. 3.1).

Aerobic batch tests

An aerobic batch activity test was executed to assess the nutrient requirements of the activated sludge biomass. For this purpose, a lab setup was assembled at the pulp mill laboratory facility. Mixed liquor activated sludge collected at the end of the aeration basin was aerated for 6 h prior to the execution of the test. Thereafter, the sludge was poured into the beaker. The pH was adjusted to 7.5 through the manual addition of HCl 0.1 M and NaOH 0.1 M solutions. Allyl-N-thiourea was added as nitrification inhibitor. In addition, 10.3 mg of urea and 53.0 mg of sodium tri-phosphate were added as N and P sources, respectively. At the start of the test, the influent was added into the batch reactor, and different samples were collected within the first 120 min. of the test, as well as after 24 and 48 h.

Analytical parameters

Parameters such as total COD, total nitrogen (TN), total phosphorus (TP), TSS, volatile suspended solids (VSS) and inorganic suspended solids (ISS) were determined at the laboratory facilities of the pulp mill according to standard methods (APHA et al., 2012). The rest of the parameters (including NO_2^- , NO_3^- , NH_4^+, BOD_{10} and PO_4^{3-}) were determined at the Technological Laboratory of Uruguay (LATU) also in accordance with standard methods (APHA et al., 2012).

Statistical analysis

Statistical parameters including mean and standard deviation were calculated for the collected data. The data computed with the model were analysed by means of a one-way analysis of variance or ANOVA (95 % confidence interval) performed using Microsoft Excel Office 365 (Microsoft, USA) when an analysis of significance was required. In this case, the dependent variables were methane production and struvite generation and the factor studied was the SRT.

3.2.3 Modelling strategy

First, the performance of the pulp mill WWTP in Uruguay was assessed by modelling the plant using BioWin v. 3.0 (EnviroSim Associates Ltd., Canada) (Bentancur et al., in preparation). The model calibration was obtained by adjusting wastewater fractions, and kinetic and stoichiometric parameters (like the aerobic decay rate and the DO half saturation constant for aerobic denitrification; nitrogen and phosphorus fractions of biomass, and the endogenous residue fraction coefficient). Aerobic batch activity tests were also conducted at the lab-facilities of the pulp mill WWTP to calibrate the model. The calibrated model was validated using data from different time periods. The calibrated and validated model provided a satisfactory description of the current and historical operation of the plant (regarding COD, TSS, TN and TP concentrations). Further details about the modelling, calibration and validation strategies can be found elsewhere (Bentancur et al., in preparation). In the present study, the model of the WWTP is used as a tool to assess different scenarios to improve the removal of TP as well as to explore potential plant upgrades and operational strategies for the recovery of resources (such as nutrients and energy through the anaerobic digestion of the excess of secondary sludge).

Fig. 3.2 shows a complete TP overview of the biological secondary treatment of the current WWTP configuration. The influent TP load to the biological treatment is 216 kgP/d. This load is divided into two parallel lines. The TP input into line 1 is 118 kgP/d, while into line 2 it is 108 kgP/d. The TP load into the secondary clarifier 1 is 15 kgP/d, whereas into the secondary clarifier 2 it is 20 kgP/d. This leads to a TP load of 35 kgP/d discharged into the Uruguay river. As observed, 84 % of the TP load discharged into the plant is removed through sludge waste (93 kgP/d through WAS_1 and 88 kgP/d through WAS_2). Only 16 % of the load is discharged into the Uruguay river. Interestingly, the TP load estimated to be present in the recirculation flow ($RAS_1 + RAS_2$) is 4887 kgP/d. Under the current operating conditions, up to 181 kgP/d may be recovered from the sludge.

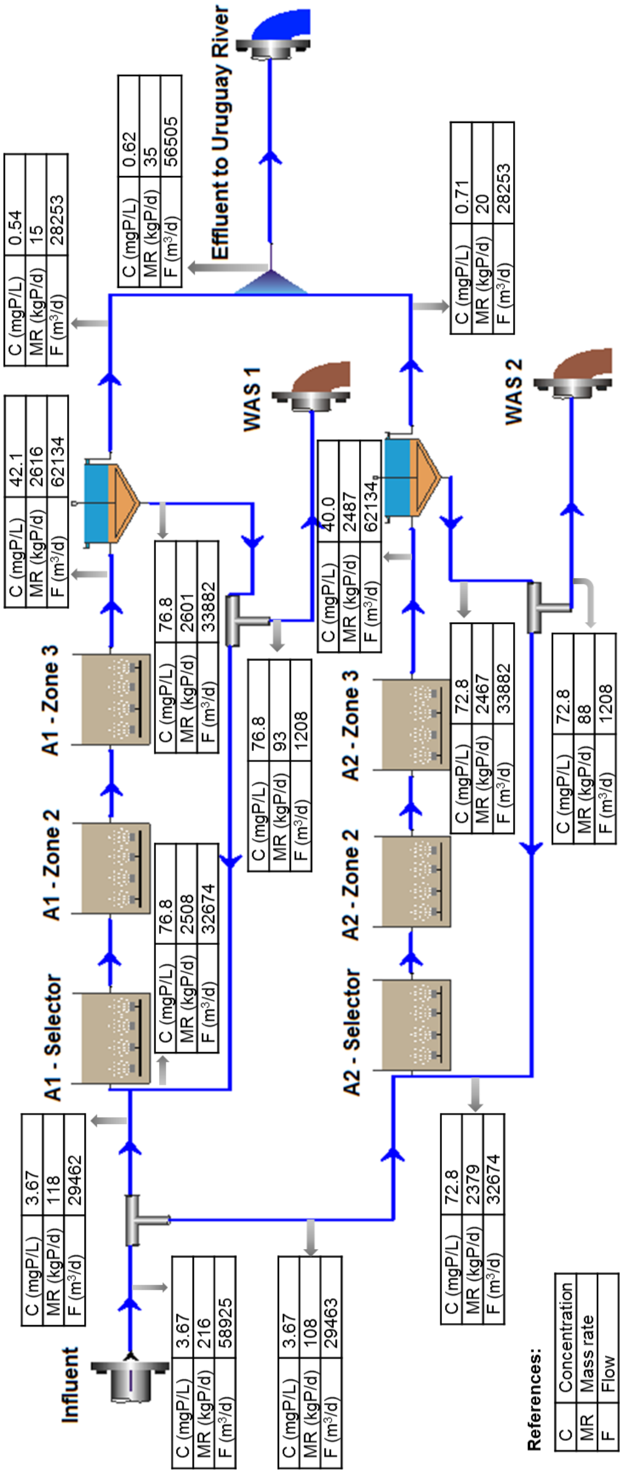
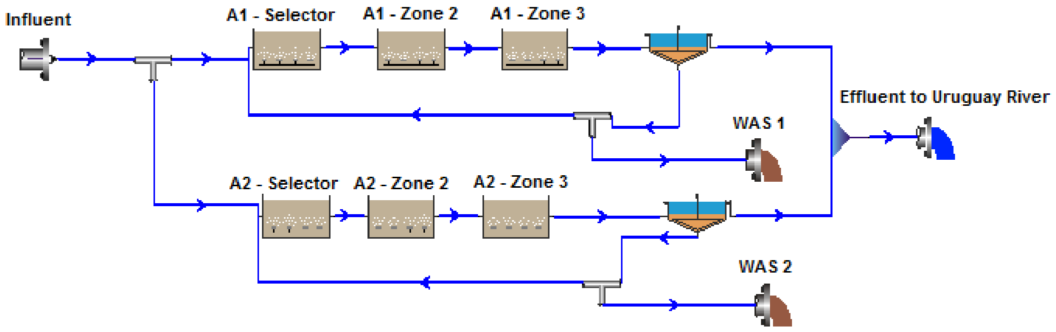


Figure 3.2 PT concentration and loads throughout the activated sludge system based on the current configuration

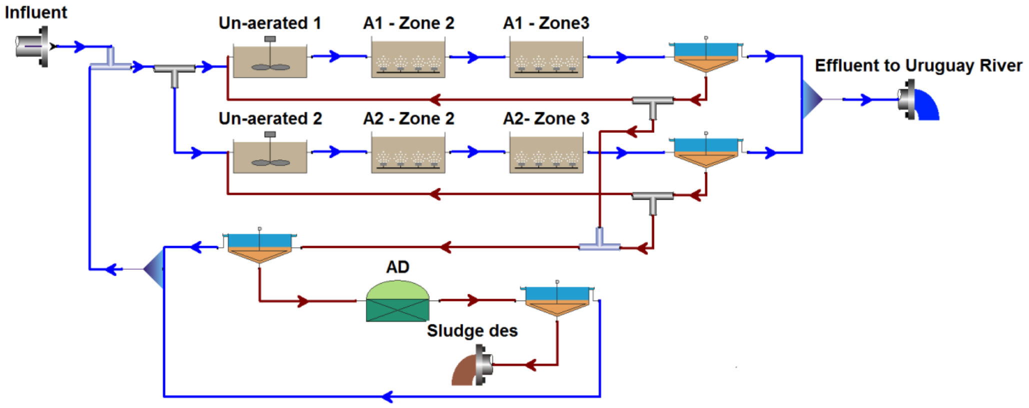
3.2.4 Assessment of resource recovery scenarios

In this research, two resource recovery scenarios were studied: (i) the implementation of an anaerobic digester to treat the generated sludge waste (Fig. 3.3B), and (ii) nutrients recovery in the AD supernatant (Fig. 3.3C). It is important to highlight that both scenarios were evaluated after considering the creation of a non-aerated zone at the beginning of the aerobic reactor. The non-aerated zone was implemented (by converting 25 % of the 35,000 m^3 aeration basin volume) to promote an Enhanced Biological Phosphorus Removal (EBPR) process in the pulp mill WWTP (further details can be found in Bentancur et al., in preparation).

A) Current WWTP configuration.



B) Scenario No.1: Implementation of an anaerobic digester in the sludge treatment stage.



C) Scenario No.2: Implementation of an anaerobic digester and a sludge precipitation tank in the sludge treatment stage.

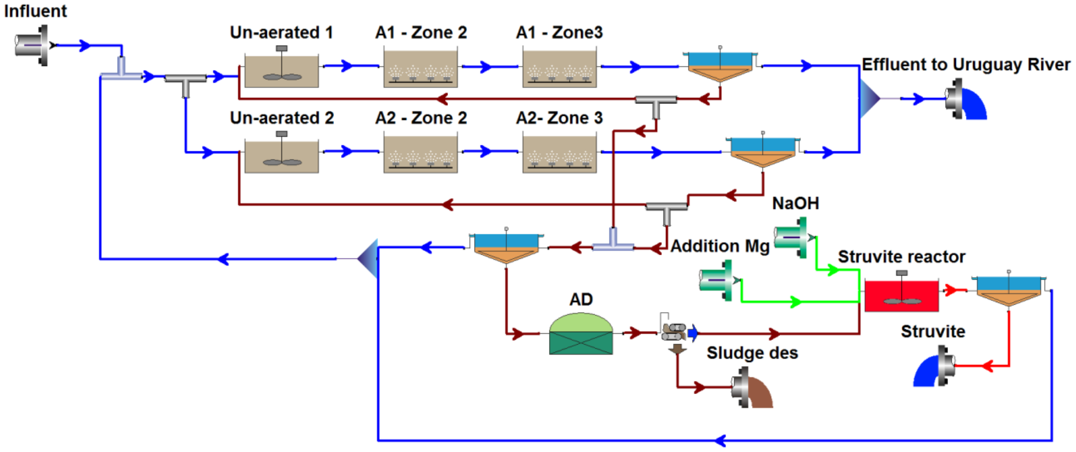


Figure 3.3 BioWin layout of a pulp mill WWTP in Uruguay

Scenario No. 1: Implementation of an anaerobic digester in the sludge treatment stage

In the CAS WWTP, the mixed primary and secondary AS can be biologically stabilized under anaerobic conditions and converted into methane (CH_4) and carbon dioxide (CO_2) through the introduction of an AD unit (Andreoli et al., 2007). The current CAS system at the pulp mill WWTP has been designed as an extended aeration process to minimize the sludge production and therefore works at an SRT of about 32 days. As previously discussed, to assess this scenario, first, an EBPR process was implemented, and an anaerobic digester was included in the process to treat the sludge generated at the WWTP. Thereafter, different scenarios were assessed by progressively shortening the SRT from 32 d to 25, 20, 15, 10 and 5 d with the aim of increasing the generation of a sludge waste with a higher content of volatile suspended solids. To assess these scenarios, the AD was designed and operated at the mesophilic temperature of 35 ^{o}C, pH of 7.0 and with a hydraulic retention time (HRT) of 21 days. Table 3.1 displays the estimated volume of the AD as a function of the sludge waste generated at the different SRTs of the mainstream CAS system.

In order to carry out a complete evaluation of the WWTP wastewater and sludge treatment lines, the energy consumption of the aeration system, methane production, energy production and net energy consumption were estimated (further details can be found in Supplementary material: Section 1).

Table 3.1 Estimated volume of an anaerobic digestion (AD) sludge treatment system as a function of the sludge waste generated at different SRT of the activated sludge system assessed in Scenario No. 1

SRT of the WWTP (days)	AD Volume (m^3)	Incoming bio-sludge flowrate (m^3 d^{-1})
32	14,600	707
25	18,562	884
20	23,772	1132
15	31,920	1520
10	48,258	2298
5	81,669	3889

Scenario No. 2: Implementation of an anaerobic digester and a sludge precipitation tank in the sludge treatment stage

After the first scenario was studied, the chemical precipitation and recovery of P as struvite in the supernatant of the AD was evaluated (Figure 3.3C). The amount of struvite generated was assessed at different SRTs in order to assess the best alternative from Scenario No. 1 (with an estimated high methane production) and find the optimal operational configuration for the recovery of resources at the WWTP.

3.3 RESULTS AND DISCUSSION

3.3.1 Assessment of resource recovery scenarios

Scenario No. 1: Implementation of an anaerobic digester in the sludge treatment stage

Fig. 1 in the Supplementary material: Section 2, shows a TP mass balance (and assumptions) throughout the modified layout of the pulp WWTP after the introduction of an AD into the sludge treatment line. The potential methane generated at the plant was estimated as a function of the SRT applied in the mainstream treatment line, which could be shortened to maximize the generation of sludge (Fig. 3.4). By shortening the SRT to increase the production of a less stabilized sludge, higher biogas productions were observed. If the SRT was shortened from 32 to 5 days, this could increase the methane production by 300 %: from 1736 m^3/d (at 32 d SRT) to 5568 m^3/d (at 5 d SRT) which was found to be statistically significant (ANOVA, P ¼ 0.0003 <0.05, more detail in Supplementary material: Section 3). However, there was a concern that the anaerobic digestion of sludge would increase the P-released in the AD unit, leading to an increase in the mainstream TP concentration through the internal recirculation flows (149 kgP/d, corresponding to 41 % of the TP mass rate in the influent to AS system) (Fig. 1 in the Supplementary material: Section 2). Nevertheless, according to the model simulations, the combined implementation of EBPR and the introduction of the AD do not jeopardize the effluent quality (which remains at 0.16 mgP/L, Fig. 1 in the Supplementary material: Section 2). For instance, regardless of the SRT applied, the effluent concentrations remain practically unchanged at around 260–280 mgCOD/L and 0.2 mgTP/L, respectively, complying consistently with the standards established by the Decree No 253/79 (Decreto 253, 1979) regulating the Uruguayan water code law 14.859 regarding the direct discharge to water courses (BOD_5 set at 60 mg/L and TP set at 5 mg/L) and enforced by the Uruguayan Environmental Agency (DINAMA).

The energy production, energy consumption (considering only the aeration requirements) and the potential net energy savings in the pulp mill WWTP were estimated considering the implementation of the previously discussed process modifications. As observed in Fig. 3.5, if an AD unit is implemented and the SRT is shortened from 32 to 5 d, the potential net energy savings could increase from 24 % to 88 % (regarding the aeration requirements). The procedure used to calculate the potential net energy savings was performed according to Spanjers (2013), and the conversion factors used are detailed in Supplementary material: Section 1. Overall, this alternative looks rather promising and deserves to be thoroughly analysed due to the potentially remarkable benefits, as observed elsewhere (Mohammadi et al., 2019). Previous research developed by Cabrera et al. (2010) studied the potential feasibility to anaerobically treat similar pulp mill primary and secondary sludges. The results showed that the biodegradability of the primary sludge was relatively low and, consequently, it is not recommended to be anaerobically digested due to its composition (mainly composed of lignin and inorganic residues). Similar results were observed by Eikelboom et al. (2018). Nevertheless, it must be underlined that the results of the modelling study rely on the potential decrease of the SRT from 32 to even 5 d. Shorter SRTs decreases the accumulation of unbiodegradable and inorganic compounds and increases the biodegradable content of the sludge (Ekama and Wentzel, 2008), which can increase the feasibility to apply an anaerobic treatment process to treat the sludge waste, as indicated by the model outcomes. In addition to increasing the biodegradable content of the secondary sludge, different pre-treatment alternatives can be evaluated (such as thermal and ultrasound, among others) in order to improve the biogas production (Veluchamy and Kalamdhad, 2017; Vaneeckhaute et al., 2017). Lopes et al. (2018) showed that the anaerobic digestion process for Kraft pulp mill secondary sludge still is not feasible on a large scale, since the energy balance is negative, as the heat necessary to maintain the temperature in the reactor is higher than the energy produced. However, Lopes et al. (2018) assessed the thermophilic anaerobic digestion of sludge, which has higher energy requirements and does not rule out that the mesophilic treatment (which is less energy intensive and, arguably, more stable) could be feasible (Nielsen et al., 2017). Last but not least, the application of heat recovery devices (Kretschmer et al., 2015) or the reuse of hot water generated by the cooling towers (Gude, 2015; Van de Bor et al., 2015; Ghoneim et al., 2016) could be explored as mechanisms to warm up the AD units. This may bring additional benefits by introducing heat recovery, which can contribute to reduce the energy requirements of the anaerobic digestion process. Further research is needed (such as pilot, detailed biomethane potential tests and energy recovery studies) to validate these potential modifications of the process configuration.

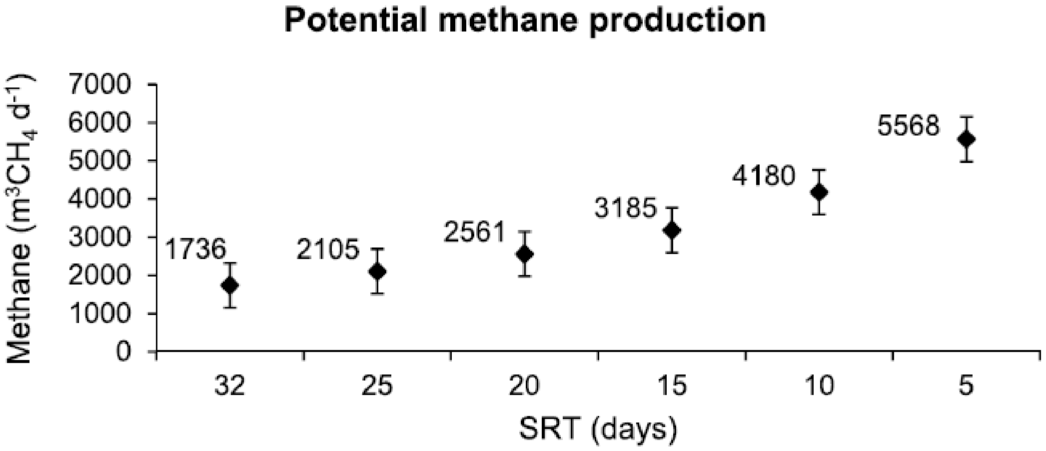


Figure 3.4 Potential methane production as a function of the SRT applied to the main wastewater treatment line

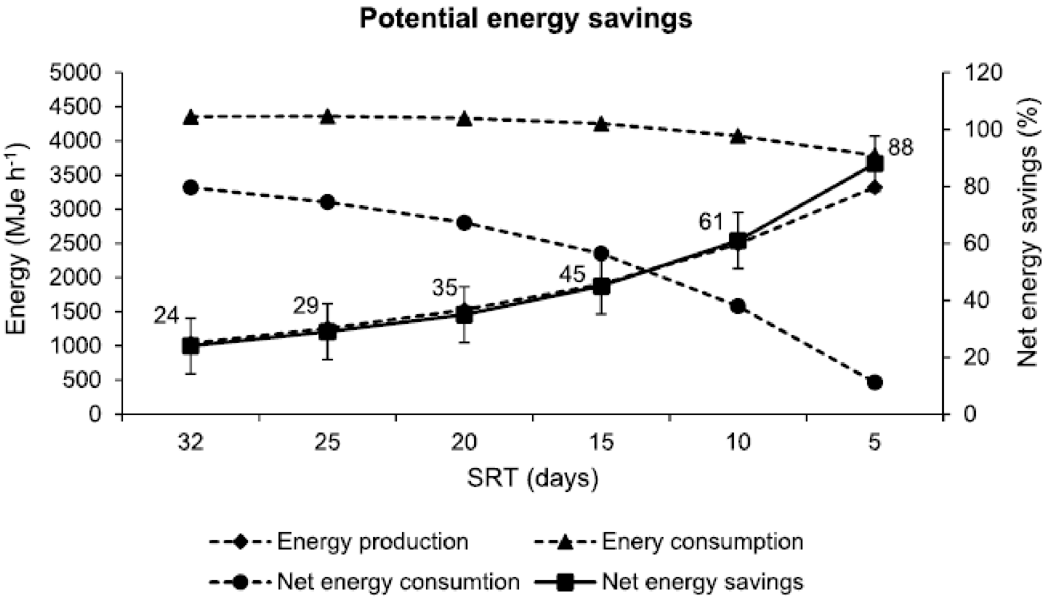


Figure 3.5 Potential energy savings at the pulp mill WWTP considering the energy consumption and potential energy generation if the excess of sludge is treated in an anaerobic digestion system and the generated methane is used for power generation

Scenario No. 2: Implementation of an anaerobic digester and a sludge precipitation tank in the sludge treatment stage

In this scenario, the precipitation of struvite from the nutrients (N and P) present in the supernatant of the AD and the addition of magnesium were assessed at different SRTs (between 32 and 5 days). Table 3.2 presents the design parameters applied for the non-aerated zone, anaerobic digester, and struvite reactor; also, it shows the methane production and generation of struvite.

The evaluation of scenario No. 2 at different SRTs showed that the highest methane production was observed at a SRT of 5 days. However, at this SRT no struvite precipitation was observed. SRT had a statistically significant effect on struvite generation (ANOVA, P ¼ 0.003 <0.05, more details can be found in Supplementary Materials: Section 3). Likely, an SRT of 5 days was too short to favour the growth of phosphate accumulating organisms (PAOs), suggesting that the EBPR process cannot be applied. In accordance with the study carried out by Brdjanovic et al. (1998) in EBPR systems, where storage polymers play an important role in bacterial metabolism, the determination of the minimum aerobic SRT is crucial. That aforementioned study indicates that the minimum aerobic SRT of PAOs at 20 ^{o}C is of about 3 days. In those experimental results, a strong dependency on temperature and the kinetics of the metabolic processes was found. Furthermore, in the WWTP evaluated in this research, the local temperature was 30 ^{o}C, and this factor likely had a negative influence over the PAO's activity. Lopez-Vazquez et al. (2008) reported that at temperatures higher than 30 ^{o}C the aerobic maintenance requirements of PAO increase considerably.

Moreover, PAOs rely on intracellular PHA storage compounds to cover aerobic maintenance requirements but also for P-uptake and growth. As such, if the aerobic maintenance rates increased considerably at 30 ^{o}C, this may result in a higher aerobic PHA consumption rate for maintenance, decreasing the PHA availability for the P-uptake and growth rates. Consequently, if these rates are slower, the SRT of 5 days resulted insufficient to allow the growth of PAOs, affecting the P-removal capacity. Nevertheless, as seen in Table 3.2, the TP concentration in the effluent discharged into the Uruguay river is low, meeting the discharge limits. The fact that P-removal was observed despite the lack of EBPR activity, suggests that the TP removal could have been achieved through chemical precipitation due to the calcium concentration observed (of 86 kg d^{-1}) at the SRT of 5 days.

From the previous evaluation, 25 days was chosen as the optimal SRT. This alternative was selected because (i) enough precipitation of struvite is achieved, (ii) a medium AD volume is required and (iii) a considerable amount of methane is produced. In addition to these factors, the pulp mill generates steam and energy for self-consumption as part of the Kraft recovery process, so for the industry the best alternative is to generate higher volumes of struvite to recover nutrients. This scenario was conducted introducing a struvite reactor with a volume of 1000 m^3, operated at an HRT of 30 h and at a pH of about 8.3. The precipitation was enhanced through the addition of magnesium hydroxide (at a flowrate of 10 m^3 d^{-1} with a concentration of 6670 mg Mg L^{-1}) and estimating the P content in the precipitate. The AD operated at a mesophilic temperature of 35 ^oC, pH 7.0 and hydraulic retention time of 21 days. The characteristics of the AD unit with the SRT of 25 days were: an 18,562 m^3 volume, area of 4111 m^2, a 4.5 m depth, a headspace volume of 2175 m^3 and a headspace pressure (absolute) of 103 KPa. The incoming bio-sludge flowrate was 884 m^3 d^{-1}. The modified layout of the WWTP and the TP mass balance is displayed in Fig. 2 in Supplementary Materials: Section 2. Table 3.3 shows the design parameters for the precipitation of struvite in the reactor, the chemical addition dosage and the effluent composition.

In the proposed configuration displayed in Fig. 2 in Supplementary Materials: Section 2, Mass balance of TP, the TP load in the influent is 216 kg P d^{-1}. The TP load in the WAS from the secondary clarifiers is about 208 kg P d^{-1}, it passes through the sludge thickener and then goes to the AD unit. The effluent of the AD system goes to the dewatering unit and the sludge contains 132 kg P d^{-1}. The output TP load from the dewatering unit that enters the struvite reactor is 76 kg P d^{-1}. This TP load in combination with a concentration of 40 kg Ammonia N/d and 17 kgMg/d can lead to up to 346 kg of struvite recovered per day. The effluent TP load (13 kgP/d), as seen in the TP mass balance shown in Fig. 2 (Supplementary Materials: Section 2), fulfils the discharge limit of the pulp mill set by DINAMA (with a maximum allowable load of 60 kgTP/d) and is also lower than the load of 35 kgP/d generated by the current WWTP configuration (Fig. 2). Despite the benefits of the proposed struvite recovery configuration, conducting the P-recovery on the digested sludge may be a better option than in the return flow line from the dewatering unit. A recent research conducted in the Amsterdam West WWTP has shown that this practice increases the performance of the sludge dewatering centrifuge (van Nieuwenhuijzen et al., 2009; Bergmans, 2011). Thus, if the P-recovery unit is installed just after the AD system, the struvite formed might increase to approximately 1611 mg/L with a load of 432.5 kg ISS/d (Table 3.4). This amount of struvite is generated with the removal and consumption of 203 kgP/d, 46 kg Ammonia N/d and 16 kgMg/d. In this WWTP configuration, the TP concentration in the effluent discharged into the river meets the standards established by DINAMA (TP set at 5 mg/L).

Assuming a general scenario and considering that 1 kg of struvite would be sufficient to cover the P requirements of 2.6 ha of arable land at an application rate of 40 kg P as P_2O_5/ha/year (Shu et al., 2006; Rahman et al., 2014), the generated struvite (433 kg ISS/d) could be used as fertilizer to cover approximately 405,000 Ha per year. This area represents only 2.3 % of the total area of Uruguay but corresponds to about 25 % of its total agricultural land (1,604,000 Ha per year) (MGAP, 2015). This means that the P (and N) recovered at the plant as struvite can be used to cover up to 24 % of the demand of fertilizers in Uruguay. Fertilizers are mostly used for the cultivation of soy (1,099,000 Ha), wheat (193,000 Ha), rice (160,000 Ha), barley (153,000 Ha), corn (71, 000 Ha) and other agricultural products in a smaller proportion (MGAP, 2018). In the Municipality where the pulp mill subject of study in this research is located, the main land uses are forestry and agricultural production (cereals and oilseeds) (MGAP, 2015; Restaino, 2019).

The potential recovery of N and P through this practice could bring an integrated resource recovery strategy while complying with the discharge limits imposed to the plant. According to Rahman et al. (2014), struvite is an effective alternative source of rock phosphate to maintain agricultural production systems. Struvite would be a useful alternative to traditional N fertilizers because it also reduces greenhouse-gas emissions and thus decreases the global warming effects due to its slow releasing pattern (decreasing the diffusion of nutrients into the land). The slower nutrient leaching loss and its fertilizer quality make struvite an eco-friendly fertilizer for crop production (Rahman et al., 2014; Sena and Hicks, 2018). Further research is needed to validate these alternative configurations for the pulp mill WWTP.

Table 3.2 Design parameters for the recovery of nutrients as struvite in the sludge treatment line at different WWTP SRT

	SRT (days)					
	5	10	15	20	25	32
Non-aerated zone in AS system (m^3)	35,000	35,000	35,000	35,000	35,000	35,000
PAOs in the non-aerated zone (mg COD L^{-1})	17	17	36	60	91	124
PAOs in the non-aerated zone (kg COD d^{-1})	2110	2138	4538	7604	11,482	15,730
Effluent TP to Uruguay River (mg L^{-1})	0.3	0.2	0.2	0.2	0.2	0.2
Anaerobic Digester volume (m^3)	81,669	48,258	31,920	23,772	18,562	14,600
Methane production (m^3 CH_4 d^{-1})	5568	4180	3185	2561	2105	1736
Struvite Reactor volume (m^3)	4375	2506	1710	1273	1000	815
Struvite Reactor HRT (hs)	30	30	30	30	30	30
Soluble PO_4–P (kg P $d^{-1)}$	50	1.6	1.2	1.2	1.8	2.4
Ammonia N (kg N d^{-1})	112	82	62	49	40	33
Total P (kg P d^{-1})	50	78	76	74	71	69
Calcium (kg d^{-1})	86	2.4	0.53	0.08	0.01	0.00
Magnesium (kg d^{-1})	44	28	22	19	17	16
Struvite (kg ISS d^{-1})	0	148	260	320	346	357

Table 3.3 Design and operating parameters for the recovery of nutrients as struvite in the sludge treatment line

Parameter	Influent	Effluent	Reactor	Struvite recovery reactor	Unit
Flowrate	58,925	58,604			$m^3\ d^{-1}$
COD	1588	266			mg COD L^{-1}
TSS	167	6.4			mg TSS L^{-1}
TN	15.8	1.5			mg TN L^{-1}
TP	3.7	0.2			mg TP L^{-1}
MLVSS			3451		mg VSS L^{-1}
MLSS			4244		mg TSS L^{-1}
Mg solution Flowrate				10	$m^3\ d^{-1}$
Mg				6670	mg Mg L^{-1}
Struvite precipitation				1430	mg ISS L^{-1}
Struvite precipitation				346	kg d^{-1}

Table 3.4 Design and operating parameters for the recovery of nutrients as struvite in the sludge treatment line

Parameter	Influent	Effluent	Reactor	Struvite reactor	Unit
Flow	58,925	58,604			m^3 d^{-1}
COD	1588	266			mg COD L^{-1}
TSS	167	6.4			mg TSS L^{-1}
TN	15.8	1.5			mg TN L^{-1}
TP	3.7	0.2			mg TP L^{-1}
MLVSS			3451		mg VSS L^{-1}
MLSS			4244		mg TSS L^{-1}
Mg solution flowrate				10	m^3 d^{-1}
Mg				8000	mg Mg L^{-1}
Struvite precipitation				1611	mg ISS L^{-1}
Struvite precipitation				432	kg d^{-1}

3.4 PRACTICAL APPLICATIONS AND FUTURE RESEARCH PERSPECTIVES

This model-based study assessed the feasibility of (i) implementing the anaerobic digestion of secondary sludge at a pulp mill WWTP located in Uruguay to estimate the potential production of methane as an energy source and (ii) implementing a reactor to precipitate struvite for nutrient recovery. These sludge recovery alternatives have been widely studied and applied in municipal WWTP (Surendra et al., 2014; Otoo and Drechsel, 2018). Regarding pulp mill WWTP, there are several studies that suggest that these strategies can be successfully applied (Veluchamy and Kalamdhad, 2017; Vaneeckhaute et al., 2017; Lopes et al., 2018; Mohammadi et al., 2019). Nevertheless, pre-treatment studies are needed to assess the potential increase in biodegradability of the secondary sludge prior to anaerobic digestion, to increase biogas production. Future research must focus on validating these results via the conduction of pilot- and detailed biomethane potential tests as well as to evaluate the adaptation of anaerobic microorganisms to the lignin compounds present in pulp mill wastewaters (to assess any potential inhibitory effect on the anaerobic digestion process). The feasibility of treating the primary sludge and a mixture of both primary and secondary sludge anaerobically should also be studied.

In addition, the efficiency of struvite as a fertilizer in crops and agricultural land in Uruguay must also be determined. Nowadays, developed countries are rapidly adapting their production chains moving from a linear to a circular economy, by giving added value to the generated waste, recycling and producing new resources that are (re-)incorporated into the economic production cycle. In coming years more resource recovery practices and strategies will be implemented around the world, emphasizing the importance of carrying out adequate and reliable feasibility studies to assess these potential alternatives.

3.5 CONCLUSIONS

According to the model used in this study, introducing an anaerobic digester to treat the excess of secondary sludge, and decreasing the SRT from 32 to 5 d can result in net energy savings of about 88 % while maximizing the compliance with effluent discharge regulations. Moreover, with an SRT of 25 days, the recovery of P via struvite precipitation can lead to the generation of 433 kg/d of fertilizer which is enough to satisfy the annual nutrient requirements of about 405,000 Ha of agricultural land. Further research is needed to validate the proposed modifications to the process configuration at an industrial-scale.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2019.109718.

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4

INITIAL SCREENING AND EVALUATION OF MAIN FACTORS AFFECTING CHEMICAL PHOSPHORUS REMOVAL AT PULP MILL WASTEWATER

This chapter is based on: Bentancur, S., López Vázquez, C. M., García, H.A., Duarte Guigou, M., Echeverría, L., Costabel, L., & Brdjanovic, D. Initial screening and evaluation of main factors affecting chemical phosphorus removal at pulp mill wastewater. In preparation

ABSTRACT

The chemical phosphorus removal (CPR) process in pulp mill wastewater treatment plant (WWTP) was studied to understand how the following key operational factors: chemical additives dosage and type, pH, temperature, and mixing intensity impact on the total phosphorus (TP) removal efficiency. Tests were carried out at laboratory scale. The effect of three precipitating agents such as: ferric chloride, aluminium sulphate, and calcium hydroxide were analysed at different temperatures (30, 45 and 60 ^oC), pH (from default, about 4.0 to 10.5) and mixing intensity (100, 200 and 300 rpm).

The higher phosphorus (P) removal efficiency was obtained at 60 ^oC and pH 10.5 for all types of precipitating agents. Furthermore, it was found that only by raising the pH to 10.5, without using any precipitating agent, the soluble P is removed. In addition, it was found that at pH less than 10.5, the precipitation of P occurs, but the P is not able to settle. The presence of calcium (Ca) and magnesium (Mg) ions in the wastewater cause precipitation of P at high pH. The optimal chemical additives dosage was found to be 600 mg$Ca(OH)_2$/L, 200 mg$Al_2(SO_4)_3\cdot 14.3H_2O$/L and 50 mg$FeCl_3\cdot 6H_2O$/L. The highest TP removal efficiency was 95 % with $Ca(OH)_2$, 98 % with $Al_2(SO_4)_3$ and 93 % with $FeCl_3$. The high temperature of the wastewater from the cellulose pulp process, approximately 60 ^oC, showed favouring the P removal process compared to lower temperatures such as 30 and 45 ^oC. The variation of mixing intensity in the coagulation process and the addition of different doses of polymer in the flocculation stage did not have a significant effect on the removal of P.

4.1 INTRODUCTION

Development of technologies for phosphorous (P) removal started in the 1950s in Switzerland in response to the issue of eutrophication and the need to reduce the levels of P affecting water bodies (Morse et al., 1998; Zahed et al., 2022; Zheng et al., 2023). Eutrophication has been one of the main environmental concerns reported in recent years (Clark et al., 1997; De-Bashan & Bashan, 2004; Rocher et al., 2023; Riza et al., 2023). The degree of eutrophication, and the related water quality problems, is largely dependent on the supply of nutrients, such as inorganic nitrogen (N) and P (Albertson & Sherwood, 2011; (Witek-Krowiak et al., 2022; Wang et al., 2023), which through the promotion of algae blooms results in oxygen depletion in the affected water bodies (Freund, 2013; Mozafari et al., 2023).

Phosphorous can be found in different forms in natural sources of water and also in wastewater. These forms can be classified into dissolved, colloidal, and particulate P. The particle size of colloidal P can vary from 0.01 to 1.0 µm (Ekama & Wentzel, 2008; Siebers et al., 2023). Phosphorous occurs in water merely as dissolved phosphates (Nassef, 2012). Because dissolved P and most of the colloidal P fractions cannot be removed by sedimentation in a reasonable period of time, chemical methods are commonly used for the removal of these fractions (Bratby, 2006) and (Tzoupanos & Zouboulis, 2008). Biological P removal can also be applied mostly to target the removal of dissolved P, although in such processes also colloidal and most of the particulate P can be also removed. In many cases, the P chemical treatment needs to be added to the conventional biological P removal treatment enhancing the P removal to meet the effluent discharge concentrations, depending on the local standards (Takács, 2008; Zhang et al., 2022; Deng & Dhar, 2023). Both the biological P removal and the chemical treatment consist in converting soluble and colloidal P into insoluble material (Albertson & Sherwood, 2011).

Chemical coagulation and chemical precipitation are the two main chemical processes applied in municipal wastewater treatment for chemical P removal (Stephenson & Duff, 1996; Ebeling et al., 2003). Coagulation is an established process which consists of the destabilization of colloidal particles, decreasing or neutralizing the electric charge on suspended particles, so that particle growth can occur as a result of particle collisions (Stephenson & Duff, 1996; Jiang & Graham, 1998; Ebeling et al., 2003). In wastewater treatment, typical applications of coagulation include the removal of suspended solids, organic matter, toxic metals, anions (i.e. phosphates), colour, and odour, among others (Semerjian & Ayoub, 2003; Tzoupanos & Zouboulis, 2008). Coagulation consists in three sequential steps: coagulant formation, colloid/particle destabilization, and particle aggregation (Ebeling et al., 2003). Flocculation is the process whereby the size of particles increases as a result of particle collisions, known as particle aggregation (Lee et al., 2014a).

When metal salts are used as coagulants (Tzoupanos & Zouboulis, 2008), the coagulant dose and coagulation pH are two of the most important factors to influence the species formed (Jiang & Graham, 1998). The removal of particles by sweep coagulation with iron occurs in a pH range between 6.5 and 10.0 with an iron dose of 2.7 to 270 mg/L (Metcalf & Eddy, 2003a). While using alum as a coagulant the pH range is similar, but the alum dose is of 20 to 200 mg/L (Metcalf & Eddy, 2003a). Because the characteristics of wastewater will vary at the different treatment plants, laboratory tests must be conducted to establish the appropriate chemical dosages (Metcalf & Eddy, 2003a; Ebeling et al., 2003).

On the other hand, chemical precipitation involves the addition of chemicals to alter the physical state of dissolved and suspended solids and facilitate their removal by sedimentation (Metcalf & Eddy, 2003a). The chemical precipitation of P can be achieved by the addition of salts of multivalent metal ions that form precipitates of sparingly soluble phosphates (Nassef, 2012). The most commonly used multivalent metal ions are calcium (Ca^{2+}), aluminium (Al^{3+}), and iron (Fe^{3+}) (Clark et al., 1997; Morse et al., 1998; Nassef, 2012). The removal of phosphate from water by means of the precipitation process, also depends on the solubility of several complexes formed in the water (Jiang & Graham, 1998). Calcium is usually added in the form of lime $Ca(OH)_2$. When lime is added to the water it reacts with the natural bicarbonate alkalinity to precipitate $CaCO_3$. When the pH values of the wastewater increase over 10, the calcium ions in excess will react with the phosphate, to precipitate hydroxylapatite $Ca_{10}(PO_4)_6(OH)_2$ (Nassef, 2012). When the phosphate precipitation is with aluminium and iron, the Al and Fe compounds react to form metallic phosphates, $AlPO_4$ or $FePO_4$, which are insoluble under specific pH conditions (Metcalf & Eddy, 2003a). In this phenomenon, 1 mol of Al or Fe will precipitate 1 mol of PO_4. However, the stoichiometric relation of this reactions cannot be used to estimate the required chemical dosage directly; many other factors need to be considered including competing reactions and their associated equilibrium constants, the effects of alkalinity, pH, and trace elements found in wastewater (Albertson & Sherwood, 2011).

The discharge of industrial wastewaters is one of the most important sources of pollution (Aniyikaiye et al., 2019; Mokarram et al., 2020; Bharagava et al., 2020), affecting the water courses and ecosystems; the diversity of pollutants in wastewater makes the wastewater treatment more difficult (Carmona-Carmona et al., 2020). Characteristics of industrial wastewaters strongly depend on the type of industrial wastewaters and industrial processes (Orhon et al., 2009), and it can usually be characterized by the basic parameters, including chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids (SS), total nitrogen (TN), total phosphorus (TP), colour and turbidity (Lin et al., 2012). In addition, in contrast with municipal wastewaters, industrial wastewaters usually have a high organic strength (Orhon et al., 2009), extreme physicochemical nature (e.g., pH, temperature, salinity), and in some cases, have high salt concentrations. Furthermore, industrial wastewaters may contain a large variety of potentially inhibiting or toxic compounds (e.g., aromatics, phenols, chlorinated compounds, volatile organic compounds, heavy metals, among others) (Munter, 2000;

Lin et al., 2012; Sharma et al., 2022). These contaminants can be removed with chemical, physical, and/or biological processes. However, in recent decades, conventional processes have not been sufficient to degrade contaminants from industrial discharges (Carmona-Carmona et al., 2020), and in some cases the combination of physicochemical treatment with biological treatment could be advantageous (Lin et al., 2012).

The complex composition of pollutants that characterizes industrial wastewaters generates modifications to the more conventional processes of chemical precipitation in municipal wastewater treatment plants. For example: i) the effectiveness of the chemical precipitation of P decreases, due to changes in the P solubility equilibrium due to the presence of complexing agents in the wastewater (Francés, 2011; Benjamin & Lawler, 2013; Gunatilake, 2015). According to El-bestawy et al., (2008) the chemical treatment with iron and aluminium in a pulp and paper mill wastewater have a strong tendency to form soluble complexes with a number of ligands, especially with polar molecules and with oxygen-containing functional groups such as hydroxyl or carboxyl groups, which provide local reacting negative charges; ii) the required dose of precipitating agents tends to be higher than in municipal setting, and it can vary considerably from one type of industry to another due to interferences in the chemical precipitation process of P by the complex composition of the wastewater (El-bestawy et al., 2008; Caravelli et al., 2008). According to Nassef (2012) the competition between hydroxy ions and phosphates for ferric ions when ferric salt ions are added causes a situation where the actual dose of ferric salts is higher than calculated by stoichiometric equations. Other important factor affecting is the eventual high temperature at which industrial wastewater is generated. It is well known that the temperature affects physical and chemical properties of water and the coagulation-flocculation processes (Fitzpatrick et al., 2004; Jin, 2005; Saritha et al., 2017). The water temperature may affect particle transport processes or particle collision rate (Duan & Gregory, 2003). An increase in temperature influences the chemical properties of water, such as reaction rates, solubilities, pH, and hydrolysis species of coagulants. Reaction rates and reaction kinetics rise with increasing temperature (Snoeyink & Jenkins, 1980); iii) the precipitate that are formed have particles stability characteristics different from those formed in a conventional treatment with municipal wastewater, due to the characteristics of industrial wastewater (Caravelli et al., 2008). Maybe the precipitate has a very small colloidal size or remains stable in the solution that does not allow it to flocculate and settle (Wang et al., 2005). According to Aguilar et al. (2002) P in form of orthophosphate is removed by precipitation of phosphate with the metal ion, while the TP is removed by a complicated combination of interaction and adsorption with the flocculated particles.

Different experiments were conducted to investigate the effect of metal salt addition in a municipal and industrial wastewater phosphorus removal (Aguilar et al., 2002; Hamdani et al., 2005; Amuda & Amoo, 2007; Takács, 2008; Szabó et al., 2008; Hauduc et al., 2015). The influence of key factors such as: metal dose, metal type, pH, alkalinity, initial and residual phosphate concentration, mixing, reaction time, age of flocs and organic content of wastewater was studied. However, little research has been conducted on the chemical precipitation of P applied to pulp and paper mill wastewater treatment (Wong et al., 2006; Leiviskä & Rämö, 2008; Leiviska, 2009; Ahmad et al., 2008).

According to Teh et al. (2016a) diverse researchers have evaluated the coagulation/flocculation treatment process at pulp and paper mill wastewater. Nevertheless, the goal of the studies was to evaluate the removal of turbidity, organic matter, total suspended solids and wood extractives efficiency (Teh et al., 2016a). In any case, P removal efficiency was studied (Wong et al., 2006; Leiviskä & Rämö, 2008; Leiviska, 2009; Ahmad et al., 2008). Usually pulp mill wastewater is deficient in nutrients (Mobius, 1991; Kenny, 2004; Kang et al., 2011; Vashi et al., 2019); therefore, in most of the occasions, nutrients need to be dosed to get an efficient biological removal of organic matter. However, at the evaluated pulp mill, in our study, the TP influent concentration is too high compared to others pulp mill in the world; due to the hardwood used to pulp production in Uruguay (Bentancur et al., 2020) and (Bentancur et al., 2021). Thus, even N is still needed to be added, P needs to be removed, rather than added.

In addition, the chemical composition of the wastewater in the pulp mill is known to have a high content of cations such as Ca, Mg and Na (Fontanier et al., 2005; Rezende et al., 2010; Doldán et al., 2011; Lucas et al., 2012). The presence of these elements in the wastewater makes it a complex matrix compared to synthetic or municipal wastewater and may be influencing the chemical precipitation of P and the particle destabilization through the coagulation process (Caravelli et al., 2008).

Due to the little research on chemical phosphorus removal carried out in pulp mill industrial wastewater worldwide (Teh et al., 2016a), and to the particular situation that occurs in the pulp mill under study in Uruguay, with high P content, it is of great interest to study in depth the chemical P removal and the effect that wastewater characteristics, such as chemical composition, pH, temperature, among others, have on this treatment.

The main objectives of the present work were to evaluate the chemical P removal process in pulp mill WWTP in Uruguay. The research was for the purpose of understand how the following key operational factors: chemical additives dosage and type, pH, temperature, and mixing intensity impact on the TP removal efficiency. Evaluations were carried out at laboratory scale, and the effect of three precipitating agents’ ferric chloride, aluminium sulphate, and calcium hydroxide were analysed at different temperatures, pH, mixing intensity and polymers addition doses. An additional objective was to evaluate the influence of water quality effects on chemical P precipitation and the effects of particle stabilization on sedimentation performance.

4.2 MATERIALS AND METHODS

4.2.1 Experimental design

In order to evaluate how the following key operational factors: chemical additives dosage and type, pH, temperature, and mixing intensity impact on the total phosphorus removal efficiency, the following experimental program was carried out.

The chemical P-removal was assessed carrying out coagulation-flocculation experiments of the industrial wastewater test at laboratory scale. Laboratory jar testing was performed to investigate the effect of the following three precipitating agents: ferric chloride, aluminium sulphate, and calcium hydroxide at different temperatures, pH, flocculants doses and coagulation mixing intensity. This study provided insight regarding the most effective combinations of the chemicals and operational factors for achieving low levels of residual phosphorus.

4.2.2 WWTP description and wastewater characteristics

The wastewater used in this experimentation was obtained from a pulp mill industry located in Uruguay. A pulp mill uses the chemical Kraft process to produce 1.3 million tons of fully bleached eucalyptus market pulp per year. The effluents generated in the pulp mill (mostly from the bleaching process) are treated in a WWTP composed of a mechanical and physico-chemical pre-treatment followed by a conventional activated sludge (CAS) system for the removal of organic matter, total suspended solids (TSS), and adsorbable halogenated (AOX) compounds. The plant configuration is shown in Figure 4.1. The WWTP was designed to treat an effluent flowrate of 25 m^3/ADT (approximately 0.8 m^3/s) (Saarela et al., 2008). The wastewater treated from WWTP is discharged in the Uruguay River.

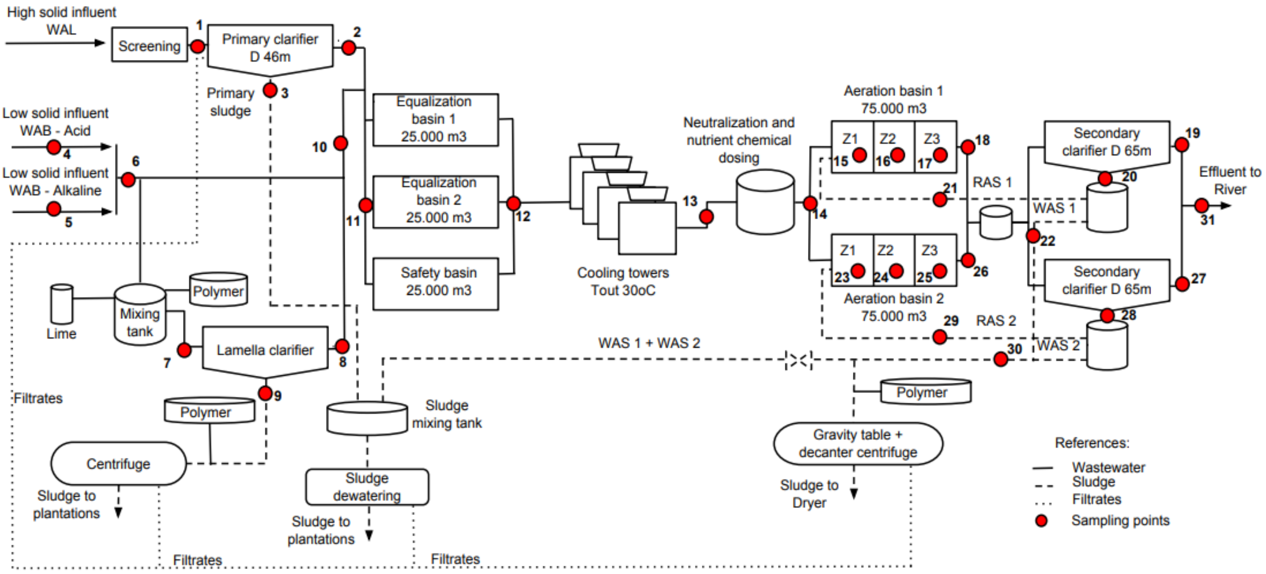


Figure 4.1 Process flow diagram of the pulp mill WWTP

There are two different lines with effluent from the pulp mill to the WWTP, one line with high solids effluent (named WAL), where point #1 is located, and the other (WAB) with low solids effluent, where points #4 and #5 are located. Point #4 represents a fraction of WAB, which includes the acid filtrate produced from what is known in the production process as the A/D1 stage (acid stage + chlorine dioxide); this fraction represents a flow of 30,240 m^3/d and a TP concentration of approximately 8 to 9 mgP/L. Whereas point #5, is the alkaline filtrate from the production process involving working with peroxide and sodium hydroxide (EOP) with a flow of 12,960 m^3/d and a TP concentration of approximately 3 to 5 mgP/L. The high solids effluent passes through screening and primary clarifier (point #2) and then is sent to the safety basins. The low solids effluent passes through a chemical P removal treatment (point #6). The total WAB stream is approximately 500 L/s; however, the P removal pre-treatment layout will allow to treat the entire stream or just a fraction of it, depending on the TP that has to be removed. After the chemical P removal plant, the wastewater is directed to the safety basins (point #8). Both flows (WAL +WAB) are mixed at the equalization basins and sent to the cooling towers system to reduce the wastewater temperature from 55 ºC to about 30 ºC. After the cooling towers, at point #13, the wastewater is neutralized and urea is added for N dosing. Point #14 is the influent to the biological activated sludge system. The activated sludge treatment was designed in two parallel lines, each including one aeration basin, one secondary clarifier and one return activated sludge flow from the secondary clarifier to the aeration tank. Finally, point #31 represents the discharge of the effluent from the WWTP to the River.

The pulp mill wastewater used in this experimentation was obtained from the sampling point #6 in Figure 4.1, since the WAB line exhibited a much higher P content compared to the WAL line. The characteristics of the pulp mill wastewater are shown in Table 4.1. The pulp mill wastewater used in the experiments contained high TP concentrations as shown in Table 4.1.

Table 4.1 Characteristics of the pulp mill wastewater used in the experiments

Parameter	**Value**
pH	3.8
Temperature (^oC)	60
COD (mgO$_2$/L)	2496
TP (total phosphorus, mgP/L)	8.4
Soluble P (soluble phosphorus with 0.45 μm filter, mgP/L)	8.2
TN (total nitrogen, mgN/L)	6.8
TSS (total suspended solids, mgTSS/L)	197

4.2.3 Experimental procedure

The experimental phase in this research includes the chemical P-removal assessment through coagulation-flocculation evaluations of the wastewater. The wastewater used for the test was collected from the WAB wastewater stream to the chemical P-removal plant (point #6 in Figure 4.1).

Coagulation-flocculation wastewater evaluations were carried out as follows: i) evaluation of different chemicals: $Ca(OH)_2$, $Al_2(SO_4)_3{\cdot}14.3H_2O$/L and $FeCl_3{\cdot}6H_2O$/L and optimization of chemical dosage, temperature and pH (Experiments 1 and 4), ii) the optimized dosages of chemicals were further examined in combination with different anionic polymer dosages to find the highest P removal efficiency. The anionic polymer used was FLOPAM AN 945 PWG with a standard molecular weight and high charge density (Experiment 2 and 6), iii) the optimized dosages of coagulant and polymer, temperature and pH were used, and different mixing intensities was assessed (Experiment 3), and iv) based on preliminary results, some Jar test was selected to repeat at pH 10.5 without precipitant agent and with $Ca(OH)_2$, $Al_2(SO_4)_3{\cdot}14.3H_2O$/L and $FeCl_3{\cdot}6H_2O$/L. The wastewater chemical composition was analysed by ICP–OES. Besides, particle size distribution was evaluated. The sludge chemical composition was analysed by SEM/EDX. In addition, X-Ray Diffractometer (XRD) was used to analyse precipitation of different crystals.

The Jar tests were carried out following the conditions presented in Table 4.2. The concentration of TP was measured before and after the Jar test execution.

Table 4.2 Coagulation-flocculation wastewater test conditions. A – Experiment # 1 to 3

Description	**Coagulant**	**Dose of coagulant (mg/L)**	**T (^{0}C)**	**pH**	**Dose of Polymer (ppm)**	**Coagulation**		**Flocculation**		**Sedimentation time (min)**
						Mixing time (min)	**Mixing intensity (rpm)**	**Mixing time (min)**	**Mixing intensity (rpm)**	
Experiment 1-A (PO$_4^{3-}$ precipitation)	$Ca(OH)_2$	400	30	Default	-	1	200	10	50	10
		600	45	9.5						
		800	60	10.5						
		1000								
Experiment 1-B (Sweep coagulation)	$Al_2(SO_4)_{3\ 14\text{-}3}H_20$	200	30	Default	-	1	200	10	50	10
		400	45	10.5						
		600	60							
		800								
Experiment 1-C (Sweep coagulation)	$FeCl_{3\cdot6}H_2O$	50	30	7.0	-	1	200	10	50	10
		100	45	10.5						
		200	60							
		300								
Experiment 2-A (different doses of polymer)	$Ca(OH)_2$	600	60	Default	0.6	1	200	10	50	10
					0.8					
					1.0					
					1.5					
Experiment 2-B (different doses of polymer)	$Al_2(SO_4)_{3\ 14\text{-}3}H_20$	800	30	10.5	0.6	1	200	10	50	10
					0.8					
					1.0					
					1.5					
Experiment 2-C (different doses of polymer)	$FeCl_{3\cdot6}H_2O$	300	60	7.0	0.6	1	200	10	50	10
					0.8					
					1.0					
					1.5					
Experiment 3-A (Optimization of mixing intensity)	$Ca(OH)_2$	600	60	Default	1.5	1	100	10	50	10
							200			
							300			
Experiment 3-B (Optimization of mixing intensity)	$Al_2(SO_4)_{3\ 14\text{-}3}H_20$	800	30	10.5	1.5	1	100	10	50	10
							200			
							300			
Experiment 3-C (Optimization of mixing intensity)	$FeCl_{3\cdot6}H_2O$	300	60	7.0	1.5	1	100	10	50	10
							200			
							300			

Table 4.2 Coagulation-flocculation wastewater test conditions. B - Experiment # 4 to 8

Description	**Coagulant**	**Dose of coagulant (mg/L)**	**T (^0C)**	**pH**	**Dose of Polymer (ppm)**	**Coagulation**		**Flocculation**		**Sedimentation time (min)**
						Mixing time (min)	**Mixing intensity (rpm)**	**Mixing time (min)**	**Mixing intensity (rpm)**	
Experiment 4-A (Increase pH with NaOH)	-	-	60	Default 8.5 9.0 9.5 10.0 10.5	-	1	200	10	50	10
Experiment 4-B (Increase pH with NaOH)	-	-	60	Default 8.5 9.0 9.5 10.0 10.5	1.5	1	200	10	50	10
Experiment 4-C (Increase pH with NaOH)	$Ca(OH)_2$	400	60	Default 8.5 9.0 9.5 10.0 10.5	1.5	1	200	10	50	10
Experiment 4-D (Increase pH with NaOH)	$Al_2(SO_4)_{3\ 14\cdot 3}H_20$	200	60	Default 8.5 9.0 9.5 10.0 10.5	1.5	1	200	10	50	10
Experiment 4-E (Increase pH with NaOH)	$FeCl_{3\cdot 6}H_2O$	50	60	Default 8.5 9.0 9.5 10.0 10.5	1.5	1	200	10	50	10
Experiment 6-A (different doses of polymer)	-	-	60	10.0	0 5 10 20	1	200	10	50	10
Experiment 6-B (different doses of polymer)	-	-	60	10.5	0 5 10 20	1	200	10	50	10
Experiment 6-C (different doses of polymer)	$Ca(OH)_2$	400	60	9.5	0 5 10 20	1	200	10	50	10
Experiment 6-D (different doses of polymer)	$Al_2(SO_4)_{3\ 14\cdot 3}H_20$	200	60	10	0 5 10 20	1	200	10	50	10
Experiment 6-E (different doses of polymer)	$FeCl_{3\cdot 6}H_2O$	50	60	10	0 5 10 20	1	200	10	50	10
Experiment 8-A	-	-	60	10.5	-	1	200	10	50	10
Experiment 8-B	$Ca(OH)_2$	400	60	10.5	1.5	1	200	10	50	10
Experiment 8-C	$Al_2(SO_4)_{3\ 14\cdot 3}H_20$	200	60	10.5	1.5	1	200	10	50	10
Experiment 8-D	$FeCl_{3\cdot 6}H_2O$	50	60	10.5	1.5	1	200	10	50	10

A fresh sample of 120 L was collected from the sampling point # 6 in Figure 4.1. For this purpose, an 8 h representative composite sample was collected.

For conducting the Jar Text experiments, a Jar Test apparatus with temperature control was used. It consists of four identical beakers of 2 litres, each equipped with a stirrer. The stirrers are driven by one rotor, thus giving each the same rotation velocity. The temperature control was made with a water bath, which was placed on a platform of Jar Test equipment. The sample pH was adjusted depending on the test to be performed, with 1 mol/L sodium hydroxide (NaOH). Then the chemical dose was added, and the sample was rapidly mixed (200 rpm) for 1 min. and slowly mixed (50 rpm) for 10 min. After sedimentation time of 10 min., the supernatant was sampled for analysis.

A total of 152 jar tests were performed to find the optimal chemical type and dose, polymer dose, pH, temperature and mixing intensity.

4.2.4 Analytical determinations

The following parameters: COD, TP, soluble P (0.45 μm filter) and TSS were analysed at the beginning and end (in the supernatant) of each coagulation-flocculation wastewater test. The analytical procedures required for the determination of parameters were performed following standardized and commonly applied analytical protocols detailed in Standard Methods (APHA et al., 2012) as follows: COD (Reactor digestion method 8000), TP and P soluble (TNT 843 Kit), and TSS (Standard Methods 2540 D Total Suspended Solids Dried at 103-105 ^{o}C).

In experiment #8 the influent and effluent (supernatant) of each jar test were further characterized: chemical composition was obtained by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) in the pulp mill laboratory. Because the analyzes were performed after obtaining the samples, they were conserved with HNO_3, with a pH between 1 and 2. In addition, particle size distribution (PSD) measurements were carried out with a Laser Diffraction Particle Size Analyzer, Microtrac S 3500 at the Laboratorio Tecnológico del Uruguay (LATU).

The sludge samples obtained from the jar test experiments carried out in the Experiment #8 were dried according to the ASTM D2216 procedure (105 °C for two hours). Samples were sent to the College of Chemistry (Udelar) and the chemical composition of the sludge and crystallographic structure of the precipitate, in Experiment #8, were performed by scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) and X-Ray Diffraction (XRD).

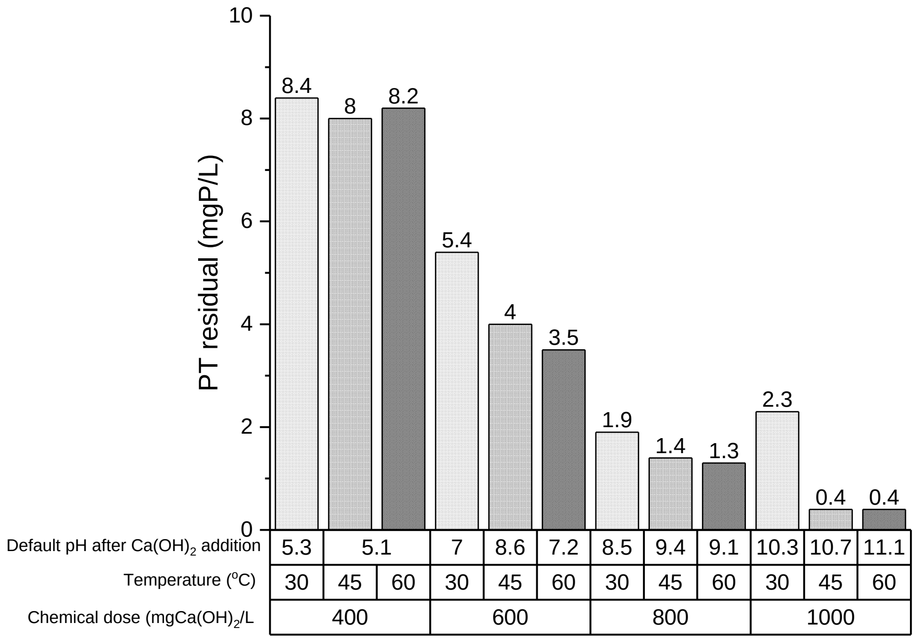
4.3 RESULTS AND DISCUSSION

4.3.1 Effect of different precipitating agents

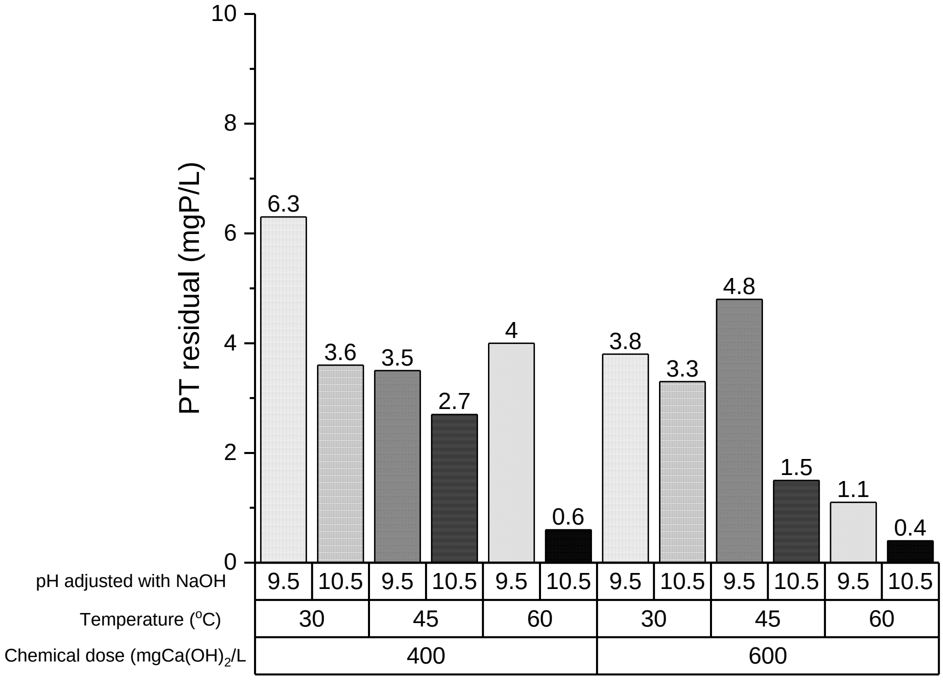
An evaluation of three commonly used precipitating agents (calcium hydroxide, aluminium sulphate and ferric chloride) was conducted for the pulp mill wastewater at WAB stream, at sampling point 6 (Figure 4.1) in order to assess the performance of the chemical P removal. The evaluations were carried out to better understand how the following key operational factors: chemical additives dosage and type, pH and temperature impact on the P removal efficiency.

Calcium hydroxide

The performance of P removal from pulp mill wastewater at WAB stream, at sampling point 6 (Figure 4.1), was evaluated with different doses of $Ca(OH)_2$ at different temperatures and pH. Figure 4.2 presents the results of the residual concentration of TP after the jar test as a function of the studied parameters. The initial wastewater concentration of TP was 8.4 mgP/L, and soluble P was 8.2 mgP/L. The initial wastewater pH was about 3.8. Using $Ca(OH)_2$ as chemical, the wastewater pH varies with the chemical doses, achieving levels as: 5.3 with 400 mg/L, 7.0 with 600 mg/L, 8.5 with 800 mg/L and 10.3 with 1000 mg/L. This evaluation was carried out to optimize the current situation at the pulp mill WWTP.



A. pH reached after calcium addition.



B. pH 9.5 and 10.5 reached with NaOH addition.

Figure 4.2 PT residual in a pulp mill wastewater with $Ca(OH)_2$ *as a function of dose of chemical, temperature and pH. Initial conditions: PT=8.4 mg/L, Psoluble=8.2 mg/L, pH=3.8. Both figures present at the horizontal axis the following parameters: pH, temperature and chemical dose*

The results of the tests with $Ca(OH)_2$ show two clear effects: i) by increasing the concentration of lime, increases the percentage removal of TP and reduces the residual concentration; however the higher the lime dose, the higher the pH values, ii) by increasing the pH of the wastewater, the percentage removal of TP also increases. In these evaluations, only the TP was analysed, so the removal is influenced by both the P precipitation as well as the ability of that precipitate to settle.

According to the literature, with lime added to water it reacts with the natural bicarbonate alkalinity to precipitate $CaCO_3$ (Jenkins et al., 1971; Mohammed & Shanshool, 2009). As the pH value of the wastewater increases beyond about 10, excess calcium ions will then react with the phosphate to precipitate hydroxylapatite (Metcalf & Eddy, 2003b). P removal with lime is a non-stoichiometric process, as the lime dosage is not dependent on the concentration of phosphate removed but on the solubility product of $Ca(OH)_2$ which is frequently exceeded as the pH of the water increases and virtually all of the PO4 will precipitate at pH values above 10 (Jiang & Graham, 1998). The quantity of lime required will depend primarily on the alkalinity of the wastewater (Metcalf & Eddy, 2003b).

Similar results, where the chemical phosphate precipitation with lime is achieved at pH range from 8.0 to 11, have been previously found by Nassef (2012); however, a synthetic phosphate solution was used as wastewater. According to Nassef (2012) when lime is added to wastewater, as the pH increases to more than 10, excess calcium ions can form the complex with phosphate and precipitate it in the solution. Furthermore, similar results were obtained by Mohammed & Shanshool (2009) where they evaluated the removal of P by alum and calcium chloride ($CaCl_2$) with a phosphate solution prepared from KH_2PO_4. The results of $CaCl_2$ showed that pH and $CaCl_2$ dosage play an important role in PO_4^{-3} removal. Phosphate removal increases with increasing pH and $CaCl_2$ dosage, and the optimum dose of $CaCl_2$ was 60 mg/l. The pH effect can be explained by the change of orthophosphate compounds with pH (Jenkins et al., 1971). However, the $CaCl_2$ dose was much lower than $Ca(OH)_2$ doses used in this research.

Mazlum & İkizoğlu, (2018) studied the P removal by chemical precipitation in a supernatant from a previously activated sludge treatment system fed municipal wastewater. When lime was added to the supernatant, and the pH was increased to 10.5, resulted in low supernatant P limits. In this case, very high doses of lime were used, from 1.80 to 1.95 g $Ca(OH)_2$ in 0.5L of wastewater. Malhotra et al. (1964) evaluated the removal of P from municipal wastewater after biochemical treatment using alum and lime. According to the results a dose of 600 mg $Ca(OH)_2$/L raised the pH of the sample to 11.0 and removed 99 % of the TP. In addition, (Malhotra et al., 1964) evaluated the removal of P from the effluent by simply raising the pH of the sample with the use of sodium hydroxide or lime. This was because from their own experiments with alum they observed that at pH above 10 better P removal were obtained than at a lower pH. Because aluminium hydroxide floc is fairly soluble at such high pH values, it was felt that the use of alum was unnecessary at such high pH values.

(Suzin et al., 2018) reported that the chemical composition of wastewater treated with $Ca(OH)_2$ plays an important effect on the process. For example, in their study chemical P precipitation was evaluated in a swine industrial wastewater; the authors reported that swine manure contained relatively high concentrations of alkalinity and ammonia; therefore, precipitation of phosphate from raw wastewater is highly difficult. According to (Suzin et al., 2018) such a high buffer capacity of the carbonate system causes excessive consumption of lime. Also, (Fernandes et al. 2012) reported that the efficiency of P removal from swine industrial wastewater using precipitation with $Ca(OH)_2$ was 90 % at pH 8.5 and higher than 98 % at pH 10.5.

Although the chemical P removal process has been well studied for synthetic, municipal and industrial wastewater, no research was found where chemical precipitation has been used for P removal in wastewater from pulp and paper industry. The effect of temperature on P removal at different pH is presented in Figure 4.2. As the temperature rises from 30 to 60 ^{o}C, the residual TP concentration decreases, so there was a higher P removal efficiency as the temperature increased. According to Snoeyink & Jenkins (1980) the solubility of solids and liquids is highly dependent on temperature, and the solubilities of most solids increase as temperature increases, with a few notable exceptions such as $CaCO_3$, $Ca_3(PO_4)_2$, $CaSO_4$, and $FePO_4$. This can explain what happened in this research, because in case of phosphate calcium precipitates when temperature increases, the solubility decreases, however, a major precipitation of P was obtained. Similar results were found by Zhu et al., (2009) where synthetic solution with hydroxyapatite was evaluated at temperature of 25 and 45 ^oC and results indicated that the solubility of hydroxyapatite decreases when the temperature increased.

At default pH obtained after adding the calcium hydroxide doses (Figure 4.2A), one of the best results were obtained when performing the jar test at 60 ^oC and dose of chemical 1000 mg$Ca(OH)_2$/L. The final PT value was 0.4 mg/L, equivalent to a TP removal efficiency of 95 %. At pH 10.5 (Figure 4.2B), the best result was obtained when performing the jar test at 60 ^oC and dose of chemical 600 mg Ca $(OH)_2$/L. The final PT value was 0.4 mg/L, equivalent to a TP removal efficiency of 95 %.

pH had a remarkable effect on the removal of P. When using lime as a precipitating agent, by default the pH increased and with high doses of lime it was seen that a P removal of 95 % was obtained. But also, by raising the pH with NaOH it was seen that it is also possible to obtain the same removal of P, so it is not the precipitating agent that is causing the removal of P. Thus, the pH plays a key role in the removal of P.

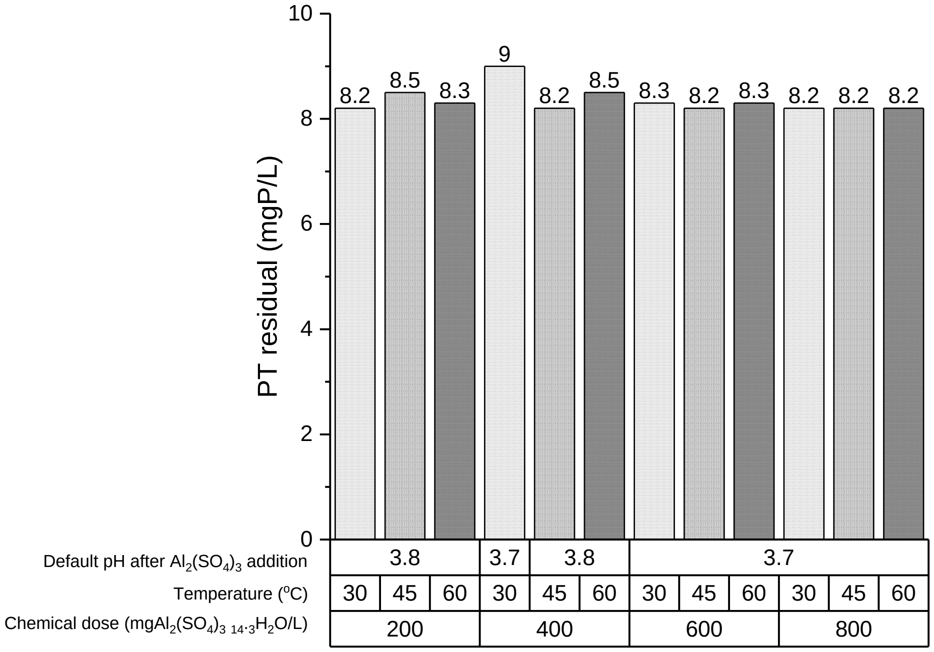
pH has a significant effect on P removal by changing the form of precipitant, which led to variations in precipitant for P removal (Qiu et al., 2015). Phosphates occur in three different forms depending on the pH. Between pH 4 and 6, the most common form is $H_2PO_4^-$. Under neutral pH conditions, HPO_4^{2-} is the predominant form, and above pH 12.5, orthophosphorus (PO_4^{3-}) is predominant. The distribution of P species at different pH values significantly dictates the removal and recovery mechanisms of phosphorus (Jenkins et al., 1971; Azam et al., 2019).

Similar results were reported by Qiu Lin et al. (2015) where the P removal using ferric or calcium salts as precipitants was significantly affected by pH and the optimal pH were 5 and 10–10.5, respectively.

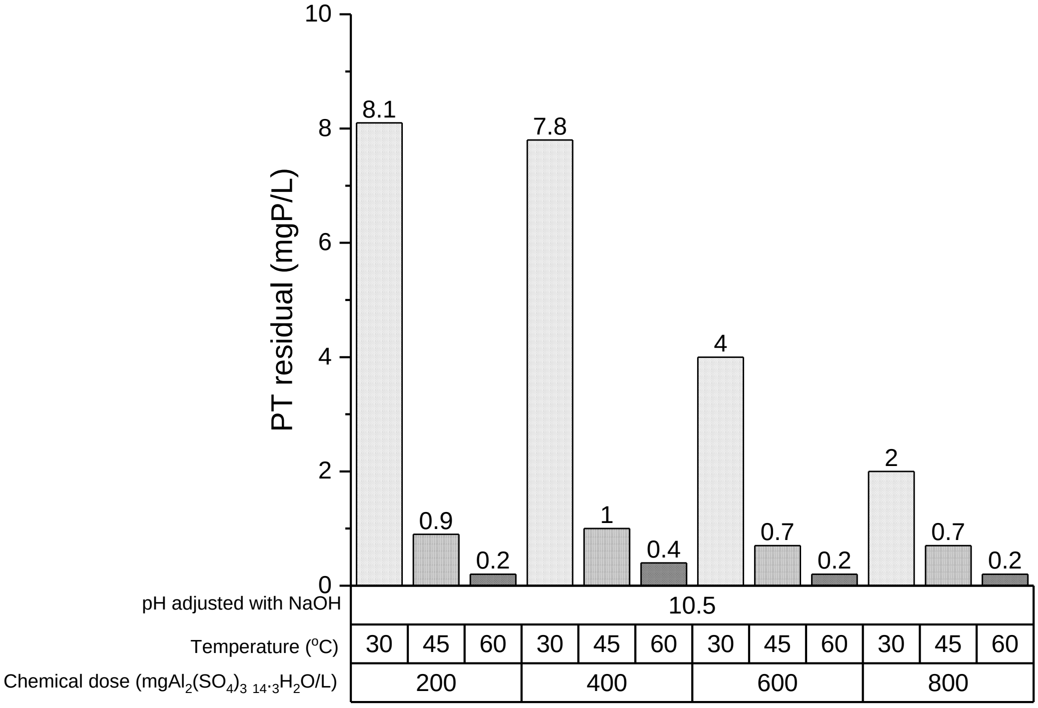
Lime used for chemical P precipitation is a promising alternative, since the cost of lime is relatively lower than that of other reagents (Suzin et al., 2018) and works properly; however, industrial application problems are produced, causing scales in the elements of the WWTP.

Aluminium sulphate

The performance of P was also evaluated with different doses of alum at different temperatures and pH. Figure 4.3 shows the results from the jar test evaluation carried out with alum as a precipitating agent. Experiments with $Al_2(SO_4)_3{\cdot}14.3H_2O$/L showed that at the pH reached after the alum addition (about 3.8) (Figure 4.3A), independent of the temperature and dose of chemical added, the TP removal efficiency was close to zero. These results are according with the results obtained by (Nassef, 2012), where they explain that solubility of aluminium salts is a function of pH and the optimum solubility for alum was reported to occur at a pH range of 5.5 to 6.5 (according to alum destabilization diagram (Bratby, 2006)). In addition, (Szabó et al., 2008) showed that in the municipal wastewater the pH range of alum is between 3.5 and 7.5 with the highest efficiency between pH 4 and 6.



A. pH reached after alum addition.



B. pH 10.5 reached with NaOH addition.

Figure 4.3 PT residual in a pulp mill wastewater with $Al_2(SO_4)_3$ *as a function of doses of coagulant, temperature, and pH. Initial conditions: PT=8.4 mg/L, Psoluble=8.2 mg/L, pH=3.8. Both figures present at the horizontal axis the follows parameters: pH, temperature and chemical dose*

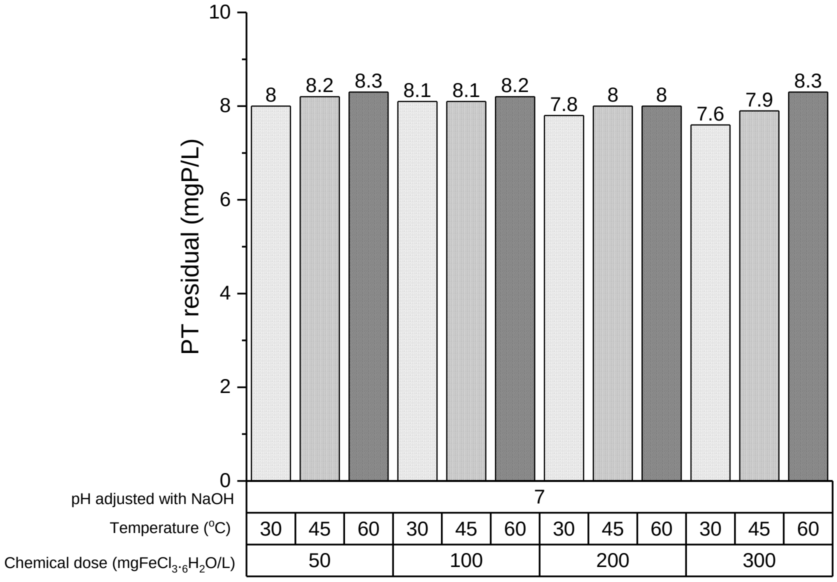
At pH 10.5 (Figure 4.3B), as the temperature increases, 30, 45 and 60 °C, the TP removal efficiency increases. (Duan & Gregory, 2003) reported that the temperature has influence on physical (such as particle transport process and collision rates) and chemical (effect on hydrolysis reactions, precipitation and solubility of the metal hydroxide) factors, and shown the hydrolysing metal coagulant perform better at high temperature. Similar result was found by (Teh et al., 2016b) who reported that at lower temperatures, the performance of metal coagulants such as alum is less effective due to decreased hydrolysis and precipitation kinetics.

In the current test, the best result was obtained when performing the jar test at 60 °C and dose of coagulant 200 mg$Al_2(SO_4)_3 \cdot 14.3H_2O$/L. The final PT value was 0.2 mg/L, equivalent to a TP removal efficiency of 98 %. pH 10.5 is over the typical optimum pH range (according to alum destabilization diagram, which is between 4 and 6 (Bratby, 2006; Szabó et al., 2008). Moreover, (Mohammed & Shanshool, 2009) reported that P removal by alum in a synthetic wastewater sample was found to be highly pH dependent with an optimum pH of 5.7-6.

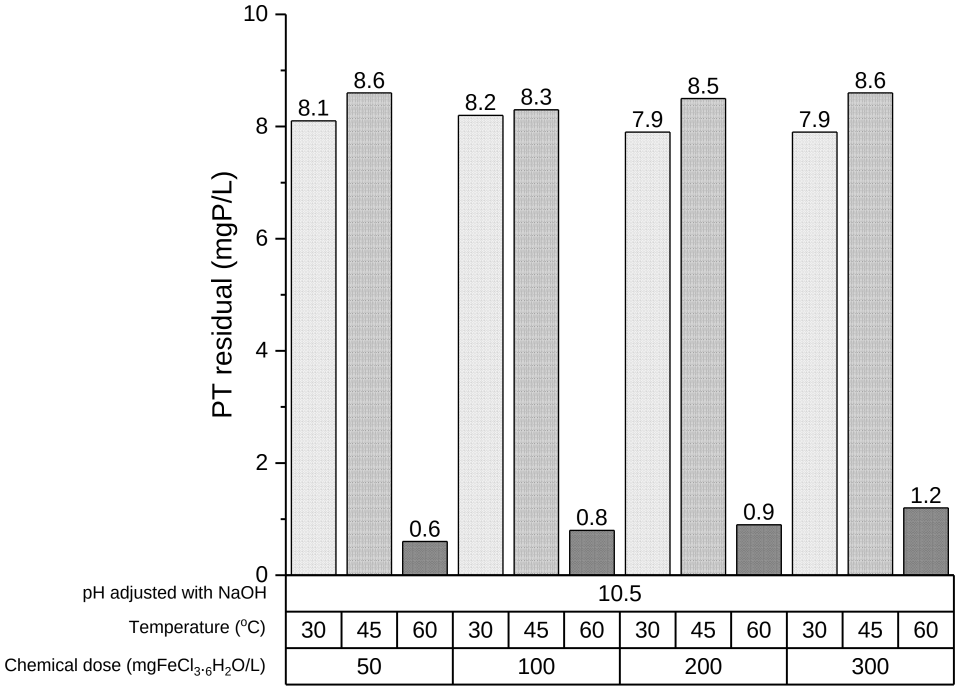
As can be seen in Figure 4.3B, at pH 10.5, the Al dose does not influence the P removal. However, the excellent P removal efficiency al pH 10.5 in this case can be attributed to chemical precipitation of P with some cation that may be present in the wastewater matrix generated in the paper industry, such as calcium or magnesium and not by alum effect in the P precipitation.

Ferric chloride

The phosphate removal process was evaluated using different doses of ferric chloride, at different operational temperatures and pH range. With $FeCl_3$ as a precipitating agent, the default pH was similar at all doses: 3.8.



A. pH 7.0 reached with NaOH addition.



B. pH 10.5 reached with NaOH addition.

Figure 4.4 PT residual in a pulp mill wastewater with $FeCl_3$ as a function of doses of coagulant, temperature, and pH. Initial conditions: PT=8.4 mg/L, Psoluble=8.2 mg/L, pH=3.8. Both figures present at the horizontal axis the following parameters: pH, temperature, and chemical dose

Figure 4.4 shows the results from a jar test carried out in this stage with ferric chloride as a precipitating agent. The jar tests were made firstly at pH 7 (Figure 4.4A), which is the recommended pH as a function of solubility diagram (Jiang & Graham, 1998). The results show that the residual TP is like the initial TP concentration, and the removal efficiency is very low. The best TP removal efficiency, 10 %, was reached at temperature 30 °C and chemical dose of 300 mg/L. If the same conditions, pH and chemical dosage were used in a clean matrix of water, such as synthetic or municipal wastewater, the P removal would be much higher (Jiang & Graham, 1998; Szabó et al., 2008), reaching residual TP values about 1.5 mgP/L or lower. (Metcalf & Eddy, 2003a).

These results show in Figure 4.4A indicates that there was some factor such as chemical composition of wastewater such as incidence of anions or presence of natural organic matter, which consists of a mixture of various organic compounds including hydrophobic (humic and fulvic acids) and hydrophilic fractions, or presence of soluble complexes that could be influencing the chemical precipitation process with iron, so no TP removal was observed. (Duan & Gregory, 2003) reported that the presence of anions, such as sulphate, can have a large effect on hydroxide precipitation. Highly charged anions can reduce the positive charge of the precipitate in the acid region, so that large flocs are formed over a wider pH range. Furthermore, the inhibition of phosphate removal of a high concentration of sulphate (sulphate-to-phosphate ratio greater than 6.0) on the wastewater was observed by (Yun et al., 2012). The ratio of the sulphate-to-phosphate on the studied wastewater is over 100. This may explain why the chemical P precipitation process does not occur as recommended pH (Jiang & Graham, 1998). Additionally, (Cichy et al., 2019) described that the chemical composition of wastewater has a great influence on precipitation process, and sulphate and carbonate anions compete with the phosphate ions.

On the other hand, complexation plays a major role in metal ion (and ligand) speciation in aquatic systems, and speciation affects chemical behavior in myriad ways (Brezonic & Arnold, 2011). Complexation may interfere with P removal (Muster et al., 2013), the presence of soluble complexes imposes limits on metal ion removal by precipitation reactions (Brezonic & Arnold, 2011). According to Wang et al. (2005) chemical precipitation has proven to be an effective technique for removing many industrial wastewater pollutants. However, the use of chemical precipitation may be limited because of interference of chelating agents and other chemical interference possible when mixing wastewater and treatment chemicals.

At pH 10.5 (Figure 4.4B), the temperature effect is relevant, at 30 and 45 ^{o}C the TP removal efficiency is near zero, but at 60 ^{o}C the residual TP concentration was 0.6 mg/L and the highest removal efficiency is 93 % at coagulant doses of 50 mg/L. It is well known that the temperature affects physical and chemical properties of water and the coagulation-flocculation processes (Heinanen, 1987; Nalco Company, 1990; Fitzpatrick et al., 2004; Jin, 2005; Saritha et al., 2017). (Heinanen, 1987) proved the temperature effect on density, viscosity and dielectric constant of water, finding that all those properties decrease as the temperature increases. The water temperature may affect particle transport processes or particle collision rate (Duan & Gregory, 2003). In general, an increase in temperature will accelerate both the rate of flocculation and settling rates of the flocculated particles (Nalco Company, 1990). An increase in temperature also influences the chemical properties of water, such as reaction rates, solubilities, pH, and hydrolysis species of coagulants. Reaction rates and reaction kinetics rise with increasing temperature. As previously described, in general, the solubility of solids and liquids is highly dependent on temperature, and the solubilities of most solids increase as temperature increases. However, $FePO_4$ is an exception (Snoeyink & Jenkins, 1980). (Kang & Cleasby, 1995) observed the differences in iron (III) solubility and speciation with varying temperature. They indicated that the impact of temperature on the $Fe(OH)_3(s)$ solubility was distinguishable. At higher temperatures the Ksp value is higher, and therefore there is a greater solubility of iron.

According to (Nassef, 2012) the competition between hydroxyl ions and phosphate for ferric ions when ferric salts are added causes a situation where the necessary dose of ferric salts is higher than calculated by stoichiometric equations.

Again, these results pointed out the importance of the pH and probably the presence of other ions in the matrix precipitates with PO_4^{3-} at high pH.

4.3.2 Effect of mixing intensity and polymer dosage

The objective of this section was to explore operational conditions: mixing intensity and different doses of polymer that can improve particle destabilization and flocculation of the precipitate. Diverse mixing intensity were studied: 100, 200 and 300 rpm. Table 4.3. shown the obtained results. From experiments with $Ca(OH)_2$, with a dose of 600 mg/L, polymer dose of 1.5 ppm and default pH after calcium addition (about 8.0): the best result was obtained for a mixing intensity of 300 rpm. At experiment with $Al_2(SO_4)_3 \cdot 14.3H_2O$/L, dose of 800 mg/L, polymer dose of 1.5 ppm and pH 10.5, the best result was obtained for a mixing intensity of 100 rpm. This result is the contradictory of that found by (Chaudhari et al., 2010), where using alum for coagulation process the adsorption and destabilization mechanisms were enhanced due to fast hydrolysis of alum and formation of hydroxide precipitates when fast mixing speed was increased.

Finally, at experiment with $FeCl_3 \cdot 6H_2O$/L, dose of 300 mg/L, polymer dose of 1.5 ppm and pH 7.0, the TP removal efficiency is near to zero, and there is no variation at different rpm.

With respect to COD removal, as can be seen in Table 4.3, there is no significant variation depending on the rpm used in the mixing process. The greatest removal occurs when aluminium is used as a precipitating agent at 100 and 300 rpm and a COD removal efficiency of 20 % is achieved. In the rest of the tests, the removal efficiency obtained is lower.

Table 4.3 Results of jar test with different mixing intensity

A - Experimental conditions.

# Test	Type of precipitating agent	Dose of precipitating agent (mg/L)	Temperature (°C)	Dose of polymer (ppm)	Initial pH	Final pH (after coagulant is added)	Adjust pH with NaOH	mL of NaOH added	Coagulation		Flocculation		Sedimentation (min)
									Time (min)	rpm	Time (min)	rpm	
1	$Ca(OH)_2$	600	60	1.5	3.9	9.7	-	-	1	100	10	50	10
2	$Ca(OH)_2$	600	60	1.5	3.9	8.8	-		1	200	10	50	10
3	$Ca(OH)_2$	600	60	1.5	3.9	7.8	-		1	300	10	50	10
4	$Al_2\,(SO_4)_{3\,.\,14.3}H_2O$	800	30	1.5	3.9	3.7	10.5	16.0	1	100	10	50	10
5	$Al_2\,(SO_4)_{3\,.\,14.3}H_2O$	800	30	1.5	3.9	3.7	10.5	16.0	1	200	10	50	10
6	$Al_2\,(SO_4)_{3\,.\,14.3}H_2O$	800	30	1.5	3.9	3.7	10.5	16.0	1	300	10	50	10
7	$FeCl_3 \cdot {}_6H_2O$	300	60	1.5	3.9	3.7	7.0	11.0	1	100	10	50	10
8	$FeCl_3 \cdot {}_6H_2O$	300	60	1.5	3.9	3.7	7.0	11.0	1	200	10	50	10
9	$FeCl_3 \cdot {}_6H_2O$	300	60	1.5	3.9	3.7	7.0	11.0	1	300	10	50	10

B - Results

# Test	Inicial PT (mg/L)	Initial Psoluble (mg/L)	Initial COD (mg/L)	Initial TSS (mg/L)	Final PT (mg/L)	Final Psoluble (mg/L)	Final COD (mg/L)	Final TSS (mg/L)	P removal (%)	P soluble removal (%)	COD removal (%)	TSS increase (%)
1	8.4	7.5	2532	242	3.4	0.3	2198	554	60	96	13	129
2	8.4	7.5	2532	242	5.1	0.7	2112	608	40	90	17	151
3	8.4	7.5	2532	242	3.0	1.0	2172	619	64	87	14	156
4	8.4	7.5	2532	242	1.4	0.5	2000	568	84	93	21	135
5	8.4	7.5	2532	242	2.4	0.4	2204	606	72	95	13	150
6	8.4	7.5	2532	242	1.5	0.5	2024	577	82	94	20	138
7	8.4	7.5	2532	242	8.2	3.6	2276	401	3	53	10	66
8	8.4	7.5	2532	242	7.8	3.8	2286	339	7	49	10	40
9	8.4	7.5	2532	242	8.5	3.6	2532	316	0	53	0	31

The variation of the TSS can be observed in the last column of Table 4.3. When lime or aluminium is used as a precipitating agent, a significant increase is seen, ranging from 129 to 156 % and no correlation is seen between the different mixing rpm. When iron is used, the percentage increase in TSS is less, from 31 % to 66 %.

With Ca or Al as precipitating agent a great increase in TSS was observed mostly due to the high pH and then, the precipitation of a lot of things at such a high pH. However, with Fe, where it was worked at pH 7.0, the increase in TSS was slight.

Stirring, also known as mixing, is a crucial step in water and wastewater treatment via coagulation-flocculation process (Teh et al., 2016a). Two mixing regimes occur in coagulation process, namely rapid mixing and slow-mixing (Subramonian et al., 2014). Rapid-mixing is required to induce uniform distribution of coagulation into suspension, and slow-mixing promotes flocs formation, complexation and adsorption of organics onto the coagulants for precipitation and settling of insoluble solids (Subramonian et al., 2014).

In accordance with (Teh et al., 2016a) in treatments using alum, the destabilization mechanisms were enhanced due to fast hydrolysis of alum and formation of hydroxide precipitates when fast mixing speed was increased. This is also contradictory to what happened in this investigation, where the best removal with aluminium occurred at 100 rpm, which was the lowest stirring speed evaluated. In this section, it is not possible to conclude about the effect of mixing intensity on P removal since similar results were obtained at 100 and 300 rpm.

On the other hand, with the aim to improve the flocculation process, different doses of polymer were considered to evaluate the effects of increasing the polymer dose on the floc formation and settling velocity. The results of the jar test are presented in Table 4.4.

Table 4.4 Effect of polymer addition on flocculation process

A – Experimental conditions

# Test	Type of precipitating agent	Dose of precipitating agent (mg/L)	Temperature (°C)	Dose of polymer (ppm)	Initial pH	Final pH (after coagulant is added)	Adjust pH with NaOH	Coagulation		Flocculation		Sedimentation (min)
								Time (min)	rpm	Time (min)	rpm	
1	$Ca(OH)_2$	600	60	-	3.9	7.2	-	1	200	10	50	10
2	$Ca(OH)_2$	600	60	0.6	3.9	7.9	-	1	200	10	50	10
3	$Ca(OH)_2$	600	60	0.8	3.9	7.7	-	1	200	10	50	10
4	$Ca(OH)_2$	600	60	1.0	4.0	8.6	-	1	200	10	50	10
5	$Ca(OH)_2$	600	60	1.5	3.9	8.8	-	1	200	10	50	10
6	$Al_2 (SO_4)_3 \cdot {}_{14.3}H_2O$	800	30	-	3.8	3.7	10.5	1	200	10	50	10
7	$Al_2 (SO_4)_3 \cdot {}_{14.3}H_2O$	800	30	0.6	3.9	3.7	10.5	1	200	10	50	10
8	$Al_2 (SO_4)_3 \cdot {}_{14.3}H_2O$	800	30	0.8	3.9	3.7	10.5	1	200	10	50	10
9	$Al_2 (SO_4)_3 \cdot {}_{14.3}H_2O$	800	30	1.0	3.9	3.6	10.5	1	200	10	50	10
10	$Al_2 (SO_4)_3 \cdot {}_{14.3}H_2O$	800	30	1.5	3.9	3.7	10.5	1	200	10	50	10
11	$FeCl_3 \cdot {}_6H_2O$	300	60	-	3.9	3.7	7.0	1	200	10	50	10
12	$FeCl_3 \cdot {}_6H_2O$	300	60	0.6	3.8	3.7	7.0	1	200	10	50	10
13	$FeCl_3 \cdot {}_6H_2O$	300	60	0.8	3.9	3.7	7.0	1	200	10	50	10
14	$FeCl_3 \cdot {}_6H_2O$	300	60	1.0	3.9	3.7	7.0	1	200	10	50	10
15	$FeCl_3 \cdot {}_6H_2O$	300	60	1.5	3.9	3.7	7.0	1	200	10	50	10
16	-	-	60	0	3.8	-	10	1	200	10	50	10
17	-	-	60	5	3.8	-	10	1	200	10	50	10
18	-	-	60	10	3.8	-	10	1	200	10	50	10
19	-	-	60	20	3.8	-	10	1	200	10	50	10
20	-	-	60	0	3.8	-	10.5	1	200	10	50	10
21	-	-	60	5	3.8	-	10.5	1	200	10	50	10
22	-	-	60	10	3.8	-	10.5	1	200	10	50	10
23	-	-	60	20	3.8	-	10.5	1	200	10	50	10
24	$Ca(OH)_2$	400	60	0	3.8	5.1	9.5	1	200	10	50	10
25	$Ca(OH)_2$	400	60	5	3.8	4.8	9.5	1	200	10	50	10
26	$Ca(OH)_2$	400	60	10	3.8	4.9	9.5	1	200	10	50	10
27	$Ca(OH)_2$	400	60	20	3.8	4.9	9.5	1	200	10	50	10
28	$Al_2 (SO_4)_3 \cdot {}_{14.3}H_2O$	200	60	0	3.8	3.7	10	1	200	10	50	10
29	$Al_2 (SO_4)_3 \cdot {}_{14.3}H_2O$	200	60	5	3.8	3.8	10	1	200	10	50	10
30	$Al_2 (SO_4)_3 \cdot {}_{14.3}H_2O$	200	60	10	3.8	3.8	10	1	200	10	50	10
31	$Al_2 (SO_4)_3 \cdot {}_{14.3}H_2O$	200	60	20	3.8	3.8	10	1	200	10	50	10
32	$FeCl_3 \cdot {}_6H_2O$	50	60	0	3.8	3.8	10	1	200	10	50	10
33	$FeCl_3 \cdot {}_6H_2O$	50	60	5	3.8	3.8	10	1	200	10	50	10
34	$FeCl_3 \cdot {}_6H_2O$	50	60	10	3.8	3.8	10	1	200	10	50	10
35	$FeCl_3 \cdot {}_6H_2O$	50	60	20	3.8	3.8	10	1	200	10	50	10

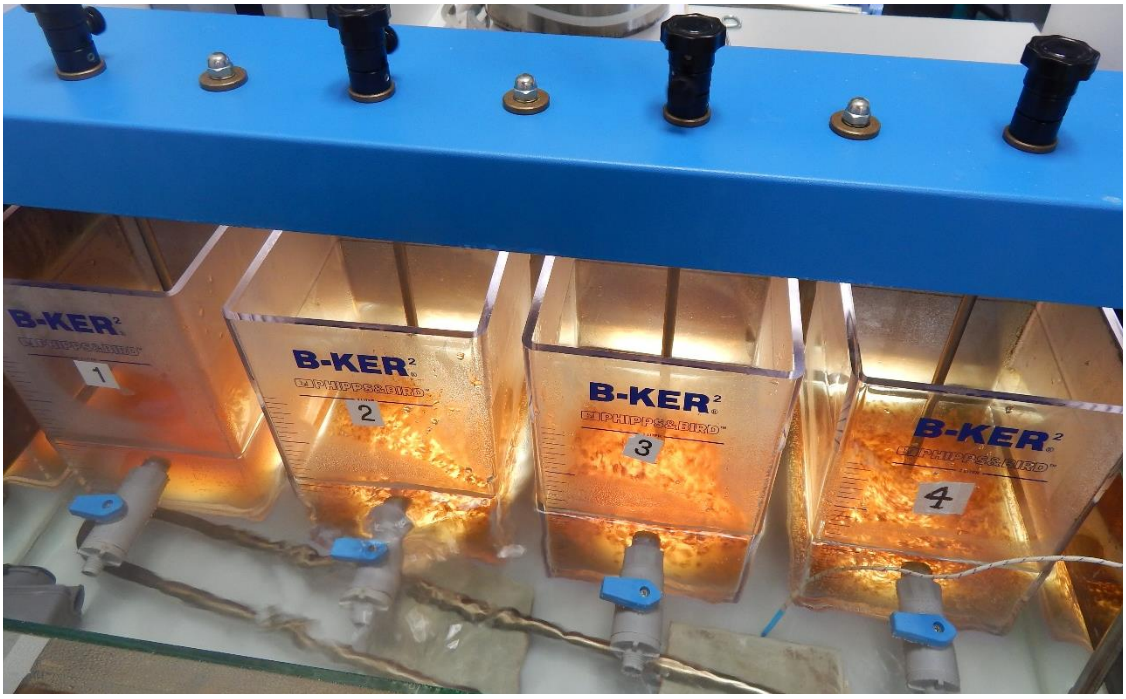
B – Results

# Test	Inicial PT (mg/L)	Initial Psoluble (mg/L)	Initial COD (mg/L)	Initial TSS (mg/L)	Final PT (mg/L)	Final Psoluble (mg/L)	Final COD (mg/L)	Final TSS (mg/L)	P removal (%)	P soluble removal (%)	COD removal (%)	TSS increase (%)
1	8.3	8.2	2522	247	3.5	2.3	2212	583	58	72	12	136
2	8.4	7.5	2532	242	9.4	0.9	2170	617	0	88	14	155
3	8.4	7.5	2532	242	2.2	0.8	2128	551	74	90	16	128
4	8.4	7.5	2532	242	4.3	3.0	2248	559	49	60	11	131
5	8.4	7.5	2532	242	5.1	0.7	2112	608	40	90	17	151
6	8.4	8.2	2496	197	2.0	0.6	2072	534	77	93	17	171
7	8.4	7.5	2532	242	3.0	0.3	2008	587	64	95	21	143
8	8.4	7.5	2532	242	2.3	0.3	2004	607	72	96	21	151
9	8.4	7.5	2532	242	3.6	0.5	2010	588	57	94	21	143
10	8.4	7.5	2532	242	2.4	0.4	2204	606	72	95	13	150
11	8.3	8.2	2522	247	8.3	2.9	2348	263	0	65	7	6
12	8.4	7.5	2532	242	8.3	4.2	2298	337	1	44	9	39
13	8.4	7.5	2532	242	8.4	3.1	2288	370	0	58	10	53
14	8.4	7.5	2532	242	9.2	3.7	2276	339	0	51	10	40
15	8.4	7.5	2532	242	7.8	3.8	2286	339	7	49	10	40
16	7.2	7.1	2680	268	6.9	1.8	2480	285	4	74	7	6
17	7.2	7.1	2680	268	6.6	1.1	2406	422	8	85	10	57
18	7.2	7.1	2680	268	5.8	1.3	2278	399	20	82	15	49
19	7.2	7.1	2680	268	5.7	1.1	2096	344	21	85	22	28
20	7.2	7.1	2680	268	7.0	0.7	2490	318	3	90	7	19
21	7.2	7.1	2680	268	6.8	0.2	2664	510	6	97	1	90
22	7.2	7.1	2680	268	6.3	0.3	2296	510	13	96	14	90
23	7.2	7.1	2680	268	5.6	0.3	2110	433	22	95	21	62
24	7.2	7.1	2680	268	3.2	0.6	2356	507	55	92	12	89
25	7.2	7.1	2680	268	3.0	0.3	2212	567	59	96	17	112
26	7.2	7.1	2680	268	3.4	0.3	2144	535	52	96	20	100
27	7.2	7.1	2680	268	2.6	0.2	1956	418	64	97	27	56
28	7.3	6.8	2708	262	2.3	0.6	2238	456	68	91	17	74
29	7.3	6.8	2708	262	0.8	0.4	2094	652	90	94	23	149
30	7.3	6.8	2708	262	0.7	0.3	1962	654	90	95	28	150
31	7.3	6.8	2708	262	0.8	0.4	1850	469	89	94	32	79
32	7.2	7.1	2680	268	7.0	3.0	2546	224	3	57	5	-16
33	7.2	7.1	2680	268	6.3	1.3	2462	533	13	82	8	99
34	7.2	7.1	2680	268	5.9	1.4	2258	453	18	80	16	69
35	7.2	7.1	2680	268	5.6	1.2	2060	456	22	83	23	70

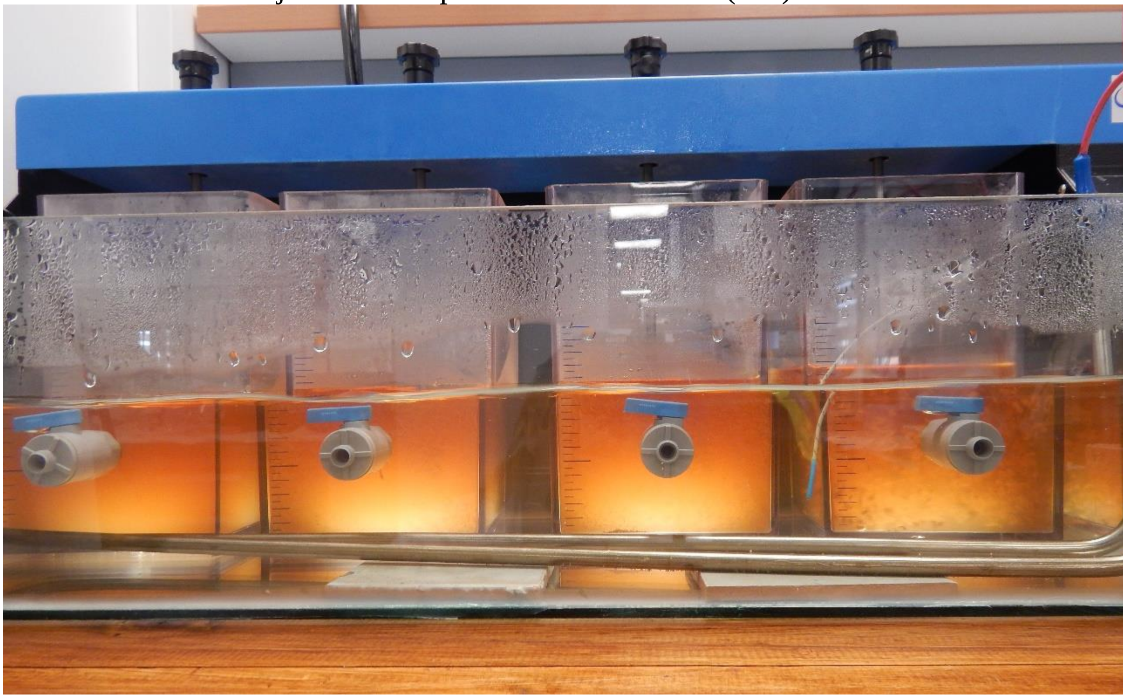
Based on the jar test results, no relevant TP removal efficiency was reached compared with jar test carried out without polymer addition. Using a doses of 600 mg$Ca(OH)_2$/L and default pH (approximately 8.0), the best removal efficiency of PT (74 %) was obtained with a polymer dose of 0.8 ppm. Under the same initial conditions, when no polymer was added, the removal efficiency of PT was 58 %. In this case, the polymer addition exhibited a slight improvement in the TP removal efficiency. With a precipitating agent dose of 800 mg$Al_2(SO_4)_3 \cdot 14.3H_2O$/L and pH 10.5, the results were completely opposite, since the highest removal efficiency of TP (77 %) was achieved when no polymer was added. Using $FeCl_3$, there was no difference between polymer addition or not.

After the chemical coagulation to precipitate the soluble P present on the wastewater, it is well known that the floc formation process can be improved with the addition of a flocculant during the slow mixing process. (Teh et al., 2016b) reported the efficiency of the solid-liquid separation process is highly influenced by the characteristics of floc, and production of small flocs is not ideal due to their fragility, lower settling velocity, and difficulty to separate them from the wastewater.

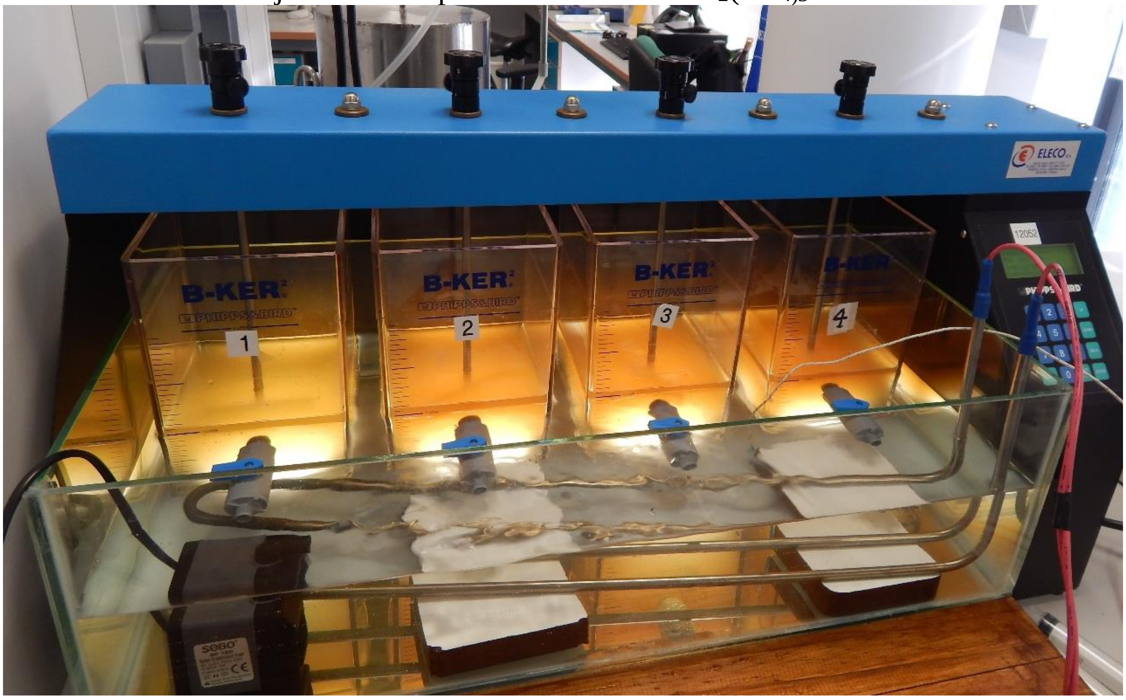
According to (Amuda & Amoo, 2007), compounds such as ferric chloride and/or polymer are added to wastewater in order to destabilize the colloidal materials and cause the small particles to agglomerate into larger settleable flocs. In the current study only larger and stronger flocs were visually observed when calcium hydroxide was used with doses higher than 600 mg$Ca(OH)_2$/L (Figure 4.5A). With alum or ferric chloride no flocs were formed (Figure 4.5B and 4.5C). This may be since the precipitation and coagulation process did not occur correctly or the colloidal particles still had a charge and caused repulsion between them.



A- Observed flocs at jar test in Experiment #2A with $Ca(OH)_2$



B- Observed flocs at jar test in Experiment #2B with $Al_2(SO_4)_3$



C-Observed flocs at jar test in Experiment #2C with $FeCl_3$.

Figure 4.5 Observed flocs in Experiment #2 with different doses of polymer

Since no significant effect on polymer aggregate was seen in the experiments shown in Table 4.4, from tests #1 to 15; The flocculation process with higher doses of polymer, 0, 5, 10 and 20 ppm, was evaluated (experiments # 16 to 35) in order to identify if high doses of polymer helped the formation of a larger floc that allowed sedimentation and better PT removal.

According to the results of the jar tests with $Ca(OH)_2$ (Table 4.4, test #24 to 27), at the default pH achieved with a dose of 400 mg$Ca(OH)_2$/L (pH about 5), no difference was seen between the doses of polymer studied.

In the case of $Al_2(SO_4)_3 \cdot 14.3H_2O$/L (Table 4.4, test #28 to 31), with a dose of 200 mg/L and a pH adjusted to 10 with NaOH, a significant effect of the polymer on PT removal can be observed. Obtaining a removal efficiency of 68 % when no polymer is added, and a removal efficiency of 90 % with doses of 5, 10 and 20 ppm were used. This agrees with what was expressed by (Lee et al., 2014b), which expresses that polyacrylamide, which is the polymer used in the jar tests during this research, received great extent of utility in the wastewater treatment in the industries due to its economic advantage and easy tailorability.

In the case of $FeCl_3$ (Table 4.4, test #32 to 35), no difference is noted in TP removal efficiency between the addition or not of polymer.

The results of removal of organic matter in the different tests, it can be seen in Table 4.4. At low added doses of polymer, from 0 to 1.5 ppm, no great variations are observed. With lime, the removal of COD is between 11 and 17 %, in the case of using aluminium, the removal of COD ranges from 13 to 21% and in the case of iron, the removal is very low, less than 10 %.

On the other hand, using high doses of polymer, of 20 ppm, higher percentages of organic matter removal are obtained, being 32 % with aluminium, 27 % with lime and 23 % with iron.

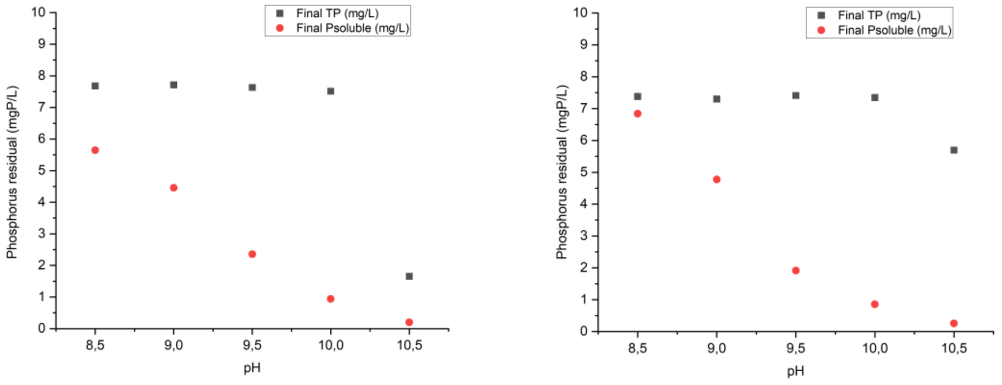
Based on the results found when evaluating the optimal conditions of mixing intensity and polymer dose, it is observed that if the particle destabilization conditions are not happened, beyond changing the mixing intensity, or adding higher doses of flocculant does not form flocs and does not allow the PT to be removed. Furthermore, to considering that adding high doses of polymer does not obtain large changes regarding the P removal efficiency, it is important to highlight that adding large doses of polymer implies an extra cost due to the large scale of the pulp mill WWTP.

With the addition of different doses of polymer, the variation in the TSS concentration of the different tests carried out can be observed in the last column of Table 4.4. With low doses of polymer, from 0 to 1.5 ppm, using lime as a precipitating agent, an increase in TSS ranging from 136 to 155 % is obtained. In the case of using aluminium, the percentage ranges from 143 to 171 % and when iron was used, the increase was much lower, from 6 to 53 %. When no precipitating agent is used, and polymer is only dosed in high doses, from 0 to 20 ppm, an increase in TSS of 0 to 90 % is obtained. With a precipitating agent, and high doses of polymer are added, from 0 to 20 ppm, an increase in TSS of 56 to 112 % can be observed in the case of lime, from 74 to 150 % in the case of aluminium, and from 0 to 99 % in the case of iron. At high doses of polymer, the increase in TSS is less than at lower doses.

According to the results obtained in this section, the mixing intensity or polymer doses variation in the flocculation process does not seem to have a great influence on the removal of P. Again, it is observed that the key factor in the removal of P is the pH. In Jar tests in which the pH is 10 or 10.5, good PT removal is obtained. It can also be highlighting that due to the complex matrix of the wastewater from pulp mill, it seems there is a high presence of certain cations, that just increased the pH promotes the precipitation of phosphate.

4.3.3 Effect of specific pH

With the aim to better understand how the pH variation affect the P precipitation processes, a new series of jar tests were carried out. The removal of TP and soluble P were evaluated with: no precipitating agent addition, 400 mg$Ca(OH)_2$/L, 200 mg$Al_2(SO_4)_3 \cdot 14.3H_2O$/L and 50 mg$FeCl_3 \cdot 6H_2O$/L at different pH levels. Figures 4.6 and 4.7 show the results from these tests.



A. without precipitating agent or polymer

B. without precipitating agent – polymer 1.5 ppm

Figure 4.6 TP and soluble P residual in a pulp mill wastewater without precipitating agent and polymer, left (A); without precipitating agent and with 1.5 ppm of polymer, right (B); and pH (from 8.5 to 10.5). Initial conditions: PT=8.3 mg/L, Psoluble=7.5 mg/L, and T=60 °C

As shown in Figure 4.6A y 4.6B, clearly the increase in pH leads to the precipitation of almost all the soluble P. On the other hand, there was no TP removal up to a pH value of 10. At pH about 10.5, only in the case of Figure 4.6A, there was a TP removal of 80 %, reaching at a residual TP value of 1.7 mgP/L. It is important to highlight that this concentration of P in the effluent represents a total load of 124 kgP/d and the permit limit (annual) established for UPM is 60 kgP/d. This could imply that their chemical precipitation of P occurred, a precipitate was formed, but it could not settle under the evaluated conditions. These results are consistent with those obtained in the jar tests presented previously, in Figure 4.2, Figure 4.3B and Figure 4.4B; where it was clearly seen that it was necessary to raise the pH to 10.5, with all the precipitating agents evaluated, to achieve a high PT removal efficiency.

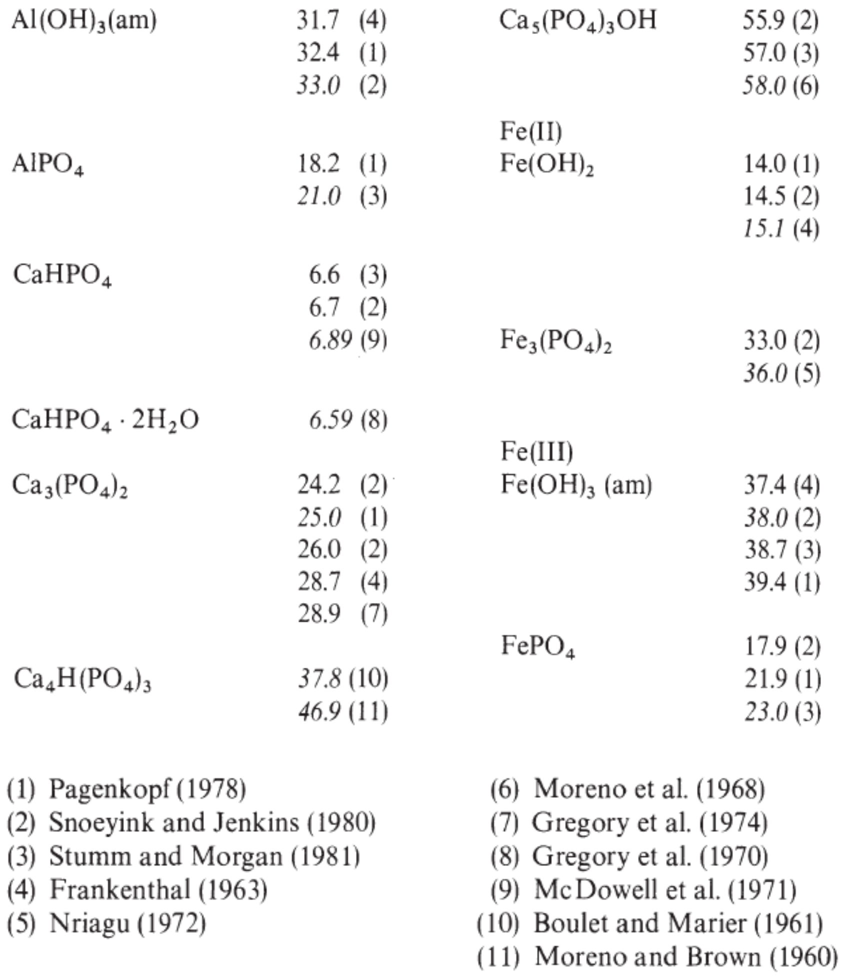
Based on these results, a first hypothesis can be established about the composition of the wastewater matrix studied. It is considered that the wastewater must contain some components, such as metals, which, when the pH is raised, they precipitate with the phosphate (from pH 8.5 they start precipitating). Metals such as Ca, Mg, Fe, Al, among others, that with OH^- and PO_4^{3-} form insoluble precipitates that are favoured at high pH. According to (Szabó et al., 2008) at pH values greater than 10, phosphate can precipitate with Mg and Ca ions available in most wastewaters and a reduction of the soluble P concentration can take place without iron or aluminium coagulant addition (A. Szabó et al., 2008).

Even precipitation of P was observed by just raising the pH, it was also observed that the precipitated P was not removed by sedimentation; that is, soluble P was removed, but not total P. Only the precipitated P was able to settle and by completely removed from the system (precipitation + sedimentation) at pH higher than 10.

It is difficult to be able to know exactly the reactions that occur in the chemical P removal at a pulp mill wastewater with different precipitating agents. A lot of reactions occur simultaneously that are not possible to predict given the complexity of the wastewater matrix in its chemical composition. Table 4.5 presents the information on the values of solubility products estimated by different authors. According to (Tomson & Vignona, 1984) only acid/base or hydrolysis reactions were included in the equations due to both numerical uncertainty in the equilibrium constants and uncertainty about the precipitation process.

As can be seen in Table 4.5, the Ksp value for $Ca_5(PO_4)_3OH$ is 10^{-57} on average for the different references. Such a small value indicates that only a very small amount of the solid dissolves at that evaluated temperature. This is consistent with what happened in the experiments with lime, since there was a good removal of PT at high pH. In the case of $AlPO_4$ and $FePO_4$, the Ksp values are higher than those of lime, being 10^{-21} and 10^{-23}, which indicates that a greater quantity of solids dissolves, so that when remaining soluble it is more difficult it can precipitate that salt. It is important to highlight that these are just the solubility products of the salts without including the complexation that could occur at such complex wastewater matrix as observed in a paper mill wastewater.

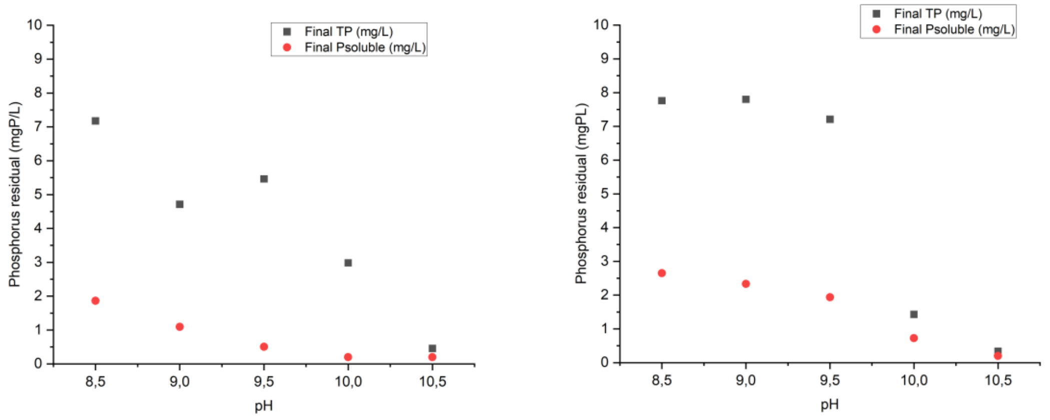
Table 4.5 Table of solubility products values at 25 °C (-log Ksp) (Tomson & Vignona, 1984)



$Al(OH)_3$(am)	31.7 (4)	$Ca_5(PO_4)_3OH$	55.9 (2)
	32.4 (1)		57.0 (3)
	33.0 (2)		*58.0* (6)
		Fe(II)	
$AlPO_4$	18.2 (1)	$Fe(OH)_2$	14.0 (1)
	21.0 (3)		14.5 (2)
			15.1 (4)
$CaHPO_4$	6.6 (3)		
	6.7 (2)		
	6.89 (9)	$Fe_3(PO_4)_2$	33.0 (2)
			36.0 (5)
$CaHPO_4 \cdot 2H_2O$	*6.59* (8)		
		Fe(III)	
$Ca_3(PO_4)_2$	24.2 (2)	$Fe(OH)_3$ (am)	37.4 (4)
	25.0 (1)		*38.0* (2)
	26.0 (2)		38.7 (3)
	28.7 (4)		39.4 (1)
	28.9 (7)		
		$FePO_4$	17.9 (2)
$Ca_4H(PO_4)_3$	*37.8* (10)		21.9 (1)
	46.9 (11)		*23.0* (3)

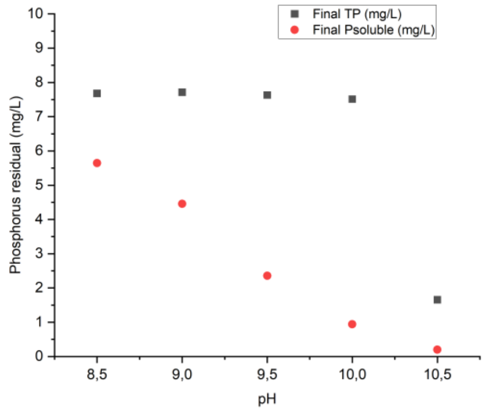
(1) Pagenkopf (1978)
(2) Snoeyink and Jenkins (1980)
(3) Stumm and Morgan (1981)
(4) Frankenthal (1963)
(5) Nriagu (1972)
(6) Moreno et al. (1968)
(7) Gregory et al. (1974)
(8) Gregory et al. (1970)
(9) McDowell et al. (1971)
(10) Boulet and Marier (1961)
(11) Moreno and Brown (1960)

Moreover, it is possible to establish a second hypothesis about the stability of the colloids. It was seen that the precipitate forms but did not settle under the evaluated conditions. The stability of the colloids could not allow them to come together, and flocculate, so they eventually remained as colloids in suspension.



A. 400 mg$Ca(OH)_2$/L – polymer 1.5 ppm

B. 200 mg$Al_2(SO_4)_3 \cdot 14.3H_2O$/L – polymer 1.5 ppm



C. 50 mg$FeCl_3 \cdot 6H_2O$/L – polymer 1.5 ppm

Figure 4.7 PT and P soluble residual in a pulp mill wastewater with $Ca(OH)_2$ *as precipitating agent and 1.5 ppm of polymer (A); with* $Al_2(SO_4)_3$ *as precipitating agent and 1.5 ppm of polymer (B); with* $FeCl_3$ *as precipitating agent and with 1.5 ppm of polymer (C); and pH (from 8.5 to 10.5). Initial conditions: PT=8.3 mg/L, Psoluble=7.5 mg/L, and T=60 °C*

When adding the precipitating agents at different pHs (Figure 4.7), the best TP removal efficiency was observed at pH 10.5, independently of the type of precipitating agents used. P soluble removal efficiency was high (about 97 %) in all studied cases. However, the TP removal efficiency was high (about 95 %) only with $Ca(OH)_2$ and $Al_2(SO_4)_3$, reaching TP residual values about 0.4 and 0.5 mgP/L respectively. With $FeCl_3$ the TP removal efficiency obtained was 80 %, with value of TP residual about 1.7 mgP/L.

As indicated in Figure 4.7, similar results were obtained to those previously shown in Figures 4.2 to 4.4. Where, when the pH increased, almost all the soluble P precipitated, but the removal of PT did not occur up to a pH value of 10.5. The results obtained are also consistent with the results presented in Figure 4.5, where it was also seen that the soluble P decreased, but the PT was not removed.

In the results presented in Figure 4.7 higher PT removals were observed as compared to the results presented in Figure 4.6.

What could happen is that by adding the precipitating agent and raising the pH, the added metal was precipitated as OH (in addition to also precipitating all the rest of the metals in the wastewater matrix). This generated a very large concentration of minerals (particles) that generates a sweeping effect in the sedimentation, also dragging the precipitated P colloids. Hydroxide precipitation could lead to the possibility of sweep flocculation, in which contaminant particles become enmeshed in the growing precipitate and thus are effectively removed (Duan & Gregory, 2003) and (Sahu & Chaudhari, 2013).

According to (Teh et al., 2016a) sweep-floc coagulation is predominant during the application of higher dosages of metal salts. This may explain why the sweep coagulation phenomenon is occurring. The optimal doses of precipitating agents obtained in Experiment #1 are much higher than the mol-mol ratio necessary for the precipitation of P. In the case of Al, a dose of 200 mg$Al_2(SO_4)_3 \cdot 14.3H_2O$/L is required, which is equivalent to a mol-mol ratio of 1:8. In the case of Fe, a dose of 50 mg$FeCl_3 \cdot 6H_2O$/L is required, which is equivalent to a mol-mol ratio of 1:4. Similar results were presented by (Duan & Gregory, 2003; Sahu & Chaudhari, 2013) where explain that the predominant removal mechanism at high doses of coagulant is sweep-floc coagulation by enmeshment in the aluminium hydroxide precipitate.

The most relevant results obtained from Figures 4.6 and 4.7 could be summarized as follows: i) without the addition of chemicals, the soluble P precipitates completely, ii) the P remains without sedimentation, but if the repulsion of the particles is overcome, or if the sweep coagulation phenomenon occurs, the TP is completely removed.

Based on the results and discussion of jar test carried out previously, some experiments were selected to be repeated analysing the TP and soluble P (Experiment #8). The objective of repeating some of the tests was to better understand the way in which the removal of P occurred. According to the results previously obtained, pH had a significant role in the removal of P, and the addition of different precipitating agents and doses did not appear to influence the removal of P. The obtained results are shown in Figure 8.

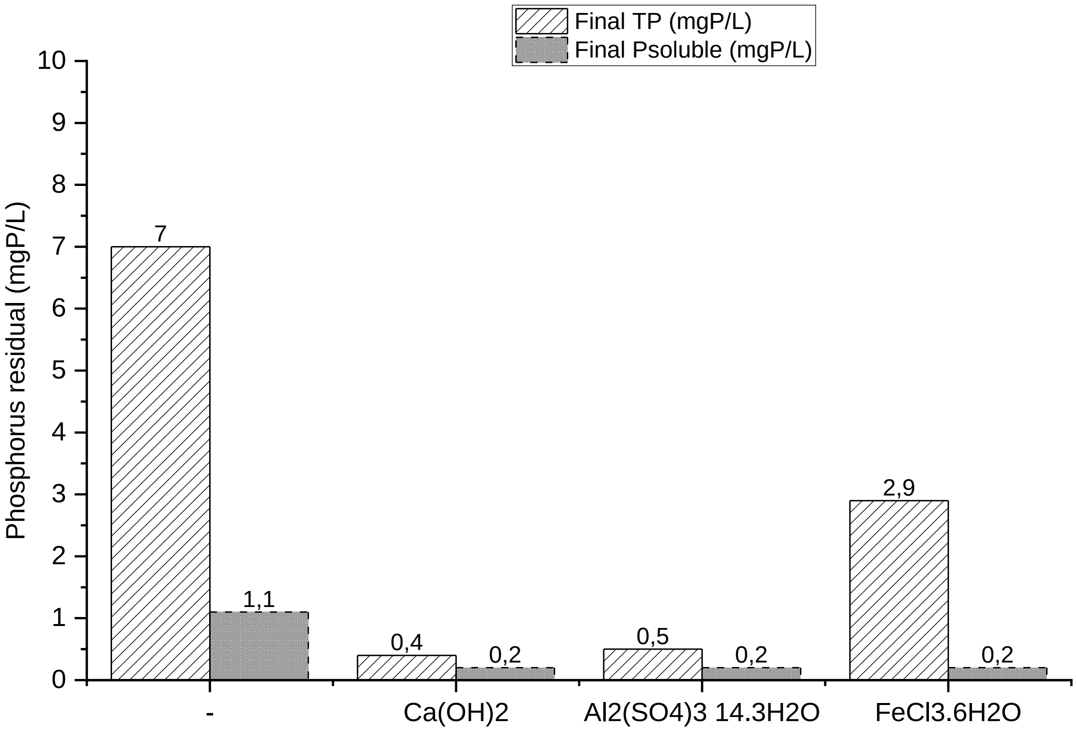


Figure 4.8 TP and soluble P residual in a pulp mill wastewater as a function of type of coagulant (without coagulant, 400 mg$Ca(OH)_2$*/L, 200 mg*$Al_2(SO_4)_3 \cdot 14.3H_2O$*/L and 50 mg*$FeCl_3 \cdot 6H_2O$*/L). Initial conditions: TP=7.6 mg/L, Psoluble=6.9 mg/L, pH 10.5 and T=60 °C*

The results of the four tests carried out at pH 10.5 and temperature 60 °C shows that the soluble P removal efficiency was high, from 84 % without chemical addition, and reaching efficiencies of 97 % for any of the other types of precipitating agents evaluated (Figure 4.8). This result agrees with that obtained in the previous experiments, shown in Figures 4.2 to 4.6. Where, as the pH increased, the soluble P precipitated, but remained without sedimentation. It was seen at pH 10.5 that the PT was not removed. With the addition of a precipitating agent, the removal of TP was achieved.

In this experiment, at a pH equal to 10.5 and without adding a precipitating agent, the PT removal efficiency is very low, 8 %, obtaining a residual PT value of 7.0 mgP/L. By adding a precipitating agent, the situation was different, and a high PT removal is noted. TP removal efficiency of 94 is achieved with $Ca(OH)_2$ and $Al_2(SO_4)_3$. Whereas, with $FeCl_3$, a maximum efficiency of 61 % was reached.

These results confirm the established hypotheses above. Firstly, increasing the pH allows cations eventually present in the pulp mill wastewater to precipitate together with P. However, the precipitated particles could be stable could come together and flocculate, so they remained as colloids in suspension. Raising the pH to 10.5 and adding the precipitating agent, the metals could precipitate as OH, and this could generate a very large concentration of particles. This eventually could cause a sweeping effect in the sedimentation, where the precipitated P colloids could be enmeshed in the floc and so removed.

4.3.4 Water quality characteristics and particle stability

From the previous jar tests, the following relevant results were obtained i) increasing the pH without the addition of chemicals would result in P precipitation and soluble P removal, even complete removals were observed at a pH of 10.5, ii) the precipitated P in most of the evaluated scenarios remains in the system without settling, but if the particles are allowed to floc, and/or if sweep coagulation could be promoted, then, the TP could be completely removed.

In order to verify such hypotheses, a new experiment was carried out (Experiment #8), where the removal of P was evaluated at pH 10.5, with and without different precipitating agents; the wastewater chemical composition was analysed in the initial sample and after precipitation and sedimentation processes, at the supernatant. Table 4.6 presents the results from this experiment.

Table 4.6 Results of experiment #8 – Wastewater chemical composition by ICP-OES

			EXP. 8-A (pH 10.5) (-)		EXP. 8-B (pH 10.5) (400 mgCa(OH)2/L)		EXP. 8-C (pH 10.5) (200 mgAl2(SO4)3/L)		EXP. 8-D (pH 10.5) (50 mgFeCl3/L)	
Element	**Total initial (mg/L)**	**Soluble inicial 0.45 µm (mg/L)**	**Total supernatant (mg/L)**	**Soluble supernatant 0.45 µm (mg/L)**	**Total supernatant (mg/L)**	**Soluble supernatant 0.45 µm (mg/L)**	**Total supernatant (mg/L)**	**Soluble supernatant 0.45 µm (mg/L)**	**Total supernatant (mg/L)**	**Soluble supernatant 0.45 µm (mg/L)**
Ca	155	118	152	112	232	267	105	96	103	103
Al	0.4	0.3	0.3	0.1	0.2	0.1	1.8	1.4	0.1	0.1
Mn	1.0	1.0	1.0	0.4	0.1	0.1	0.1	0.0	0.4	0.1
Cr	0.0	0.0	0.0	0.0	<0.006	0.0	<0.006	0.0	<0.006	0.0
Fe	0.5	0.3	0.5	0.1	0.2	0.1	0.1	0.1	3.3	1.1
Cu	0.1	0.1	0.0	0.0	0.0	0.0	<0.03	0.03	0.0	0.0
P	6.5	6.4	6.4	0.7	0.4	0.1	0.4	0.16	2.6	0.3
Si	10	6.3	10	4.2	6.6	5.5	6.1	5.6	6.8	5.4
Mg	24	24	23	18	12	12	2.9	2.0	13	9.1
Ba	0.4	0.2	0.4	0.1	0.1	0.1	0.1	0.1	0.2	0.1
Na	797	746	1249	1243	917	1012	1243	1168	1093	1223
K	18	17	21	19	20	18	20	18	20	18
S	432	374	435	447	387	441	431	424	383	432

The results of the water quality presented in Table 4.6 show that the chemical composition of the pulp mill wastewater evaluated presents a high concentration of some cations such as calcium: 155 mgCa/L, magnesium: 24 mgMg/L and sodium: 797 mgNa/L and high sulphur concentration: 432 mgS/L. The presence of these elements in the wastewater makes it a complex matrix compared to synthetic or municipal wastewater. Table 4.6 also shown that initial soluble concentration of sample after filtration with 0.45 µm.

Several studies have shown a high content of cations such as Ca, Mg and Na in pulp mill wastewater (Fontanier et al., 2005; Rezende et al., 2010; Doldán et al., 2011; Lucas et al., 2012). (Doldán et al., 2011) observed that Ca, Mg and K as the main cations found in the wood chips that is processed in the plant, and which then reach the effluent to be treated. On the other hand, other studies report high values of cations such as Ca, Mg and Na in the effluent from the pulp mill after secondary treatment. (Rezende et al., 2010) reports values of 46 mgCa/L, 77 mgMg/L and 742 mgNa/L. Similarly, (Lucas et al., 2012) found that the pulp mill wastewater after secondary treatment was composed of: 229 mgCa/L, 210 mgMg/L and 454 mgNa/L.

Table 4.6 present results from 4 test caried out: i) Exp 8-A, at pH 10.5 and without precipitating agent, ii) Exp 8-B, at pH 10.5 and doses of 400 mg$Ca(OH)_2$/L, iii) Exp 8-C, at pH 10.5 and doses of 200 mg$Al_2(SO_4)_3$/L, and Exp 8-D, at pH 10.5 and doses of 50 mg$FeCl_3$/L.

In all experiments from 8-A to 8-D it can be observed that the soluble P concentration decreases from the initial to the final supernatant sample, going from 6.4 mgP/L to 0.7 mgP/L in Exp 8-A, to 0.1 mgP/L in Exp 8-B, to 0.2 mgP/L in Exp 8-C and to 0.3 mgP/L in Exp 8-D. This indicates that at pH 10.5 P precipitation occurs. This may be due to the high wastewater content of Ca or Mg or because a phenomenon of sweep coagulation occurs. For example, the concentration of soluble Ca decreases 6 mgCa/L between the initial value of 118 to 112 mgCa/L in the case of Exp 8-A. This can explain that the Ca precipitated with the soluble P, since it also decreases 6 mgP/L. Evaluated in terms of moles, can be see that 0.15 mol of Ca reacts with 0.16 mol of P. It is also seen that the Mg concentration decreases between the initial soluble value and the final value in all the experiments. In the case of Exp 8-A, it decreases from 24 to 18 mgMg/L. In Exp 8-B to 12 mgMg/L, in Exp 8-C to 2.0 mgMg/L and in Exp 8-D to 9.1 mgMg/L; however, in these three experiments a massive concentration of counter cations was added (Ca, Al and Fe) and greater competition for phosphate is generated. This decrease in soluble Mg also justifies the precipitation of soluble P.

Exp 8-A showed that the TP was not removed, but the soluble P was removed almost completely, like results presented in Figure 4.5. This indicates that the P was precipitated, but this precipitate could eventually have a very small colloidal size or remains stable, so it could not flocculate and settle; nevertheless, P was removed by microfiltration. The results obtained in Table 4.6, Exp 8-B, C and D were similar to the results presented in Figure 4.7, where increasing the pH to 10.5 and adding a precipitating agent achieved almost complete removal of TP. With reported efficiencies for TP removal of 94 % with $Ca(OH)_2$ and $Al_2(SO_4)_3$, and 60 % with $FeCl_3$.

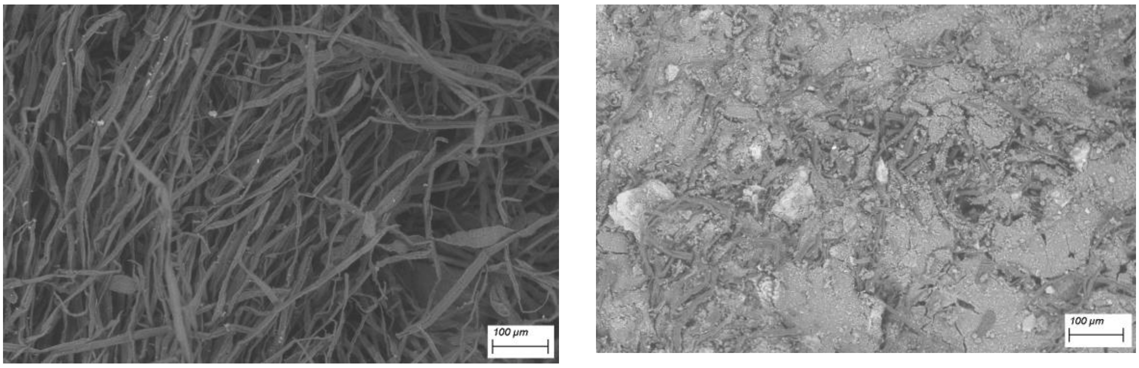
The final analysis of the sample in all experiments shown that the concentration of some elements remained unchanged, and the only case in which great variation were observed is in Na; Na increased since this was added to the initial sample to raise the pH to 10.5 in the form of NaOH.

Wang et al. (2005) showed that the PO_4^{3-} removal efficiency was higher than the removal efficiency of TP for different coagulants. The result showed that the coagulants mainly removed the PO_4^3 fraction of the P present in the wastewater. This can be explained that the P in form of PO_4^3 is removed by precipitation of phosphate with the metal ion. According to (Caravelli et al., 2012) at high pH conditions, sweep flocculation produces large aggregates of ferric hydroxide when ferric salts are added to water. As the sweep flocs settle, the colloidal particles will be removed by the sweep action of the settling flocs.

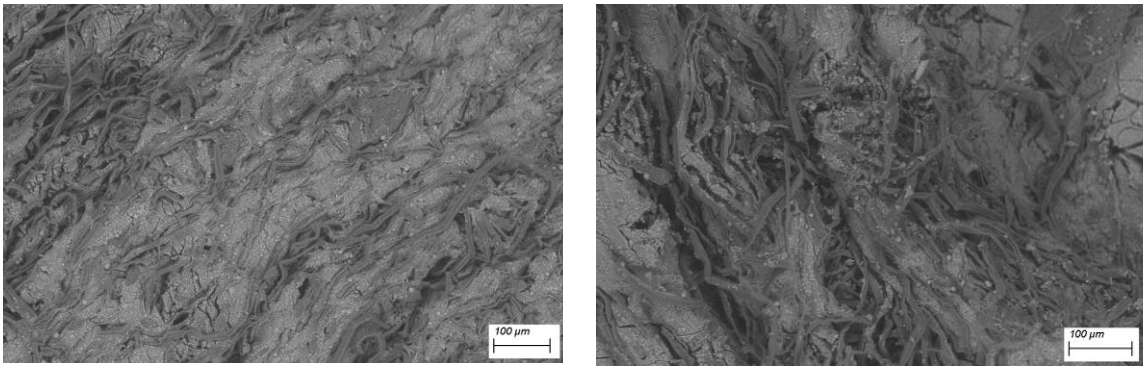
From previous studies is know that PO_4^{3-} and Mg could precipitate as trimagnesium phosphate ($Mg_3(PO_4)_2$), bobierrite ($Mg_3(PO_4)_2 . _8H_2O$) or newberyite ($MgHPO_4 . _3H_2O$) (Crutchik et al., 2013). The solid formed depends directly on the operational pH. Newberyite precipitates at pH values below 6.0. Bobierrite precipitates at pH values between 8 and 10, but with slow precipitation kinetics, in the order of days (Crutchik et al., 2013). According to Crutchik et al., (2013) results, at pH 10.5 none of these salts precipitated. On the other hand, the nature of the calcium phosphate precipitates depends mainly on pH and wastewater composition. Hydroxyapatite $Ca_5(PO_4)_3OH$ is thermodynamically the most stable calcium phosphate form, but this does not precipitate readily. Amorphous calcium phosphate: $Ca_3(PO_4)_2.nH_2O$, dicalcium phosphate dihydrate or brushite: $CaHPO_4 . _2H_2O$, dicalcium phosphate anhydrous or monenite: $CaHPO_4$ and octacalcium phosphate: $Ca8H_2(PO_4)_6 . _5H_2O$ can be precursors of hydroxyapatite, depending on the conditions (Crutchik et al., 2013). In the case of wastewater containing Mg, the first phases that precipitate are dicalcium phosphate dihydrate and amorphous calcium phosphate. Dicalcium phosphate dihydrate precipitates at low pH values (<7.0) whereas pH values higher than 7.0 enable the precipitation of amorphous calcium phosphate (Crutchik et al., 2013).

4.3.5 X-ray Diffraction and Scanning Electron Microscopy characterization

With the aim to know the morphology and chemical composition of the sludge generated in the jar test in Exp 8, samples were tested through SEM-EDS and XRD. Figure 4.9 shows the SEM images of the different samples analysed. In figure 8.A, refers to the evaluation where only the pH of the wastewater sample was raised to 10.5 and no precipitating agent was used. It can be seen in the image that only the cellulose fibre emerges (without other precipitates). In contrast, in the other images, 8.B, C and D, it is clearly seen that several minerals precipitated, and two phases are identified, i) the cellulose fibres and ii) a solid matrix with the precipitate. This can be verified with the chemical composition of the sludge by means of SEM-EDS in the different tests. As shown in Table 4.7, the chemical composition in Exp 8-A is different to the rest of the tests: Exp 8-B, C and D.



A Exp 8-A (pH a 10.5) B Exp 8-B (400 mg/L de $Ca(OH)_2$ and pH a 10.5)



C Exp 8-C (200 mg/L de $Al_2(SO4)_3$ and pH 10.5) D Exp 8-D (50 mg/L de $FeCl_3$ and pH 10.5)

Figure 4.9 SEM images of sludge produced by Exp 8-A, B, C, and D

The atomic percentage of each element in the chemical composition of the sludge can be observed. The table presents in the upper part the information detected on the cellulose fibre, and in the lower part the data referring to the precipitate. As can be seen, in all experiments, EDS analysis of precipitates shows that Ca and Mg, are the most abundant elements, whereas Na, S, Cl, Si, P y are detected at relatively low concentrations. These results evidence that the coagulation-flocculation process does not only remove P, but also traps other pollutants from the wastewater inside the flocs, such as metal ions. The chemical composition obtained verifies the presence of metals such as Ca and Mg in the treated wastewater, which indicates that the precipitation of P occurred with these metals when the pH increased to 10.5.

Table 4.7 Chemical composition of the sludge in experiments 8-A, B, C and D calculated by scanning electron microscopy energy dispersive spectroscopy (SEM-EDS)

Element	Exp 8-A	Exp 8-B	Exp 8-C	Exp 8-D
Chemical composition of fibre - Atomic%				
C	56.55 +/- 0.00	60.96 +/- 0.00	58.99 +/- 0.00	59.77 +/- 0.00
O	42.83 +/- 0.00	37.67 +/- 0.00	38.32 +/- 0.00	38.76 +/- 0.00
Na	0.22 +/- 0.00	0.15 +/- 0.00	0.32 +/- 0.00	-
S	0.08 +/- 0.00	0.06 +/- 0.00	0.12 +/- 0.00	-
Cl	0.06 +/- 0.00	0.04 +/- 0.00	0.09 +/- 0.00	-
Ca	0.25 +/- 0.00	0.67 +/- 0.00	0.88 +/- 0.00	0.77 +/- 0.00
Mg	-	0.28 +/- 0.00	0.77 +/- 0.00	0.46 +/- 0.00
Si	-	0.07 +/- 0.00	0.13 +/- 0.00	0.24 +/- 0.00
P	-	0.08 +/- 0.00	0.15 +/- 0.00	-
Al	-	-	0.22 +/- 0.00	-
Chemical composition of precipitate - Atomic%				
C	57.92 +/- 0.00	50.07 +/- 0.00	46.90 +/- 0.00	48.81 +/- 0.00
O	41.53 +/- 0.00	43.56 +/- 0.00	44.79 +/- 0.00	42.76 +/- 0.00
Na	0.29 +/- 0.00	0.39 +/- 0.00	0.63 +/- 0.00	-
S	0.08 +/- 0.00	0.22 +/- 0.00	0.30 +/- 0.00	0.41 +/- 0.00
Cl	0.04 +/- 0.00	0.15 +/- 0.00	0.18 +/- 0.00	-
Ca	0.14 +/- 0.00	2.74 +/- 0.00	3.26 +/- 0.00	4.91 +/- 0.00
Mg	-	1.77 +/- 0.00	2.30 +/- 0.00	1.93 +/- 0.00
Si	-	0.57 +/- 0.00	0.44 +/- 0.00	0.52 +/- 0.00
P	-	0.47 +/- 0.00	0.58 +/- 0.00	0.65 +/- 0.00
Al	-	0.07 +/- 0.00	0.61 +/- 0.00	-

To complement the previous results, XRD tests were carried out to identify the compounds that precipitated in each of the test in Exp 8. Figure 4.9 presents the graphs corresponding to each test. In Exp 8-A, the presence of only cellulose was identified, this is consistent since no precipitating agent was added in that test. In Exp 8-B, the XRD showed the main mineral species component were Hydroxyapatite ($Ca_5(PO_4)_3(OH)$) and Calcite ($CaCO_3$). Which are expected given that hydrated lime was added as a precipitating agent. In Exp 8-C, the presence of Weddellite ($CaC_2O_42H_2O$), Aluminium phosphate hydrate ($AlPO_4 \cdot xH_2O$) and Silvialite ($(Ca,Na)_4(Si,Al)_{12}O_{24}[(SO_4),(CO_3)]$) is observed. Finally, in Exp 8-D, the main mineral species component was Weddellite ($C_2CaO_4 \cdot 2.25H_2O$) and Potassium hydrogen carbonate phosphate hydrate ($Ca_8H_2(PO_4)_6 \cdot H_2O\text{-}KHCO_3\text{-}H_2O$).

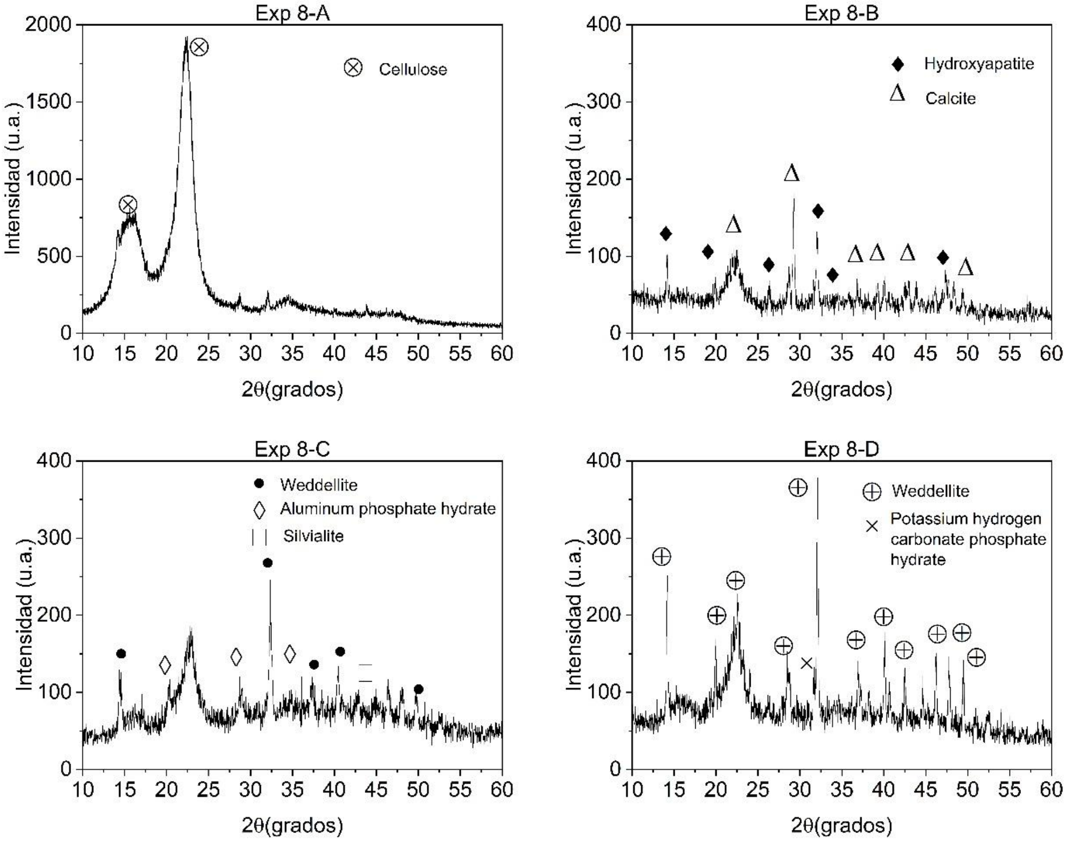


Figure 4.10 Electron diffraction spectra of sludge after coagulation-flocculation process

From Figure 4.10, the diffraction peak of Hydroxyapatite in Exp 8-B indicates that calcium ions formed precipitates with phosphate. Similar results in Exp 8-C, where the diffraction peak of aluminium phosphate hydrate show that aluminium ions formed precipitates with phosphate. However, in Exp 8-D iron phosphates were not found in the XRD patterns of the sludge. The P could have been removed by the Ca or Mg present in the wastewater. The presence of the diffraction peak of Potassium hydrogen carbonate phosphate hydrate confirms that the precipitation occurred with lime.

4.4 CONCLUSIONS

- Chemical P removal processes as pre-treatment of the pulp mill wastewater is a good alternative to get a high TP removal efficiency.
- The pH showed a great influence on P removal, with an optimal pH of 10.5 for the best TP removal. Only by raising the pH to 10.5, without using any precipitating agent, the soluble P is removed. The precipitation of P occurs, but the P is not able to settle.
- The highest TP removal efficiency was 95 % with $Ca(OH)_2$, 98 % with $Al_2(SO_4)_3$ and 93 % with $FeCl_3$.
- As the pH rises, the precipitation of P occurs with the metals Ca and Mg present in the wastewater.
- As the pH increased the precipitation of P was observed (even without adding any chemical); however, the precipitates were not able to settled. Thus, higher soluble P removal was observed, but little TP removal was reported. The P precipitation but just raising the pH seemed to form some sort of colloidal P precipitates not able to flocculate and settle.
- The high temperature of the wastewater from the cellulose pulp process, approximately 60 ^oC, showed favoring the P removal process compared to lower temperatures such as 30 and 45 ^oC.
- The variation of mixing intensity in the coagulation process and the addition of different doses of polymer in the flocculation stage did not have a significant effect on the removal of P.

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5

EVALUATION OF A CHEMICAL PHOSPHORUS REMOVAL PROCESS AT A PULP MILL WWTP IN URUGUAY

This chapter is based on: Bentancur. S., Dutra, I., Pereyra, P., López Vázquez, C. M., García, H.A., Echeverría, L., De Los Santos, E., & Brdjanovic, D. Evaluation of a chemical phosphorus removal process at a pulp mill WWTP in Uruguay. In preparation

ABSTRACT

In this study, the potential biological and chemical removal of phosphorus were assessed in an industrial effluent from a full-scale pulp mill wastewater treatment plant that had a relatively higher influent P-concentration compared to other plants from the same sector. For that purpose, the potential biological removal of phosphorus was evaluated in a lab-scale SBR under fully aerobic conditions for merely biomass synthesis. The chemical P-removal (CPR) process was studied following a co-precipitation (through the addition of coagulants to the lab-scale SBR) and a post-precipitation approach (conducting different jar-tests with the effluent from the SBR). Three coagulants ($FeCl_3$, $Al_2(SO_4)_3$, and $Ca(OH)_2$) were tested at different concentrations. The treatment of the pulp mill effluent by merely biological means was unable to contribute to a considerable P-removal due to the low P growth requirements of the biomass. The co-precipitation CPR approach showed to be highly effective independently of the coagulant used (at doses of 300 $mgFeCl_3{\cdot}6H_2O/L$, 300 $mgAl_2(SO_4)_3{\cdot}14.3H_2O/L$ or 400 $mgCa(OH)_2/L$) resulting in removal efficiencies of between 79 and 82 % and achieving final soluble P wastewater concentrations in the range of 0.28 to 0.34 mgP/L. However, it struggled to comply with the discharge standard permit limit (annual) of 60 kg TP/d. On the other hand, the post-precipitation approach (with the addition of $Al_2(SO_4)_3$ at a PO_4^{3-}/metal salt ratio (mol-to-mol) of 1:10 or when dosing 400 mg $Ca(OH)_2/L$) allowed to achieve the lowest observed TP and soluble P concentrations (lower than 0.5 and 0.2 mgP/L, respectively). Thus, the most suitable CPR approach to treat the pulp mill industrial effluent was post-precipitation since it was able to consistently comply with the maximum discharge standard of 60 kg TP/d.

5.1 INTRODUCTION

In the world, the most widely treatment applied to pulp and paper effluents is the biological activated sludge system (Hubbe et al., 2016; Toczyłowska-Mamińska, 2017). In general, industrial effluents generated by pulp and paper mills are deficient in nutrients (nitrogen (N) and phosphorus (P)) and they often need to be dosed (Vashi et al., 2018; Vashi et al., 2019). In Uruguay, on the other hand, the hard wood (eucalyptus) used as raw material has a different P composition compared to other hard woods processed elsewhere (in terms of chemical structure and content) (Bentancur et al., 2021). According to data provided by pulp mill from Uruguay, the hard wood that they process has a high P-content, which has continued to increase in the last 10 years. Consequently, their effluents have a higher P concentration than other paper mill effluents.

The pulp mill subject of study in this research, located in Uruguay, uses the chemical Kraft process to produce 1.3 million tons of fully bleached eucalyptus pulp per year. The effluent generated by the pulp mill (mostly from the bleaching process) is treated in a WWTP composed of a conventional activated sludge (CAS) system with an installed capacity of approximately 73,000 m^3/day (Bentancur et al., 2021). Originally, the WWTP was built without any nutrient removal process, since it was expected that the industrial effluent was going to be deficient in nutrients. However, in 2015 given the high P-content of the hard wood, a chemical pre-treatment stage with $Ca(OH)_2$ addition was implemented. In this way, the industry increased its production from 1.1 to 1.3 million tons of cellulose per year while continuing to comply with the total phosphorus (TP) discharge limits established by the environmental regulations in Uruguay (60 kgTP/d as an annual load average).

Phosphorus can be found in aqueous media in different compounds and species. As such, phosphorus can be classified as dissolved (mostly composed of orthophosphate, PO_4^{3-}-P), colloidal (non-stabilized PO_4^{3-}-P) or particulate phosphorus (mostly organic phosphorus) (APHA et al., 2012).

The enhanced biological phosphorus removal (EBPR) process in wastewater treatment activated sludge systems is the most studied and applied P-removal process in the world, being able to achieve discharge concentrations lower than 1 mg/L (De Haas et al., 2000; López-Vázquez et al., 2008; López-Vázquez et al., 2009). EBPR can be very effective, but there are still certain disadvantages, like the higher construction and operating costs and the highly sophisticated operation required (Zhen-hua & Kai, 2011). For industrial applications, and particularly in the pulp and paper industry, its implementation is still a challenge since the effluents contain complex and diverse harmful compounds, such as resin acids and sterols (Lindholm-Lehto et al., 2015). Besides, temperatures higher than 30 ^oC may jeopardize the performance of the EBPR process (López-Vázquez et al., 2008; Kazadi Mbamba et al., 2019). On the other hand, the chemical phosphorus removal (CPR) process has also been effectively applied in wastewater treatment to achieve consistent P removal efficiencies (Takács et al., 2005). In the CPR process, metal salts (mostly based on Al, Fe or Ca) are dosed into the wastewater for P precipitation (Metcalf & Eddy, 2003; Smith et al., 2008; Li et al., 2018). The two main chemical processes applied for P removal are coagulation and chemical precipitation. Coagulation consists on the destabilization of colloidal particles, decreasing or neutralizing the electric charge of suspended particles, so that particle growth can occur as a result of particle collisions (Stephenson & Duff, 1996; Jiang & Graham, 1998; Ebeling et al., 2003). Chemical precipitation involves the addition of chemicals to alter the physical state of dissolved and suspended solids and facilitate their removal in a following settling stage (Metcalf & Eddy, 2003).

When metal salts are used as coagulants (Tzoupanos & Zouboulis, 2008), the coagulant dose and the pH are two of the most important factors that determine the removal mechanisms and the species formed (Jiang & Graham, 1998). The removal of particles by sweep coagulation with iron occurs in a pH range between 6.5 and 10.0 at iron doses from 2.7 to 270 mg/L (Metcalf & Eddy, 2003a). When dosing alum the pH range is similar, but alum dosages between 20 and 200 mg/L are often applied (Metcalf & Eddy, 2003a). The Al and Fe ratios between added salt and precipitate is 1:1, considering also potential competitive reactions, the effects of alkalinity and the pH (Bratby, 2006).

Regarding the precipitation mechanism, calcium is added as $Ca(OH)_2$. First, it reacts with soluble calcium bicarbonate to precipitate $CaCO_3$ (Albertson & Sherwood, 1969). Then the pH increases over 10 and the excess of calcium ions react with phosphate producing $Ca_{10}(PO_4)_6(OH)_2$ (Albertson & Sherwood, 1969). The amount of lime required to precipitate phosphorus depends largely on the alkalinity and not on the phosphorus concentration (Metcalf & Eddy, 2003).

The precipitation of P from wastewater can occur in different locations with regard to the (biological) secondary treatment stage as: pre-precipitation, co-precipitation and post-precipitation (De Haas et al., 2000; Metcalf & Eddy, 2003). There are different factors that influence on the location of the application: the influent P concentration, wastewater suspended solids concentration, alkalinity, chemical costs, reliability of the chemical supply, sludge handling facilities, ultimate disposal methods and compatibility with other treatment processes (Metcalf & Eddy, 2003). Iron and aluminium can be added on different points along the treatment process, but because polyphosphates and organic phosphorus are not as easily removed as orthophosphate, the addition of aluminium or iron salts after secondary treatment (post-precipitation) usually leads to the best results (Metcalf & Eddy, 2003).

The CPR processes have shown to be robust and reliable. They can be used as a single P-removal process in the main side-stream treatment lines or be complementary to EBPR (Takács et al., 2005). However, in the pulp and paper industry in Uruguay, satisfactory results have not been obtained using the most common coagulants ($FeCl_3$ and $Al_2(SO_4)_3$) at the doses and pH ranges suggested in literature (Triany, 2020). Thus, the objective of this research was to evaluate different CPR alternatives, such as a co- and post-precipitation using $Ca(OH)_2$, $FeCl_3$ and $Al_2(SO_4)_3$, using a lab-scale biological reactor operated under similar conditions to those applied at the full-scale WWTP.

5.2 MATERIALS AND METHODS

5.2.1 WWTP description

The process flow diagram of the wastewater treatment plant (WWTP) of study (Figure 5.1) consisted of a mechanical and physico-chemical pre-treatment followed by a biological activated sludge treatment for the removal of organic matter. The WWTP was designed for an influent flowrate of approximately 73,000 m^3/day.

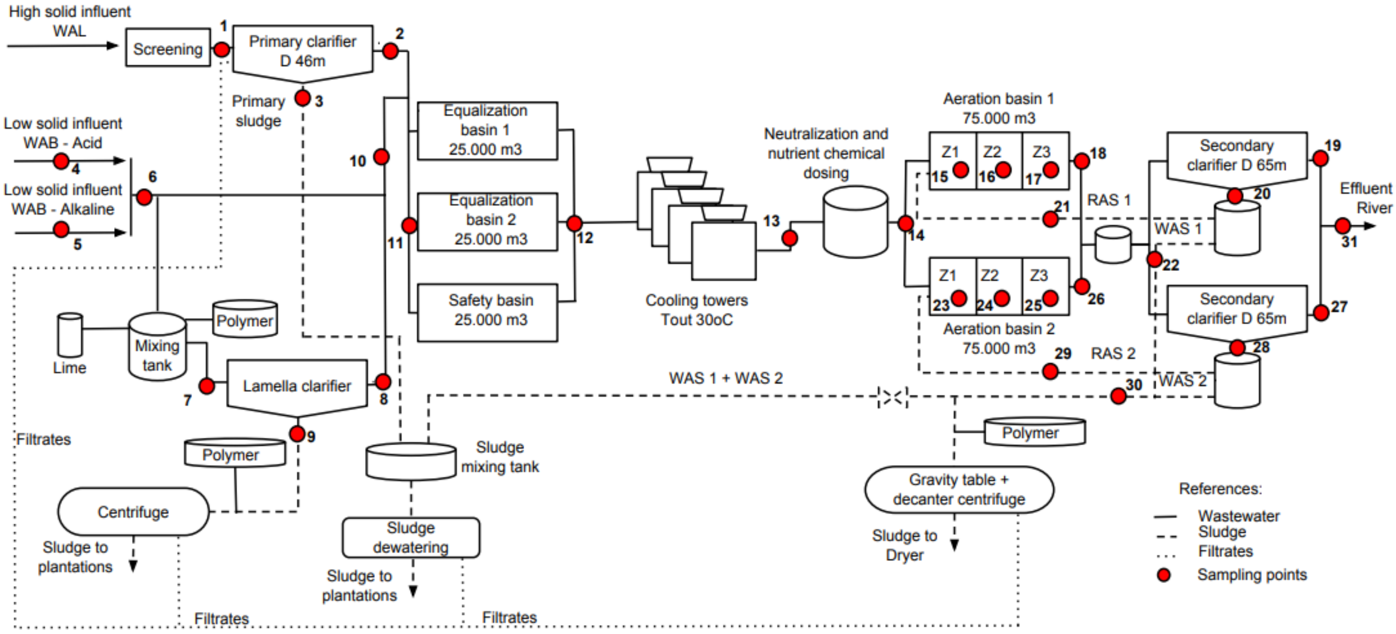


Figure 5.1 Process flow diagram of the pulp mill WWTP

The plant has two effluents from the pulp and processing factory, one with a high solids effluent (named WAL) (sampling point 1) and the other (identified as WAB) with a low solids effluent (sampling point 6 composed of two flowrates that flow through sampling points 4 and 5). Actually, the WAB effluent is composed of (a) 30,240 m^3/d of acid filtrate from the A/D1 stage that contains chlorine dioxide and a TP concentration of approximately 8 to 9 mgP/L and (b) 12,960 m^3/d of an alkaline filtrate containing peroxide, sodium hydroxide (EOP) and a TP concentration of approximately 3 to 5 mgP/L. The WAL effluent passes through a screening stage and a primary clarifier (sampling point 2) and then continues to the safety basins. The WAB effluent is treated in a recently implemented CPR process (sampling point 7). After the chemical P removal stage, the wastewater flows to the safety basins (Sampling point 8). Both flows (WAL plus WAB) are mixed at the equalization basins and sent to the cooling towers to adjust the wastewater temperature from 55 ^{o}C to about 30 ^{o}C. After the cooling towers (sampling point 13), the neutralization stage and urea addition, the combined effluent flows to the activated sludge system (sampling point 14). The activated sludge system was designed with two parallel lines, each including one aeration basin, one secondary clarifier and one return of activated sludge from the secondary clarifier to the aeration tank. Finally, the effluent is discharged into the river (sampling point 31). The sludge treatment line processes the primary sludge, the sludge generated in the CPR treatment and the waste of activated sludge.

5.2.2 Experimental phases

The experimental work of this research was carried out at the Environmental Engineering Laboratory (EEL) of the Catholic University of Uruguay (UCU) in Montevideo, Uruguay. The experimental plan was divided in three different phases.

Experimental phase No. 1

In phase 1, a lab-scale sequencing batch reactor (SBR) was used with the aim of mimicking and evaluating the operational conditions that prevail in the extended aeration process currently applied at the pulp mill WWTP. In the first stage, a mixture of the two raw effluents WAL and WAB was supplied to the SBR. Afterwards, an equalized and stabilized mixture of the pre-treated effluents was tested (as currently practiced in the full-scale WWTP).

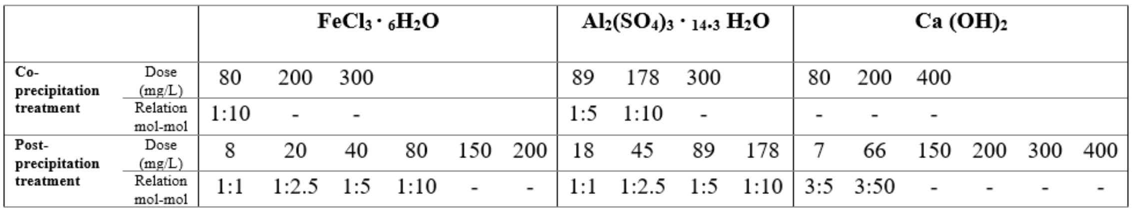
Once the bioreactor was stabilized (after the system had operated for more than 3 times the applied SRT and when no major changes were observed in the analytical parameters in the following weeks), the SBR was assumed to have reached pseudo steady-state conditions.

Experimental phase No. 2

In the experimental phase 2, the main purpose was to assess the CPR process in jar-tests simulating a co-precipitation stage in the SBR and a post-precipitation stage. For the co-precipitation, coagulants were dosed during the aerobic phase into the SBR. Meanwhile, for the post-precipitation tests, mixed liquor and settled effluent were collected at the end of the operational cycle and used to conduct jar-tests.

The jar tests were conducted in four identical beakers with a capacity of 2 litres, each one with its corresponding stirrer. First, a rapid agitation (200 rpm) was provided for 1 min followed by slow mixing (50 rpm) for 10 min and a settling stage that had a duration of 10 min. Table 5.1 shows the chemicals and doses used in the co-precipitation and tertiary treatment tests.

Table 5.1 Different types of coagulants and their doses used in the jar-tests conducted in experimental phase No. 2



		$FeCl_3 \cdot {}_6H_2O$						$Al_2(SO_4)_3 \cdot {}_{14\cdot3} H_2O$				$Ca(OH)_2$					
Co-precipitation treatment	Dose (mg/L)	80	200	300				89	178	300		80	200	400			
	Relation mol-mol	1:10	-	-				1:5	1:10	-		-	-	-			
Post-precipitation treatment	Dose (mg/L)	8	20	40	80	150	200	18	45	89	178	7	66	150	200	300	400
	Relation mol-mol	1:1	1:2.5	1:5	1:10	-	-	1:1	1:2.5	1:5	1:10	3:5	3:50	-	-	-	-

For each co-precipitation test, 300 mL of mixed liquor extracted from the biological reactor was used.

For the purpose of evaluate the P-removal process for tertiary treatment purposes, a similar approach to that followed in the co-precipitation tests was applied. However, instead of using mixed liquor from the biological reactor, 1 L of final effluent from the reactor was used in each beaker of the jar-tests. The doses used are shown in Table 5.1.

Samples were collected before and after carrying out each jar-test to determine the TP and soluble P concentrations.

Experimental phase No. 3

In the experimental phase No. 3, the effects of the continuous addition of coagulants to the extended aeration process mimicked in the lab-scale SBR were studied. For this purpose, a combination of effluents (as currently practiced in the full-scale WWTP and explained in the following sub-section) was supplied to the SBR.

This experimental phase was conducted after the efficiency and the dosage of coagulants were optimized in the jar-tests performed in the experimental phase 2. Based on those tests, iron chloride ($FeCl_{3.6}H_2O$) was selected to carry out the P-precipitation tests in the SRB itself. Iron chloride was dosed 15 minutes before the end of the aerobic stage. Three different doses of $FeCl_{3.6}H_2O$/L were assessed: 40, 80 and 240 mg/L.

5.2.3 Pulp mill effluents used as a feed to the SBR

To carry out this study, pulp mill effluent samples were taken three times a week from the full-scale WWTP. The samples were sent to the EEL at UCU in Montevideo and stored in a refrigerated room at 4 °C.

In order to perform the experimental phase 1, initially, the raw effluents were collected from June to August 2019, from sampling point 2 (4 L of WAL stream) and 6 (8 L of WAB stream) (Figure 5.1). Afterwards, from the second stage of the experimental phase 1 as well as in the experimental phases 2 and 3, the effluent was collected from sampling point 12, which contains a combined and equalized mixture of the pre-settled WAL effluent with the partially pre-treated (with calcium hydroxide) WAB effluent.

5.2.4 Continuous operation of the sequential batch reactor (SBR)

To carry out the three experimental phases, a double-jacketed lab-scale sequencing batch reactor with a maximum volume capacity of 3 L was continuously operated in cycles of 8 hours. Each cycle was composed of a 5 min. influent filling, 6 h 50 min. aerobic phase, 60 min. settling phase, and 5 min. of effluent withdrawal.

The temperature was set at 30.0 ± 0.1 °C and the pH was adjusted to 7.0 ± 0.1 through the automatically addition of acid (HCl 0.4 M) and base (NaOH 0.4 M). Aeration was supplied by compressed air and the dissolved oxygen concentration was maintained at a concentration of 2.0 mgO_2/L. In order to have an adequate mixture of the wastewater and the sludge during the aerobic phase, the mixing speed of the SBR was set at 150 rpm.

The reactor was inoculated with 1 L of activated sludge from the full-scale pulp mill WWTP previously aerated for 6 h.

In the first stage of phase 1, the SBR was fed in the beginning of each cycle with 1.0 L of wastewater prepared and preserved at the EEL and applying a hydraulic retention time (HRT) of 16 h. The influent was prepared twice a week with 4 L of effluent from the high solids WAL stream (point 2, Figure 5.1) and 8 L from the low solids WAB stream (point 6, Figure 5.1). In this stage, the SBR working volume was 2 L and 62.5 mL of waste sludge was withdrawn every day to operate the system at a SRT of 32 days.

From the second stage of phase 1 onwards, each cycle was fed with 0.83 L of wastewater collected at the sampling point 12 in order to reach a HRT of 24 h. The SBR had a working volume of 2.5 L and 78.1 mL of sludge were withdrawn daily to reach a SRT of 32 days.

All influents fed to the SBR in the different experimental phases were prepared twice a week. Urea was also supplied as N-source to cover the biological growth requirements. The prepared influents were stored in the fridge (4 °C) in a 20 L bucket.

5.2.5 Analysis

For more than five months (from June to October 2019), influent and effluent samples were taken weekly from the lab-scale reactor for the analytical determination of different parameters: such as Chemical Oxygen Demand (COD), Total Phosphorus (TP), Total Nitrogen (TN), Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS). Also, the TSS and VSS biomass in the reactor were analysed weekly. The parameters were determined at the Environmental Engineering Laboratory facilities at of the Catholic University of Uruguay (Montevideo, Uruguay). The analytical procedures were performed following standardized and commonly applied analytical protocols described in Standard Methods (APHA et al., 2012): COD (Standard Methods 5220 D), TP (Standard Methods 4500-P E), TN (Standard Methods 4500-N C), TSS (Standard Methods 2540 D), VSS (Standard Methods APHA 2540-E), and ISS (Standard Methods APHA 4500-E).

5.3 RESULTS AND DISCUSSION

5.3.1 Experimental phase 1. Operation of the lab-scale SBR

Raw pulp mill effluent treatment

With the intention of reaching the objective in this phase, it was necessary to simulate the operation of the activated sludge system of the pulp mill WWTP on a laboratory-scale SBR. In this experimental phase, the reactor was operated for 86 days. Different parameters were monitored weekly with special focus on COD, TP, TN and TSS.

Regarding the organic matter removal, the performance of the SBR in terms of COD (influent, effluent and removal efficiency) is shown in Figure 5.2A. As shown in Figure 5.2A, a good COD removal efficiency was observed during the entire period of study, the average influent and effluent COD concentrations and the removal efficiency were 2172 ± 219 mg/L, 603 ± 198 mg/L and 73 ± 8.0 %, respectively.

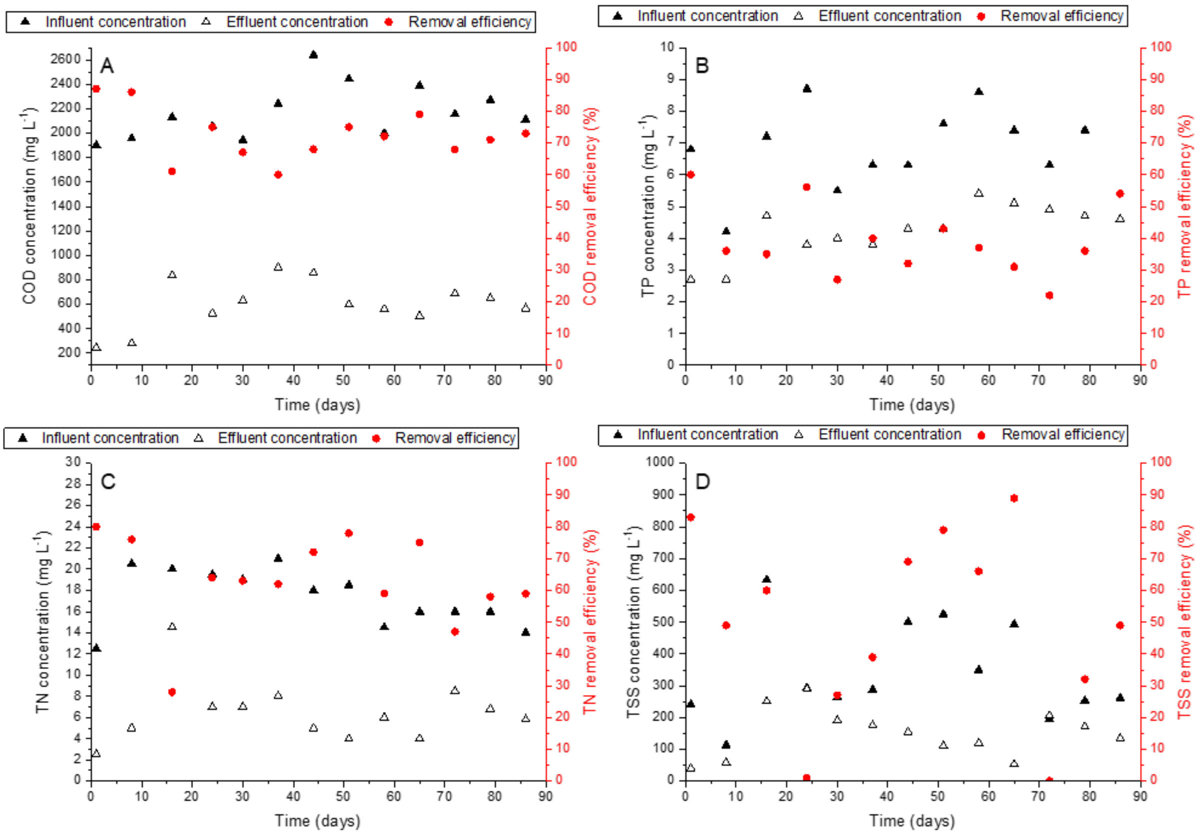


Figure 5.2 Influent, effluent concentrations and removal efficiencies observed in the operation of the lab-scale SBR operated with raw effluent from the pulp mill: (A) COD, (B) TP, (C) TN and (D) TSS

The operation of the lab-scale SBR was not designed to perform the EBPR process. As observed in Figure 5.2B, the average influent TP was 7.1 ± 1.5 mg/L while the average TP effluent concentration was 4.2 ± 0.8 mg/L, resulting in a TP removal efficiency of about 39 ± 11 %. The TP removal can be attributed to the amount of P required for bacterial growth. These results are in accordance to those observed in conventional activated sludge systems without EBPR processes (Von Sperling, 2015). Under these conditions, if the plant had not had the CPR pre-treatment (Figure 5.1), it had not been able to comply with the corresponding discharge standards established by the environmental agency in Uruguay. This pulp mill industry, due to the high daily wastewater discharge (of approximately 73,000 m^3/d), is allowed to discharge 60 kg TP/d. Thus, considering the flowrate discharged into the river, the effluent TP concentration needs to be lower than 1 mgTP/L to meet the discharge standard.

With regard to TN removal, the influent wastewater fed into the SBR was previously prepared with urea in order to comply with the N required for biomass growth (Chan et al., 2010). The nutrients should be supplied following a COD:N:P ratio of 100:10:1 (Burgess et al., 1999). In this study, the COD:N:P ratio was about 100:0.8:0.3. This result is consistent with previous studies carried out in this pulp mill WWTP (Bentancur et al., 2021) where the nutrient requirements were evaluated through aerobic batch activity tests, and a low nutrient assimilation was observed.

The average TN influent, effluent and removal efficiency were 17 ± 2.7 mg TN/L, 6.5 ± 3.0 mg TN/L and 63 ± 14 %, respectively (Figure 5.2C). The TN effluent concentration was higher than the effluent concentration observed at the WWTP (which is about 2.0 mg/L). Nevertheless, this can be adjusted by decreasing the urea addition.

As observed in Figure 5.2D, the influent TSS concentration varied considerably. Actually, the influent TSS concentration was higher than the concentration that reaches the secondary treatment stage of the full-scale pulp mill WWTP. The mean reason for that difference is that, in this phase, a raw combined effluent of WAL and WAB was fed into the lab-scale SBR since the objective was to evaluate the biological conversions (in particular the P-removal process) without any CPR pre-treatment. As such, the raw effluent was collected at a sampling point located before the CPR process (which also contributes to the removal of suspended solids) and also before the equalization basins (that generate a homogenous flow in terms of quantity and quality). This induced certain TSS dynamics that may explain why the effluent TSS concentration also varied (Figure 5.2D), likely influencing the TSS removal. Randomly and due to unknown reasons yet, at the end of the settling phase the sludge bed in the lab-scale SBR was sometimes higher than expected, resulting in certain loss of solids through the effluent, and also influencing the TSS concentrations in the reactor. As such, the average TSS influent, effluent and removal efficiency was 339 ± 152 mg/L, 150 ± 75 mg/L and 62 ± 29 %, respectively.

Figure 5.3 shows the TSS and VSS biomass concentrations in the SBR. The average TSS concentration was about 9.0 ± 1.1 g/L. This value was much higher, almost twice, than the concentration of biomass observed in the WWTP, which was approximately 5.5 g/L. This can be explained by the higher solids and organic content fed into the lab-scale SBR, as discussed previously. In the CPR pre-treatment and primary treatment stages of the full-scale WWTP, there was also certain removal of organic matter, and the average COD input into the biological reactor of the WWTP was about 1500 mg/L.

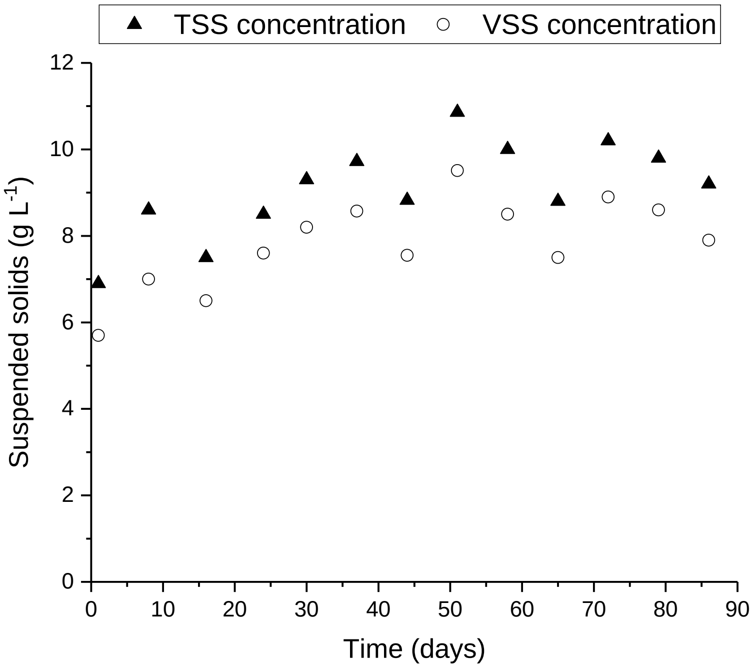


Figure 5.3 Biomass concentrations (as TSS and VSS) in the lab-scale SBR operated with raw effluent from the pulp mill

After the operation of the SBR for 86 days and evaluating the obtained results with supervisors and technical staff from the pulp mill, on September 4th, 2019, it was decided to change the collection of wastewater to feed the SBR to the sampling point No. 12 (Figure 5.1). The wastewater collected at point 12 had already passed through the CPR system and the equalization basins prior to its treatment in the conventional activated sludge system. Thus, it had the required characteristics to perform the P-coprecipitation tests and the chemical P-precipitation as a potential tertiary treatment.

Treatment of a mixture of raw effluent and chemically pre-treated effluent

In this experimental phase, the reactor was operated for 28 days. Like in the previous phase, different parameters were monitored weekly with special focus on COD, TP, TN and TSS concentrations in order to assess the activated sludge system and compare its performance with that from the full-scale WWTP.

Regarding the organic matter removal, as shown in Figure 5.4A, satisfactory COD removal efficiencies were observed with average influent, effluent and COD removal efficiency values of around 1478 ± 71 mg/L, 317 ± 14 mg/L and 79 ± 1.1 %, respectively.

In particular, the COD removal efficiency was like what was observed in the full-scale WWTP (of around 80%).

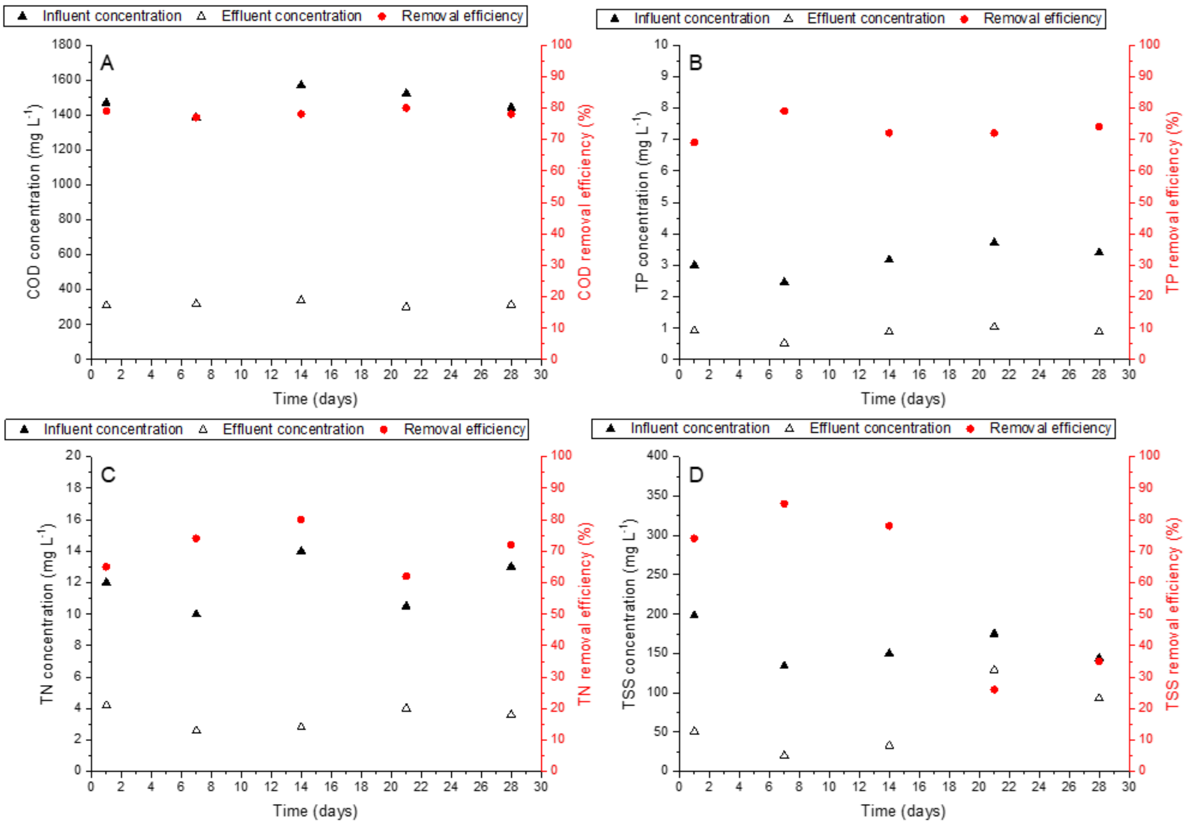


Figure 5.4 Influent, effluent concentrations and removal efficiencies observed in the lab-scale SBR operated with a mixture of raw effluent and chemically pre-treated effluent from the full-scale pulp mill WWTP: (A) COD, (B) TP, (C) TN and (D) TSS

Concerning the TP removal, as observed in Figure 5.4B, the influent average concentration was about 3.2 ± 0.5 mg TP/L, while the average effluent TP concentration was 0.8 ± 0.2 mg TP/L, reaching a removal efficiency of 73 ± 3.7 %, which is similar to that one recorded in the full-scale WWTP.

In this experimental phase, as shown in Figure 5.4C, a satisfactory TN removal efficiency of 71 ± 7.2 % was observed with is close to that weekly recorded in the full-scale WWTP. This results as a consequence of the average influent and effluent TN concentrations measured in the lab-scale SBR of around 12 ± 1.7 mg/L and 3.4 ± 0.7 mg/L, respectively.

In this experimental phase, the average influent and effluent TSS concentrations were about 160 ± 26 mg TSS/L and 65 ± 45 mg/L, respectively (Figure 5.4D), resulting in an average removal efficiency of 60 ± 27 %. These TSS concentration values would comply with the discharge standards set by the Legislation Law No.14.859 from Uruguay (Decree 253, 1979) for direct effluent discharges into surface water courses that establishes a maximum allowable TSS concentration of 150 mg/L.

With regard to the biomass concentration in the SBR, the average TSS concentration was about 6.9 ± 1.4 g/L (Figure 5.5). Nevertheless, the TSS concentration tended to decrease throughout the days approaching a concentration of 5.5 g/L in the last days of this experimental phase, which is the average concentration reported in the full-scale pulp mill WWTP.

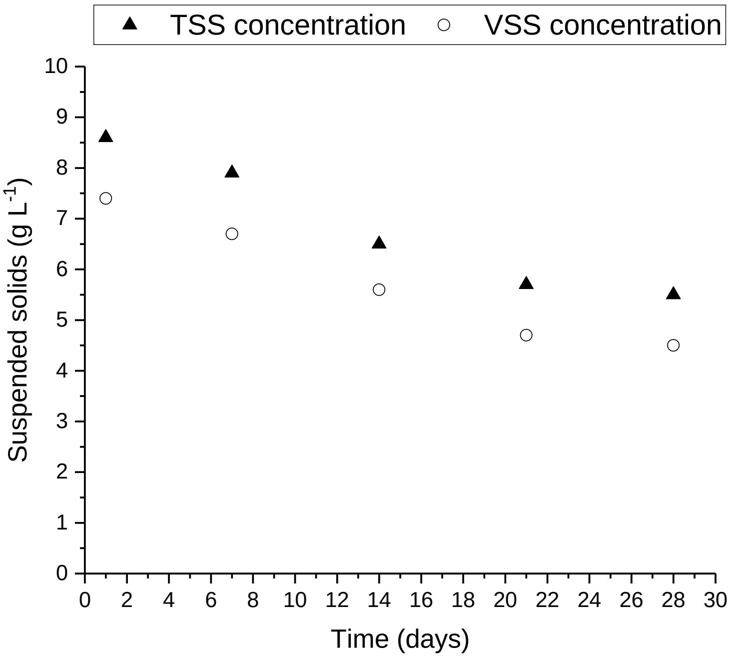


Figure 5.5 Biomass concentrations (as TSS and VSS) in the lab-scale SBR operated with a mixture of raw effluent and chemically pre-treated effluent from the full-scale pulp mill WWTP

Overall, in this experimental phase, a stable operation of the lab-scale SBR was achieved, obtaining removal efficiencies close to those observed in the full-scale pulp mill WWTP. This allowed to continue with the conduction of the chemical P-removal tests in experimental phase 2.

5.3.2 Experimental phase 2. Chemical P-removal

Co-precipitation jar-tests

The most common coagulants used for chemical P-removal via co-precipitation are Fe and Al-based inorganic salts (Mbamba et al., 2019). Different factors, such as the water characteristics (presence of lignin, adsorbable organic halide (AOX) or toxic compounds), the initial pH, the coagulant type and dosage (mol-mol Metal/P ratio), influence the P-removal efficiency (Metcalf & Eddy, 2003). Thus, in order to evaluate the potential chemical P-removal, different coagulants and doses were tested (Bratby, 2006). As previously described (in section 2.2), three different chemicals were assessed ($FeCl_3$, $Al_2(SO_4)_3$ and $Ca(OH)_2$). The results of the co-precipitation jar-tests conducted are shown in Table 5.2.

Table 5.2 TP and soluble TP concentrations and removal efficiencies observed in the co-precipitation jar-tests conducted with different types and doses of coagulants

	$FeCl_3 \cdot 6H_2O$			**$Al_2(SO_4)_3 \cdot 14.3H_2O$**			**$Ca(OH)_2$**		
Beaker	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Dosage (mg/L)	80	200	300	89	178	300	80	200	400
PO_4^{3-}/metal ion ratio	1:10	-	-	1:5	1:10	-	-	-	-
Initial TP (mg/L)	3.80	3.80	3.80	3.80	3.80	3.80	3.80	3.80	3.80
Final TP (mg/L)	2.40	2.60	1.30	1.90	2.00	0.80	5.00	2.20	1.40
TP removal (%)	37	32	**66**	50	47	**79**	0.0	42	**63**
Initial soluble TP (mg/L)	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60
Final soluble TP (mg/L)	0.80	0.80	0.30	1.00	0.90	0.30	1.60	0.90	0.30
Soluble TP removal (%)	49	53	**82**	35	43	**83**	0.0	44	**79**
Initial pH (after adding the coagulant)	6.5	6.3	6.5	6.6	6.5	6.9	6.9	7.8	10
Final pH (after settling)	6.7	6.5	6.9	6.7	6.8	7.1	7.1	7.9	10.2

According to the results shown in Table 5.2, all the three tested coagulants showed a similar trend: the removal efficiencies increased as the doses increased, reaching up to 83 % removal of soluble TP and 79 % TP removal at the highest dosage of aluminium sulphate (of 300 mg/L) followed by that of iron chloride (82 and 66 % for soluble TP and TP at 300 mg/l) and that of calcium hydroxide (79 and 63 % for soluble TP and TP with a dosage of 400 mg/L).

The Fe and Al doses were higher than the suggested stoichiometric ratios of 1 mole of Fe^{3+} or Al^{3+} assumed to be necessary to precipitate 1 mole of PO_4^{3-}. These results are in agreement with other studies that found that there is certain competition between hydroxyl ions and phosphate ions for the iron ions at the point of addition. In addition, the reaction of bicarbonate ions forming iron hydroxides and the need to destabilise colloids, probably account for the higher concentrations of ferric iron often required for phosphate precipitation (Jenkins et al., 1971; De Haas et al., 2000; Bai et al., 2010; (Hauduc et al., 2015) and (Mbamba et al., 2019).

In all the jar-tests, the initial pH was slightly acid (at around 6.5). After the coagulation-flocculation tests, when dosing $FeCl_3$ or $Al_2(SO_4)_3$, the pH remained stable. On the other hand, at the highest doses of $Ca(OH)_2$ the final pH increased up to 10. In spite of the higher $Ca(OH)_2$ dosage and higher pH, the final TP concentration in the supernatant was 1.4 mg/L, while the soluble P was 0.3 mg/L resulting in a lower TP removal efficiency (of only 63 %) compared to the addition of the Fe and Al coagulants. Nevertheless, the soluble TP removal efficiency (79 %) was like what was that observed with the other coagulants (of 82-83 %).

In accordance with these results and the literature, the simultaneous precipitation of phosphorus or co-precipitation is a suitable process to generate low P-concentration effluents. De Haas et al. (2000) reported certain advantages about this approach such as the ease of operation, flexibility to dynamic conditions, low capital costs, relatively small additional solids production (in the case of Al or Fe), improvements in sludge settleability and dewaterability, among others.

Post-precipitation jar-tests

As previously mentioned, this experimental phase was conducted using clarified effluent from the lab-scale SBR. This effluent, in addition to have been biologically treated in the SBR, underwent a primary treatment with $Ca(OH)_2$ for P removal in the full-scale system.

In order to perform this phase, first, a sample was taken to run the post-precipitation jar-tests with $FeCl_3$ and $Al_2(SO_4)_3$. This sample had a TP concentration of 0.74 mgP/L, of which 0.42 mg/L was composed of soluble P. Afterwards, another sample was collected to carry out the $Ca(OH)_2$ post-precipitation tests. This sample had a concentration of 0.66 mgP/L with 0.46 mg/L of soluble P. In both samples, the initial pH before adding the coagulant was 7.9. The results obtained in this experiment are shown in Tables 5.3 and 5.4.

Table 5.3 Total and soluble TP concentrations and removal efficiencies observed in the post-precipitation jar-tests conducted with different doses of $FeCl_3$ *and* $Al_2(SO_4)_3$

	$FeCl_3·6H_2O$						$Al_2(SO_4)_3·14.3H_2O$			
Beaker	**1**	**2**	**3**	**4**	**5**	**6**	**1**	**2**	**3**	**4**
Dosage (mg/L)	8	20	40	80	150	200	18	45	89	178
PO_4^{3-}/metal ion ratio	1:1	1:2.5	1:5	1:10	-	-	1:1	1:2.5	1:5	1:10
Initial TP (mg/L)	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74
Final TP (mg/L)	0.65	0.64	0.63	0.63	0.61	0.63	0.62	0.62	0.64	0.62
TP removal (%)	12	14	15	15	**18**	15	**16**	**16**	14	**16**
Initial soluble TP (mg/L)	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.42
Final soluble TP (mg/L)	0.39	0.33	0.32	0.28	0.45	0.32	0.32	0.42	0.42	0.16
Soluble TP removal (%)	7	21	24	**33**	0	24	24	0	0	**62**
Initial pH (after adding the coagulant)	8.0	7.9	7.8	7.8	6.7	6.6	7.8	7.6	7.4	6.7
Final pH (after settling)	7.9	7.7	7.5	7.2	6.8	6.7	7.8	7.7	7.5	6.8

According to the results and data presented in Table 5.3, both the $Al_2(SO_4)_3$ and $FeCl_3$ showed low TP removal efficiencies at dosing ratios between 1:1 and 1:10 PO_4^{3-}-to-Me, the highest removal obtained was 15 % in the case of $FeCl_3$ and 16% when dosing $Al_2(SO_4)_3$.

A higher removal was achieved with regard to soluble P, reaching a removal of 33 % with $FeCl_3$ at a 1:10 mol-to-mol ratio. This led to a concentration of 0.3 mgP/L in the final effluent, which would comply with the established TP discharge limit. Two additional tests were performed at higher doses (beakers 5 and 6 with 150 and 200 mg/L, respectively) to induce a sweep coagulation mechanism. However, the P removal efficiency did not improve compared to the previous tests.

Regarding the results when $Al_2(SO_4)_3$ was dosed, a significant increase in the removal of soluble P was observed at a 1:10 PO_4^{3-}-to-Me ratio, reaching 62 % removal with a final concentration lower than 0.2 mgP/L.

Table 5.4 Total and soluble TP concentrations and removal efficiencies observed in the post-precipitation jar-tests conducted with different doses of $Ca(OH)_2$

	$Ca(OH)_2$					
Beaker	**1**	**2**	**3**	**4**	**5**	**6**
Dosage (mg/L)	7	66	150	200	300	400
PO_4^{3-}/metal ion ratio	3:5	3:50	-	-	-	-
Initial TP (mg/L)	0.66	0.66	0.66	0.66	0.67	0.67
Final TP (mg/L)	0.67	0.61	0.56	0.49	0.44	0.47
TP removal (%)	0	8	15	26	**34**	30
Initial soluble TP (mg/L)	0.46	0.46	0.46	0.46	0.43	0.43
Final soluble TP (mg/L)	0.47	0.46	0.33	0.26	0.24	0.18
Soluble TP removal (%)	0	0	28	43	44	**58**
Initial pH (after adding the coagulant)	8.1	8.9	9.6	10.1	10.5	11.2
Final pH (after settling)	8.3	9.3	10.0	10.3	10.8	11.3

Analysing the results of total and soluble P removal with $Ca(OH)_2$ shown in Table 5.4, at a higher dose, the P-removal efficiency increases, obtaining the highest TP removal with a dose of 300 mg/L. In the case of soluble P, the highest removal was 58 % when dosing 400 mg/L of $Ca(OH)_2$. However, the best dosage seems to be 300 mg/L since the final TP and soluble TP concentrations were 0.4 and 0.2 mg/L, respectively.

These results are consistent with previous studies performed in the same full-scale WWTP (Bentancur et al., 2021) where it was found that, applying the CPR process within the sweep coagulation range as a potential post-treatment and with final effluent filtration, it is possible to reach soluble concentrations lower than 0.2 mgP/L.

5.3.3 Experimental phase 3. Co-precipitation in the lab-scale SBR

For the last experimental stage, a continuous P-removal by co-precipitation was assessed in the lab-scale SBR. Thus, the continuous addition of $FeCl_3$ was evaluated for 14 days. The influent, effluent and TP removal efficiency are shown in Table 5.5 and Figure 5.6.

Table 5.5 Total and soluble TP concentrations and removal efficiencies observed in the co-precipitation tests performed in the lab-scale SBR for 14 days at different $FeCl_3$ doses

Time (days)	**PO_4^{3-}: Fe ratio (mol-to-mol)**	**Dose ($mgFeCl_3 \cdot 6H_2O/L$)**	**Influent TP (mg/L)**	**Effluent TP (mg/L)**	**TP removal Efficiency (%)**
1	1:5	40	3.3	1.1	68
2	1:5	40	3.3	0.8	75
3	1:5	40	3.6	1.0	72
7	1:10	80	3.5	0.8	76
8	1:10	80	3.5	1.0	73
9	1:10	80	3.5	1.1	69
10	sweep coagulation	240	3.5	1.3	62
11	sweep coagulation	240	3.5	1.6	54
12	sweep coagulation	240	4.2	1.6	62
13	sweep coagulation	240	4.2	1.7	59
14	sweep coagulation	240	4.2	1.7	59

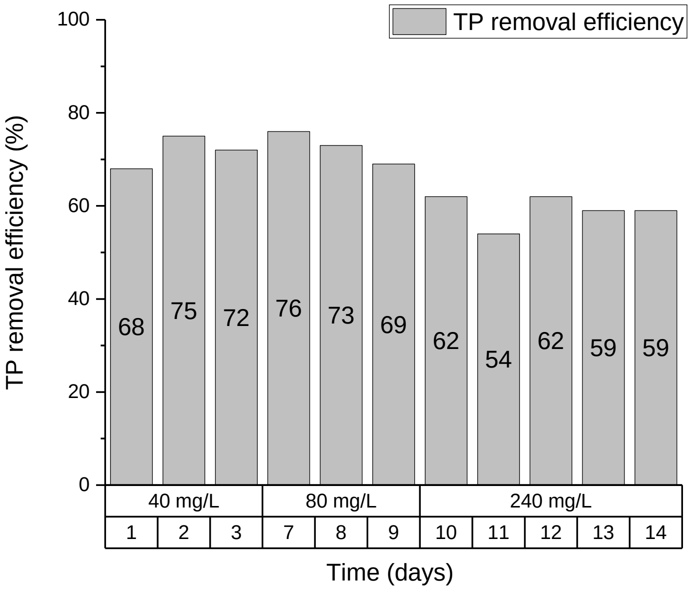


Figure 5.6 TP removal efficiency observed in the co-precipitation tests performed in the lab-scale SBR for 14 days at different $FeCl_3$ doses

In the first cycles, for the first 3 days with the addition of 40 mg$FeCl_3 \cdot 6H_2O$/L, the TP removal efficiency remained stable (Figure 5.6) at an average value of about 71 %. Thus, the dose was increased to 80 mg$FeCl_3 \cdot 6H_2O$/L; however, no improvements were observed. Consequently, the dose was increased to 240 mg$FeCl_3 \cdot 6H_2O$/L, which is slightly lower than the concentration of 300 mg/L that led to the best results in the co-precipitation jar tests (Table 5.2).

Regarding the TP removal efficiency, the results obtained in the co-precipitation tests in the SBR with a dose of 240 mg$FeCl_3 \cdot 6H_2O$/L were similar to those observed in the co-precipitation jar tests. When the coagulant dosage in the reactor increased, going from 80 to 240 mg$FeCl_3 \cdot 6H_2O$/L, the removal efficiency slowly decreased from an average of 71 % in the first days of evaluation to 59 % in the final stage. Interestingly, regardless the coagulant dosage, the actual net removed TP concentration was around 2.4 ± 0.2 mgP/L throughout all the tests (Table 5.5). This suggests that there is a P-fraction that can be efficiently removed but a concentration of residual P that cannot be subject to removal. Furthermore, since the influent TP and influent PO_4-P concentrations were similar, it appears that the residual P-fractions could be composed of PO_4-P incorporated into certain colloidal particles that did not allow them to be removed via the CPR process in the co-precipitation tests. Further research is needed to elucidate the factors that limited the co-precipitation CPR process.

When compared to other P-removal mechanisms, the TP removal efficiency in the lab-scale SBR without the addition of any coagulant was about 73 % (Figure 5.4B), with a net P-removal of about 3.0 mgP/L and, when $FeCl_3$ was dosed in the co-precipitation tests, a net P-removal of about 2.5 mgP/L was observed (average value for 14 days, resulting in a removal efficiency of about 66 %). As such, co-precipitation in the lab-scale SBR was not the most efficient CPR process in this study.

In addition, previous studies have reported certain limitations regarding the co-precipitation of P-removal in activated sludge systems (Clark et al., 2000; De Gregorio et al., 2010; and Caravelli et al., 2012). The results indicate that overdosing coagulants can affect the biological processes and the settling characteristics. According to Clark et al. (2000), the settleability of the sludge may occur due to an excessive presence of filamentous bacteria at excessive doses of $FeCl_3$. This phenomenon causes the loss of sludge, affecting the effluent quality. De Gregorio et al. (2010) assessed the feasibility to achieve P-removal by co-precipitation with $FeCl_3$ in a laboratory-scale activated sludge reactor fed with synthetic wastewater from the dairy industry. In that research, the application of different doses of ferric chloride (at Fe:P molar ratios of 1.5–2.3:1) to the aeration stage of an activated sludge reactor, led to a soluble P removal efficiency of between 96 and 98 %, and a TP removal higher than 90 %. However, the application of high $FeCl_3$ doses for an extended period caused a gradual accumulation of Fe-salts in the activated sludge. This led to the formation of dispersed flocs affecting the final effluent quality.

Overall, co-precipitation does not seem to have strong advantages compared to post-precipitation, which allows to reaching P-concentrations lower than 0.6 mgP/L, and if a filtration step is implemented, likely P-effluent concentrations as low as 0.2 mgP/L could be obtained. As such, post-precipitation appears to be the most promising CPR approach to consistently achieve low effluent P-concentrations. Further research is needed to assess the economic feasibility of this approach also taking into consideration the additional generation of sludge and the need to implement a filtration stage.

5.4 CONCLUSIONS

- The treatment of the pulp mill effluent by merely biological means was unable to contribute to a considerable P-removal due to the low P growth requirements of the biomass.
- The co-precipitation CPR approach showed to be highly effective independently of the coagulant used (at doses of 300 mg$FeCl_3 \cdot 6H_2O$/L, 300 mg$Al_2(SO_4)_3 \cdot 14.3H_2O$/L or 400 mg$Ca(OH)_2$/L) resulting in removal efficiencies of between 79 and 82 % and achieving final soluble P wastewater concentrations in the range of 0.28 to 0.34 mgP/L but it struggled to comply with the discharge standard permit limit (annual) of 60 kgTP/d.
- The post-precipitation led to the lowest soluble P concentrations observed (as low as 0.16 to 0.18 mgP/L) with the addition of $Al_2(SO_4)_3$ at a PO_4^{3-}/metal salt ratio (mol-to-mol) of 1:10 and when dosing 400 mg $Ca(OH)_2$/L.
- Based on the continuous evaluation of the co-precipitation CPR with $FeCl_3$ and despite that the total net P-removal was the highest (of around 2.4 mgP/L), the post-precipitation approach is preferable because it allowed to achieve the lowest observed TP and soluble P concentrations (lower than 0.5 and 0.2 mgP/L, respectively), being able to consistently comply with the maximum discharge standard of 60 kgTP/d.

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6

REFLECTIONS AND OUTLOOK

6.1 REFLECTIONS

The main objective of this thesis was to investigate and assess the performance of the most relevant physico-chemical and biological processes at the WWTP of the UPM pulp industry in Fray Bentos, Uruguay, and to evaluate different operational and configuration alternatives to enhance the overall plant performance with emphasis on the chemical phosphorus removal process.

The study began with a visit to the plant to get a sense of the size of the system to be studied. Historical data of the operation of the WWTP were then analysed to understand its operation and assess the evidence of the removal of different contaminants from the wastewater.

The first activity that was carried out was to develop a mathematical model that can describe the operation of the plant and that would allow analysis of different operating strategies and configuration alternatives. After having the plant model calibrated and validated, we proceeded to study several scenarios to analyse opportunities for improvement regarding the removal of phosphorus from wastewater, as well as regarding the recovery of resources, such as biogas and struvite as a fertilizer rich in nitrogen and phosphorus.

Then, laboratory-scale research was carried out to evaluate different precipitating agents as an alternative to the current phosphorus removal that the UPM WWTP had in the period this study was carried out. The removal of P was studied through jar tests, where the effect of temperature, pH, different types and doses of chemicals, mixing intensity on the coagulation-flocculation process, among other parameters, was evaluated.

The chemical composition of the wastewater was assessed both initially and after undergoing physicochemical treatment, along with an analysis of particle size distribution. Additionally, the chemical composition of the sludge was examined for each type of precipitating agent employed, and the crystallographic structure of the precipitated sludge was investigated in each test.

Finally, the chemical phosphorus removal (CPR) as a post-treatment was evaluated on a laboratory scale with three different precipitating agents: calcium hydroxide ($Ca(OH)_2$), aluminium sulphate ($Al_2(SO_4)_3$) and ferric chloride ($FeCl_3$), and the co-precipitation of P with $FeCl_3$ was evaluated simultaneously in the biological reactor with the WWTP current activated sludge system.

The reflections made here are about the entire research process carried out to understand the characterization of the wastewater from this cellulose pulp industry in Uruguay, the complex composition of the wastewater, its influence on the different types of treatment at the WWTP and the way in which the WWTP under study removes contaminants.

The reflection is based on the research objectives addressed throughout the study.

6.1.1 Objective 1: To apply steady-state mathematical modelling to describe the performance of the current wastewater treatment plant of UPM

The UPM pulp mill uses the chemical Kraft process to produce 1.3 million tons of fully bleached eucalyptus market pulp per year. The effluents generated in the pulp mill (mostly from the bleaching process) are treated in a WWTP composed of a mechanical pre-treatment followed by the conventional activated sludge (CAS) system with an installed capacity to treat approximately 73,000 m^3/day. Originally, the CAS system was designed only to remove suspended solids and organic matter. The WWTP was designed without nutrient removal capacities, since pulp and paper wastewater are usually deficient in nutrients. Nonetheless, nutrients such as N and P need to be dosed for sustaining the wastewater treatment biological processes (Mobius, 1991; Kenny, 2004; Kang et al., 2011; Vashi et al., 2019). However, the hard wood (eucalyptus) which is processed in UPM WWTP has a higher phosphorus content compared to other types of woods, and part of the phosphorus ended up in the raw wastewater which requires treatment.

Municipal CAS systems modelling has become a useful tool and well-established practice supported by several robust models developed over the years (Brdjanovic et al., 2015). Despite the broad application of mathematical models, there is still a limited number of studies regarding mathematical modelling of pulp and paper mill WWTPs; particularly, with respect to models that can describe the performance of pulp mill WWTPs with different P-assimilation and P-removal as observed in conventional WWTPs. The situation is that either the results of the modelling studies are confidential (being only available for the internal use of industries), or in general, seemingly limited research have been carried out in this type of industries.

In this research the performance of a UPM WWTP was assessed using the software (simulator) BioWin aiming at providing alternatives for further reduction of even phosphorus concentration in the effluent. BioWin developed its own integrated activated sludge/anaerobic digestion (AS/AD) model which is applied in the software (EnviroSim Associates Ltd., n.d.). This model is a combination of the models ASM1, ASM2d, and ASM3 published by the International Water Association (IWA) incorporating the anaerobic digestion model (ADM) as well (Elawwad et al., 2019).

A sampling program and measuring campaign was carried out at the UPM WWTP to characterize the wastewater according to the Dutch STOWA protocol (Hulsbeek et al., 2002). The UPM pulp mill wastewater had higher organic matter concentrations (including the biodegradable organic fraction) than a typical raw municipal wastewater. For instance, the COD/BOD ratio of the UPM wastewater in Uruguay was lower than 2, indicating a considerable presence of biodegradable components in the influent (Rodrigues et al., 2008; Zaher & Hammam, 2014). The pulp mill wastewater at the plant in Uruguay had similar characteristics (in terms of total COD, TN, TSS and NH_4^+) to those reported from other pulp and paper mill wastewaters (Lindblom et al., 2004;

Barañao, P. A., & Hall, 2004; Keskitalo & Leiviskä, 2010). However, the BOD_5 and TP concentrations were considerably higher. This could be attributed to the composition of the wood used as raw material which had a higher P content in comparison with other pulp and paper mill wastewater.

The COD fractions of the UPM wastewater differed considerably with respect to those from a municipal wastewater. The UPM wastewater had higher concentrations of readily biodegradable COD (S_S: 64 %) (Bentancur, 2014) than a typical municipal wastewater (S_S: 43 %) (ASM3 default). The slowly biodegradable substrates (X_S) together with the particulate inert organic material (X_I) account for 22 % of the pulp mill wastewater influent COD. For a typical municipal wastewater, the particulate fraction is much higher (approximately 44 % of the influent COD) (ASM3 default). In addition, the readily biodegradable COD (RBCOD) (S_S) of 0.64 is higher than the SS observed for other pulp mill WWTP from Canada (0.49) (Barañao & Hall, 2004), and Stora Enso Fine Paper Oulu pulp mill in Finland (0.31) (Keskitalo & Leiviskä, 2010), whereas the slowly biodegradable COD (X_S) and the particulate non-biodegradable (X_I) are lower (0.19 and 0.03, respectively).

The model calibration was obtained by adjusting selected wastewater fractions, and kinetic and stoichiometric parameters as follows: (i) kinetic parameters: aerobic decay rate and aerobic denitrification DO half saturation; and (ii) stoichiometric parameters: nitrogen and phosphorous in biomass, and endogenous residue. In addition to the wastewater characterization, an aerobic batch evaluation was carried out at the laboratory facilities of the UPM WWTP aiming at obtaining the necessary information to calibrate the model. Once of the model was calibrated, the performance of the WWTP was properly predicted. Wastewater data from different periods of time was used aiming at validating the model. The model proved capable of describing the current plant operation, as well as its (plant's) historical performance. The following key effluent parameters were used to validate the model: COD, TSS, TN and TP. Modelling the plant allows the prediction of different future scenarios. Different potential scenarios were evaluated to reduce the TP concentration in the effluent.

Although the BioWin software was primarily developed for modelling municipal wastewater treatment plants, the performance of the UPM pulp mill WWTP was correctly predicted by the model. Minor adjustments were needed, including the modification of some kinetic and stoichiometric parameters such as the ordinary hetherotrophic organisms (OHOs) and ammonia oxidizing biomass (AOB) aerobic decay rates, and the N and P fractions in the biomass as an endogenous residue. At the end of the study, the main objective was achieved; the assessment of the different scenarios to enhance the plant's performance was carried out successfully.

By doing this, the WWTP is provided with the best available technology; the WWTP exhibited a good performance, and the water quality of the effluent in most of the times met the local standards established by DINACEA (Decree 253/79). In addition, the nutrient concentrations observed in the effluent were lower than other reported effluent from similar plants in Europe. The modelling proved once again as a useful tool for describing the operation of a WWTP – despite the fact that the model is originally developed for domestic sewage treatment, with some modifications (which is a standard and expected practice in modelling), the model was able to describe sufficiently well the plant treating the pulp mill effluent.

6.1.2 Objective 2: Through the application of mathematical modelling, to evaluate and optimize the current operational parameters regarding the phosphorus removal

The previously developed model for UPM WWTP was used to evaluate different upgrading scenarios for the treatment plant aiming at increasing the plant performance regarding the P removal. According to the model, the implementation of an anaerobic phase to assess introduction of enhanced biological phosphorus removal (EBPR) prior to the aerobic stage showed to be a feasible scenario contributing to the decrease of TP concentration in the effluent by approximately 58 %. The EBPR process could be achieved by, for example, converting the current aerobic selector (V = 35,000 m^3) located in the beginning of the aeration basin, into an unaerated reactor. The modelling results show that the TP concentration in the effluent can be decreased from 0.62 to 0.26 mgP/L. For the EBPR process to develop, anaerobic conditions must be created, and a different group of heterotrophic microorganisms (known as PAOs) shall proliferate to enhance the biological P-uptake (Henze et al., 2008; (López-Vázquez et al., 2008). The proposed configuration may be a good option to further remove P biologically. The only intervention needed here is to convert the current selector to an anaerobic selector by simply switching off the aeration in that unit.

However, further research activities such as piloting-test or detailed studies may be needed to validate this configuration for industrial-scale application. The wastewater exhibited an average temperature of 30 °C, and these conditions (high temperature) may have a negative influence over the PAO’s activity (Whang & Park, 2002; Lopez-Vazquez et al., 2009; Ong et al., 2014; Izadi et al., 2020). In addition, the recommended sludge retention time (SRT) for implementing EBPR processes ranges between 10–25 days and the nominal hydraulic retention time (HRT) from 10 to 24 hours (Henze et al., 2008; Roots et al., 2020). Onnis-Hayden et al. (2020) and Srivastava et al. (2023) found that P removal is highly affected by the SRT, with lower and more stable effluent P level achieved at SRT < 10 days. In the currently evaluated pulp mill WWTP the SRT was set to 32 days and the HRT to 48 hours. Therefore, further research is needed to validate the implementation of an EBPR system. On a lab-scale, the efficiency of an EBPR system can be assessed by treating pulp mill wastewater in a bach-type experimental system. It can be evaluated how different factors, such as temperature, pH, and SRT, influence the removal of phosphorus. Besides, it can be helpful to investigate if there are contaminants in wastewater that cause inhibition or even toxicity and that may affect the proliferation of PAOs. The professionals responsible for the operation of the WWTP stated that on some previous occasions, they had turned off the aeration of the selector zone of the reactor, but they had not obtained a better TP removal efficiency. Since the start of the plant at the end of 2007 and until 2010, the plant operated with the initial zone of the reactor as anoxic, without the addition of oxygen. However, this modification in the reactor was primarily to achieve better removal of chlorides in the wastewater. After 2010, adjustments were made to the equalization basins and chloride removal occurred there. In that period, no variation was noted in P removal when changing the selector zone of the reactor from aerobic to anoxic. Then in 2018, when the plant occasionally had P concentrations in the effluent close to the established limit, they tried leaving the reactor selector zone without aeration, but this test was for a short period, less than a month, and no effect was seen regarding P removal compared to having the entire reactor aerated.

The industrial applicability of pulp mill anaerobic treatment should be indeed studied considering that lignin compounds from pulp mill wastewater could be inhibitors for PAOs (Leiviska et al., 2009; Pessala et al., 2010). The temperature of the wastewater of 30 ◦C can also positively (faster kinetics regarding the COD removal) and negatively (PAO-GAO competition in case of EBPR) influence the performance (Lopez-Vazquez, 2009).

Another scenario evaluated to obtain a greater removal of P, was to apply chemical precipitation as post-treatment. This additional treatment can further decrease the TP concentration below 0.1 mg/L. CPR with $FeCl_3$ was evaluated since it is a cost-effective coagulant (Barman et al., 2018; Karam et al., 2021). With the objective of determining the optimal $FeCl_3$ dosage for CPR, different jar tests were carried out at the pulp mill laboratory facilities. The coagulant addition could take place at the end or after the aerobic tank, following a sweep coagulation mechanism, at the regular pH observed at the plant (pH 7.2) without requiring pH adjustment. The coagulant concentration and dosage point were included in the BioWin model, leading to a similar outcome of 0.1 mg P/L in the effluent of the WWTP. Assuming an average effluent TP concentration of 0.62 mg P/L (this value was predicted by the calibrated and validated model without applying additional strategies for P-removal) and an effluent flowrate of 58,925 m^3/d, the estimated P load is 36.5 kgP/d. Furthermore, if CPR is applied and an effluent TP concentration of 0.1 mgP/L is achieved, the effluent P load will be reduced to 6.5 kgP/d, which is far lower than the discharge limit of 60 kgP/d imposed by the environmental authorities to the plant.

A cost analysis was performed to estimate the annual costs for chemicals. For this purpose, the total coagulant requirements were quantified considering the coagulant characteristics (a commercial 40 % ferric chloride solution); a commercial price of € 100 per ton was considered (Paul et al., 2001). The addition of 100 mg $FeCl_3$/L appears to be a satisfactory option to decrease and secure a low P concentration in the plant at an estimated annual cost of 1.2 million of euros (no sludge disposal costs were considered since the waste activated sludge - WAS is returned to evaporation process at the pulp mill at the time this study was conducted).

Further research activities such as pilot-testing may be needed to validate the previous recommendations of applying chemical P removal at such pulp mill effluent treatment. Likewise, it is necessary to evaluate other consequences regarding chemical addition for TP removal, such as: sludge's metal composition, additional chemical sludge volume, and economic aspects. The study confirmed usefulness of laboratory experimentation in the evaluation of WWTP performance and optimization. Unlike biological processes, scaling up of physio-chemical processes may be less challenging and more straightforward, thus is recommended for further study.

6.1.3 Objective 3: To explore different configuration alternatives to enhance the phosphorus removal efficiency of the plant (using mathematical modelling) and to evaluate resource recovery potential

After having the mathematical model that satisfactorily describes the operation of the WWTP of UPM, different scenarios were evaluated for the recovery of resources. Namely, the potential production of methane from secondary sludge, with its inherent energy savings, and the recovery of P as struvite were estimated.

In the CAS WWTP, the mixed primary and secondary AS (WAS) can be biologically stabilized under anaerobic conditions and converted into methane (CH_4) and carbon dioxide (CO_2) through the introduction of an AD unit (Andreoli et al., 2007). The current CAS system at the pulp mill WWTP has been designed as an extended aeration process to minimize the sludge production and therefore works at an SRT of about 32 days. To assess these scenarios, the AD was designed and operated at the mesophilic temperature of 35 ˚C, pH of 7.0 and with an HRT of 21 days.

Considering the current WWTP configuration with a SRT of 32 days, and according to the model, the study indicates that the implementation of EBPR with an unaerated zone in the existing reactor and an anaerobic digester to treat the excess sludge can lead to a methane production of approximately 1,736 m^3 CH_4/d and can be a promising alternative to increase the WWTP treatment performance. Furthermore, the model predictions suggest that by shortening the SRT from 32 to 5 days, the methane production could increase by up to 5,568 m^3 CH_4/d. If the methane produced is used to generate electrical energy to operate the WWTP, energy savings of about 88 % can be achieved.

Overall, this alternative looks rather promising and deserves to be thoroughly analysed due to the potentially remarkable benefits, as observed elsewhere (Mohammadi et al., 2019). Previous research published by Cabrera et al., (2010) studied the potential feasibility to anaerobically treat similar pulp mill primary and secondary sludges. The results showed that the biodegradability of the primary sludge was relatively low and, consequently, it is not recommended to be anaerobically digested due to its composition (mainly composed of lignin and inorganic residues). Similar results were observed by Eikelboom et al., (2018). Nevertheless, it must be underlined that the results of the modelling study rely on the potential decrease of the SRT from 32 to even 5 d. Shorter SRTs decrease the accumulation of unbiodegradable and inorganic compounds and increase the biodegradable content of the sludge (Ekama & Wentzel, 2008), which can increase the feasibility of applying an anaerobic digestion to treat the sludge waste, as indicated by the model outcomes. In addition to increasing the biodegradable content of the secondary sludge, different pre-treatment alternatives can be evaluated (such as thermal and ultrasound, among others) to improve the biogas production (Veluchamy & Kalamdhad, 2017; Vaneeckhaute et al., 2017). Lopes et al. (2018) showed that the anaerobic digestion process for Kraft pulp mill secondary sludge still is not feasible on a large scale, since the energy balance is negative, as the heat necessary to maintain the temperature in the reactor is higher than the energy produced.

Nevertheless, pre-treatment studies are needed to assess the potential increase in biodegradability of the secondary sludge prior to anaerobic digestion, to increase biogas production. Future research should focus on validating these results via the conduction of pilot- and detailed biomethane potential tests as well as to evaluate the adaptation of anaerobic microorganisms to the lignin compounds present in pulp mill wastewaters (to assess any potential inhibitory effect on the anaerobic digestion process). The feasibility of treating the primary sludge and a mixture of both primary and secondary sludge anaerobically should also be studied.

Another important topic is that the UPM industry generates energy from biomass, has self-consumption of the generated electrical energy and in turn dumps the surplus generated into the national electrical grid. Therefore, the proposal of installing an anaerobic sludge digester to treat the sludge and generate energy is not attractive from the perspective of the company.

Regarding the potential recovery of P as struvite, the precipitation of struvite from the nutrients (N and P) present in the supernatant of the AD and the addition of magnesium were assessed at different SRTs (between 32 and 5 days). 25 days was chosen as the optimal SRT. This alternative was selected because (i) sufficient precipitation of struvite is achieved, (ii) a medium-size AD volume is required and (iii) a considerable amount of methane is produced. In addition to these factors, the pulp mill generates steam and energy for self-consumption as part of the Kraft recovery process, so for the industry the best alternative is to generate higher volumes of struvite to recover nutrients. This scenario was conducted introducing a struvite reactor with a volume of 1,000 m^3, operated at an HRT of 30 hours and at a pH of about 8.3.

The addition of a struvite reactor could be an efficient option to recover approximately 1,611 mg/L of struvite (corresponding to a load of about 433 kg/d). Assuming a general scenario and considering that 1 kg of struvite would be sufficient to cover the P requirements of 2.6 ha of arable land at an application rate of 40 kg P as P_2O_5/ha/y (Shu et al., 2006; Rahman et al., 2014) the generated struvite (433 kg ISS/d) could be used as fertilizer to cover approximately 405,000 ha per year. This area represents only 2.3 % of the total area of Uruguay but corresponds to about 25 % of its total agricultural land (1,604,000 ha/y) (MGAP, 2015). This means that the P (and N) recovered at the plant as struvite can be used to cover up to 24 % of the demand of fertilizers in Uruguay. By optimizing the process performance, these findings highlight the potential recovery of resources in pulp mill WWTP, while complying with stringent effluent discharge standards.

According to Rahman et al. (2014), struvite is an effective alternative source of rock phosphate to maintain agricultural production systems. Struvite would be a useful alternative to traditional N fertilizers because it also reduces greenhouse-gas emissions and thus decreases the global warming effects due to its slow releasing pattern (decreasing the diffusion of nutrients into the land). The slower nutrient leaching loss and its fertilizer quality make struvite an eco-friendly fertilizer for crop production (Rahman et al., 2014; Sena & Hicks, 2018).

The efficiency of struvite as a fertilizer in crops and agricultural land in Uruguay must also be determined. Nowadays, developed countries are rapidly adapting their production chains moving from a linear to a circular economy, by giving added value to the generated waste, recycling and producing new resources that are (re-)incorporated into the economic production cycle. In coming years resource recovery practices and strategies will be implemented around the world at increased pace, emphasizing the importance of carrying out adequate and reliable feasibility studies to assess these potential alternatives. In addition, further research activities such as pilot-test or detailed laboratory studies may be needed to validate the previous recommendations for industrial-scale application.

6.1.4 Objective 4: to evaluate the chemical P removal process proposed by UPM and assess how other operational factors (like the dosage and type of chemical, pH, time and mixing intensity) affect the chemical P removal process

The chemical phosphorus removal process in UPM WWTP was studied to understand how the following key operational factors: chemical additives dosage and type, pH, temperature, and mixing intensity impact on the total phosphorus removal efficiency. Tests were carried out at laboratory scale. The effect of three precipitating agents such as: ferric chloride, aluminium sulphate, and calcium hydroxide were analysed at different temperatures (30, 45 and 60^{o}C), pH (from default, about 4.0 to 10.5) and mixing intensity (100, 200 and 300 rpm).

The higher phosphorus removal efficiency was obtained at 60 ^{o}C and pH 10.5 for all types of precipitating agents. Furthermore, it was found that only by raising the pH to 10.5, without using any precipitating agent, the soluble P is removed. In addition, it was found that at pH less than 10.5, the precipitation of P occurs, but the P is not able to settle. The presence of calcium (Ca) and magnesium (Mg) ions in the wastewater cause precipitation of P at high pH. The optimal chemical additives dosage was found to be 600 mg$Ca(OH)_2$/L, 200 mg$Al_2(SO_4)_3 \cdot 14.3H_2O$/L and 50 mg$FeCl_3 \cdot 6H_2O$/L. The highest TP removal efficiency was 95 % with $Ca(OH)_2$, 98 % with $Al_2(SO_4)_3$ and 93 % with $FeCl_3$. The high temperature of the wastewater from the cellulose pulp process, approximately 60 ^oC, showed favouring the P removal process compared to lower temperatures such as 30 and 45 ^oC. The variation of mixing intensity in the coagulation process and the addition of different doses of polymer in the flocculation stage did not have a significant effect on the removal of P.

The chemical P removal processes as pre-treatment of the pulp mill wastewater is a good alternative to get a high TP removal efficiency. The pH showed a great influence on P removal, with an optimal pH of 10.5 for the best TP removal. As the pH rises, the precipitation of P occurs with the metals Ca and Mg present in the pulp mill wastewater. The study shows that in the process with variable temperatures, treatment units positioning plays and important role and can influence performances in both directions.

6.1.5 Objective 5: Evaluation of chemical P removal such as a co-precipitation treatment and as tertiary treatment after activated sludge system

The objective of this research was to simulate on a laboratory scale, by means of a biological reactor, the full-scale conditions of the UPM WWTP and to evaluate different alternatives for chemical P removal such as a co-precipitation treatment and as tertiary treatment. The feasibility of the three metal salts, including $FeCl_3$, $Al_2(SO_4)_3$, and Ca $(OH)_2$ for the P removal from pulp mill wastewater was investigated in the present study.

This study improved the understanding of the fact that if the chemical P removal as primary treatment had not been implemented in the pulp mill WWTP, it would not be possible to comply with the discharge limit established by Uruguayan legislation for TP discharged into the river, a maximum monthly average of 60 kgP/day.

To obtain a TP concentration close to zero in the final wastewater discharged into the river (this to satisfy the above standard), it is necessary to implement a chemical P treatment.

The experimental results showed that the chemical coagulation method implemented as co-precipitation treatment effectively removed P from pulp mill wastewater. The optimal metal salts dosages for soluble P removal using $FeCl_3$, $Al_2(SO_4)_3$ and $Ca(OH)_2$ were: 300 mg$FeCl_3 \cdot 6H_2O$/L, 300 mg$Al_2(SO_4)_3 \cdot 14.3H_2O$/L and 400 mg$Ca(OH)_2$/L. The optimal removal efficiency of soluble P by co-precipitation using the $FeCl_3$, $Al_2(SO_4)_3$, and $Ca(OH)_2$ were 82 %, 83 % and 79 %, respectively, achieving final soluble P wastewater concentration about: 0.29, 0.28 and 0.34 mgP/L.

The experimental results showed that the chemical precipitation method implemented as tertiary treatment effectively removed P from pulp mill wastewater. The metal salts/P mole ratio is the key factor influencing TP removal efficiency. The optimal metal salts/P mole ratios for soluble P removal using $FeCl_3$ and $Al_2(SO_4)_3$ were 10:1 and 10:1. In the case of lime, the optimal dosage was 400 mg $Ca(OH)_2$/L. The optimal removal efficiency of soluble P by using the $FeCl_3$, $Al_2(SO_4)_3$, and $Ca(OH)_2$ were 33 %, 62 % and 58 %, respectively, achieving final soluble P wastewater concentration about: 0.28, 0.16 and 0.18 mgP/L.

Based on the continuous evaluation in the reactor of the co-precipitation of P with $FeCl_3$, a favourable result was not obtained with respect to the treatment without the addition of precipitating agent. The removal of TP decreases with increasing dose of the $FeCl_3$ as precipitating agent.

The best alternative to achieve a final effluent with a P concentration of less than 0.5 mg P/L is to apply chemical phosphorus precipitation as post-treatment.

6.2 OUTLOOK

This thesis introduces the model- and experimentation-based evaluation of a pulp mill WWTP in Uruguay. The study includes improved understanding of the production process of obtaining cellulose to appreciate the different points where liquid effluents are generated and familiarizing to a greater detail with the configuration of the wastewater treatment system.

A hydraulic model of the WWTP was made, through the BioWin software, with a control volume limited to the activated sludge biological system, to simulate the operation of the plant and thus evaluate configuration and operation alternatives that favors the removal of P from wastewater.

A characterization of the plant's wastewater was carried out, in accordance with the STOWA protocol, and for this a sampling campaign was carried out and experimental data was obtained that helped the calibration of the model, complementing the historical data provided by the plant personnel. After having the model calibrated, historical data was used to validate the model results. The model was able to correctly predict the operation of the plant, and this allowed different study scenarios to be evaluated. Some were focused on obtaining greater efficiency in P removal in the WWTP, for example: incorporating a EBPR in the activated sludge system and/or incorporating chemical P precipitation as a post-treatment. Others were to evaluate the possibility of recovering resources such as biogas (energy) and P through the generation of struvite.

Then, through an extensive experimental plan carried out in situ at the UPM plant, and in the Environmental Engineering Laboratory at the Catholic University of Uruguay, an evaluation was carried out to optimize the current operation system at UPM WWTP, which include the removal of P through a primary treatment. The use of other precipitating agents was evaluated as an alternative to the calcium hydroxide currently used, and different operating conditions such as temperature, pH, mixing intensity, among others, were evaluated.

On the other hand, on a laboratory scale, using a biological reactor, it was possible to simulate the operating conditions of the WWTP, operating the system for more than three months, and evaluate the chemical precipitation of P as a tertiary treatment and as co-precipitation in the same reactor.

After finishing the experimental stage of the doctoral process, which consisted of researching different aspects, such as developing a mathematical model, being able to evaluate different WWTP operation scenarios, analysing different alternatives to the current P removal treatment on a laboratory scale. It can be said that there are still several aspects to deepen and continue research studies in order to obtain increased confidence in that the results obtained through the evaluation with the model, will be reoccurring when tested on a scale of laboratory or pilot scale. And in cases of results obtained on a laboratory scale, further research is required to evaluate the industrial-scale scaling-up of the proposed alternatives.

6.2.1 Opportunities for improvement regarding the WWTP model

Throughout this research the performance of the UPM WWTP was assessed by applying standard wastewater treatment modelling tools. The hydraulic model of the plant was built and structured using the software/simulator BioWin. After the model was structured, it was calibrated following a step-wise approach adjusting both key wastewater fractions, as well as kinetic and stoichiometric model parameters. The model correctly predicted the operation of the plant and allowed the evaluation of different study scenarios. The model helped evaluate configuration alternatives to improve the efficiency of P removal from the plant's wastewater, and, thus, obtain an effluent with very low P concentrations.

The model boundary selected for the UPM WWTP model-based assessment was the biological activated sludge treatment, but this WWTP includes additional processes that increase complexity. It has a pre-treatment, followed by a primary treatment to remove solids and P, and cooling towers that lower the wastewater temperature from 60 to 30 ^{o}C, and finally, the activated sludge system. To assess the most relevant physico-chemical and biological processes in the WWTP it would be necessary to carry out a plant-wide modelling including other relevant chemical reactions that occur in wastewater treatment.

The other thing that occurs is that industries experience periods when something becomes challenging in the production system and such events may cause wastewater to change standard composition that can have a in turn a specific impact on the biological treatment system. In general, in comparison to municipal sewage, industrial effluents exhibit much higher variability and irregularity in both the quantity and quality, the UPM effluents not being the exemption in this respect.

According to the model outputs, including an anaerobic phase prior to the aerobic process may reduce the TP concentration in the effluent by approximately 58 %. In addition, CPR at the sweep coagulation range (between 2.7 and 270 mg/L) showed that the P concentrations can be further reduce to concentrations below 0.1 mg/L. However, further research activities such as pilot-testing or detailed studies may be needed to validate the EBPR or chemical P removal for industrial-scale applications. In addition, the industrial applicability of pulp mill anaerobic treatment should be indeed studied considering that lignin compounds from pulp mill wastewater could be inhibitors for a biological treatment. Likewise, it is necessary to evaluate other consequences such as: sludge production increase, metals composition in the sludge that can influence sludge recovery, economic aspects due to the use of chemicals, among others, regarding chemical addition for TP removal.

6.2.2 Laboratory scale evaluation to optimize P removal

The main objective of this research was to evaluate the CPR process in pulp mill WWTP in Uruguay. The research was to understand how the following key operational factors: chemical additives dosage and type, pH, temperature, and mixing intensity impact on the TP removal efficiency. Tests were carried out at laboratory-scale and the effect of three precipitating agents such as: ferric chloride, aluminium sulphate, and calcium hydroxide were analysed at different temperatures, pH, mixing intensity and polymers addition doses. An additional objective was to evaluate the influence of water quality effects on chemical P precipitation and the effects of particle stabilization on sedimentation performance.

The main objective was completely achieved in this study. A comprehensive evaluation could be carried out to identify how to optimize the CPR at the UPM WWTP. The main finding was that only by raising the pH of the wastewater to 10.5 (without the addition of precipitating agent) was it possible to remove soluble P. In the current case of the WWTP, they carry out P removal as a primary treatment and using $Ca(OH)_2$, which by default already raises the pH of the wastewater to values close to 10 and this favours the removal of P. What happens with the current solution is that $Ca(OH)_2$ generates scale in the pipes, tanks, sinks, clarifier, among other elements of the plant. To solve this, raising the pH was tried using sodium hydroxide, and other precipitating agents such as $FeCl_3$ and $Al_2(SO_4)_3$ were tested, and TP removal results of 98 % with $Al_2(SO_4)_3$ and 93 % with $FeCl_3$ were obtained.

Currently, the UPM WWTP has resolved the removal of P by applying CPR as a pre-treatment. However, given the problem of scale that is generated in the different equipment and pipes of the system, it would be good in the future to be able to change the type of precipitating agent used for the removal of P. The wastewater pH can be rise to 10.5 using sodium hydroxide and then filter to obtain final PT concentrations close to zero. Another alternative is to raise the pH to 10.5 with sodium hydroxide and use a precipitating agent such as Al or Fe.

The second objective was to evaluate the influence of water quality effects on chemical P precipitation and the effects of particle stabilization on sedimentation performance. This objective was partially met, since, although the quality of the water and its effects on the CPR were evaluated, some treatment still needs to be identified to ensure that the P that precipitates when we raise the pH to 10.5 can settle and remove that P through the sludge.

With respect to this evaluation of CPR, different possibilities were evaluated, whether applied as pre-treatment, as co-precipitation and as post-treatment. Within these options, different operating alternatives were evaluated in each of them, so it is possible to say that the objectives set at the beginning were fully met.

Through this research it was possible to verify that the concentration of P in wood has been increasing rapidly over the years, doubling the concentration in 10 years. In the WAB line the TP concentration increases from 3.7 mg P/L in 2009 to 7.0 mg P/L in 2019. This indicates that the concentration of P in the wood could continue to increase over the years, and this generate an increase in the wastewater concentration of P.

Based on what has been studied, it seems interesting to carry out a detailed evaluation in the future on the possibility of implementing an EBPR system in the plant and thus achieve a good P removal. The advantages of biological over chemical P removal (high removal efficiency, economy, environmentally friendly operation, and potential phosphorus recovery (Lopez-Vazquez, 2009; Diaz et al., 2022) aroused the interest of scientists who continued studying and investigating about the EBPR metabolic mechanisms, optimization process configurations, among other research.

6.2.3 Final remarks

The results of this research showed the potential and the value of the use a mathematical model to evaluate the pulp mill WWTP operation and simulate different study scenarios. Based on the model results, it was possible to find a suitable options to enhance the P removal at the WWTP and some alternatives to resource recovery, such as biogas (as energy saving) and recovery of P as struvite.

Through the extensive study carried out in the cellulose pulp plant, it was possible to deepen the understanding of the complex chemical composition of the wastewater and its physical characteristics. After analysing the chemical removal of phosphorus as pre-treatment, co-precipitation, and post-treatment, it was found that it is possible to reach phosphorus concentration values close to zero in the final effluent. The best results were obtained with the chemical removal of P applied as pre-treatment, using precipitating agents such as $Ca(OH)_2$, $Al_2(SO_4)_3$ and $FeCl_3$ at pH around 10.5. From the evaluation it was also obtained that it is possible to apply chemical phosphorus removal as post-treatment, but this would imply a greater cost for the plant since in that case it is the entire flow that would be treated unlike pre-treatment, which is only the low solid content line that passes through the treatment, being two thirds of the total flow.

Further research activities such as pilot-testing or detailed studies may be needed to validate the CPR for industrial-scale application. Likewise, it is necessary to evaluate other consequences regarding chemical addition for TP removal, such as sludge composition, treatment and disposal and economic aspects.

All in all, the study significantly contributed to understanding of the plant operations and provided insightful added value to this particular pulp-processing industry to be more efficient and more environmentally friendly at minimal additional investments.

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LIST OF ACRONYMS

AC	Anaerobic contact
AD	Anaerobic digester
ADM	Anaerobic digestion model
ADT	Air dry ton
AF	Anaerobic filter
ANII	National Research and Innovation Agency in Uruguay
AOB	Ammonia oxidizing bacteria
AOX	Adsorbable organic halides
AS	Activated sludge
ASM1	Activated Sludge Model No 1
ASM2	Activated Sludge Model No 2
ASM2d	Activated Sludge Model No 2d
ASM3	Activated Sludge Model No 3
ATP	Adenosine triphosphate
BAT	Best available techniques
BOD	Biological oxygen demand
CAS	Conventional activated sludge
CH_4	Methane
CO_2	Carbon dioxide
COD	Chemical oxygen demand
CPR	Chemical phosphorus removal
DO	Dissolved oxygen
DPAO	Denitrifying polyphosphate-accumulating organisms
DSFF	Down-flow stationary fixed film
EBPR	Enhanced biological phosphorus removal
ECF	Elemental chlorine free
EEL	Environmental engineering laboratory
EGSB	Expanded granular sludge blanket
FB	Fluidized bed
GAO	Glycogen-accumulating organisms
GMEM	Materials, Energy and Environment Research group
HCl	Hydrochloric acid
HRT	Hydraulic retention time
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
ISS	Inorganic suspended solids
IWA	International Water Association
LATU	Technological Laboratory of Uruguay
MBR	Membrane bioreactor

MF	Microfiltration
N	Nitrogen
NaOH	Sodium hydroxide
NF	Nanofiltration
NH_4^+	Ammonia
NO_2^-	Nitrite
NO_3^-	Nitrate
OHO	Ordinary heterotrophic organisms
P	Phosphorus
PAO	Polyphosphate-accumulating organisms
PH2MV	Poly-β-hydroxy-2-methyl-valerate
PHA	Poly-β-hydroxyalkanoates
PHB	Poly-β-hydroxybutyrate
PHV	Poly-β-hydroxyvalerate
PO_4^{3-}	Orthophosphate
Poly-P	Polyphosphates
PSD	Particle size distribution
RAS	Recirculation of activated sludge
RBCOD	Readily biodegradable chemical oxygen demand
RO	Reverse osmosis
SBCOD	Slowly biodegradable chemical oxygen demand
SBR	Sequential batch reactor
SEM-EDS	Scanning electron microscopy energy dispersive spectroscopy
SRT	Sludge retention time
SS	Suspended solids
TDS	Total dissolved solids
TN	Total nitrogen
TP	Total phosphorus
TSS	Total suspended solids
UASB	Upflow anaerobic sludge blanket
UCU	Catholic University of Uruguay
UF	Ultrafiltration
VFA	Volatile fatty acids
VOC	Volatile organic compounds
VSS	Volatile suspended solids
WAB	Low solids effluent stream
WAL	High solids effluent stream
WAS	Waste activated sludge
WWTP	Wastewater treatment plant
XRD	X-Ray Diffraction

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ABOUT THE AUTHOR

Silvia María Bentancur Caballero completed her bachelor's degree in Industrial Engineering at the Catholic University of Uruguay (UCU) in Montevideo, Uruguay, in 2011. After graduation, she gained valuable practical experience in engineering in Uruguay. Later, in 2012, she received a full scholarship from the Uruguayan Research and Innovation Agency (ANII) to pursue a Master's in Municipal Water and Infrastructure with a specialization in Sanitary Engineering at UNESCO-IHE Institute for Water Education in Delft, The Netherlands. She completed her master's degree in 2014. Since then, she has been working as an Adjunct Professor at the Catholic University of Uruguay, where she teaches, manages, and conducts research duties.

In 2016, she received a full scholarship from ANII in collaboration with UPM pulp mill in Uruguay and UCU to follow her doctoral studies at IHE DELFT Institute for Water Education and Delft University of Technology (TU Delft). She was a PhD fellow in the Environmental Engineering and Water Technology Department at IHE DELFT, conducting her research in a sandwich modality between Uruguay and The Netherlands. Her research topic focused on the 'Plant-wide modelling of pulp mill wastewater treatment plants in Uruguay.

As part of the doctoral research activities in Uruguay, S. Bentancur designed and built an Environmental Engineering Laboratory (EEL) at UCU. The laboratory was established in 2018, allowing S. Bentancur to conduct the entire experimental part of her Ph.D. in Uruguay. She introduced a new research line in the Department of Engineering at UCU, specifically in wastewater treatment. It was she who promoted the field of environmental engineering within the University through her research and applied projects with the industry.

The EEL has facilitated the execution of numerous projects related to the treatment and modelling of wastewater treatment plants. This contribution to the University was significant, as the EEL enables the development of research and played a crucial role in the creation of a new undergraduate degree in Environmental Engineering at UCU, which initiated in 2021, with S. Bentancur doing as the Academic Director.

Journals publications

Bentancur, S., López-Vázquez, C. M., García, H. A., Duarte, M., Travers, D., & Brdjanovic, D. (2020). Resource recovery assessment at a pulp mill wastewater treatment plant in Uruguay. Journal of Environmental Management, 255. https://doi.org/10.1016/j.jenvman.2019.109718

Bentancur, S., López-Vázquez, C. M., García, H. A., Duarte, M., Travers, D., & Brdjanovic, D. (2021). Modelling of a pulp mill wastewater treatment plant for improving its performance on phosphorus removal. Process Safety and Environmental Protection, 146, 208–219. https://doi.org/10.1016/j.psep.2020.08.029

Bentancur, S., López Vázquez, C. M., García, H.A., Duarte Guigou, M., Echeverría, L., Costabel, L., & Brdjanovic, D. Initial screening and evaluation of main factors affecting chemical phosphorus removal at pulp mill wastewater. *In preparation.*

Bentancur. S., Dutra, I., Pereyra, P., López Vázquez, C. M., García, H.A., Echeverría, L., De Los Santos, E., & Brdjanovic, D. Evaluation of a chemical phosphorus removal process at a pulp mill WWTP in Uruguay. *In preparation.*

Conference proceedings

Bentancur. S., López Vázquez, C.M., García, H. A., & Brdjanovic, D. (2023) Evaluación de los principales factores que afectan la remoción química de fósforo en aguas residuales de industria de celulosa en Uruguay. V Congreso Nacional de Ciencia y Tecnología Ambiental, Argentina y Ambiente 2023.

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The Netherlands research school for the
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(SENSE) declares that

Silvia Maria Bentancur Caballero

born on the 17th of January 1985 in Montevideo, Uruguay

has successfully fulfilled all requirements of the
educational PhD programme of SENSE.

Delft, 24 June 2024

Chair of the SENSE board	The SENSE Director
Prof. dr. Martin Wassen	Prof. Philipp Pattberg

The SENSE Research School has been accredited by the Royal Netherlands Academy of Arts and Sciences (KNAW)

KONINKLIJKE NEDERLANDSE
AKADEMIE VAN WETENSCHAPPEN

The SENSE Research School declares that **Silvia Maria Bentancur Caballero** has successfully fulfilled all requirements of the educational PhD programme of SENSE with a work load of 38.8 EC, including the following activities:

SENSE PhD Courses

- Environmental research in context (2017)
- Research in context activity: Organized a Conference and a Workshop to inform and raise awareness among young students from schools and high schools on issues related to environmental protection in Uruguay (2019)

Selection of Other PhD and Advanced MSc Courses

- Advanced coaching and facilitation program, TU Delft (2017)
- Cross Cultural Communication Skills in Academia, TU Delft (2017)
- Leadership, Teamwork and Group Dynamics, TU Delft (2017)
- Foundations of teaching, learning and assessment, TU Delft (2017)
- 6th Summer School on Sustainable Chemistry for Sustainable Development, Leuphana University, Germany (2020)

Management and Didactic Skills Training

- Supervising five BSc students (2019 2021) and three MSc students (2020-2022) with thesis

Oral Presentations

- *Evaluación a escala de Laboratorio de la remoción de P en efluentes de planta de celulosa por tratamiento primario, secundario y co-precipitación*. Sistemas de tratamiento para remoción de fósforo y nitrógeno de efluente. Centro Tecnológico del Agua, 09 September 2020, Motevideo, Uruguay
- *Laboratory-scale evaluation of phosphorus removal in pulp mill effluents by primary, secondary and co-precipitation treatment*. 2nd Technical Conference on Effluents and Waste. Removal and recovery of phosphorus at an industrial level in Uruguay, 19 August 2022, Durazno, Uruguay
- *A plant-wide modelling of pulp mill wastewater treatment plant in Uruguay*. The 14th IHE PhD Symposium- Collaboration for Sustainability: Inter- and trans-disciplinary research to solve water-related issues. 07-08 October 2020, Delft, The Netherlands
- *Evaluación de los principales factores que afectan la remoción química de fósforo en aguas residuales de industria de celulosa en Uruguay*. V Congress of Environmental Science and Technology, Argentina and Environment, 03- 05 May 2023, San Luis, Argentina

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IHE DELFT
Institute for Water Education
under the auspices of UNESCO

TU Delft
Delft University of Technology

This research evaluates the performance of a state-of-the-art pulp mill, UPM, wastewater treatment plant (WWTP) focusing on phosphorus (P). The WWTP, designed for a daily influent flow of around 73,000 m^3, applies a conventional aerobic activated sludge system. Utilizing BioWin software, that involves an integrated activated sludge/anaerobic digestion model, the WWTP was effectively modeled describing both current and historical WWTP operation. The model allows for predicting diverse future scenarios. Various approaches were explored to reduce effluent TP concentration, including introducing an anaerobic phase and chemical phosphorus removal (CPR). Additionally, resource recovery potential was assessed, considering methane production from secondary sludge and P recovery as struvite. Lab-scale studies investigated CPR operational factors like chemical additives, pH, temperature, and polymer doses, highlighting optimal conditions for total phosphorus (TP) removal. The research also examined the biological removal of P in a lab-scale sequencing batch reactor (SBR) under fully aerobic conditions. Both co-precipitation and post-precipitation CPR approaches were considered for their efficacy in TP meeting discharge standards. Overall, the study aimed to enhance WWTP performance, exploring innovative strategies for P removal and resource recovery in the context of a pulp mill environment.

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