Evaluation of a chemical phosphorus removal process at a pulp mill WWTP in Uruguay

Bentancur, S.; Dutra, I.; Pereyra, P.; López Vázquez, C. M.; García, H. A.; Echeverría, L.; De Los Santos, E.; Brdjanovic, D.

DOI
10.1016/j.jenvman.2025.126391

Publication date
2025

Document Version
Final published version

Published in
Journal of Environmental Management

Citation (APA)
Bentancur, S., Dutra, I., Pereyra, P., López Vázquez, C. M., García, H. A., Echeverría, L., De Los Santos, E., & Brdjanovic, D. (2025). Evaluation of a chemical phosphorus removal process at a pulp mill WWTP in Uruguay. *Journal of Environmental Management*, *390*, Article 126391. https://doi.org/10.1016/j.jenvman.2025.126391

Journal of Environmental Management 390 (2025) 126391

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Evaluation of a chemical phosphorus removal process at a pulp mill WWTP in Uruguay

S. Bentancur [a,b,*], I. Dutra [b], P. Pereyra [b], C.M. López Vázquez [a], H.A. García [a], L. Echeverría [b], E. De Los Santos [b], D. Brdjanovic [a,c]

[a] Department of Environmental Engineering and Water Technology, IHE-DELFT Institute for Water Education, Westvest 7, 2611 AX, Delft, the Netherlands
[b] Department of Engineering, UCU Universidad Católica del Uruguay, Av. 8 de Octubre 2738, CP 11600, Montevideo, Uruguay
[c] Department of Biotechnology, Delft University of Technology, Van der Maasweg 9, 2629 HZ, Delft, the Netherlands

ARTICLE INFO

Keywords:
Chemical phosphorus removal
Co-precipitation
Post-precipitation
Industrial wastewater treatment
Pulp mill

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 (WWTP) 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 resulting in removal efficiencies of between 79 and 82 % and achieving final soluble P wastewater concentrations in the range of 0.28–0.34 mgP L^{-1}. However, it struggled to comply with the discharge standard permit limit (annual) of 60 kg TP d^{-1}. 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^{-1}) allowed to achieve the lowest observed TP and soluble P concentrations (lower than 0.5 and 0.2 mgP L^{-1}, respectively).

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, 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 d^{-1} (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^{-1} 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, AWWA

---

* Corresponding author. Department of Engineering, UCU Universidad Católica del Uruguay, Av. 8 de Octubre 2738, CP 11600, Montevideo, Uruguay.
E-mail address: sbentanc@ucu.edu.uy (S. Bentancur).

https://doi.org/10.1016/j.jenvman.2025.126391
Received 20 May 2025; Received in revised form 17 June 2025; Accepted 25 June 2025

and WEF, 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^{-1} (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 °C may jeopardize the performance of the EBPR process (López-Vázquez et al., 2008; Kazadi Mbamba et al., 2019; Inario, 2020; van Hoff Anciaux, 2021). 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 and Eddy, 2003; Smith et al., 2008; Li et al., 2018; Cardoso et al., 2025). 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 and Duff, 1996; Jiang and 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 and Eddy, 2003).

When metal salts are used as coagulants (Tzoupanos and 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 and 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^{-1} (Metcalf and Eddy, 2003). When dosing alum the pH range is similar, but alum dosages between 20 and 200 mg L^{-1} are often applied (Metcalf and Eddy, 2003). 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 and Sherwood, 1969). Then the pH increases over 10 and the excess of calcium ions react with phosphate producing $\mathrm{Ca_{10}(PO_4)_6(OH)_2}$ (Albertson and Sherwood, 1969). The amount of lime required to precipitate phosphorus depends largely on the alkalinity and not on the phosphorus concentration (Metcalf and 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 and 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 and 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 and Eddy, 2003).

In recent years, there has been a global shift toward circular economy approaches, with growing interest in recovering P from wastewater to generate added value. In a previous study conducted at the same pulp industry, the potential implementation of an anaerobic digester for the treatment of activated sludge was evaluated, with the aim of recovering struvite as a natural fertilizer (Bentancur et al., 2020). This approach aligns with current trends that seek to transform waste into resources. Additionally, Minh T. Vu (2023) highlighted that P recovery provides both financial and environmental benefits. Revenue from recovered products such as struvite and calcium phosphate for use as fertilizers can help offset the costs of recovery.

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). In addition, pre-polymerized coagulants and various flocculants were also tested in an effort to identify the most effective combination for the CPR process, but without favourable outcomes (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.

2. Materials and methods

2.1. WWTP description

The process flow diagram of the WWTP of study (Fig. 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 $m^3\ d^{-1}$.

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 $m^3\ d^{-1}$ of acid filtrate from the A/D1 stage that contains chlorine dioxide and a TP concentration of approximately 8–9 mgP L^{-1} and (b) 12,960 $m^3\ d^{-1}$ of an alkaline filtrate containing peroxide, sodium hydroxide (EOP) and a TP concentration of approximately 3–5 mgP L^{-1}. 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 °C to about 30 °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.

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.

2.2.1. 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

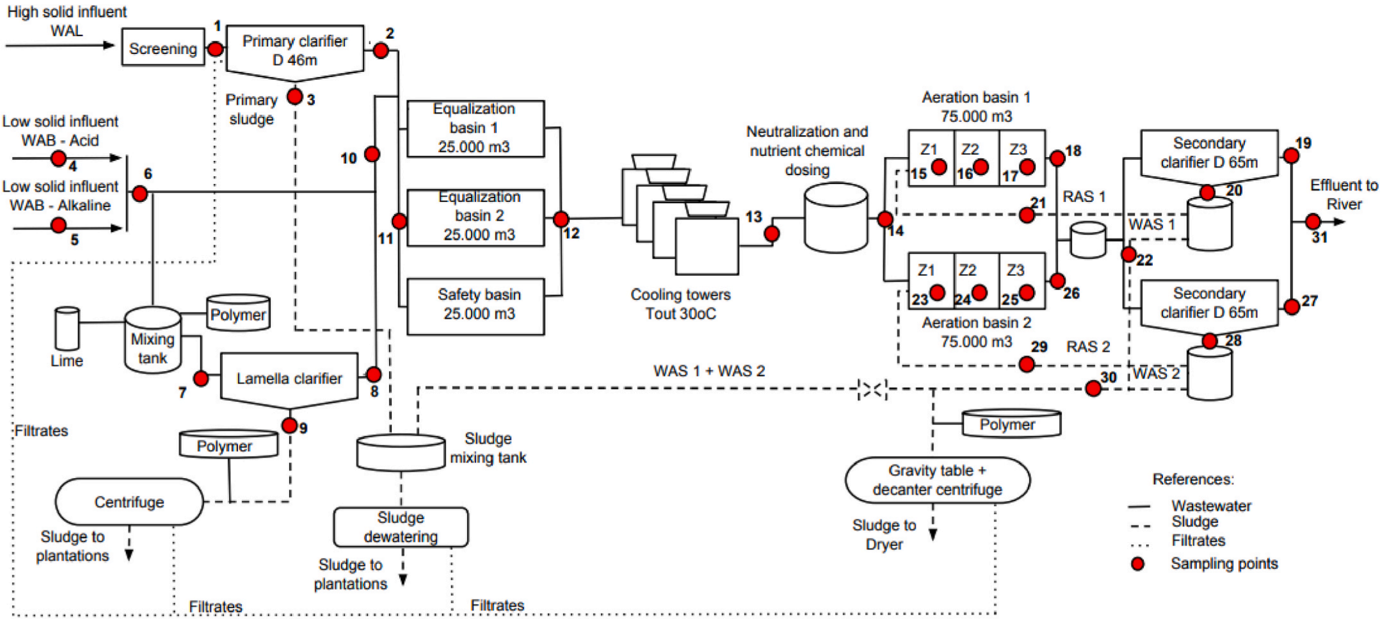

Fig. 1. Process flow diagram of the pulp mill WWTP.

practiced in the full-scale WWTP).

To carry out this experimental phase, a double-jacketed lab-scale sequencing batch reactor (SBR) with a maximum working volume of 3 L was used and operated in 8-h cycles. The reactor was inoculated with 1 L of activated sludge sourced from a full-scale pulp mill WWTP and previously aerated for 6 h. Each cycle consisted of four phases: influent filling (5 min), aerobic reaction (6 h and 50 min), settling (60 min), and effluent withdrawal (5 min). The system was equipped with an automated control program that precisely timed the operation of the influent and effluent pumps, ensuring consistent volumes were fed into and discharged from the reactor in each cycle. The temperature was maintained at 30.0 ± 0.1 °C using a thermal jacket, while the pH was automatically adjusted to 7.0 ± 0.1 via the controlled addition of acid (0.4 M HCl) and base (0.4 M NaOH).

Aeration was provided by compressed air injected at a flow rate of 60 $L\ h^{-1}$ through a compressor, maintaining a dissolved oxygen concentration of 2.0 mg $O_2\ L^{-1}$ during the aerobic phase. The reactor was equipped with sensors that provided real-time data on pH, temperature, and dissolved oxygen, allowing for continuous monitoring and automatic adjustment when necessary. A mixing speed of 150 rpm was applied during the aerobic phase to ensure proper contact between the wastewater and sludge. The system's full automation allowed for precise control of environmental conditions, improving the stability and reproducibility of the experimental operation.

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, Fig. 1) and 8 L from the low solids WAB stream (point 6, Fig. 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. 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.

2.2.2. *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 and post-precipitation tests, mixed liquor and settled effluent were collected at the end of the operational cycle on the SBR and used to conduct jar-tests.

The coagulants used in this phase were prepared in the laboratory. To calculate the molar ratio of coagulant to be used, the starting point is the concentration of soluble P, which is mostly in the form of PO_4^{3-}. The number of moles of PO_4^{3-} to be removed was calculated, and based on this, the required moles of $FeCl_3{\cdot}6H_2O$ were determined, from which the dosage mass was obtained. A 10 $g\ L^{-1}$ solution was prepared, and for example, if 80 mg are to be added to 1 L of wastewater, 8 mL of the prepared solution were used. For $Al_2(SO_4)_3{\bullet}14.3H_2O$ the same procedure was applied.

For $FeCl_3$, a 10 $g\ L^{-1}$ solution was prepared by dissolving 10 g of ferric chloride hexahydrate ($FeCl_3{\bullet}6H_2O$, 40 % concentration) in 1 L of distilled water. The same procedure was followed for aluminium sulphate ($Al_2(SO_4)_3{\bullet}14.3H_2O$, 40 % concentration), dissolving 10 g in 1 L of distilled water. In the case of calcium hydroxide ($Ca(OH)_2$), no solution was prepared, as it was added directly in solid form.

The jar tests for co-precipitation and post-precipitation test were conducted in four identical beakers with a capacity of 2 L, 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 shows the chemicals and doses used in the co-precipitation and tertiary treatment tests.

Each co-precipitation test was conducted using 300 mL of mixed liquor withdrawn from the SBR. 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 SBR, 1 L of final effluent from the reactor was used in each beaker of the jar-tests. The doses used are shown in Table 1.

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

2.2.3. *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-

Table 1
Different types of coagulants and their doses used in the jar-tests conducted in experimental phase No. 2.

		$FeCl_{3\cdot6}H_2O$						$Al_2(SO_4)_{3\ 14\cdot3}\ H_2O$				$Ca\ (OH)_2$					
Co-precipitation treatment	Dose (mg L^{-1})	80	200	300				89	178	300		80	200	400			
	Relation mol-mol	1:10	–	–				1:5	1:10	–		–	–	–			
Post-precipitation treatment	Dose (mg L^{-1})	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	–	–	–	–

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, $FeCl_3$ coagulant prepared during phase 2 was used, with a concentration of 10 g L^{-1} was selected to carry out the P-precipitation tests in the SRB itself. Ferric chloride was dosed 15 min before the end of the aerobic stage and a stirring speed of 150 rpm was maintained during this stage. Three different doses of $FeCl_{3.6}H_2O$ L^{-1} were assessed: 40, 80 and 240 mg L^{-1}.

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) (Fig. 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.

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.

2.4. 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, AWWA and WEF, 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).

In the case of experimental phase No 3, the SBR was evaluated over a continuous period of 14 days, with daily sampling and analysis of both influent and effluent. In all cases, only one analysis was performed per sample due to the high cost associated with each test.

3. Results and discussion

3.1. Experimental phase 1. operation of the lab-scale SBR

3.1.1. 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 Fig. 2A. As shown in Fig. 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^{-1}, 603 ± 198 mg L^{-1} and 73 ± 8.0 %, respectively.

The operation of the lab-scale SBR was not designed to perform the EBPR process. As observed in Fig. 2B, the average influent TP was 7.1 ± 1.5 mg L^{-1} while the average TP effluent concentration was 4.2 ± 0.8 mg L^{-1}, 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 (Fig. 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^{-1}), is allowed to discharge 60 kg TP d^{-1}. Thus, considering the flowrate discharged into the river, the effluent TP concentration needs to be lower than 1 mgTP L^{-1} 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^{-1}, 6.5 ± 3.0 mg TN L^{-1} and 63 ± 14 %, respectively (Fig. 2C). The TN effluent concentration was higher than the effluent concentration observed at the WWTP (which is about 2.0 mg L^{-1}). Nevertheless, this can be adjusted by decreasing the urea addition.

As observed in Fig. 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

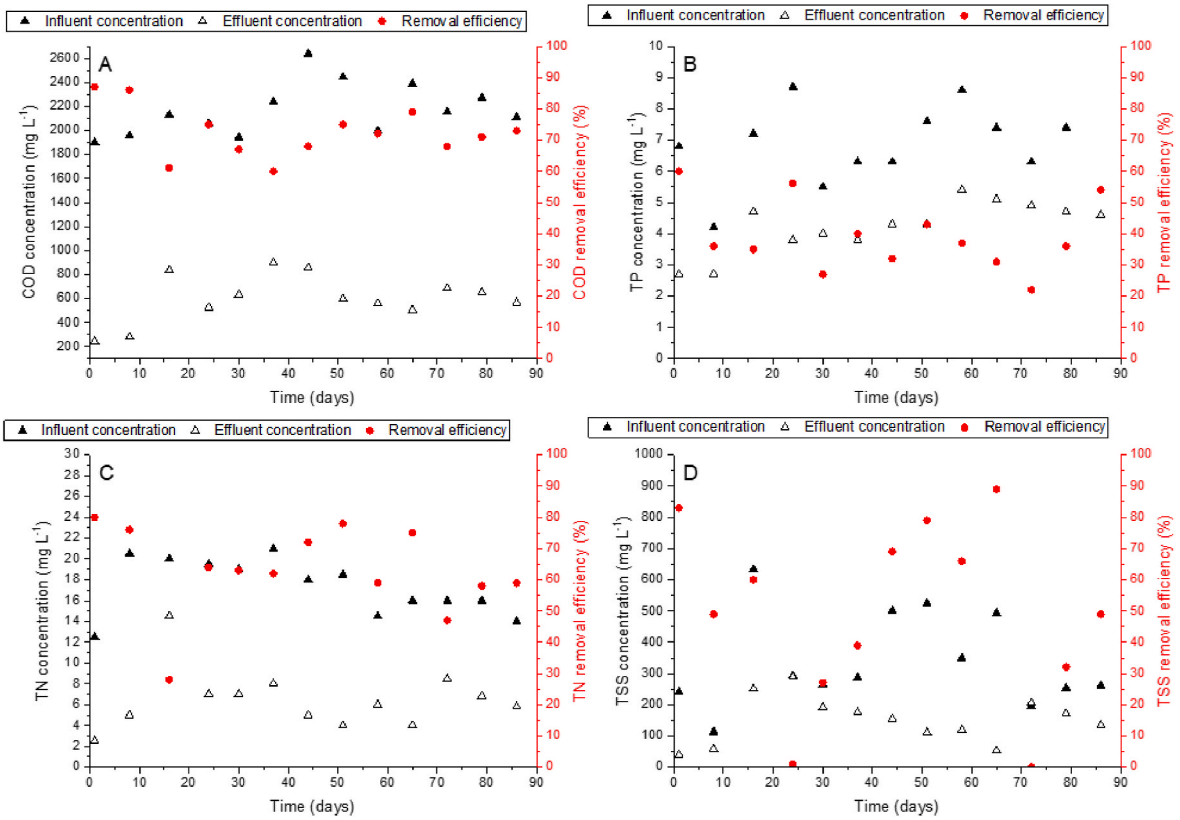

Fig. 2. Influent, effluent concentrations and removal efficiencies observed in the operation of the lab-scale SBR operated with raw effluent from the pulp mill: (A) COD, (B) TP, (C) TN and (D) TSS.

a homogenous flow in terms of quantity and quality). This induced certain TSS dynamics that may explain why the effluent TSS concentration also varied (Fig. 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^{-1}, 150 ± 75 mg L^{-1} and 62 ± 29 %, respectively.

Fig. 3 shows the TSS and VSS biomass concentrations in the SBR. The average TSS concentration was about 9.0 ± 1.1 g L^{-1}. This value was much higher, almost twice, than the concentration of biomass observed in the WWTP, which was approximately 5.5 g L^{-1}. 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^{-1}.

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 (Fig. 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.

3.1.2. *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.

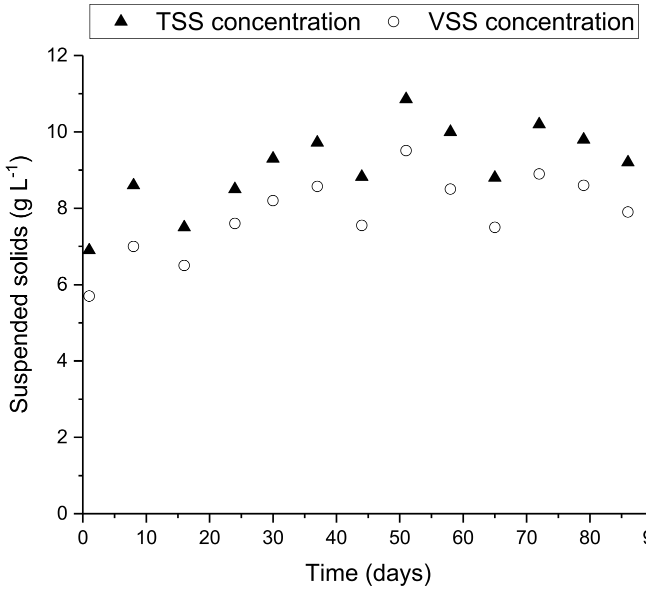

Fig. 3. Biomass concentrations (as TSS and VSS) in the lab-scale SBR operated with raw effluent from the pulp mill.

Regarding the organic matter removal, as shown in Fig. 4A, satisfactory COD removal efficiencies were observed with average influent, effluent and COD removal efficiency values of around 1478 ± 71 mg L^{-1}, 317 ± 14 mg L^{-1} and 79 ± 1.1 %, respectively. In particular, the

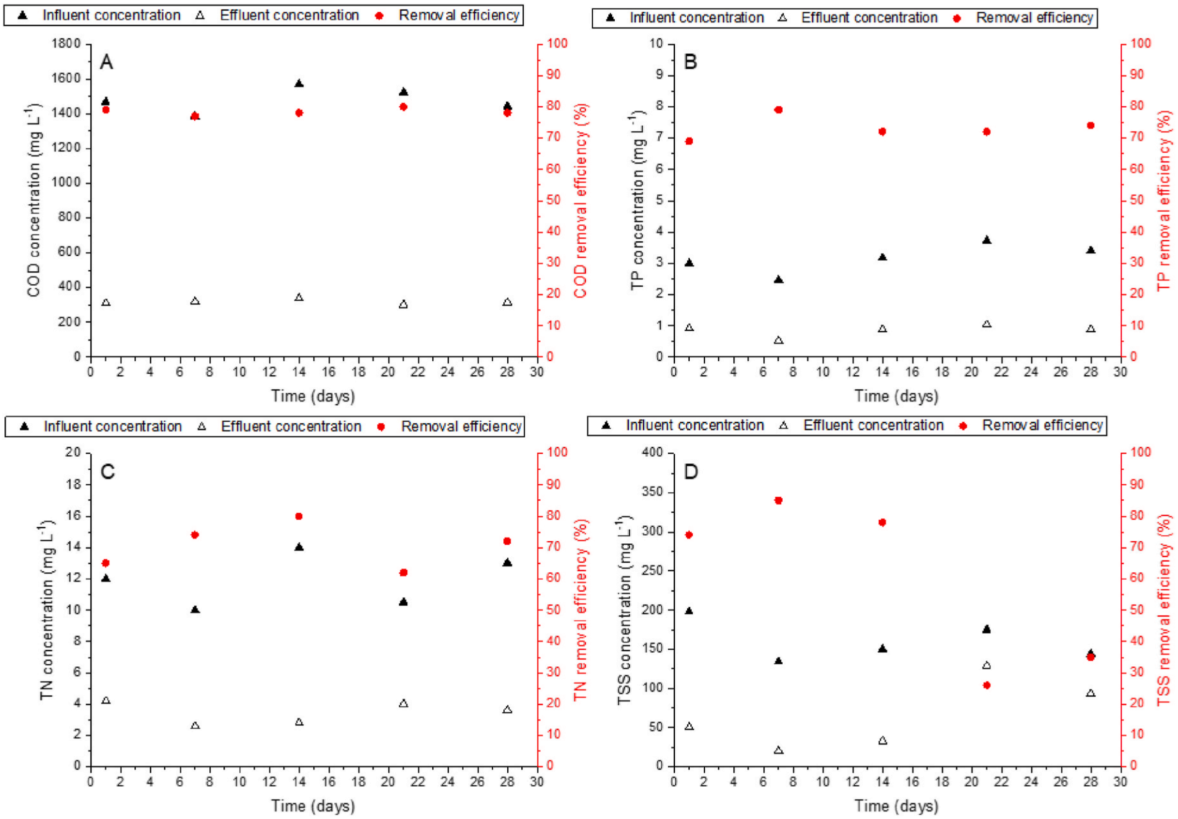

Fig. 4. Influent, effluent concentrations and removal efficiencies observed in the lab-scale SBR operated with a mixture of raw effluent and chemically pre-treated effluent from the full-scale pulp mill WWTP: (A) COD, (B) TP, (C) TN and (D) TSS.

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

Concerning the TP removal, as observed in Fig. 4B, the influent average concentration was about 3.2 ± 0.5 mg TP L^{-1}, while the average effluent TP concentration was 0.8 ± 0.2 mg TP L^{-1}, 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 Fig. 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^{-1} and 3.4 ± 0.7 mg L^{-1}, respectively.

In this experimental phase, the average influent and effluent TSS concentrations were about 160 ± 26 mg TSS L^{-1} and 65 ± 45 mg L^{-1}, respectively (Fig. 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^{-1}.

With regard to the biomass concentration in the SBR, the average TSS concentration was about 6.9 ± 1.4 g L^{-1} (Fig. 5). Nevertheless, the TSS concentration tended to decrease throughout the days approaching a concentration of 5.5 g L^{-1} in the last days of this experimental phase, which is the average concentration reported in 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.

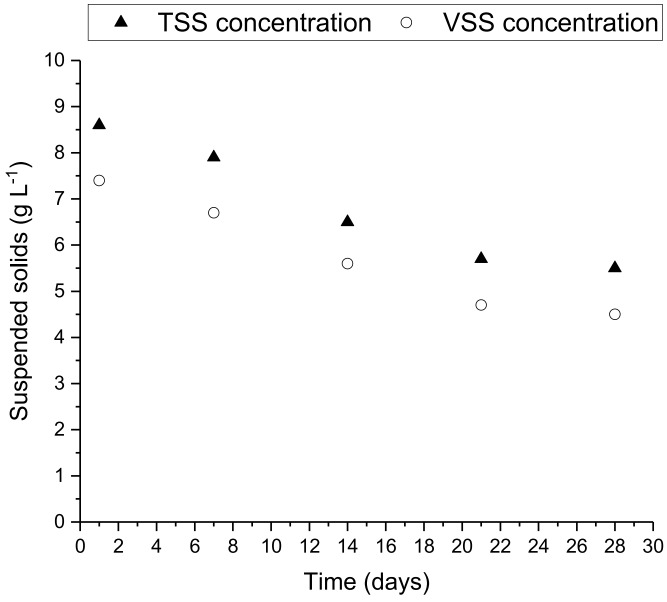

Fig. 5. Biomass concentrations (as TSS and VSS) in the lab-scale SBR operated with a mixture of raw effluent and chemically pre-treated effluent from the full-scale pulp mill WWTP.

3.2. *Experimental phase 2. chemical P-removal*

3.2.1. *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 and 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 2.

According to the results shown in Table 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^{-1}) followed by that of iron chloride (82 and 66 % for soluble TP and TP at 300 mg L^{-1}) and that of calcium hydroxide (79 and 63 % for soluble TP and TP with a dosage of 400 mg L^{-1}). Based on these removal efficiencies and considering a daily flow of 73,000 m^3, the application of the optimal co-precipitation dose of aluminium sulphate (300 ppm) would result in a TP discharge of approximately 58.4 kg TP d^{-1}, thereby complying with the discharge limits established by current environmental regulations.

The Fe and Al doses were higher than the suggested stoichiometric ratios of 1 mol of Fe^{3+} or Al^{3+} assumed to be necessary to precipitate 1 mol 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; 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^{-1}, while the soluble P was 0.3 mg L^{-1} 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 %).

The difference in P removal efficiency between aluminium sulphate and iron chloride in the co-precipitation step is primarily due to the chemical characteristics of the pulp industrial wastewater and the diverse precipitation mechanisms of the two coagulants. When $FeCl_3$ is used as a coagulant, the optimal pH range for sweep coagulation to occur is between 6 and 9. In the case of $Al_2(SO_4)_3$, sweep coagulation occurs within a similar pH range, from 6.5 to 10, but it is also accompanied by adsorption mechanisms, which can further increase P removal from the wastewater. Besides, aluminium tends to form more stable and less soluble aluminium-phosphate complexes, especially at a pH range around 6.0–7.5 than iron (Metcalf and Eddy, 2003).

There are other previous studies where a similar behaviour was observed, in which the use of aluminium sulphate showed better removal efficiency than ferric chloride (Luk, 1999; El-Bestawy et al., 2005).

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.

However, if the economic aspects of implementing the co-precipitation treatment process are analysed, the operating costs emerge as a key factor in the selection of the most suitable alternative. In a pulp mill WWTP treating 73,000 m^3 d^{-1}, three coagulants were assessed: $FeCl_3$, $Al_2(SO_4)_3$ and $Ca(OH)_2$) with optimal dosages determined through jar tests: 300 ppm for $FeCl_3$ and $Al_2(SO_4)_3$, and 400 ppm for $Ca(OH)_2$. Based on current market prices in Uruguay (USD 1.10/kg for $FeCl_3$ and $Al_2(SO_4)_3$, and USD 0.60/kg for $Ca(OH)_2$), the estimated daily coagulant cost is USD 24,243.3 for $FeCl_3$ and $Al_2(SO_4)_3$, and USD 16,162.2 for $Ca(OH)_2$. On an annual basis, this corresponds to approximately USD 8.85 million for $FeCl_3$ and $Al_2(SO_4)_3$, and USD 5.90 million for $Ca(OH)_2$. These results highlight the importance of including a cost-benefit analysis when selecting coagulants, as reagent costs can significantly impact the economic sustainability of the treatment process.

3.2.2. *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^{-1}, of which 0.42 mg L^{-1} 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^{-1} with 0.46 mg L^{-1} 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 3 and 4.

According to the results and data presented in Table 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^{-1} 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^{-1}, 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

Table 2
TP and soluble TP concentrations and removal efficiencies observed in the co-precipitation jar-tests conducted with different types and doses of coagulants.

Beaker	$FeCl_3•6H_2O$			$Al_2(SO_4)_3•14.3H_2O$			$Ca(OH)_2$		
	1	2	3	1	2	3	1	2	3
Dosage (mg L^{-1})	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^{-1})	3.80	3.80	3.80	3.80	3.80	3.80	3.80	3.80	3.80
Final TP (mg L^{-1})	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})	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60
Final soluble TP (mg L^{-1})	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

Table 3
Total and soluble TP concentrations and removal efficiencies observed in the post-precipitation jar-tests conducted with different doses of $FeCl_3$ and $Al_2(SO_4)_3$.

Beaker	$FeCl_3•6H_2O$						$Al_2(SO_4)_3•14.3H_2O$			
	1	2	3	4	5	6	1	2	3	4
Dosage (mg L^{-1})	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^{-1})	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.74
Final TP (mg L^{-1})	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^{-1})	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^{-1})	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

Table 4
Total and soluble TP concentrations and removal efficiencies observed in the post-precipitation jar-tests conducted with different doses of $Ca(OH)_2$.

Beaker	Ca $(OH)_2$					
	1	2	3	4	5	6
Dosage (mg L^{-1})	7	66	150	200	300	400
PO_4^{3-}/metal ion ratio	3:5	3:50	–	–	–	–
Initial TP (mg L^{-1})	0.66	0.66	0.66	0.66	0.67	0.67
Final TP (mg L^{-1})	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^{-1})	0.46	0.46	0.46	0.46	0.43	0.43
Final soluble TP (mg L^{-1})	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

Table 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 (mg $FeCl_3•6H_2O$ L^{-1})	Influent TP (mg L^{-1})	Effluent TP (mg L^{-1})	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

ratio, reaching 62 % removal with a final concentration lower than 0.2 mgP L^{-1}.

Analysing the results of total and soluble P removal with $Ca(OH)_2$ shown in Table 4, at a higher dose, the P-removal efficiency increases, obtaining the highest TP removal with a dose of 300 mg L^{-1}. In the case of soluble P, the highest removal was 58 % when dosing 400 mg L^{-1} of $Ca(OH)_2$. However, the best dosage seems to be 300 mg L^{-1} since the final TP and soluble TP concentrations were 0.4 and 0.2 mg L^{-1}, 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^{-1}.

Since in both processes the wastewater flow rate to be treated is the same, 73,000 m^3/d, the removal of P by chemical co-precipitation requires a higher amount of coagulant. To achieve low values of TP and soluble P, doses of 300 mg L^{-1} are needed for both $FeCl_3$ and $Al_2(SO_4)_3$. In the case of lime, a dose of 400 mg L^{-1} is required to achieve the best removal of TP and soluble P. This can be seen in Table 2.

In the case of post-precipitation, using a dose of 80 mg L^{-1} of $FeCl_3$ or 178 mg L^{-1} of $Al_2(SO_4)_3$ can achieve low concentrations of TP and soluble P in compliance with discharge standards established by regulations (Table 3). When using $Ca(OH)_2$, the consumption remains the same at 400 mg L^{-1} (Tables 2 and 4).

In terms of daily TP load discharged into the receiving water body, the use of these chemical agents resulted in a notable reduction. When applying $FeCl_3$, the final TP load was estimated at 45.9 kg TP d^{-1}, while $Al_2(SO_4)_3$ dosing yielded a slightly lower load of 45.3 kg TP d^{-1}. The best performance was achieved with $Ca(OH)_2$, resulting in a discharge of only 34.3 kg TP d^{-1}. These values not only comply with the established discharge limits but also contribute significantly to environmental protection by reducing the amount of TP released into the aquatic ecosystem, thereby supporting improved water quality and ecosystem health.

The cost analysis for the post-precipitation treatment was conducted following the same methodology as the previously presented co-precipitation analysis. This evaluation considered a daily wastewater flow of 73,000 m^3 in the pulp mill. The coagulants assessed were $FeCl_3$, $Al_2(SO_4)_3$, and $Ca(OH)_2$, with optimal dosages obtained from jar tests of 80 ppm, 178 ppm, and 400 ppm, respectively. Coagulant costs, including taxes, were USD 1.10/kg for $FeCl_3$ and $Al_2(SO_4)_3$, and USD 0.60/kg for $Ca(OH)_2$. Based on these values, the estimated daily operating costs were USD 6464.9 for $FeCl_3$, USD 14,384.4 for $Al_2(SO_4)_3$, and USD 16,162.2 for $Ca(OH)_2$. On an annual basis, this results in total coagulant costs of approximately USD 2.36 million for $FeCl_3$, USD 5.25 million for $Al_2(SO_4)_3$, and USD 5.90 million for $Ca(OH)_2$. These results provide a comparative economic perspective on coagulant selection for optimizing post-precipitation treatment strategies.

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 and Fig. 6.

In the first cycles, for the first 3 days with the addition of 40 mg$FeCl_3•6H_2O$ L^{-1}, the TP removal efficiency remained stable (Fig. 6) at an average value of about 71 %. Thus, the dose was increased to 80 mg$FeCl_3•6H_2O$ L^{-1}; however, no improvements were observed. Consequently, the dose was increased to 240 mg$FeCl_3•6H_2O$ L^{-1}, which is slightly lower than the concentration of 300 mg L^{-1} that led to the best results in the co-precipitation jar tests (Table 2).

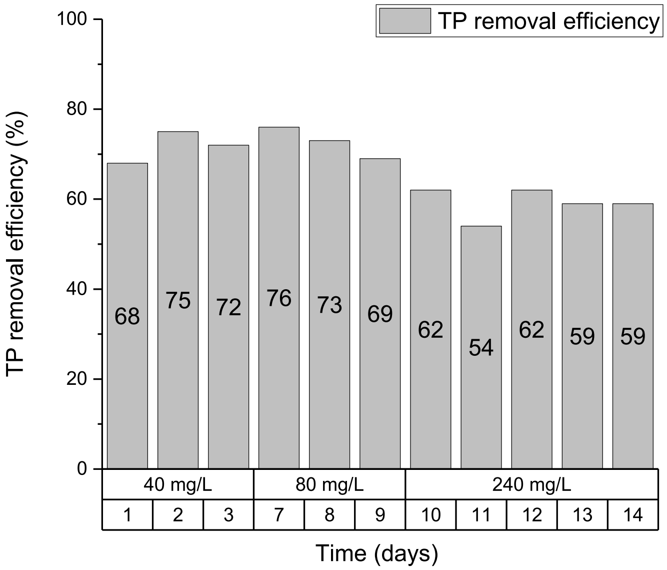

Fig. 6. TP removal efficiency observed in the co-precipitation tests performed in the lab-scale SBR for 14 days at different $FeCl_3$ doses.

Regarding the TP removal efficiency, the results obtained in the co-precipitation tests in the SBR with a dose of 240 mg$FeCl_3$•$6H_2O$ L^{-1} 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$FeCl_3$•$6H_2O$ L^{-1}, 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^{-1} throughout all the tests (Table 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 % (Fig. 4B), with a net P-removal of about 3.0 mgP L^{-1} and, when $FeCl_3$ was dosed in the co-precipitation tests, a net P-removal of about 2.5 mgP L^{-1} 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; 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^{-1}, and if a filtration step is implemented, likely P-effluent concentrations as low as 0.2 mgP L^{-1} 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.

4. Practical applications and future research perspectives

Since 2015, WWTP has operated a P removal system as a primary treatment step (pre-precipitation), specifically treating the WAB line, which exhibits a high TP concentration (approximately 11–14 mg L^{-1}). This stream represents a treated flow of around 43,200 m^3 d^{-1}, about two-thirds of the total influent flow to the WWTP. However, the system is flexible and can be adjusted to treat the full or partial flow depending on the required TP removal.

One operational challenge identified in the use of $Ca(OH)_2$ for P removal pre-treatment has been the formation of scale and incrustations in the plant's infrastructure, which significantly hindered process efficiency and reliability. As a result, the pulp mill has considered and evaluated alternative approaches for P removal. The evaluation revealed that CPR could also be applied at different stages of the treatment process, such as co-precipitation or post-treatment. Nevertheless, these alternatives would involve treating the entire influent flow, approximately 73,000 m^3 d^{-1}, leading to considerably higher operational costs.

Preliminary economic assessments reveal that both co-precipitation and post-precipitation strategies demand considerable amounts of chemical coagulants, leading to high annual operating costs that may challenge the economic feasibility of large-scale industrial implementation. However, among the alternatives evaluated, the post-precipitation treatment appears to be more economically viable, particularly when $FeCl_3$ is selected as the primary coagulant, due to its lower required dosage and associated reagent costs. Moreover, to achieve the target TP concentration and comply with the established discharge limits, it would be necessary to incorporate a tertiary microfiltration treatment step. Therefore, further studies, including pilot-scale testing and detailed technical-economic assessments, are essential to validate the feasibility and efficiency of CPR under real operating conditions. Additionally, the long-term implications of chemical addition on sludge generation, sludge composition, treatment and disposal processes, and overall plant economics must be thoroughly investigated. Previous studies have shown that the application of CPR processes results in the generation of sludge with a complex composition, which requires proper management and disposal (Mainardis et al., 2022; Cardoso et al., 2025).

An important future line of research includes studying the continuous dosing of ferric chloride directly into the aerobic reactor of the activated sludge system. While this method may enhance TP removal, it may also pose a risk of inhibiting key microbial communities, potentially affecting biological treatment performance.

Given these considerations, a promising future direction would be a comprehensive evaluation of the potential implementation of an EBPR system. In addition, it is suggested to explore integrated approaches such as synergistic biological and CPR, specifically the coupling of EBPR with post-precipitation, as a means to improve overall removal efficiency while potentially reducing the required dosage of chemical agents and minimizing operational costs and environmental impact. Such studies could provide the scientific and operational basis for a sustainable and efficient P management strategy in large-scale industrial wastewater treatment.

5. 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 $mgFeCl_3\bullet 6H_2O$ L^{-1}, 300 $mgAl_2(SO_4)_3\bullet 14.3H_2O$ L^{-1} or 400 $mgCa(OH)_2$ L^{-1}) resulting in removal efficiencies of between 79 and 82 % and achieving final soluble P wastewater concentrations in the range of 0.28–0.34 mgP L^{-1} but it struggled to comply with the discharge standard permit limit (annual) of 60 kgTP d^{-1}.
- The post-precipitation led to the lowest soluble P concentrations observed (as low as 0.16 to 0.18 mgP L^{-1}) 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^{-1}.
- 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^{-1}), 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^{-1}, respectively), being able to consistently comply with the maximum discharge standard of 60 kgTP/d.

CRediT authorship contribution statement

S. Bentancur: Writing – original draft, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **I. Dutra:** Methodology. **P. Pereyra:** Methodology. **C.M. López Vázquez:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Conceptualization. **H.A. García:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Conceptualization. **L. Echeverría:** Methodology, Data curation, Conceptualization. **E. De Los Santos:** Methodology, Data curation, Conceptualization. **D. Brdjanovic:** Writing – review & editing, Validation, Supervision, Conceptualization.

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.

Acknowledgments

The authors acknowledge: i) the financial support of the National Agency for Research and Innovation (ANII) from Uruguay and that of the Dutch government; ii) the Catholic University of Uruguay (UCU) due to their support to cover the costs of the analytical work conducted in the field, and iii) our thankfulness and high appreciation to the entire staff of the pulp mill company of this study.

Data availability

The data that has been used is confidential.

References

Albertson, O.E., Sherwood, R.J., 1969. Phosphate extraction process. Water Pollut. Control Fed.-J 41 (8 pt 1), 1467–1490.

APHA, AWWA, WEF, 2012. Stand. Methods Exam. Water Wastew. 1496.

Bai, S., Zhu, Y., Zhang, X., Zhang, H., Gong, Y., 2010. Enhanced phosphorus removal from municipal wastewater by coagulation with alum and iron salts. In: 2010 4th International Conference on Bioinformatics and Biomedical Engineering, ICBBE 2010, pp. 2–5. https://doi.org/10.1109/ICBBE.2010.5517496.

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. J. Environ. Manag. 255. https://doi.org/10.1016/j.jenvman.2019.109718. May 2019.

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 Saf. Environ. Prot. 146, 208–219. https://doi.org/10.1016/j.psep.2020.08.029.

Bratby, J., 2006. Coagulation and Flocculation in Water and Wastewater Treatment, second ed. IWA Publishing.

Burgess, J.E., Quarmby, J., Stephenson, T., 1999. Role of micronutrients in activated sludge-based biotreatment of industrial effluents. Biotechnol. Adv. 17 (1), 49–70. https://doi.org/10.1016/S0734-9750(98)00016-0.

Caravelli, A.H., De Gregorio, C., Zaritzky, N.E., 2012. Effect of operating conditions on the chemical phosphorus removal using ferric chloride by evaluating orthophosphate precipitation and sedimentation of formed precipitates in batch and continuous systems. Chem. Eng. J. 209, 469–477. https://doi.org/10.1016/j.cej.2012.08.039.

Cardoso, C.E.D., Almeida, J.C., Rocha, J., Pereira, E., 2025. Application of Box-Behnken design to optimize the phosphorus removal from industrial wastewaters using magnetic nanoparticles. Environ. Sci. Pollut. Control Ser. 32 (11), 6804–6816. https://doi.org/10.1007/s11356-025-36152-6.

Chan, Y.J., Chong, M.F., Law, C.L., 2010. Biological treatment of anaerobically digested palm oil mill effluent (POME) using a Lab-Scale Sequencing Batch Reactor (SBR). J. Environ. Manag. 91 (8), 1738–1746. https://doi.org/10.1016/j.jenvman.2010.03.021.

Clark, T., Burgess, J.E., Stephenson, T., Arnold-Smith, A.K., 2000. The influence of iron-based co-precipitants on activated sludge biomass. Process Saf. Environ. Prot. 78 (5), 405–410. https://doi.org/10.1205/095758200530916.

De Gregorio, C., Caravelli, A.H., Zaritzky, N.E., 2010. Performance and biological indicators of a laboratory-scale activated sludge reactor with phosphate simultaneous precipitation as affected by ferric chloride addition. Chem. Eng. J. 165 (2), 607–616. https://doi.org/10.1016/j.cej.2010.10.004.

De Haas, D.W., Wentzel, M.C., Ekama, G.A., 2000. The use of simultaneous chemical precipitation in modified activated sludge systems exhibiting biological excess phosphate removal Part 1: literature review. Water SA 26 (4), 439–452. https://doi.org/10.4314/wsa.v27i2.4989.

Ebeling, J.M., Sibrell, P.L., Ogden, S.R., Summerfelt, S.T., 2003. Evaluation of chemical coagulation-flocculation aids for the removal of suspended solids and phosphorus from intensive recirculating aquaculture effluent discharge. Aquac. Eng. 29 (1–2), 23–42. https://doi.org/10.1016/S0144-8609(03)00029-3.

El-Bestawy, E., Hussein, H., Baghdadi, H.H., El-Saka, M.F., 2005. Comparison between biological and chemical treatment of wastewater containing nitrogen and phosphorus. J. Ind. Microbiol. Biotechnol. 32 (5), 195–203. https://doi.org/10.1007/s10295-005-0229-y.

Hauduc, H., Takács, I., Smith, S., Szabo, A., Murthy, S., Daigger, G.T., Spérandio, M., 2015. A dynamic physicochemical model for chemical phosphorus removal. Water Res. 73, 157–170. https://doi.org/10.1016/j.watres.2014.12.053.

Hubbe, M.A., Metts, J.R., Hermosilla, D., Blanco, M.A., Yerushalmi, L., Haghighat, F., Lindholm-Lehto, P., Khodaparast, Z., Kamali, M., Elliott, A., 2016. Wastewater treatment and reclamation: a review of pulp and paper industry practices and opportunities. BioResources 11 (3), 7953–8091. https://doi.org/10.15376/biores.11.3.hubbe.

Inario, S., 2020. High Temperature Effects on the EBPR Process when Treating pulp-mill Wastewater. IHE Delft, Institute for Water Education.

Jenkins, D., Ferguson, J.F., Menar, A.B., 1971. Chemical processes for phosphate removal. Water Res. 5 (7), 369–389. https://doi.org/10.1016/0043-1354(71)90001-7.

Jiang, J.Q., Graham, N.J.D., 1998. Pre-polymerised inorganic coagulants and phosphorus removal by coagulation - a review. Water SA 24 (3), 237–244.

Li, R.H., Cui, J.L., Li, X.D., Li, X.Y., 2018. Phosphorus removal and recovery from wastewater using Fe-Dosing bioreactor and cofermentation: investigation by X-ray absorption near-edge structure spectroscopy [Research-article]. Environ. Sci. Technol. 52 (24), 14119–14128. https://doi.org/10.1021/acs.est.8b03355.

Lindholm-Lehto, P.C., Knuutinen, J.S., Ahkola, H.S.J., Herve, S.H., 2015. Refractory organic pollutants and toxicity in pulp and paper mill wastewaters. Environ. Sci. Pollut. Control Ser. 22 (9), 6473–6499. https://doi.org/10.1007/s11356-015-4163-x.

López-Vázquez, C.M., Oehmen, A., Hooijmans, C.M., Brdjanovic, D., Gijzen, H.J., Yuan, Z., Loosdrecht, M. C. . van, 2009. Modelling the PAO – GAO competition : effects of carbon source , pH and temperature. Water Res. 43 (2), 450–462. https://doi.org/10.1016/j.watres.2008.10.032.

López-Vázquez, C.M., Song, Y., Hooijmans, C.M., Brdjanovic, D., Moussa, M.S., Gijzen, H. J., Loosdrecht, M.C.M. Van, 2008. Temperature effects on the aerobic metabolism of glycogen-accumulating organisms. Biotechnol. Bioeng. 101 (2), 295–306. https://doi.org/10.1002/bit.21892.

Luk, G.K., 1999. Removal of phosphorus by metallic coagulation: an experimental aid to dose computations. Trans. Modell. Simulat. 21, 553–562. www.witpress.com.

Mainardis, M., Mulloni, S., Catenacci, A., Danielis, M., Furlani, E., Maschio, S., Goi, D., 2022. Sustainable alternatives for tertiary treatment of pulp and paper wastewater. Sustainability 14 (10), 1–18. https://doi.org/10.3390/su14106047 (Switzerland).

Mbamba, C.K., Lindblom, E., Flores-Alsina, X., Tait, S., Anderson, S., Saagi, R., Batstone, D.J., Gernaey, K.V., Jeppsson, U., 2019. Plant-wide model-based analysis of iron dosage strategies for chemical phosphorus removal in wastewater treatment systems. Water Res. 155, 12–25. https://doi.org/10.1016/j.watres.2019.01.048.

Metcalf, Eddy, 2003. Wastewater Engineering: Treatment and Reuse, fourth ed. Tata McGraw-Hill Publishing Company Limited, New Delhi, India. https://doi.org/10.1016/0309-1708(80)90067-6.

Smith, S., Takács, I., Murthy, S., Daigger, G.T., Szabo, A., 2008. Phosphate complexation model and its implications for chemical phosphorus removal. Water Environ. Res. 80 (5), 428–438. https://doi.org/10.2175/106143008X268443.

Stephenson, R.J., Duff, S.J.B., 1996. Coagulation and precipitation of a mechanical pulping effluent - I. Removal of carbon, colour and turbidity. Water Res. 30 (4), 781–792. https://doi.org/10.1016/0043-1354(95)00213-8.

Takács, I., Murthy, S., Fairlamb, P.M., 2005. Chemical phosphorus removal model based on equilibrium chemistry. Water Sci. Technol. 52 (10–11), 549–555. https://doi.org/10.2166/wst.2005.0735.

Toczyłowska-Mamińska, R., 2017. Limits and perspectives of pulp and paper industry wastewater treatment – a review. Renew. Sustain. Energy Rev. 78, 764–772. https://doi.org/10.1016/j.rser.2017.05.021. April.

Triany, R., 2020. Chemical Phosphorus Removal of a Pulp Mill Wastewater at High Temperature (>30°C). IHE DELFT Institute for Water Education, The Netherlands.

van Hoff Anciaux, C.B., 2021. Treatment of Pulp and Paper Mill Effluent with an EBPR Process. IHE DELFT Institute for Water Education.

Vashi, H., Iorhemen, O.T., Tay, J.H., 2018. Aerobic granulation: a recent development on the biological treatment of pulp and paper wastewater. Environ. Technol. Innovat. 9, 265–274. https://doi.org/10.1016/j.eti.2017.12.006.

Vashi, H., Iorhemen, O.T., Tay, J.H., 2019. Extensive studies on the treatment of pulp mill wastewater using aerobic granular sludge (AGS) technology. Chem. Eng. J. 359, 1175–1194. https://doi.org/10.1016/j.cej.2018.11.060. August 2018.

Von Sperling, M., 2015. Activated Sludge and Aerobic Biofilm Reactors. IWA Publishing. https://doi.org/10.2166/9781780402123. Water Intelligence Online (Vol. 6, Issue 0).

Zhen-hua, L.I., Kai, Y., 2011. Notice of retraction modelling chemical phosphorus removal from municipal wastewater using coagulation. In: 2011 International Conference on Multimedia Technology, ICMT 2011, pp. 1056–1059.