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Calcium removal from calcium rich paper mill wastewater by microbial $CaCO_3$ precipitation

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Abstract

High concentrations of calcium present in paper mill wastewaters are considered as they lead to some important problems during the treatment process. Recently, submerged membrane bioreactor (sMBR) system have been commonly used to industrial wastewater treatment and it is observed that membrane scaling or fouling is one of the most important problems which causes many operational difficulties. A decrease in membrane flux is observed after the formation of $CaCO_3$ film on the membrane surface as inorganic membrane fouling is encountered during the operation of the sMBR. Microbial carbonate precipitation (MCP) process is a natural microbial process and the mechanism of MCP is defined as the ability of microorganism to alkalinise an environment through various physiological activities. The purpose of this study was to investigate the application of MCP to paper-mill wastewater as a pre-treatment method prior to submerged membrane bioreactor. The potential for $CaCO_3$ removal from wastewater through urea was investigated at optimum operation conditions obtained from the batch tests using a sequencing batch reactor (SBR). The optimum dosage of urea and HRT were determined 4 g/L and 72 h. The results obtained indicated that the calcium removal efficiency was found to be 90.16% at optimum experimental conditions in the SBR operation. It was found out that the MCP was a suitable method for calcium removal and it can be used as a pre-treatment method of paper-mill wastewater treatment to avoid calcium scaling and inorganic fouling in sMBR in the study.

Keywords: *Calcium removal, microbial carbonate precipitation, paper-mill industrial wastewater, urea hydrolysis.*

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Yüksek kalsiyum içeren kağıt endüstrisi atıksuyundan mikrobiyal $CaCO_3$ çöktürmesi ile kalsiyum giderimi

Özet

Yüksek konsantrasyonda kalsiyum içeren kağıt endüstrisi atıksuları arıtma prosesleri esnasında bazı önemli problemlere sebep olduğu için dikkate alınmaktadır. Son zamanlarda batık membran biyoreaktör (bMBR) sistemi endüstriyel atıksuların arıtımında yaygın şekilde kullanılmaya başlanmıştır ve işletmede pek çok zorluklara sebep olan problemlerden biri olarak membran tıkanma problemleri gözlenmektedir. bMBR'de işletme esnasında membran yüzeyinde $CaCO_3$ film tabakası oluştuktan sonra inorganik membran tıkanması oluştuğu için membran akısında düşüş gözlenmektedir. Mikrobiyal karbonat çöktürme (MCP) prosesi doğal bir mikrobiyal prosestir ve mikroorganizmaların değişik fizyolojik aktiviteleri vasıtası ile çevrede alkalinite üretme yetenekleri olarak tanımlanır. Bu çalışmanın amacı MCP uygulamasının kağıt endüstrisi atıksuyu için batık membran biyoreaktör öncesinde ön arıtım metodu olarak kullanımının araştırılmasıdır. Üre vasıtasıyla atıksudan $CaCO_3$ giderim potansiyeli ön testler ile belirlenen optimum işletme şartlarında ardışık kesikli reaktör (SBR) sistemi kullanılarak araştırılmıştır. Ön çalışmalar ile optimum üre dozu ve hidrolik bekleme süresi (HRT) 4 g/L ve 72 sa olarak belirlenmiştir. SBR'de optimum deneysel koşullar altında elde edilen sonuçlar %90.16 kalsiyum giderim verimi elde edildiğini göstermiştir. Bu çalışmada MCP prosesinin kalsiyum giderimi için uygun bir metot olduğu ve bMBR'de kalsiyum tıkanması ve inorganik tıkanmayı önlemek için kağıt endüstrisi atıksuyunun arıtımında ön arıtım metodu olarak kullanılabileği bulunmuştur.

Anahtar kelimeler: *Kalsiyum giderimi, mikrobiyal karbonat çöktürmesi, kağıt endüstrisi atıksuyu, üre hidrolizi.*

1. Introduction

The pulp and paper industry is one of the most important industries in the world [1]. One of the major raw materials used in the pulp and paper industry is wood, and it consists of cellulose fibres, carbohydrates (starch and sugars), and lignin (as an adhesive substance for the cellulose fibres) [2]. The wood pulping and production of paper products produce substantial amounts of pollutants characterized by suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), toxicity and color [1]. On the other hand, produced wastewater can include more than 200-300 different organic compounds and approximately 700 organic and inorganic compounds, which may contain adsorbable organic halogens, phenolic compounds etc., depending on the applied pulping process, addictive chemicals and consumed water [3, 4]. As known, the pulp and paper wastewater characterization varies depending upon the type of process applied and the process technology. For this type of wastewaters, the COD concentration can be as high as 11000 mg/L [2]. On the other hand, recycled waste papers are increasingly being used during the last decades, instead of producing paper using virgin fiber resulting in protection of natural resources and reduction in both emissions and solid waste generation [5]. The amount of wastewater from the process producing paper via waste paper is quite small compared to the virgin pulp and paper production process [6]. The paper recycling process requires high amounts of calcium

and the wastewater contains high calcium concentrations reaching between 10 to 40 mM [7]. Calcium carbonate ($CaCO_3$) is used to improve paper surface properties, to obtain high whiteness, opacity, and to produce high quality paper. Using high amount of calcium causes clogging of pipelines, boilers and heat exchanger or aerobic and anaerobic treatment systems [7]. $CaCO_3$ also causes scaling or fouling in the membrane, when wastewater is treated with sMBR [8].

The pulp and paper wastewater treatment methods include physicochemical, biological and integrated treatment processes. Physicochemical processes are used to remove colloidal matter, SS, toxic compounds and color from pulp and paper wastewater, and include screening, sedimentation, flotation, ultrafiltration, coagulation and flocculation and ozonation [9]. Aerobic and anaerobic biological treatment processes can be used to remove organic contaminants in pulp and paper wastewater. Recently, the performance of MBR technology for different applications in the pulp and paper processes have been investigated, and the overall review indicated that this technology, in most cases, is feasible [1, 10]. However, it is known that membrane fouling because of calcium carbonate scaling and biofouling proved to be very serious and can cause severe flux reduction in MBR. Therefore, MBR systems treating pulp and paper mill wastewaters require proper and more complicated maintenance systems, when compared to a classical activated sludge system. Lerner et al. [8] who investigated full scale activated sludge plant (AS) and a pilot membrane bioreactor (MBR) having flat sheet membranes for the treatment of paper mill wastewater mentioned scaling problem. In a later study, Simstich et al. [11] investigated the treatment of paper mill de-inking wastewater using an sMBR under thermophilic aerobic conditions and have concluded that the COD removal rates were around only 83%. The authors have also observed calcium scaling.

Calcium ions in water and wastewater precipitates as carbonate minerals both in presence of microorganism and interactions of these microorganism with the precipitated minerals. MCP is one of the natural processes and occurs as a by-product of common microbial metabolic processes, such as photosynthesis, urea hydrolysis and sulphate reduction [7, 12, 13]. MPC via urea hydrolysis has been used in bioremediation previously [14]. Urea degradation is a simple process and it can be integrated in a biological wastewater treatment system. Furthermore, urea is not an expensive chemical. Urea provides hydrolysis which cause simultaneously a pH and dissolved inorganic carbon increase, both of which are essential to precipitation [12]. In the process, the microbial urease enzyme hydrolyzes urea to produce dissolved ammonium, dissolved inorganic carbon and CO_2. The ammonia is released and therefore the pH increases, then it leads to the accumulation of insoluble $CaCO_3$ in a calcium rich wastewater. In the process, 1 mole urea is hydrolysed to 2 moles of ammonia (Eqs. (1-3)).

$$H_2NCONH_2 + H_2O \rightarrow 2NH_3 + CO_2 \quad (1)$$

$$2NH_3 + CO_2 + H_2O \leftrightarrow 2NH_4^+ + CO_3^{2-} \quad (2)$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \quad (3)$$

These reactions occur under natural environment. The pH is above the 6.5 and the optimum pH is around 9. The optimum temperature ranges from 20 to 37 °C.

In the previous study carried out by the authors of this study, pulp and paper mill wastewater treatment with an sMBR system was investigated and urea was added to the system in order to balance the COD/TKN ratio of the feed wastewater. Calcium precipitation and accumulation was observed on the sMBR walls, air diffuser and hollow fibre membrane surfaces. When the reason of this problem was investigated, it was found out that the enzymatic hydrolysis of urea caused $CaCO_3$ precipitation in the reactor. The calcification in the sMBR was observed as a result of microbial calcium precipitation (MCP). Hammes et al. [7, 12] reported that it was possible to remove Ca^{2+} from industrial wastewaters such as paper recycling, bone processing and citric acid production, and landfill leachate by MCP to prevent calcification and scaling problems in pipelines and reactors. However, during this study, this natural reaction occurred in the sMBR and, therefore, caused scaling on the membrane and the air diffuser. As a result, membrane flux and dissolved oxygen concentration decreased in the reactor.

In this study, therefore, MCP was investigated to remove calcium from the pulp and paper wastewater to prevent the scaling and fouling problem in the sMBR studied.

2. Material-Method

2.1. Characterization of wastewater

The recycled paper mill wastewater was taken from the wastewater treatment plant of a paper mill factory located in Istanbul. The full scale treatment plant has a pre-sedimentation tank for solids separation, an anaerobic treatment followed by an activated sludge reactor. The characteristics of raw wastewater were summarized in Table 1. As can be seen in Table 1, the calcium concentration of the raw wastewater was very high, as was the case for the study carried out by Simstich et al. [11]. The ammonia and phosphate concentrations were very low, as was expected for paper mill wastewater. The C/N/P ratio for the studied paper mill wastewater was found to be about 100/0.7/0.069.

Table 1. Characteristics of raw paper mill wastewater.

Parameter	Unit	Raw wastewater
COD (Chemical oxygen demand)	mg/L	11415
BOD_5 (Biochemical oxygen demand)	mg/L	7155
TS (Total solids)	mg/L	11140
TSS (Total suspended solids)	mg/L	127
TKN (Total Kjeldahl nitrogen)	mg/L	79.7
NH_3-N (Ammonia nitrogen)	mg/L	12
TP (Total phosphorus)	mg/L	7.9
PO_4-P (Orthophosphate)	mg/L	1.3
pH	-	5.93
Alkalinity	mg $CaCO_3$/L	2380
Calcium	mg/L	2074

2.2. Experimental set-up

Determination of optimum urea concentration: Batch experiments were conducted with 100 mL raw paper mill wastewater in Erlenmeyer. The urea concentration of 0, 0.25,

0.5, 1, 2, 4, 8, 16 g/L were added in each erlenmayer, respectively. These were then incubated at 100 rpm, 20 °C for 4 days. At the end of 4 days, the floated and precipitated materials were withdrawn and the clarified effluent sample was pipetted out from the Erlenmeyer, and then allowed to settle for a few hours in a polyethylene flask. Finally, the clarified supernatant liquid was collected and preserved according to the standard methods and stored for characterization [15]. Calcium, pH, NH_3-N analysis were carried out to determine the optimum urea concentration.

Determination of hydraulic retention time (HRT): In order to determine optimum HRT, batch tests were performed at optimum urea concentration that was specified before. The HRT of 18, 24, 48, 72, 96 hours were chosen. At the end of each batch test, samples were taken and analysed for Calcium, pH and NH_3-N. All experiments were carried out in duplicate and average values of datas were used in results.

Operating Sequencing Batch Reactors (SBR): In order to evaluate the SBR performance for calcium, NH_3-N and COD removal efficiencies, it was operated 2 L working volume of SBR at optimum urea dosage and HRT which was determined by batch tests previously. SBR was operated on the principles of four phases. These phases were fill, react, settle, and draw. The wastewater was continuously mixed at a magnetic stirrer for the specified HRT value. Followed by 2 h of settling and 0.2 h discharge of 1.5 L top clear solution. This completed an operating cycle of the SBR process. Then 1.5 L of wastewater were added to start the next cycle.

2.3. Sampling and analysis

The calcium analysis were measured using a flame atomic adsorption spectrometry (Perkin Elmer Analyst 400). The pH in all batch tests were measured by a WTW Multiline P4 multimeter (SenTix 41 pH probe). All other analyses were performed in accordance with the Standard Methods [15]. All the chemicals used were of analytical-reagent grade.

3. Results and Discussion

3.1. Optimization of urea dosage

Figure 1 shows that urea dosage versus calcium concentration and calcium removal efficiencies. As can be seen from Figure 1, optimum urea concentration under the experimental conditions was 4 g/L. The calcium removal efficiency was found 92.7% and calcium concentration was measured 151 mg/L in this urea dosage.

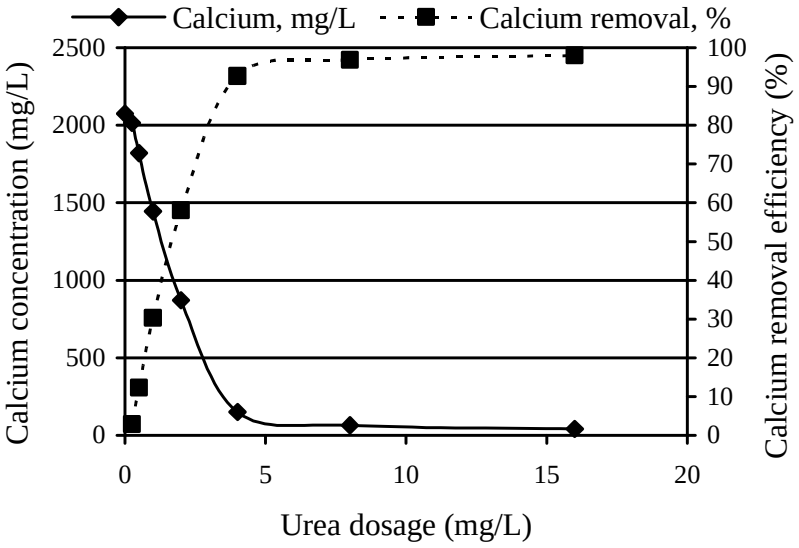

Figure 1. Determination of optimum urea dosage (HRT: 4 days).

The pH variations under the experimental conditions can be seen in Figure 2. As can be seen in Figure 2, the pH value of raw paper mill wastewater was 5.64. The pH value increased gradually as urea dosage increased from 0 to 16 g/L after 4 days of incubation at 20 °C. The pH value was measured 8.5 at the urea dosage of 4 g/L. The pH value did not exceed 9.26 at all urea dosage because of the ammonium buffer equilibrium as it was given in Equation 4 [12].

$$NH_4^+ \leftrightarrow NH_3 + H+ (pK_1=9.26) \quad (4)$$

Figure 3 shows that the theoretical and measured NH_3-N concentration versus urea dosage at experimental conditions. Theoretically, 1 g urea equals 467.4 mg NH_3-N. As seen from Figure 3, the NH_3-N concentration increased with an increase in urea dosage. The theoretical and measured concentration of NH_3-N was same under the urea dosage of 2 g/L, however, the NH_3-N concentrations were slightly lower than expected for the urea dosage of 4, 8 and 16 g/L. The pH values were found 8.5, 8.89, 9.06 for the urea dosage of 4, 8 and 16 g/L, respectively. As is known, NH_3-N can be removed by ammonium or air stripping process. In air stripping process, NH_3-N is transferred from the waste stream into the air and then fluxed into the ambient air. The NH_3-N will likely escape to the atmosphere unless it reacts with water to form NH_4^+. In this study, the NH_3-N concentration of sample could be ascribed to ammonium volatilisation. As seen from the Figure 3, the maximum NH_3-N volatilisation was found 20.4% for the urea dosage of 16 g/L.

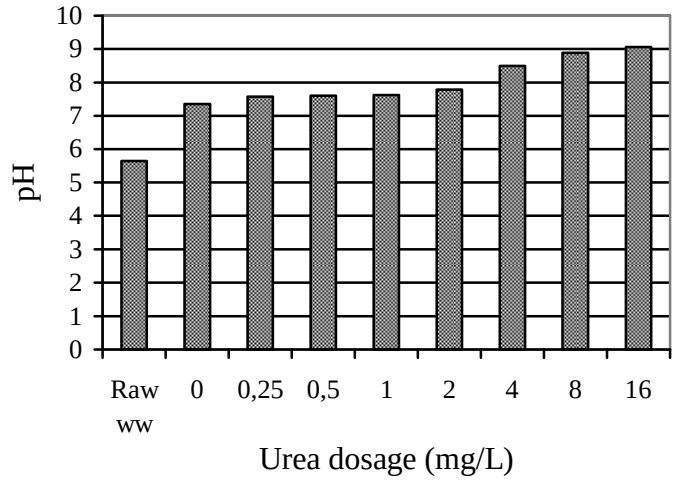

Figure 2. The pH variations of batch test for determination of urea dosage (HRT: 4 days).

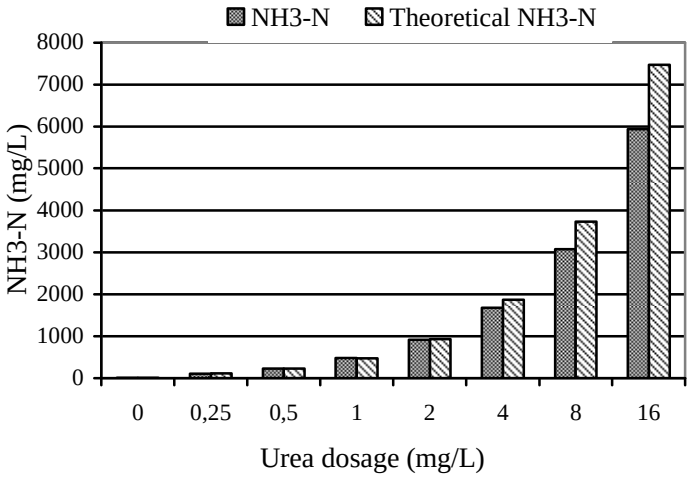

Figure 3. The NH_3-N variation of batch test for determination of urea dosage (HRT: 4 days).

3.2. Optimization of hydraulic retention time

Figure 4 shows the relationship between HRT and calcium concentration and calcium removal efficiencies which was obtained via batch tests at optimum urea dosage of 4 g/L, 20 °C and 100 rpm. As seen from Figure 4, the calcium removal efficiency was found 90.16% at HRT of 72 hours. The pH value was found 7.98 at this experimental condition (Figure 5). The NH_3-N concentration was shown in Figure 6 and NH_3-N concentration was measured 1817 mg/L, as the theoretical NH_3-N concentration was 1870 mg/L.

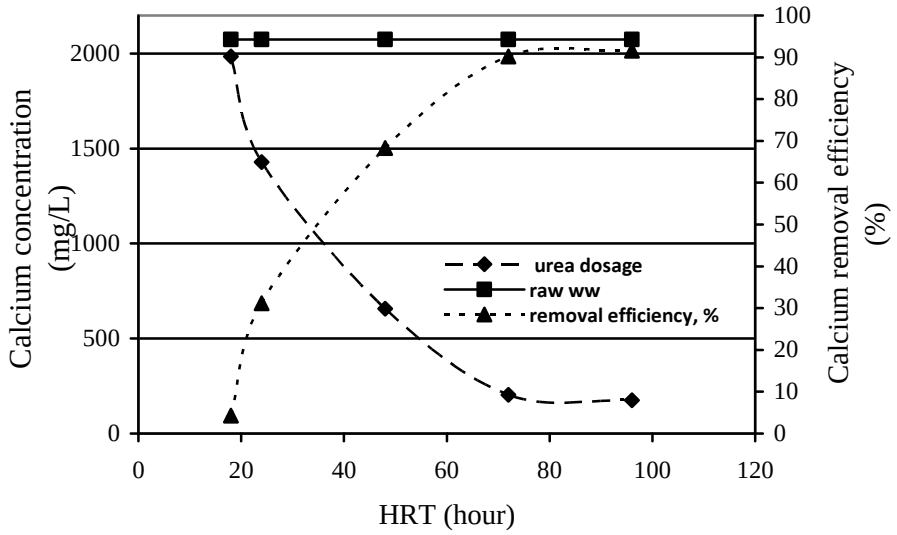

Figure 4. Determination of HRT values at optimum urea dosage of 4 g/L.

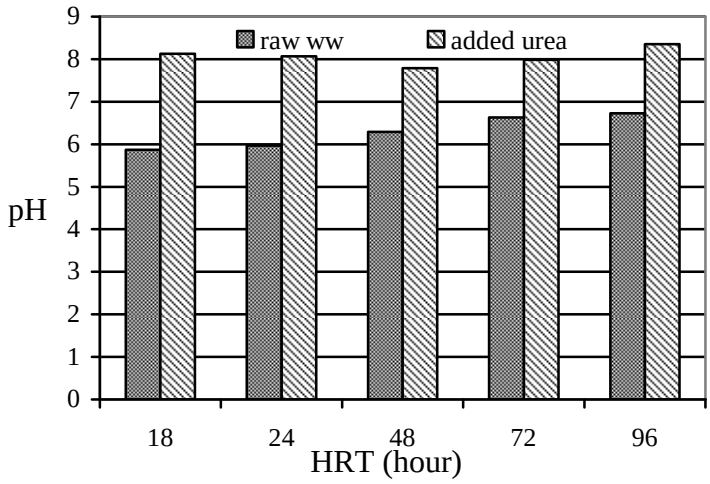

Figure 5. The pH variations of batch test for determination of HRT (optimum urea dosage: 4 g/L).

Based on the results of the experiments which were conducted to determine the optimum urea dosage and HRT, it was determined that the optimum urea dosage is 4 g/L and the optimum HRT is 72 hours.

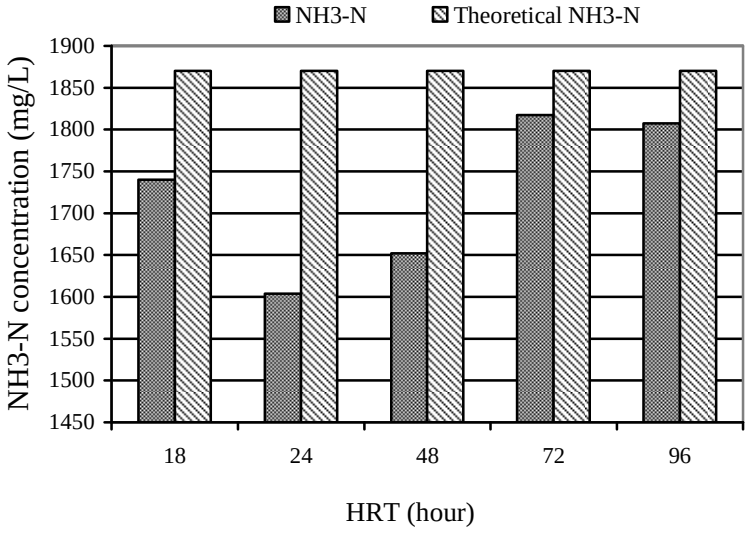

Figure 6. The NH_3-N variation of batch test for determination of HRT (optimum urea dosage: 4 g/L).

3.3. Performance evaluation for sequencing batch reactor (SBR)

The SBR was operated just over 30 days at optimum urea dosage and HRT values in order to remove calcium present in paper mill wastewater via microbial calcium precipitation process, which is a natural process. Figure 7 shows the calcium and COD removal efficiencies for both control reactor and the SBR. As seen from the Figure 7, calcium removal efficiencies exceeded 90% after 6 days of operation in the SBR, however, only 5.6% average calcium removal efficiency was obtained in the control reactor. Hammes et al. [12] investigated calcium removal from industrial wastewater using a bio-catalytic $CaCO_3$ precipitation. In the study, anaerobic effluent was chosen and the authors obtained 85% and 13% calcium removal in the process for reactor and control effluent, respectively. On the other hand, they obtained 8.1% and 15% COD removal efficiencies for reactor and control, respectively. In this study, it was obtained 17.3% and 18.5% COD removal efficiencies for control reactor and SBR.

The variations of NH_3-N concentration and pH for both reactors were shown in Figure 8. The NH_3-N concentration decreased slightly from 12 mg/L to 9.11 mg/L for control reactor throughout the operation. The average value of NH_3-N concentration was found 1830 mg/L in the SBR. The pH increased slightly from 6 to 6.85 for control reactor. The pH values for SBR varied between 7.85 and 8.23 throughout the operation.

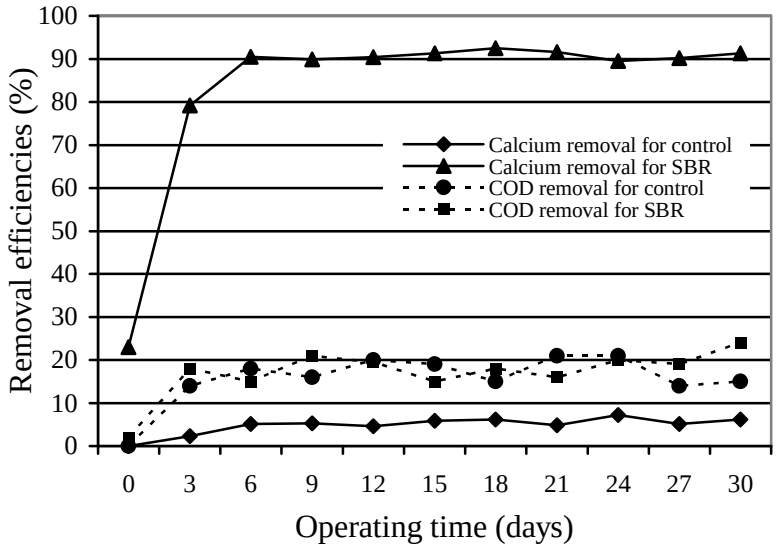

Figure 7. Calcium and COD removal efficiencies for control reactor and SBR.

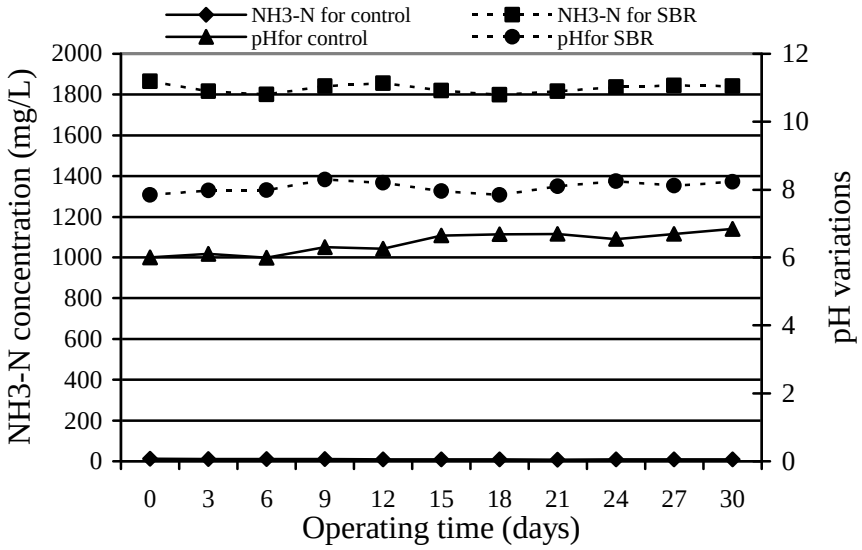

Figure 8. NH_3-N concentrations in control reactor and SBR.

4. Conclusion

This study investigated the effectiveness of MCP for the pre-treatment of pulp and paper mill wastewater. In order to determine optimum urea dosage and HRT, batch tests were conducted in the incubator at 20 °C and 100 rpm. After the determination of urea dosage and HRT, the SBR was operated at these conditions over 30 days. The obtained results respresented that the calcium removal efficiency was very satisfactory and the MCP was a suitable process to remove excess calcium in pulp and paper mill wastewater. According to the COD results obtained from SBR, the COD removal efficiency was only 18.5%. With using MCP process before the sMBR, the main

operational problem was calcification in the sMBR was eliminated in the sMBR systems which caused scaling and fouling on the reactor wall, air diffuser and hollow fibre membrane surfaces. As a final remark, it can be said that the MCP process was used for pre-treatment for pulp and paper mill wastewater, thus, the excess calcium should be removed before the wastewater is introduced to the MBR system to prolong membrane filterability.

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