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Effect of clinoptilolite addition on nutrient removal in a membrane bioreactor

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ABSTRACT

This work aimed to investigate the efficiency of nutrient removal in a modified membrane bioreactor (MBR) used for treatment of wastewater containing high level of ammonium. Due to high selectivity of ammonium for clinoptilolite (a natural kind of zeolite) and its unique characteristics, this sort of clay was studied in combination with MBR. Experiments were in two parallel simultaneous MBRs with an hydraulic retention time (HRT) of 8 h within 33 days. Then, the control membrane bioreactor without clinoptilolite (CMBR) and the zeolite membrane bioreactor with clinoptilolite (ZMBR) were studied. Thereafter, nutrient removal from synthetic wastewater in the CMBR and ZMBR were compared. In ZMBR, about 24% more N-NH_4 removal was achieved owing to combination of nitrification and cation exchange. It was also found that ZMBR application resulted in 10% increase in TN removal in comparison with CMBR. In contrast, no significant difference was observed in chemical oxygen demand (COD) removal. Only low amounts of nitrate and phosphate were removed during the first days of experiments. The results demonstrated that clinoptilolite is highly effective in reducing ammonium content of wastewaters.

Keywords: Ammonium; MBR; Zeolite; Clinoptilolite; Nutrient removal

1. Introduction

The presence of nutrients as a consequence of excessive use of fertilizers or other nitrogen or phosphate-containing compounds is progressively increasing in water and wastewater. The negative impact of such substances on the environment is undeniable [1,2]. Therefore, the treatment of wastewaters is gaining considerable attention by scientists [3,4]. Several methods for nutrient removal are investigated, among which biological methods are used frequently [5,6]. The micro-organisms are capable of degrading many chemicals and accordingly are often used for effective removal of pollutants from waters [7]. Traditional methods such as activated sludge have their own difficulties including inability to meet effluent standards or requiring a lot of space. Previous studies have focused on finding alternative ways for treatment. Membrane bioreactor (MBR) has been proposed as one of the best alternatives for conventional activated sludge process [8].

Using membrane filtration, MBR technology combines the biological degradation through the activated sludge process with a direct solid–liquid separation. By using a micro or ultra filtration membrane [9], MBR system allows complete physical retention of bacterial flocks and virtually all suspended solids

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within the bioreactor. As a result, the MBR has many advantages over conventional wastewater treatment processes including presence of highly concentrated mixed liquor volatile suspended solid (MLVSS), hydraulic retention time (HRT) reduction, small footprint and reactor requirements, high effluent quality, good disinfection capability, higher volumetric loading, and lower sludge production. The MBR process has now become a suitable option for the treatment and reuse of industrial and municipal wastewaters, as evidenced by their constantly rising numbers and capacity [10,11]. In spite of all these advantages, MBR sometimes cannot provide necessary standards for highly polluted wastewaters such as petrochemical wastewater. As a result, a combined supplementary process such as adsorption or cation exchange is regarded as crucial.

Recently, many kinds of adsorbents, coagulants, and cations have been applied in wastewater treatment plants to improve MBR performance [12,13]. Agricultural byproducts, sugar-beet, orange peel, activated carbon, zeolite, silicon based particles, MCM, and polymeric adsorbents such as chitosan are some examples of such adsorbents. Some adsorbents, especially synthetic or polymeric and ion exchange resins, are expensive. There are, however, cheap alternative materials such as zeolite, which are abundant in nature. Natural zeolites are the most important inorganic cation exchangers that exhibit high ion exchange capacity, selectivity, and compatibility with environment [14]. Clinoptilolite is the most abundant natural zeolite that exists in relatively large mineral sedimentary deposits with high degree of purity in many parts of the world. One of the cations, is ammonium ion for which the natural zeolites and especially clinoptilolite have high selectivity. The use of clinoptilolite unit would be an applicable tool to meet stringent standards of ammonia or other forms of total inorganic nitrogen. Clinoptilolite is abundant in Japan, USA, Russia, Iran, and Hungary. Both natural and synthetic zeolites are able to remove some cations from solutions by adsorption or ion exchange features [15].

Natural zeolite or surface-modified zeolite has been widely used as an adsorbent or cation exchanger for water purification or wastewater treatment in the form of clay or filtration [16–18]. This particle has been investigated to some extent in combination with activated sludge or has been used as a biocarrier in biological systems. In addition, effects of zeolite on sludge properties and nutrient removal were discussed before [19–22]. With regard to nitrogen content increase in municipal and industrial wastewaters, inefficiency to meet the required standards for effluents of plants, clinoptilolite ability for nitrogen removal, and a worldwide tendency for using MBR, the idea of combining physical and biological methods in the form of a zeolite membrane bioreactor (ZMBR) has been generated. Zeolite has been rarely investigated in combination with MBR. Jung et al. studied the sequential combination of MBR and zeolite columns [23]. Damayanti et al. comparatively examined zeolite, powered activated carbon (PAC), and Moringa oleifera as biofouling reducers on MBR [24]. Malamis et al. and Katsou et al. investigated heavy metal removal using MBR combined with zeolite [25,26]. Sheng-bing et al. compared nutrient removal, filtration characteristic, micro-organism activity, and permeability of membranes between control MBR and the MBR with zeolite [8]. In addition, according to another researcher, a better permeate quality and lower membrane fouling will be achieved by using particles due to biofilm formation [27]. Literature on combination of zeolite and MBR is quite scarce, so further comprehensive studies should be conducted.

The aim of this study is to investigate the effects of clinoptilolite on nutrient removal in a MBR and to find a way to improve MBR performance for removing pollutants from rich wastewaters especially petrochemicals that usually contain high levels of ammonium. Considering this, physical adsorption and cation exchange in combination with MBR are preferable and a MBR is modified as a ZMBR. Clinoptilolite, which is known as one of the most appropriate types of zeolite in cation exchange, is utilized in combination with MBR to investigate its influence on MBR nutrient removal. Then, chemical oxygen demand (COD) and nutrient removal in both the control membrane bioreactor (CMBR) and the ZMBR, which operated in similar conditions, were assessed in this study.

2. Materials and methods

2.1. Experimental setup

Fig. 1 shows the schema of the experimental setup consisting of a Plexiglas reactor divided into two similar bioreactors working in parallel. In both sides, a membrane module is submerged in the middle. The bioreactors are cube-shaped with a total volume of 16 L and working volume of 15 L. The membrane modules used in this study were Kubota flat microfiltration for polyethylene with a pore size of 0.4 μm and a filtration area of 0.11 m^2. A peristaltic pump was used for both permeate flows. The pump was switched off for 1 h for relaxation purposes every day. In case of fouling on membranes, the membranes were cleaned during the relaxation time. The permeated effluent had a constant flow rate of 31.25 (mL/min) to provide an 8 h

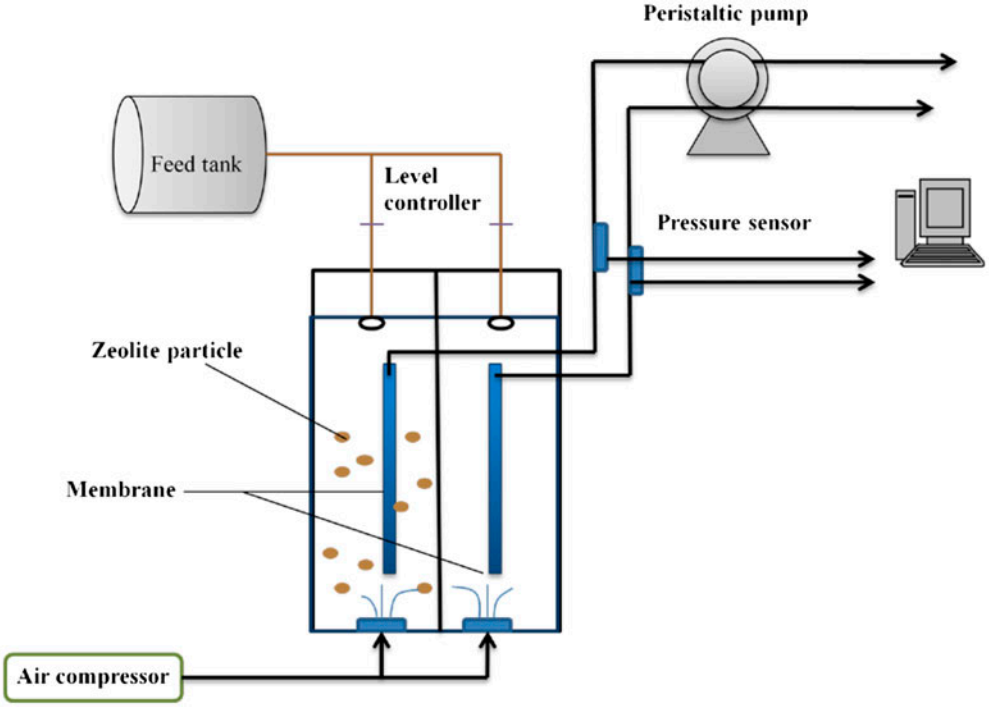

Fig. 1. The schematic of experimental setup.

HRT in both reactors. Air diffuser was installed in the bottom of each reactor to supply the air and mix the micro-organisms. Temperature was the same as the laboratory temperature (19–24˚C). In ZMBR, 8 g/L clinoptilolite was added, which was an optimized amount of clinoptilolite according to previous study [24].

2.2. Feeding medium

The feed tank was installed above the bioreactors with a volume of 100 L. The influent composition that has been fed continuously into the bioreactors is shown in Table 1. The feed flow rate was controlled by a level controller.

Table 1
Synthetic wastewater composition

Material	mg/L
Glucose ($C_6H_{12}O_6$)	110.3
Ammonium phosphate ($(NH_4)_2HPO_4$)	25.56
Ammonium sulfate ($(NH_4)_2SO_4$)	210.3
COD	1,000
TN	50
P	6

2.3. Analysis and experiments

The COD, ammonium (N-NH_4), nitrite (N-NO_2^-), nitrate (N-NO_3^-), total nitrogen (TN), phosphate (P-PO_4^{3-}), and mixed liquor suspended solid (MLSS) contents were determined according to Standard Methods. Dissolved oxygen (DO) concentration, pH, and temperature were measured using a multimeter sensor (WTW-Multi 340i, Germany).

The experiments proceeded 33 days in both CMBR and ZMBR systems. Each measurement has been repeated twice, and the average amount calculated for these measurements has been reported.

2.4. Preparation and measurement of zeolite samples

Zeolite samples used in this study were taken from Semnan mines, Iran. The samples were ground and sieved to an average particle size of 115 μm and then were washed with distilled water several times to remove any non-adhesive impurities and small particles. Then, it was shaked with distilled water in a shaker for 24 h to remove any remaining fine impurities, and thereafter it was dried at 105˚C in an oven for 24 h. Chemical composition of zeolite samples was determined using Philips PW1730 X-ray diffractometer and is presented in Table 2.

Table 2
Clinoptilolite composition and properties

Sample composition	% (wt)
SiO_2	67.44
Al_2O_3	10.90
Fe_2O_3	0.84
TiO_2	0.19
CaO	1.24
MgO	0.33
Na_2O	3.71
K_2O	4.39
S	0.47
LOI[a]	11.05
Physical characteristic	
Density	$2.2\,kg/m^3$
Surface area	$40\,m^2/g$

[a] Loss on ignition.

3. Results and discussion

3.1. Effect of clinoptilolite on ammonium removal

The experiments were conducted simultaneously in two MBRs, one CMBR, and one ZMBR under the same operating conditions. Fig. 2 demonstrates that the initial ammonium ($N-NH_4$) removal is about 97% in ZMBR. As clinoptilolite is a well-known cation exchanger with NH_4, the high NH_4 elimination suggests that cation exchanging with clinoptilolite cations happens. The clinoptilolite, as a sort of clay, has a total negative charge with great cation adsorption tendency. As a result, NH_4 molecules were adsorbed into the clay. During the initial 13 days, $N-NH_4$ elimination was as a result of cation exchange, adsorption, and biological removal altogether, thus the result of these three mechanisms resulted in high $N-NH_4$ removal according to Fig. 2. As other researchers have stated, clinoptilolite, added to activated sludge, eliminates some inhibitors which have reverse effects on nitrification. Furthermore, the stabilized bacteria on particles improve the rate of mass transfer through the particles [21,22]. Consequently, nitrification development was expected as represented in Fig. 2. Despite high removal efficiency of $N-NH_4$ in ZMBR, the amount of this contaminant in the effluent increased and cation exchange with clinoptilolite diminished steadily over the time in phase (a) during 13 days. According to Fig. 2, the amount of $N-NH_4$ in the effluent became stable and no more reduction was observed in phase (b). In phase (a), during the first 13 days, gradual surface saturation of clinoptilolite particles happened with different ions and cations, after the 13th day. As shown in phase (b), adsorption stopped and cation exchange became steady, subsequently $N-NH_4$ was removed biologically. This behavior guides us towards the idea that accumulation of $N-NH_4$ inside and outside of the particles facilitates the growth and activity of nitrifier bacteria. Recovery of saturated zeolite from $N-NH_4$ is performed by nitrifiers. In fact, clinoptilolite particles provide a suitable space for the delivery of nutrients to nitrifiers. Consumption of $N-NH_4$ by nitrifiers results in a concentration gradient in particles. This gradient leads to the re-adsorption of fresh cations. Zeolite particles are recovered by nitrifiers and, due to the lack of positive charge on particles and the generation of concentration slope, the cycle repeats continuously. Recovery of zeolite by nitrifiers was also studied by Soleimani et al. [16]. As illustrated in Fig. 2, $N-NH_4$ removal in ZMBR reached 56% that is 24% more than that of the CMBR. This trend suggests that zeolite has a superior adsorption capability for NH_4 cation which makes it possible for nitrifiers to be attached on the surface and into the pores of clinoptilolite, which in turn enhances nitrification. In addition, nitrifiers prefer attached growth and the biofilm formed on particles mostly contains these kinds of bacteria. Temperature and pH have a significant influence on nitrification. The optimum temperature for the growth of nitrifier was between 28 and 36°C. Also the pH value varied from 8 to 9 [28]. The above optimal conditions were not applied and controlled during experiments. Therefore, the nitrification performance in both systems was lower than the values reported by other researchers [28,29]. However, the goal of this study was to compare CMBR and ZMBR under the same conditions.

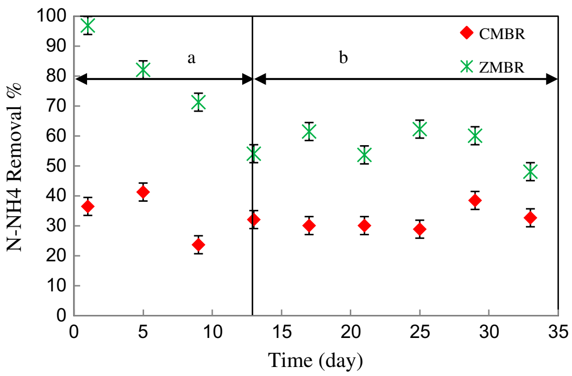

Fig. 2. Removal efficiency of $N-NH_4$ for both CMBR and ZMBR.

3.2. Effect of clinoptilolite on nitrate removal

The effluent nitrate nitrogen concentrations in both ZMBR and CMBR are shown in Fig. 3. In both

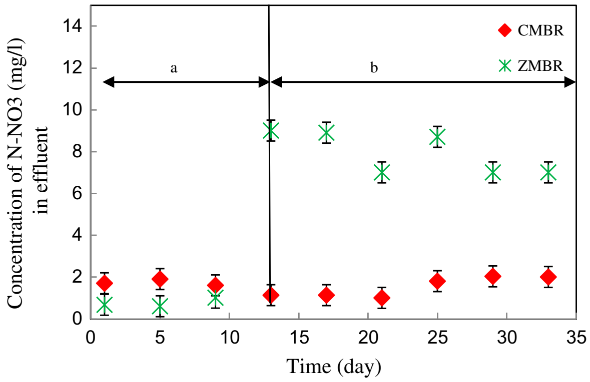

Fig. 3. Concentration of N-NO_3 in effluent for both CMBR and ZMBR.

bioreactors considerable denitrification took place, 72% in ZMBR and 90% in CMBR. Denitrification percentage was calculated using the following equation:

$$\frac{[(\text{N-NH}_{4\text{in}}) - (\text{N-NH}_{4\text{eff}})] - (\text{N-NO}_{3\text{eff}})}{(\text{N-NH}_{4\text{in}}) - (\text{N-NH}_{4\text{eff}})} \times 100 = \text{Denitrification percentage} \qquad (1)$$

"in" and "eff" stand for influent and effluent, respectively. Denitrification percentage shows the percentage of total produced nitrate through nitrification which has been consumed by denitrifiers. The term $(\text{N-NH}_{4\text{in}})-(\text{N-NH}_{4\text{eff}})$ was considered as the amount of ammonium nitrogen converted to nitrate nitrogen during nitrification, so this term shows nitrate nitrogen production. If $(\text{N-NO}_{3\text{eff}})$ is subtracted from nitrate nitrogen production $(\text{N-NH}_{4\text{in}})-(\text{N-NH}_{4\text{eff}})$, the amount of denitrified (N-NO_3) is obtained. The ratio of denitrified nitrate nitrogen to total produced nitrate nitrogen equals to denitrification percentage. The N-NO_3 concentration of effluent in ZMBR during the first 10 days was significantly lower than that of CMBR. Furthermore, N-NO_3 removal was about 98.5% during this period in ZMBR. This quantity is attributed to simultaneous effect of biological elimination and adsorption, the latter being due to the porous structure of clinoptilolite. Phase (a) includes the period during which adsorption surface of clinoptilolite was active and removal process included adsorption in addition to biological removal. After a transition from phase (a), N-NO_3 concentration of effluent enhanced sharply and then it leveled off. As shown in Fig. 3, in phase (b), in spite of the presence of adsorbent in ZMBR, the N-NO_3 concentration of effluent from the ZMBR was more than that of CMBR. As mentioned before, as a result of cation exchange capacity of clinoptilolite with NH_4, nitrification increased 24% within ZMBR in comparison with CMBR. In other words, N-NO_3 production soared. Nevertheless, in response to this growth there was not a significant compensating process for removing the excess NO_3 produced and only biological denitrification occurred. Phase (b) shows the saturation period during which no adsorption happened. In phase (b), whatever is considered as increased NO_3 production is attributed to the modification of nitrification, and the micro-organisms are only able to remove some amount of these excess nitrates while the rest are remained. According to the above equation, a 19% reduction in denitrification in ZMBR happened as a result of extensive nitrification.

It is well known that the formation of biofilm can generally provide an anaerobic region in the depth of biofilm so enhancing denitrification. However, Ivanovic et al. stated several other advantages for biofilm formation in MBR systems [30]. As a noticeable feature, the depth of oxygen permeation through a biofilm is 100–150 μm [31] and a thicker layer is needed for establishing anaerobic condition. During this experiment, the depth of biofilm formed on clinoptilolite was always less than this value. As a result, anaerobic condition which engenders a better denitrification did not happen in ZMBR. In case of longer experiments, depth of biofilm formed on particles will become thicker and due to the provision of anaerobic circumstance in inner layer of biofilm, nitrate consumption could improve. However, assessing the effect of biofilm formation on particles is not the aim of this article and it will be investigated in future studies.

3.3. *Effect of clinoptilolite on total nitrogen removal*

Herein, TN includes total nitrogen nitrate, nitrogen ammonium, and nitrogen nitrite. Nitrite was measured in some cases and was seldomly detected. Due to negligible amounts of nitrite, it was disregarded. Fig. 4 illustrates, the amount of total nitrogen effluent from both CMBR and ZMBR. Total nitrogen amount of CMBR effluent was steady over the time, but in ZMBR during the early days of experiment in phase (a), total effluent nitrogen was too low. High level of nitrate adsorption and ammonium along with enhanced nitrification led to lower amount of total nitrogen in effluent of ZMBR. The graph shows a rising trend in ZMBR behavior. It stems from saturating clinoptilolite cation exchange capacity with ammonium and adsorbing capacity of nitrate. Although stability is observed in ZMBR graph, phase b, it is obvious that the total effluent nitrogen in ZMBR is less

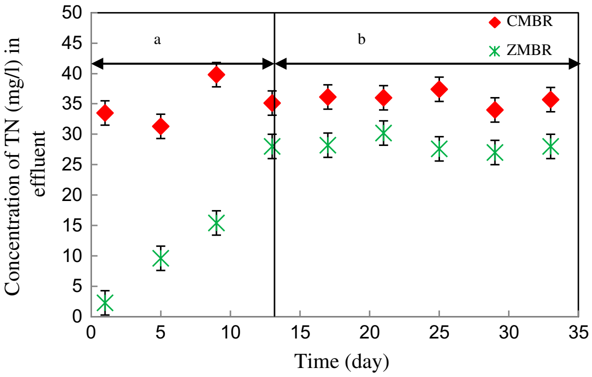

Fig. 4. Concentration of total nitrogen in effluent for both CMBR and ZMBR.

than that of CMBR. In spite of greater nitrate generation in ZMBR, total nitrogen elimination in ZMBR enhanced and removal was 10% more in ZMBR than CMBR. This can be attributed to better efficiency of ammonium removal and elevated rate of nitrification. Other researchers also reported the enhanced nitrogen removal in the presence of clinoptilolite in MBR [8]. Wang et al. stated that hybrid MBR, performed the nitrogen removal much better than the conventional MBR owing to presence of biofilm under the same operating conditions [32].

3.4. Effect of clinoptilolite on COD removal

As illustrated in Fig. 5, clinoptilolite does not affect COD removal significantly, for organic carbons such as COD neither has anionic or cationic charge to be adsorbed on zeolite, nor can exchange with its cations.

Other researchers have confirmed that zeolite does not have any potential to enhance COD elimination [21].

3.5. Effect of clinoptilolite on phosphate removal

Fig. 6 demonstrates that over 70% of P-PO_4 is removed during the first days since addition of particles in ZMBR. But this trend declined till the 13th day, and then ZMBR graph leveled off and both zeolite and control schemes showed the same approximate 20% elimination. In phase (a), clinoptilolite adsorbed P-PO_4 ions, and then as the clinoptilolite got more saturated, the adsorption declined until it stopped completely. In phase (b) of the ZMBR scheme in Fig. 6, the only mechanism was biological removal as seen in the CMBR. This mechanism operated exactly similar to nitrate adsorption. The clinoptilolite behavior was the same when facing small negative charged particles and this behavior was due to the mesoporous structure of zeolite particles. In addition, biological phosphate removal needs anaerobic conditions, since phosphate ions in anaerobic phase convert to radical phosphor and subsequently this radical phosphor is adsorbed into phosphate-accumulating organisms (PAOs). So in this case, due to the lack of anaerobic condition, phosphate removal was less than what was supposed before. Other researchers have also confirmed that sequencing aerobic and anaerobic treatments result in more phosphorous removal [33]. As other researchers have mentioned, adding biofilm carriers to MBR improves phosphorous removal much more than the conventional MBR [32].

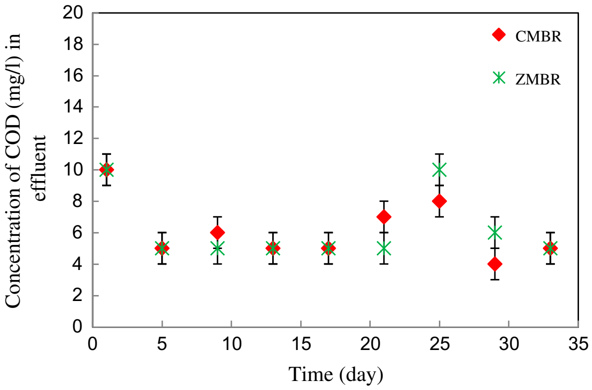

Fig. 5. Concentration of COD in effluent for both CMBR and ZMBR.

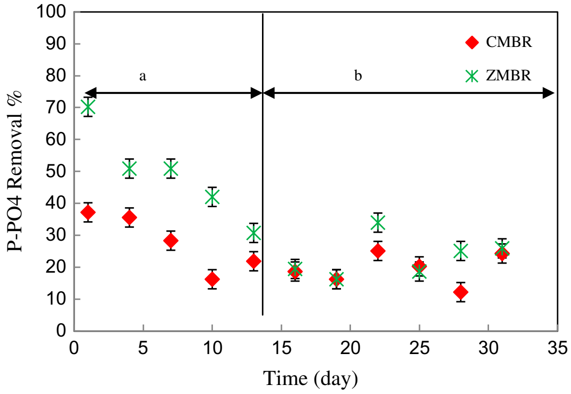

Fig. 6. Removal efficiency of P-PO_4 for both CMBR and ZMBR.

4. Conclusions

In this study a control submerged MBR and a zeolite powder added MBR operated in parallel to investigate the effect of zeolite powder addition on the elimination capability of a MBR. It was concluded that:

In ZMBR, clinoptilolite particles influence removal of ammonium cation. Based on the cation exchange capacity of clinoptilolite and increasing attached growth of micro-organisms on particles, ammonium and total nitrogen elimination both increased significantly while COD removal was negligible. Although nitrate elimination did not decrease in these experiments, it could diminish in a long-term operation due to the formation of a biofilm layer and under anaerobic conditions. In addition, natural zeolites, modified by surfactants, could successfully bind anionic species of nitrate which were not mentioned in this study. No significant reduction in phosphate amounts within ZMBR compared to CMBR was observed. In conclusion, this method is recommended for industries with highly polluted ammonium-containing wastewaters in which the common treatments cannot easily produce the effluent with necessary standards.

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Nomenclature

MBR — membrane bioreactor
MLVSS — mixed liquor volatile suspended solid
MLSS — mixed liquor suspend solid
HRT — hydraulic retention time
PAC — powered activated carbon
CMBR — control membrane bioreactor
ZMBR — zeolite membrane bioreactor
COD — chemical oxygen demand
DO — dissolved oxygen
TN — total nitrogen
PAO — phosphate accumulating organisms

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