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# The influence of zeolite (clinoptilolite) on the performance of a hybrid membrane bioreactor

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## HIGHLIGHTS

- Clinoptilolite as a bio carrier cause 24% more activated sludge growth in MBR.
- Clinoptilolite in MBR causes sorption of SMP and improves sludge properties.
- Clinoptilolite particles reduce fouling of membrane more than 66%.
- Biological nutrient removal especially ammonium removal improves 24% in hybrid MBR.

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## ABSTRACT

This work aims to investigate the effect of clinoptilolite on the performance of membrane bioreactor (MBR). The control membrane bioreactor without clinoptilolite (CMBR) and the hybrid membrane bioreactor with clinoptilolite (HMBR), in two parallel simultaneous MBRs within long and short term filtration experiments, were studied. Sludge properties, transmembrane pressure (TMP) rise as an index for membrane fouling and nutrient removal from synthetic wastewater in the CMBR and HMBR were compared. In HMBR, sludge properties improvement such as 22.5% rise in MLSS, 7% more accumulation of large particles, reduction of soluble microbial products (SMP) to half of this value in CMBR, no increase in sludge volume index (SVI) and 66% TMP reduced. The results of short term filtration showed that the trend of TMP increase in terms of flux will be slower in HMBR. Improvement of biological wastewater treatment quality and ease of membrane operation are concluded from this study.

## 1. Introduction

Membrane bioreactor (MBR) has been widely used as a leading technology to treat different wastewaters (Koseoglua et al., 2008; Hwang et al., 2007). In spite of MBR advantages such as small footprint (Pajoum Shariati et al., 2013; Chang et al., 2002), control of solids (Gil et al., 2010), high effluent quality (Pajoum Shariati et al., 2013; Chang et al., 2002; Gil et al., 2010), and good retention of microorganisms (Koseoglua et al., 2008; Gil et al., 2010), fouling has been discussed in many published studies as a major obstacle in MBR technology (Chang et al., 2002; Gil et al., 2010; Stoller, 2011; Koseoglua et al., 2012; Wang et al., 2008; Mennitia et al., 2009) which brings about a significant cost and energy burden on the system (Wang et al., 2008; Mennitia et al., 2009).

Three parameters are involved in membrane fouling including operating condition (Pajoum Shariati et al., 2013), sludge characteristic (Koseoglua et al., 2008; Pajoum Shariati et al., 2013; Chang et al., 2002) and membrane materials (Pajoum Shariati et al., 2013; Homayoonfal et al., 2010). Various publications indicate that different sludge characteristics such as viscosity (Koseoglua et al., 2012; Pajoum Shariati et al., 2013), extracellular polymeric substance (EPS) (Koseoglua et al., 2012; Pajoum Shariati et al., 2013; Azami et al., 2011), floc size (Koseoglua et al., 2012; Pajoum Shariati et al., 2013), soluble microbial product (SMP) (Pajoum Shariati et al., 2013; Koseoglua et al., 2012), and MLSS (Pajoum Shariati et al., 2013) influence membrane fouling. As MBR is a costly technology and most expenses are due to solving fouling problems such as back washing, aeration, chemical and physical cleaning, it will be advisable to adopt an appropriate method to modify sludge characteristics as an important parameter in membrane permeability.

Some additives have been recently used in MBRs to improve its applications either in effluent quality or in membrane fouling

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mitigation (Koseoglua et al., 2012; Sheng-bing et al., 2006; Yang et al., 2006). PAC, zeolite, chitosan and polymeric coagulants are some examples of additives which have been used in combination with MBR (Damayanti et al., 2011; Wu et al., 2006). Both natural and synthetic zeolites have the ability to remove some cations from solutions by adsorption and cation exchange processes (Soleimani et al., 2009; Mažeikien et al., 2008). Some aspects of clinoptilolite, as the most abundant natural zeolite, have been investigated in combination with activated sludge and its effects on sludge properties or nutrient removal were discussed (Park et al., 2002; Sool Lee et al., 2002; Jung et al., 2006).

Damayanti et al. (2011) used this particle in combination with membrane. The results showed that zeolite addition to activated sludge will increase permeability and decrease membrane resistance. In comparison with the control reactor, it enhances critical flux up to 20% (Damayanti et al., 2011). Park et al. (2002) indicated that clinoptilolite particles accelerate nitrification due to clinoptilolite ammonium adsorption. They suggested that clinoptilolite provides a relatively low C/N ratio for nitrifiers in activated sludge. Moreover, MLSS and MLVSS elevate in the zeolite reactor and oxygen uptake rate (OUR) enhances due to higher nitrification. Nitrate production rate is also higher in zeolite reactors owing to better nitrification (Park et al., 2002). Other researchers reported nitrification development in the presence of clinoptilolite (Park et al., 2003). Wu et al. (2008) showed that ammonium removal efficiency enhanced over 27% in a zeolite reactor in comparison with an activated sludge reactor.

Since the combination of clinoptilolite particles and activated sludge has shown some improvements in sludge properties and also in nutrient removal, it seems a good idea to embed this particle in MBR for both enhancing nutrient removal and the likely improvement of sludge characteristics and thereby reduce membrane fouling. Few studies have been done in this field. Yang et al. (2006) reported that flexible porous suspended carriers increase critical flux by 20% and decrease cake resistance of MBR by 86%. Malamis et al. (2009) and Katsou et al. (2010) investigated metal removal from wastewater in a combined system using sludge, clinoptilolite and filtration membrane.

Although zeolite is well-known in wastewater industry and many researchers have studied clinoptilolite in activated sludge, fewer pieces of research have studied MBR in combination with zeolite comprehensively. Therefore, clinoptilolite effects on MBR are not obvious. The aim of this study is to investigate the effects of clinoptilolite addition on sludge characteristics, fouling mitigation and nutrient removal in a MBR. Considering this purpose, clinoptilolite is utilized in a MBR called hybrid MBR (HMBR) system and its performance is compared with the control membrane bioreactor (CMBR) in terms of nutrient removal, sludge properties including MLSS, sludge volume index (SVI), particle size distribution (PSD) and SMP. Transmembrane pressure (TMP) increase trend, membrane permeability and short term filtration are compared in these MBR systems as well.

## 2. Methods

### 2.1. Experimental setup

Experimental setup consists of a Plexiglas reactor which is 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 are of Kubota polyethylene flat microfiltration type with pore size of 0.4 μm and filtration area of 0.11 $m^2$. A peristaltic pump is used for both of the permeate flows. In case of any TMP augmentation more than maximum allowable TMP, the membranes are cleaned physically. In case of constant rise in short time, the membranes are cleaned chemically according to their procedure. With regard to Judd (2006), HRT between 6 and 16 h is popular in municipal and domestic wastewater treatments using MBR. Also it was experimented that in HRTs lower than 8 h COD removal and process efficiency will decrease in this study. So the permeated effluent has a constant flow rate of 31.25 ml/min to provide a HRT of 8 h in both reactors. Air diffuser is installed in the bottom of each reactor to supply air and mix the sludge. Temperature is the same as laboratory temperature (18–20 °C). The long term filtration is done during ninety days. 8 g/l clinoptilolite is an optimized amount according to Wu et al. (2008). Also Sool Lee et al. (2002) expressed that in case of low clinoptilolite dosage there is no difference between control and clinoptilolite added sludge. In some other research, 5 g/l (Park et al., 2003) and 4 g/l (Park et al., 2002) clinoptilolite added sludge are studied as minimum amount of this additive. In this work, 8 g/l is considered for HMBR in order to study the influence of clinoptilolite on MBR performance.

### 2.2. Feed medium

The feed tank is installed above the bioreactors with a volume of 100 L. The influent has been fed into the bioreactors continuously and consists of 1103 mg/l glucose ($C_6H_{12}O_6$), 25.56 mg/l ammonium phosphate ($(NH_4)_2HPO_4$), and 210.3 mg/l ammonium sulfate ($(NH_4)_2SO_4$). The ratio of COD:TN:TP is 1000:50:6. The feed flow rate is controlled by a level controller.

### 2.3. Analysis

The composition of COD, ammonium ($N{-}NH_4$), nitrite ($N{-}NO_2^-$), nitrate ($N{-}NO_3^-$), total nitrogen (TN), phosphate ($P{-}PO_4^{3-}$) and MLSS contents are determined according to Standard Methods APHA et al. (1998). Sludge characteristics including MLSS, sludge PSD, SVI and SMPs are measured according to Standard Methods. DO concentration, pH and temperature are measured using a multimeter sensor (WTW-Multi 340i, Germany).

### 2.4. Preparation and measurement of zeolite samples

Zeolite samples used in this study are taken from Semnan mines, Iran. The samples are ground and sieved to average particle size of 115 μm and then washed with distilled water several times to remove any non-adhesive impurities and small particles. Then, it is shaken with distilled water in a shaker for 24 h to remove any remained fine impurities. Then, it is dried at 105 °C in an oven for 24 h. Density and surface are of clinoptilolite are 2.2 $kg/m^3$ and 40 $m^2/g$. Chemical composition of zeolite sample is determined using Philips PW1730 X-ray diffractometer. The clinoptilolite is mainly composed of 67.44% $SiO_2$, 10.9% $Al_2O_3$, 4.39% $K_2O$ and 3.71% $Na_2O$.

### 2.5. Short-term filtration

A short-term filtration within 160 min took place in order to investigate the effects of clinoptilolite on TMP elevation, fouling rate and membrane permeability versus flux. The first step of the experiment starts with a flux equaling to 3 LMH. This method included 10 min of operation at each tested flux, from 3 to 33 LMH. In other words, the fluxes are increased by 3 LMH increments and experiments are done at 3, 6, 9, 12, 15, 18, 21, 24, 27, 30 and 33 LMH. For example, for testing each step, the protocol was as follows: operation at 3 LMH for 10 min, 0 LMH (no permeate production, only aeration) for 5 min, 6 LMH for 10 min and so on.