Desalination and Water Treatment 9 (2009) 201–210
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Natural and modified zeolite utilization in submerged membrane reactor for potable water treatment

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Received 15 September 2008; Accepted 10 August 2009

ABSTRACT

In this study, zeolite addition as a pretreatment step in a submerged membrane system was investigated. The effect of natural and modified zeolite, modified zeolite concentration, particle size fractionation of modified zeolite and feed organic matter concentrations as well as turbidity were studied with synthetic solutions. Additionally, experiments were performed to evaluate the effect of modified zeolite concentration and combination of zeolite and $FeCl_3$ with natural raw water. It was found that natural zeolite should be modified prior to use for improving the performance as a pretreatment in the submerged membrane system. Also, it was observed that smaller particle sizes of zeolite improved the performance further. In contrast to turbidity, zeolite and organic matter concentrations have a considerable effect on membrane performance. Natural raw water caused nearly two-fold increase in the vacuum pressure in comparison to the synthetic water. However, addition of $FeCl_3$ in the presence of modified zeolite compensated the high pressure increasing in the permeate line with raw water.

Keywords: Zeolite (clinoptilolite); Surface modification; Submerged membrane system; Ferric chloride; Organic matter removal

1. Introduction

Membrane technology has been widely used for solid/liquid separation in water treatment. As recent regulations get more stringent for drinking water, microfiltration (MF) and ultrafiltration (UF) membranes are being considered for the replacement of conventional water treatment plants.

Natural organic matter (NOM) generally found in surface water is not desired in membrane water treatment due to reversible and irreversible fouling on membrane surfaces [1]. Not only flux declines but also transmembrane pressure increases with membrane fouling, causing an increase in operating costs. This turns up as vacuum pressure increase for submerged membrane systems.

MF and UF systems are not sufficient to remove soluble materials such as dissolved organic matters when used alone. Hybrid systems such as membrane-adsorption systems can be considered as an alternative method to achieve a high removal efficiency of natural organic matter (NOM) and low pressure increase.

Powdered activated carbon (PAC) was used as an adsorbent in the previous studies for both pressurized and submerged membrane systems and satisfactory results were obtained in these studies [2–4] for NOM fouling. Additionally, natural zeolite which is used as an adsorbent was also used in water treatment applications [5]. The results indicated that there is a significant potential for the natural zeolite as an adsorbent material for ammonium removal from aqueous solutions.

Natural zeolite was used as an adsorbent in submerged membrane system for wastewater treatment [6–7]. They obtained good results with the addition of natural zeolite in terms of pressure increase. However, natural zeolite adsorption as a pretreatment method in submerged membrane system for water treatment has not been studied before.

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Presented at the Conference on Membranes in Drinking and Industrial Water Production, 20–24 October 2008, Toulouse, France.

In this study, natural Turkish zeolite was evaluated due to its low cost as well as its extensive adsorption capacity in submerged microfiltration membrane studies for water treatment. Studies were carried out both with natural zeolite and its surface modified form. The effect of natural and modified zeolite, modified zeolite concentration, particle size fractionation of modified zeolite and feed organic matter concentrations and turbidity were studied with synthetic solutions on membrane performance. Additionally, experiments were performed with raw water to evaluate the effect of modified zeolite concentration and combination of zeolite and $FeCl_3$.

2. Materials and methods

2.1. Synthetic and natural feed waters

Synthetic and natural raw waters were used in the experiments similar to previous study [8]. Synthetic water was prepared in a composition thus it represents a typical surface water. Predetermined amounts of calcium chloride, magnesium sulphate, sodium bicarbonate, potassium bromate, humic acid and clay were added to the deionized water to obtain the synthetic water. Deionized water was obtained by using a reverse osmosis system and the conductivity of this water was about 10 µS/cm. Effect of organic matter on membrane fouling was studied by changing the humic acid content of synthetic water during the experiments. Humic acid was obtained from Sigma Aldrich Company. Natural raw water was obtained from the intake of Kagithane water treatment plant of Istanbul (which comes from Terkos Lake). The chemical characterizations of waters are given in Table 1.

2.2. Zeolite – submerged MF system operation

The same experimental set-up was used with the previous study [8]. Polypropylene hollow fiber microfiltration (MF) membranes (Zena Membranes, Czechoslovakia) were used in the experiments. The modules were operated in an "outside-in" configuration by peristaltic pump. The pore size of the MF membrane was about 0.1 µm. The MF membrane was pretreated with ethanol for 30 min followed by rinsing with deionised water to clear its surface. The membrane area was 0.047m2. Technical characteristics of MF membrane are given in Erdim et al. [8].

The hybrid submerged membrane reactor was made of Plexiglas. The volume of the reactor was 6.6 L. The reactor was separated into two parts with a baffle. The first compartment serves as an adsorption zone while the second part was used for submerged membrane. Raw water was introduced to the first part and flows through the second part by a bottom flow channel. A water level controller was used to maintain a constant water level in the reactor by controlling the inlet pump (Watson Marlow 323E)which pumped the raw water into the reactor. Permeate was vacuumed from the reactor for 60 min using a peristaltic pump (Watson Marlow 323E). Backwashing was performed once every hour for 5 min with pump (ALLDOS M 208-0.3-10,000). Permeating and backwashing were performed automatically with automatic control system. Samples were taken at once a day from the permeate line, reactor and the raw water tank. Permeate flow rate was kept constant at 20 mL/min and was monitored daily during the experiments. The operating flux was set as 425.5 L/m^2 min. The transmembrane pressure (TMP) was measured by a pressure gauge (Siemens SITRANS P ZD) placed in the vacuum line in the experiments. The pressure data was monitored online and stored by using a HACH model SC1000 data logging system [8] (Fig. 1).

Air was supplied from a porous ceramic plate below the membrane module in order to provide turbulence along the membrane surface which helps to remove foulants and particles that deposit on the outside of the membrane fiber. Experiments continued for one week and MF membranes were cleaned between each experiment. Different chemicals were used during chemical cleaning procedure of each membrane [8]. The MF membrane module was cleaned according to the following steps: (i) surface cleaning with deionized

Table 1
The characterization of synthetic and raw waters [8].

Parameter	Synthetic water	Natural raw water
Total hardness, mgCaCO$_3$/L	110–120	150–160
Alkalinity, mgCaCO$_3$/L	95–100	100–110
Dissolved organic carbon (DOC), mg/L	1.5	4.5–5.0
pH	7.8–8.0	8.1–8.3
SO_4^{2-}, mg/L	25–30	35–40
Conductivity, µS/cm	400–450	650–670
Turbidity, NTU	5	8
UV_{254} (absorbance at 254 nm), L/cm	0.13–0.14	0.10–0.15

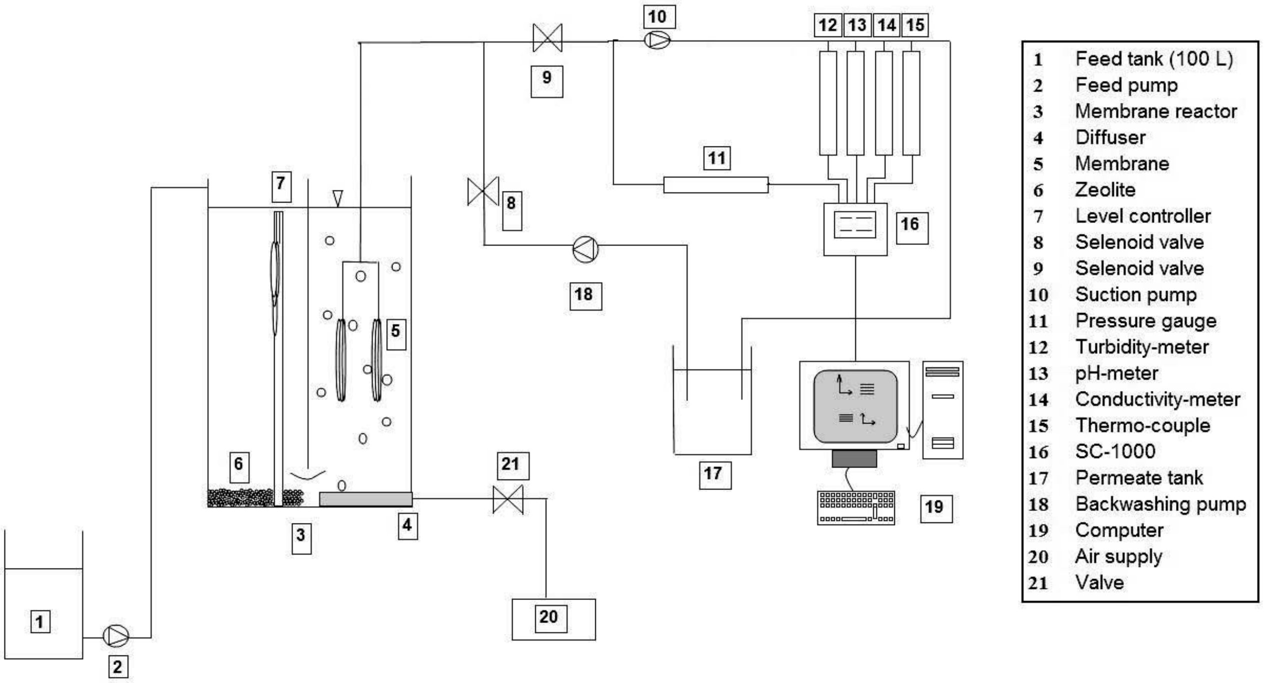

Fig. 1. Schematic diagram of the hybrid adsorption/submerged membrane experimental set-up.

water (ii) acidic wash in 2% HCl solution for 2 hours (iii) basic wash with 1 N NaOH solution for overnight (iv) final cleaning in 0.4% NaOCl for 2 h [4]. Membranes were rinsed with deionized water after every step and prior to all experiments. Figure 2 shows the recovery of MF membranes after each cleaning which have been conducted with pure water.

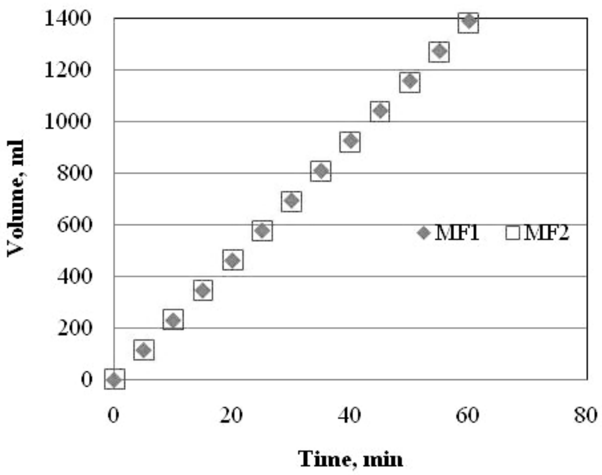

Fig. 2. Flux recovery of MF membrane after each cleaning conducted with pure water.

2.3. Preparation of modified natural zeolite

Zeolite (clinoptilolite) was supplied by Enli Mining (Izmir) and modified with an analytical grade HDTMA (Hexadecyltrimethylammonium). 200 g of natural zeolite was added to HDTMA of 3 g/L concentration and shaked for 2 h in the orbital shaker. Subsequently, the liquid phase was drained and zeolite was washed with deionized water several times until no foam was observed. Then the modified zeolite was dried at 103°C–105°C prior to use.

2.4. Analytical methods

Treatment efficiencies were measured by analyzing removal of dissolved organic carbon and UV_{254} absorbance. Other parameters such as turbidity (Hach-Lange Solitax t-line sc), pH (Hach-Lange DPD1P1.99) and conductivity (Hach-Lange D3412.99) were also monitored with online monitoring system (Hach-Lange SC1000) continuously [8]. All analytical methods were performed according to the standard methods [9]. UV absorption was determined at 254 nm using a 1 cm quartz cell. Dissolved organic carbon (DOC) was determined by combustion catalytic oxidation/NDIR method (Shimadzu TOC-V_{CPH}) [8].

3. Results and discussions

Adsorption isotherm studies were performed at the beginning of the experiments. After that, the performance of natural and modified zeolite as a pretreatment was

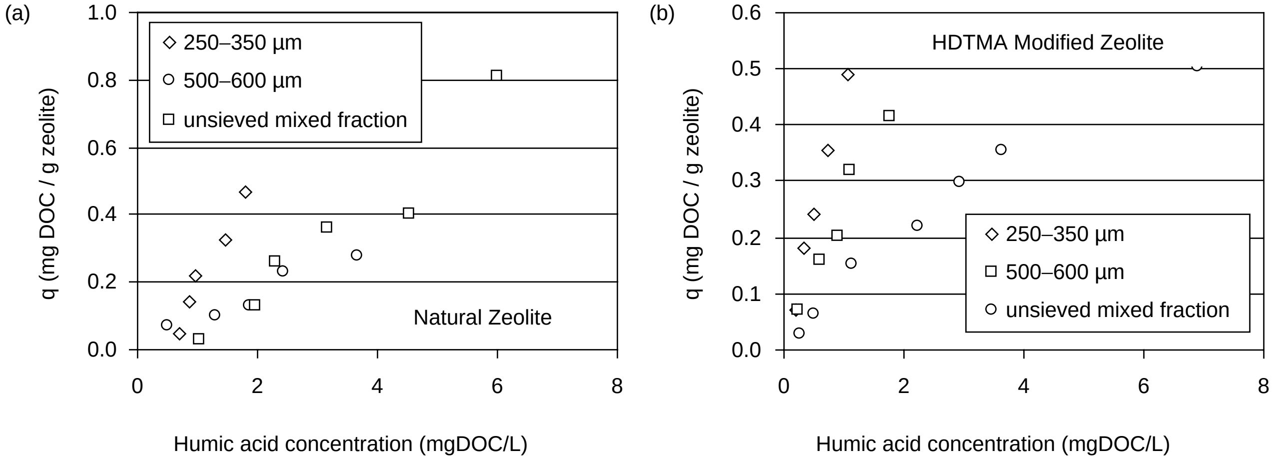

Fig. 3. Isotherm experiments studied at batch conditions for natural and modified zeolite.

evaluated. For this purpose, different zeolite and organic matter concentrations as well as turbidity values were studied with synthetic water experiments. Also, natural raw water was studied to compare the results with synthetic water experiments.

3.1. Isotherm studies

Isotherm studies were performed with natural and modified zeolites. Three different size fractions were studied for both of the zeolite types: 250–350 µm, 500–600 µm and unsieved mixed fraction. The particle diameter in the unsieved mixed fraction was higher than 700 µm. Batch tests were used for isotherm studies. Adsorption capacities are shown in (Fig. 3) for both types of zeolites. It was obtained that small size fractionation of both zeolite types (250–350 µm) showed better performance than the mixed type. 0.1 mg DOC was adsorbed with 1 gr natural zeolite at 1.5 g DOC/L for both the mixed and 500–600 µm fractions. Almost three times adsorption capacity was obtained with 250–350 µm size fraction. Adsorption capacity of modified zeolite increased almost two times after modification with HDTMA. On the basis of these results it was decided to perform the membrane experiments with modified zeolite.

3.2. Membrane studies with synthetic water

3.2.1. Comparison of natural and modified zeolite

The performance of modified and natural zeolite was evaluated and results were assessed in terms of pressure increase and organic matter removal efficiency. The

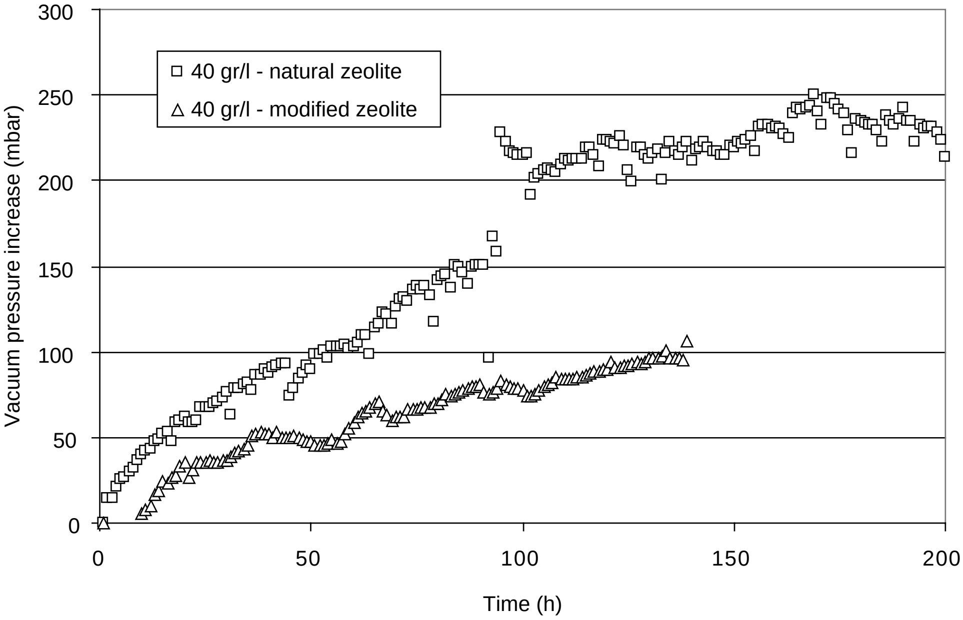

Fig. 4. Pressure increase for natural and modified zeolite.

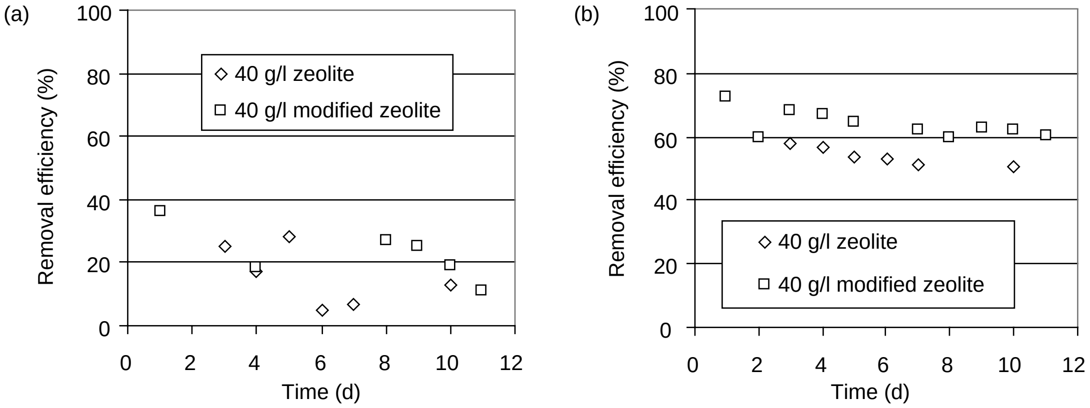

Fig. 5. Removal efficiencies of (a) DOC and (b) UV_{254} for natural and modified zeolite.

main effect of modified zeolite was observed on pressure increase as shown in (Fig. 4). For modified zeolite, the pressure increase was about 100 mbar after 140 h operation while 225 mbar pressure was obtained with natural zeolite at 40 g/L concentration. Although the significant effect of modified zeolite was observed on pressure increase, there was a slight effect on organic removals (Fig. 5).

Nearly 10% difference was obtained for UV_{254} absorbance removal efficiencies while almost no change was observed for DOC removal. This situation can be attributed to the characteristics of humic acid. The molecular weight of humic acid changes between 2000 and 300000 Da. It generally contains long chain organics and the fraction of small molecular weight content is not dominant. The effect of zeolite decreases with increasing molecular weight of humic acid (aromatic groups). The size fraction of zeolite is also important on removal efficiencies. The 10% difference on modified and natural zeolites on removal efficiencies can be due to the aliphatic groups which can be adsorbed on modified zeolite surface easily. The pressure increase during the experiments with natural zeolite was due to continuous membrane fouling which can be caused by the small size organics. However, in the modified zeolite case, the small molecular weight organics adsorbed onto surface of modified zeolite and did not foul the MF membrane surface thus causing low pressure increase on the

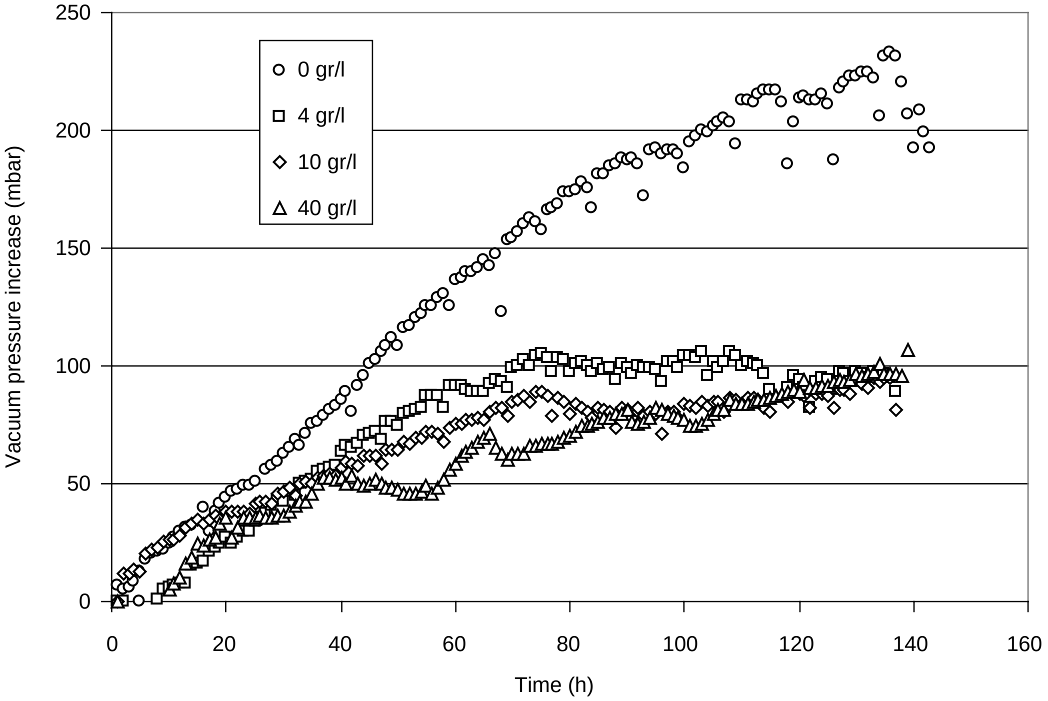

Fig. 6. Effect of modified zeolite concentration on pressure increase.

permeate line. Additionally, small molecular weight fraction (aliphatic groups) which was adsorbed on modified zeolite caused small differences on removal efficiencies.

3.2.2. Effect of modified zeolite concentration

Three different types of modified zeolite concentrations were studied with synthetic water: 4, 10 and 40 g/L. Slower development in vacuum pressure at higher concentration of zeolite as shown in Figure 6 indicates that membrane fouling was mitigated due to higher removal of aliphatic groups at higher concentration of zeolite. The concentration of DOC and UV_{254} increased in the reactor during experimental runs. The DOC concentration increase at low zeolite concentrations (4 and 10 g/L) was due to the low adsorption capacity in contrast to 40 g/L. At the end of the experiments, increase of the DOC concentration in the reactor was nearly 110% at 10 g/L of zeolite concentration while it was about only 34% at 40 g/L. Similar results were obtained also for UV absorbance values at 254 nm. The permeate UV_{254} absorbance values were similar for 4 and 10 g/L of zeolite concentrations whereas low permeate UV_{254} absorbances were obtained at 40 g/L (Fig. 7). The effect of zeolite concentration on the permeate DOC values was not noticeable.

3.2.3. Effect of particle size fractionation of modified zeolite

As stated in the isotherm experiments, the adsorption capacity increases as the size of the particles decrease. Two different fractions were studied in this study: 250–350 µm and unsieved mixed zeolite. The pressure increase at 10 g/L of zeolite concentration is shown in (Fig. 8) for fractions at 250–350 µm and mixed zeolite.

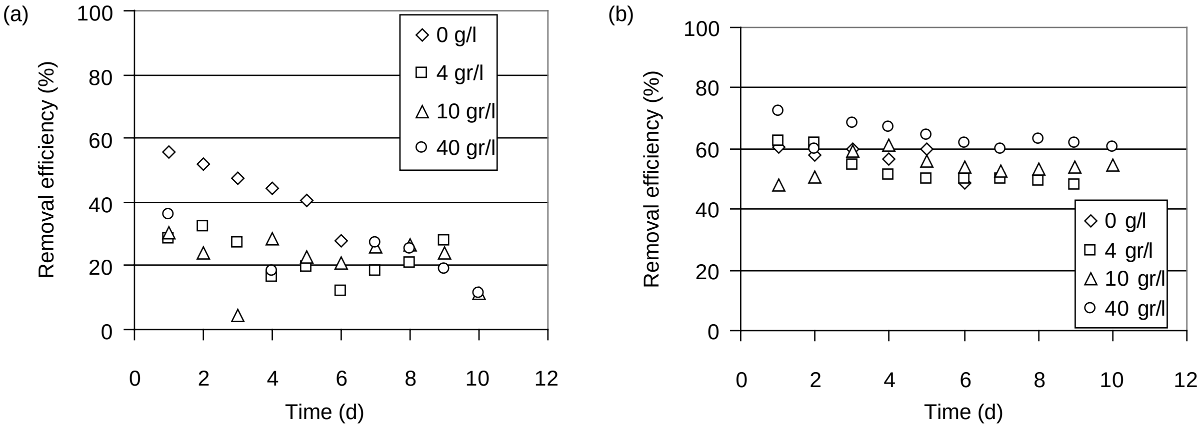

Fig. 7. Effect of modified zeolite concentration on (a) DOC and (b) UV_{254} removal efficiencies.

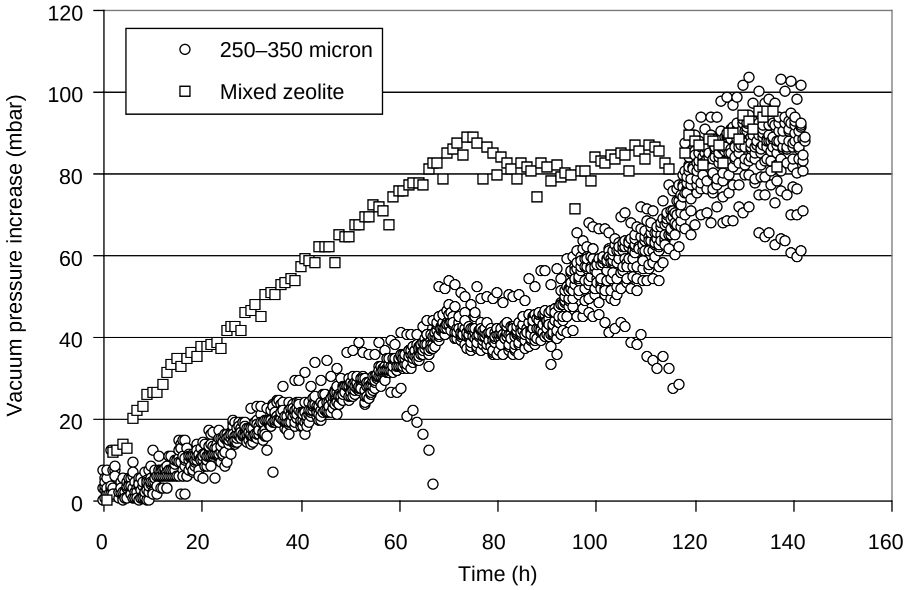

Fig. 8. Effect particle size fractionation on pressure increase.

The pressure increase was slower at lower particle size fractionation due to the higher adsorption capacity. This also affected the DOC and UV_{254} removal efficiencies as shown in (Fig. 9.) Adsorption area of the zeolites increased at low particle size fractionation and this yielded high organic removal efficiencies.

3.2.4. *Effect of organic matter concentration and turbidity*

The effects of organic matter concentrations and turbidity on pressure increase were investigated. 10 g/L of zeolite concentration was used during experiments. A substantial increase in DOC concentration was observed in the reactor with increasing feed organic matter concentration. At the final stage of the experiments the DOC concentration increase in the reactor was about 140%, 189% and 220% for 1.1, 3.1 and 5.4 g/L of DOC concentrations, respectively. The effect of feed concentration on permeate was also remarkable. The DOC concentrations in the permeate increased with feed DOC concentrations. This was due to the limited adsorption capacity of 10 g/L of zeolite at different organic matter concentrations. The effect of various organic matter concentrations on the vacuum pressure increase is illustrated in Fig. 10(a).

Although, nearly the same vacuum pressure increase was observed for all of the organic matter concentrations within 200 h of run time, it was noticed that the acceleration rate in the pressure increase was different. In the first hours of the experiment, the medium-high organic matter concentrations showed a rapid pressure increase whereas the lowest organic matter concentration presented a slower increase. Figure 10(b) indicates that turbidity did not create any outstanding effect on pressure increase. However, the higher pressure increase for 10 and 20 NTU experiments can be assigned to enhanced adsorption of organic matter on clay.

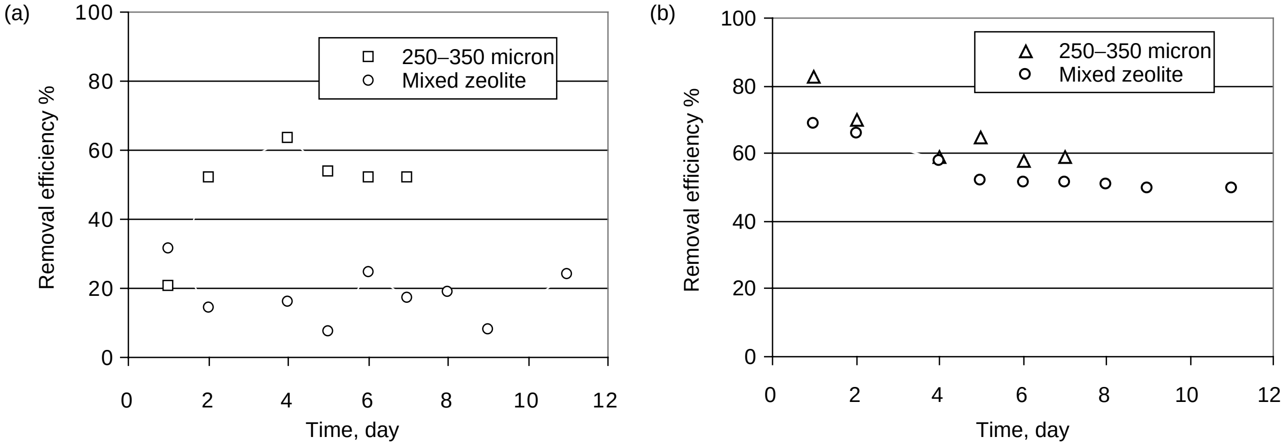

Fig. 9. Effect particle size fractionation on (a) DOC and (b) UV_{254} removal efficiencies.

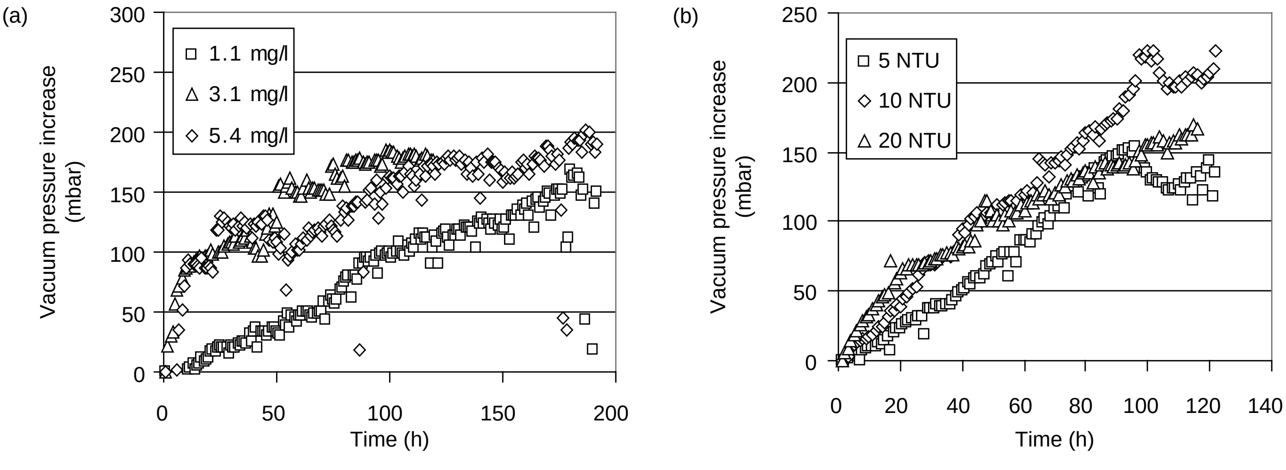

Fig. 10. Effect of (a) organic matter and (b) turbidity concentrations on pressure increase.

3.3. Membrane studies with raw water

The aforementioned experiments were also performed with natural raw water. Furthermore, effect of ferric chloride ($FeCl_3$) on pressure increase and removal efficiencies in presence of 10 g/L zeolite concentration was investigated.

3.3.1. Effect of modified zeolite concentration

Two different modified zeolite concentrations were studied with raw water, namely 10 and 40 g/L. The results obtained without any zeolite addition was compared to those found for 10 and 40 g/L zeolite concentrations. The change in pressure increase as a function of time is shown in Figure 11. The vacuum pressure decreased at high-zeolite concentrations similar to the synthetic water experiments. However, vacuum pressure attained with raw water was almost two-fold high than the synthetic water experiments which can be explained with the complex characteristics of raw water. The concentration of DOC and UV_{254} absorbance increased in the reactor during experimental runs and this affected the removal efficiencies. The DOC concentration increase at 40 g/L of zeolite concentration was low due to the high adsorption capacity. High DOC and UV_{254} removal efficiencies were achieved at 40 g/L compared to the experiments with 10 g/L of zeolite concentration and without any zeolite addition (Fig. 12).

3.3.2. Effect of $FeCl_3$ addition in the presence of modified zeolite

To challenge with the high-pressure increase, flocculation with $FeCl_3$ in the membrane reactor was studied. The

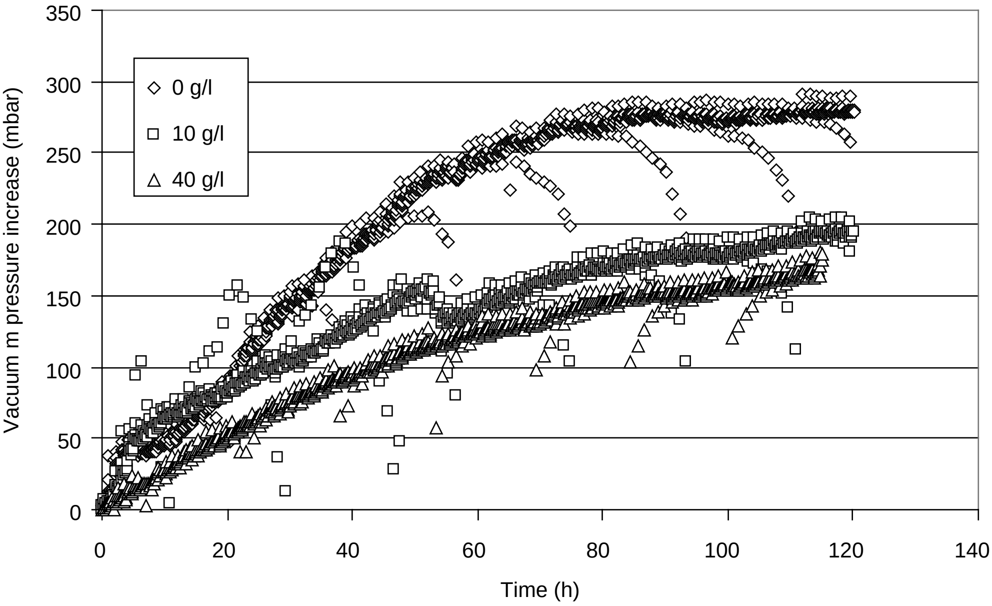

Fig. 11. Effect of modified zeolite concentration on pressure increase for raw water.

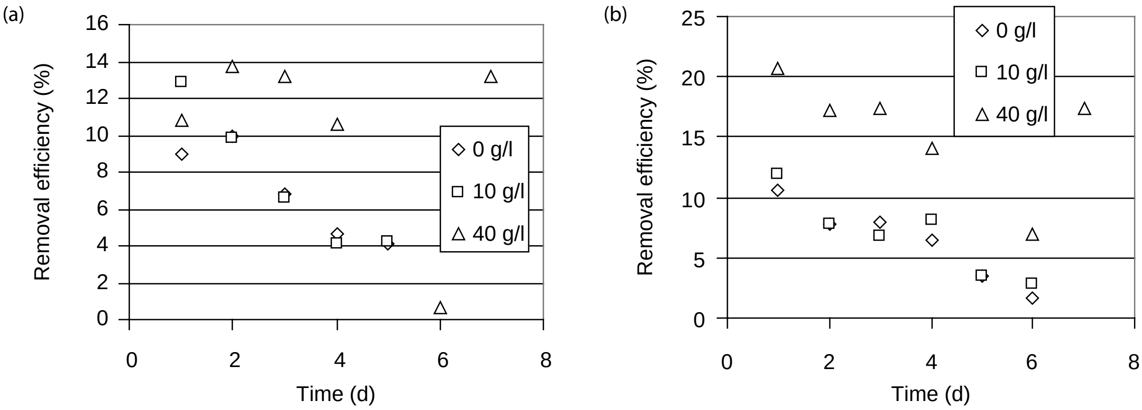

Fig. 12. Effect of zeolite concentration (a) DOC and (b) UV_{254} removal efficiencies for raw water.

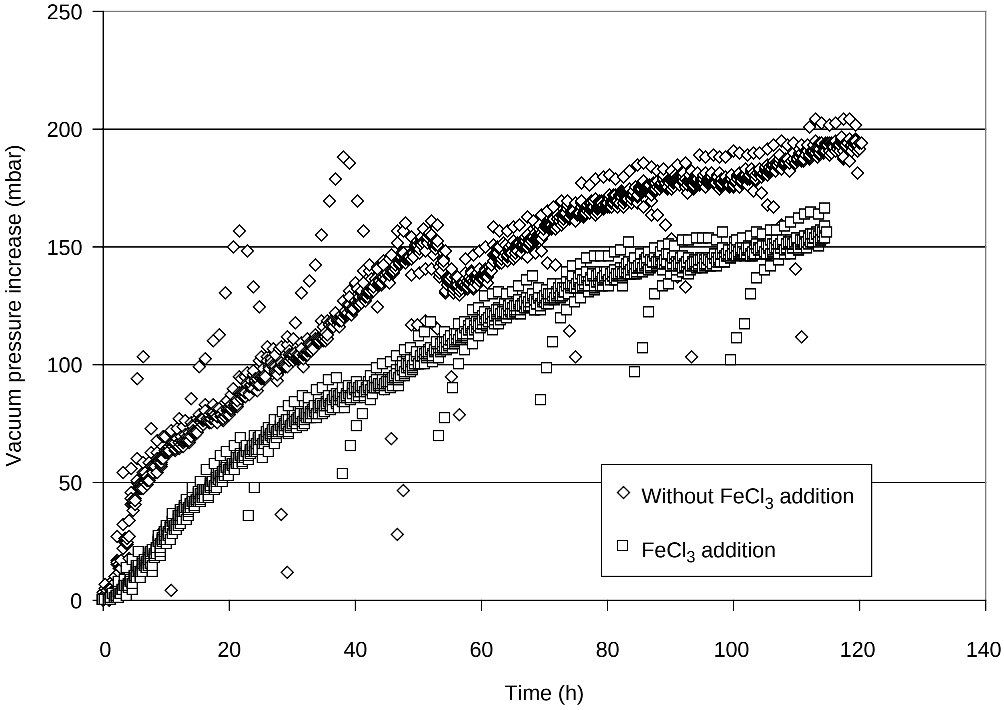

Fig. 13. Effect of $FeCl_3$ addition on pressure increase for raw water.

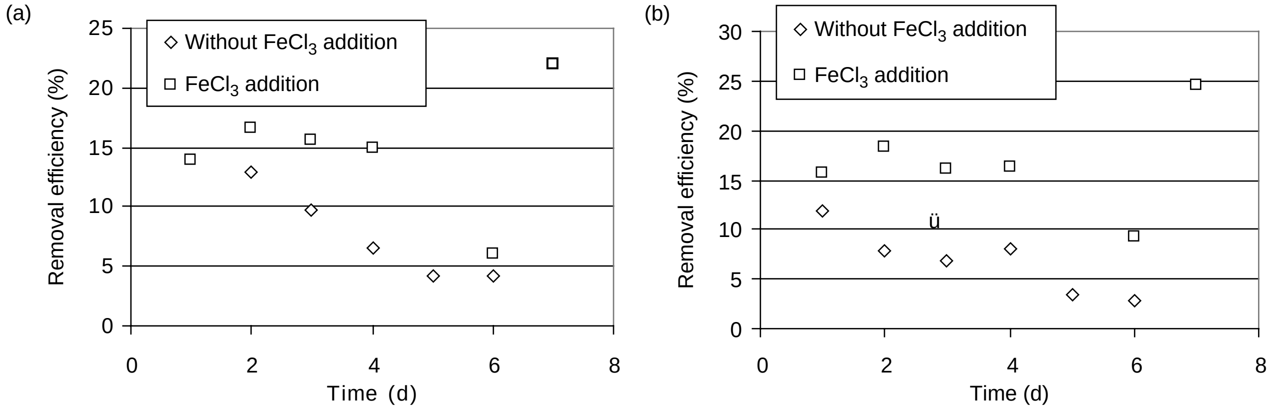

Fig. 14. Effect of $FeCl_3$ addition (a) DOC and (b) UV_{254} removal efficiencies for raw water.

pressure increase in time is given in (Fig. 13). The addition of $FeCl_3$ increased the removal rate of organic materials (Fig. 14) which in turn caused lower pressure increase. The vacuum pressure increase decreased almost 25% in comparison to the experiment without $FeCl_3$ addition. It can be concluded that combination of zeolite and coagulants improves the submerged membrane system performance for raw water by decreasing membrane fouling.

4. Conclusions

This study evaluated the utilization of zeolite on the performance of submerged membrane systems for synthetic and raw water. The main effect of zeolite was observed on vacuum pressure increase although a less pronounced effect on organic matter removal was achieved. The pressure increase was reduced by half for modified zeolite. Moreover, vacuum pressure and organic matter removal efficiencies decreased at high zeolite concentrations. Adsorption capacity of zeolite was enhanced by size fractionation which gave rise to decrease in vacuum pressure increase. Increasing feed organic matter concentrations bring about a substantial increase in DOC concentration in the reactor as well as vacuum pressure increase. Turbidity did not create any outstanding effect on pressure increase. The results of the natural raw water experiments showed that vacuum pressure decreased at high zeolite concentration similar to synthetic water experiments. However, vacuum pressure attained with raw water was almost two-fold high than the synthetic water experiments which can be explained with the complex characteristics of raw water. The addition of $FeCl_3$ increased the removal rate of organics which resulted in low pressure increase. The results of this research suggest that combination of zeolite and coagulant addition can be used as a pretreatment in submerged membrane system.

Acknowledgements

This research was supported by The Scientific and Technological Research Council of Turkey (TÜBİTAK) project number 106Y171. The authors would like to thank to Zena Membranes, Czechoslovakia for supplying the membranes.

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