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Hybrid photocatalysis/submerged microfiltration membrane system for drinking water treatment

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ABSTRACT

In this study, the potential of UV/TiO_2 photocatalytic oxidation method to control of membrane fouling caused by natural organic matter (NOM) was investigated under various conditions in submerged MF membrane system. Effect of TiO_2 concentration, UV irradiation in the absence of TiO_2, TiO_2 in the absence of UV irradiation and combination of UV/TiO_2 photocatalytic oxidation were investigated. Additionally, intermittent and continuous UV application and initial NOM concentration on the pressure increase and rejections were also studied. The results of synthetic and raw water experiments were compared. It was found that TiO_2 concentration is very important parameter by means of permeate pressure increase and removal efficiencies. UV irradiation in the absence of TiO_2 or TiO_2 in the absence of UV irradiation was not effective and combination of UV/TiO_2 photocatalytic oxidation gave better results. Also, intermittent UV application was not as effective as UV/TiO_2. The increase in NOM concentration also increased the pressure increase. Synthetic and raw water experiments were compared and raw water experiments gave higher pressure increase and lower removal efficiencies.

Keywords: Submerged membrane system; UV/TiO_2 photocatalytic oxidation; Microfiltration; NOM removal; Adsorption

1. Introduction

In water treatment, the disinfection by-products (DBPs) were formed from chlorination of water containing natural organic matter. Therefore, control of organic matter plays an important role in treating the surface water [1–3]. The main components of natural organic matter are humic acid (HA) and fulvic acid (FA) in natural waters [1].

Some studies have reported that NOM is difficult parameter to remove by the conventional treatment processes [4]. Therefore, advanced treatment techniques should be used to remove organic matter. Membrane systems are one of the common methods used for drinking water treatment. However, membrane fouling due to natural organic matter is one of the most common problems encountered in microfiltration (MF) and ultrafiltration (UF) applications in water treatment [5]. Permeate quality, flux values and operating costs are adversely affected by NOM which is often represented by dissolved organic matter. This situation limits the usage of membrane systems for drinking water treatment purposes.

Membrane systems are used in two different forms for water treatment. The first one is pressurized system. Two different streams are produced under pressure in this system. While concentrate flow is discharged, permeate is used as treated water. The second system is submerged membrane systems. Treated water is vacuumed from membrane which is in the tank at this system. Recently, many pilot scale experiments have been carried out with submerged membrane system (especially in the United States). In these studies, it has been indicated that submerged membrane systems can

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be adapted to water treatment plants and there will be 30%of decrease for space requirement. Additionally, it has also been remarked that operating of this type system is cheaper than the membrane system which works under pressure [6].

Recently, hybrid systems such as submerged membrane photocatalysis reactor (SMPR), adsorption and membrane photocatalysis reactor were developed to eliminate the effect of NOM fouling [1, 7–9]. Photocatalysis using catalysts such as TiO_2 is gaining interest for removal of organic compounds from water. Fu et al [1] studied the degradation of fulvic acid by nano-structured TiO_2 in a submerged membrane photocatalysis reactor (SMPR). They reported that the permeate flux rate of MF was improved and thus the membrane fouling phenomenon is reduced with the addition of nano-structured TiO_2 catalyst. Chin et al [8] used the low-pressure submerged membrane photoreactor (SMPR) to retain the TiO_2 particles in the system and bisphenol A (BPA) was used as a model pollutant. The SMPR appeared to be very effective and can achieve removal of low-concentration organics (such as BPA) in a compact, low-energy system. Lee et al [7] studied, first the TiO_2 adsorption and then photocatalytic degradation of bisphenol A in the submerged membrane reactor.

As mentioned above, hybrid submerged membrane photocatalysis reactor studies have been carried out recently by different researches. However, these studies were performed at short term and we do not know the long-term effect of UV light on the membranes. Additionally, there is no study on the efficiency of this process for natural raw water. The aim of this study is to investigate the effect of titanium dioxide (TiO_2) photocatalyst under ultraviolet (UV) illumination on membrane fouling during treatment of highly contaminated drinking waters by organic matter with new submerged membrane systems. Different TiO_2 and organic matter concentrations were studied. UV radition and TiO_2 was applied continuously as well as intermittently during experimental runs. The results of synthetic and natural raw water were also compared.

2. Materials and methods

2.1. Membranes

Polypropylene hollow fiber microfiltration (MF) membranes (Zena Membranes, Czechoslovakia) were used in the experiments. The modules operate in an "outside-in" configuration, where a vacuum pressure provided by the pump induces a flow of water from outside to the inside of the membrane fibres. The technical characteristics of the MF membranes are shown in Table 1. The MF membrane was pretreated with ethanol for 30 min followed by rinsing with deionised water to clear its surface [10].

2.2. Feed water

Synthetic and natural raw waters were used in the experiments. Natural raw water was obtained from the intake of Kagithane water treatment plant of Istanbul which comes from Terkos Lake. Synthetic water were 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. Effect of organic matter on membrane fouling was achieved by changing the humic acid content of synthetic water during the experiments. Characterizations of both waters are given in Table 2 [10].

2.3. Hybrid photocatalysis/submerged microfiltration membrane system

The same experimental set-up was used with the previous study [10] except UV/TiO_2 part. The hybrid

Table 1
Technical specifications of MF membrane used in the experiments (Zena Membranes).

Polypropylene membrane characteristic	Nominal Value	Min Value	Max Value	Units
Fiber Inside Diameter	0.240	0.220	0.260	Mm
Fiber Outside Diameter	0.310	0.290	0.320	Mm
Fiber Wall Thickness	0.035	0.030	0.040	Mm
Fiber Pore Size	0.1 × 0.7		0.2 × 0.9	Micron
Fiber Volumetric Porosity	50	43	57	%
Fiber Burst Pressure	6.0	5.0		Bar
Fiber Collapse Pressure	3.5	3.0		Bar
Tap Water Flux	300	250	400	Lmh @ 1.0 bar, 25 C
Strength	2	1.7		N/fiber

Table 2
The characteristics of synthetic and raw waters [10].

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), 1/cm	0.13–0.14	0.10–0.15

photocatalysis/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 a photocatalytic oxidation zone while the second part was used for submerged membrane. Feed water was introduced to the first part and flows through the second part by a bottom flow channel. First part where the UV lamp was placed in was isolated from second part to prevent the membranes from UV light. 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 208-0.3-10000). Permeating and backwashing were performed automatically with automatic control system. Samples were taken at once a day from the permeate line, reactor and feed water tank. Permeate flow rate was kept constant at 20 mL/min and was monitored daily during the experiments. The transmembrane pressure (TMP) was measured by a pressure gauge (Siemens SITRANS P ZD) online placed in the vacuum line in the experiments.

Air was supplied from a porous ceramic plate below the membrane module in order to provide dissolved oxygen for photoreaction. Air flow also fluidizes the TiO$_2$ particles and creates turbulence along the membrane surface which helps to remove foulants and particles that deposit on the outside of the membrane fibre. Experiments continued for one week and MF membranes were cleaned between each experiment. Different chemicals were used during chemical cleaning procedure of each membrane. The MF membrane module was cleaned according to the following steps [11]: (i) surface cleaning with deionized water (ii) acidic wash in 2% HCl solution for 2 h (iii) basic wash with 1 N NaOH solution for overnight (iv) final cleaning in 0.4%

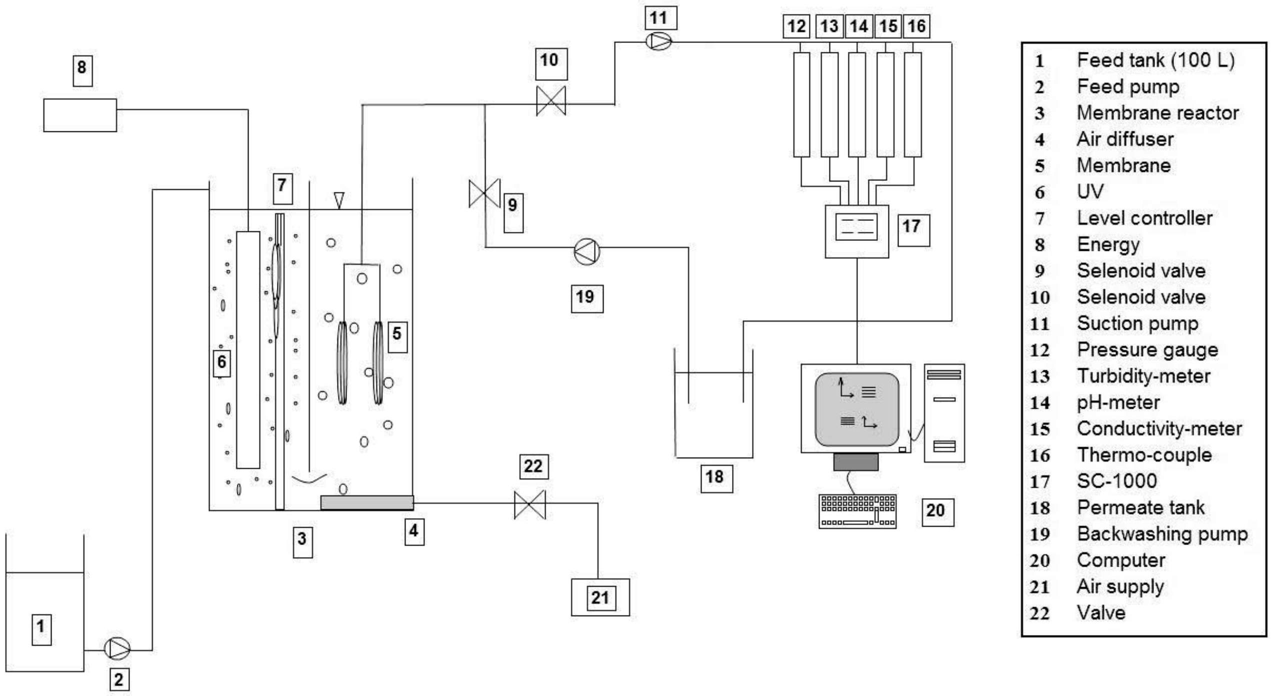

Fig. 1. A schematic diagram of the hybrid photocatalysis/submerged membrane experimental set-up.

NaOCl for 2 h. Membranes were rinsed with deionized water after every step and prior to all experiments.

The UV source was a 11 W immersed low pressure mercury lamp with a major emission at 254 nm. The lamp was housed in a 2.1 cm diameter quartz tube located at the first compartment of the hybrid photocatalysis/submerged membrane reactor. The application time of UV irradiation was adjusted with timer. TiO_2 catalyst used in the study was AEROXIDE P25 (Degussa, Frankfurt, Germany). It is stated that the average particle size was 21 nm by the manufacturer.

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 [10]. All analytical methods were performed according to the standard methods [12]. 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}).

3. Results and discussion

3.1. MF membrane performance – synthetic raw water

Photocatalytic oxidation experiments were performed in a MF submerged membrane system as described above for the evaluation of TiO_2/UV pretreatment for NOM removal. At the first stage of the pretreatment experiments, photocatalytic oxidation with different amounts of TiO_2 concentration was studied. After that only UV photoxidation, only TiO_2 adsorption and combination of UV/TiO_2 were studied to evaluate the photodegradation under UV irradiation, adsorption on TiO_2 surface and both. Additionally, different durations of UV light were also investigated. Finally, the impacts of initial NOM concentration were also evaluated. Experiments were continued for at least 7 days.

3.1.1. Effect of TiO_2 concentration

The photocatalytic efficiency of TiO_2 depends on its concentration [1, 13]. TiO_2 nanoparticles that are one of the most widely used photocatalysts produce electrons and holes by ultraviolet irradiation, which makes it possible to form the hydroxyl radicals and superoxides that have a strong oxidizing power. Those radicals contribute to the mineralization of NOM, the decolorizaion of humic acids, and the destruction of toxins [14]. As TiO_2 dosage increases, the rate of oxidation increases due to increase of free OH radicals. However, high TiO_2 concentrations decrease the effect of UV radiation due to increase in turbidity which in turn affects the reaction rate negatively [13]. It has been reported that TiO_2 concentration higher than 0.3 g/L, increases the turbidity and decreases the effect of UV radiation. Therefore experiments were conducted with three different TiO_2 concentrations ranging from 0.10 to 0.50 g/L. UV radiation was applied continuously during the experiments. Vacuum pressure increase was given in Fig. 2. Additionally, photooxidation of humic acid in the absence of TiO_2 catalyst is included in

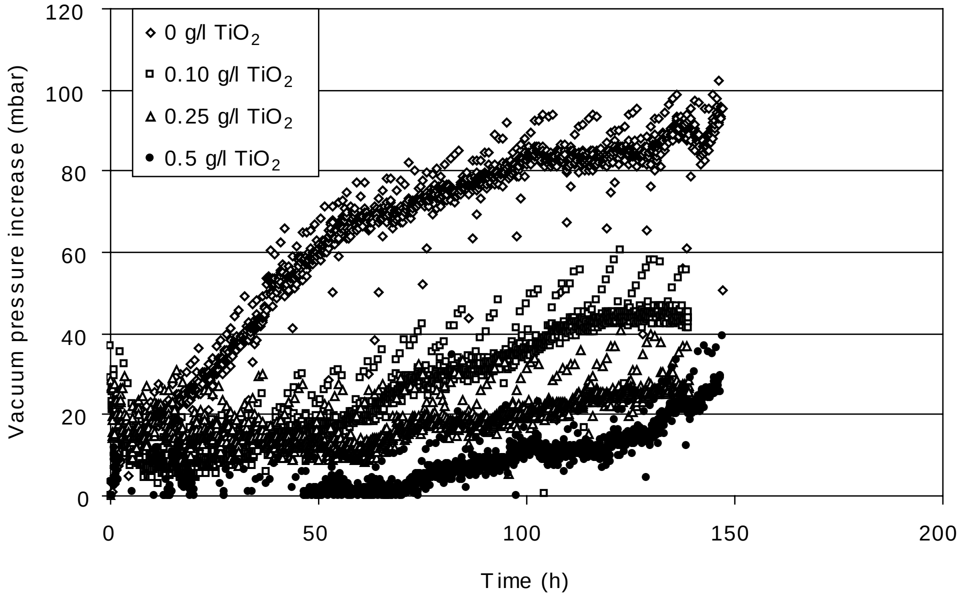

Fig. 2. Vacuum pressure increase at different TiO_2 concentrations.

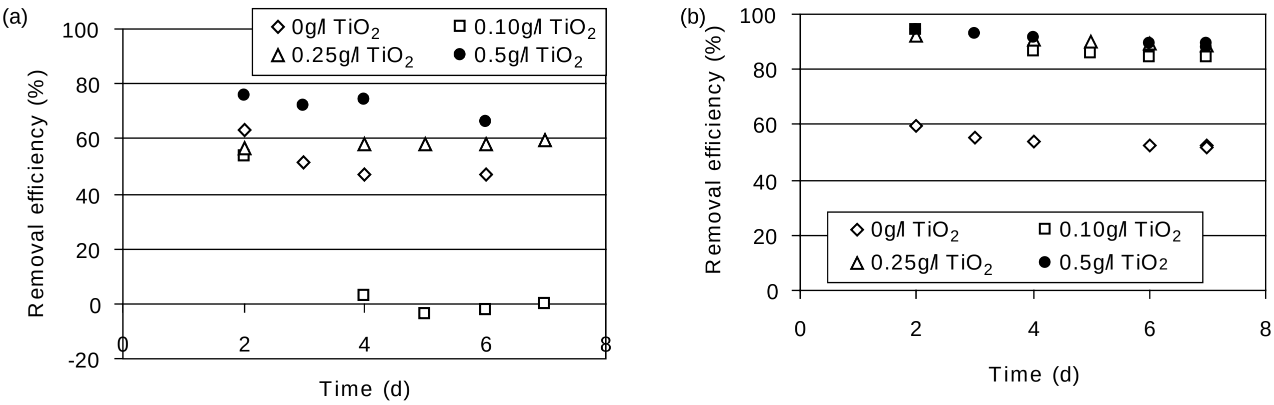

Fig. 3. Removal efficiencies of (a) DOC and (b) UV_{254} at different TiO_2 concentrations.

the same figure. Calculated amounts of TiO_2 powder for desired concentrations were added at once at the beginning of the experiments. Pressure increase decreased with increasing TiO_2 concentrations due to the increase in the adsorption capacity of TiO_2 and reached to plateau after 3 days. Therefore, it was decided to use 0.5 g/L TiO_2 dosage for the following experiments.

Fig. 3 shows the DOC and UV_{254} removals as a function of time using different doses of TiO_2. As shown in these figures, DOC and UV_{254} removals were high at high TiO_2 concentrations. Approximately, 70% of DOC and 90% of UV_{254} removals were achieved at 0.5 g/L of TiO_2 and permeate DOC and UV_{254} concentrations approached a plateau after 7 days. There were small differences on UV_{254} removals with TiO_2 concentration. However, DOC removals were significant at high TiO_2 concentrations. After the addition of TiO_2 at the beginning of the experiments, DOC and UV_{254} concentrations in the reactor decreased to below of feed concentrations due to the rapid adsorption of organics on TiO_2. Depending to the TiO_2 concentration in the reactor, DOC and UV_{254} concentrations in the reactor increased and this affected the removal efficiencies and also pressure increase in the permeate line. Rapid decrease at the beginning of experiments and the following increase in DOC and UV_{254} can be due to the adsorption and the release of oxidized intermediate products, respectively [13].

3.1.2. Comparison of UV irradiation, TiO_2 adsorption and UV/TiO_2

Vacuum pressure increase with time is shown in Fig. 4 for different runs containing UV irradiation in the absence of TiO_2 catalyst, TiO_2 adsorption in the absence of UV irradiation and UV irradiation and TiO_2 adsorption together (UV/TiO_2).

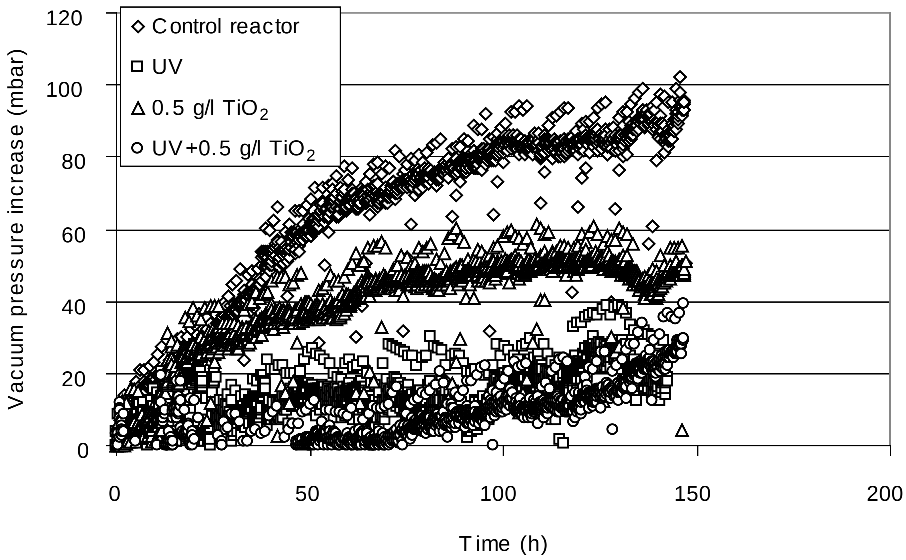

Fig. 4. Vacuum pressure increase for UV irradiation, TiO_2 adsorption and UV/TiO_2.

UV/TiO_2 combination showed better performance by means of pressure increase at the TiO_2 concentration of 0.5 g/L. Additionally, pressure increase with UV irradiation in the absence of TiO_2 was low due to the degradation of organics at low intensity. However, DOC removal efficiency was also low for this experiment due to low molecular weight organic matter after degradation (Fig. 5). There was a similar result with Le-Clech et al [15] while Le-Clech et al [15] obtained high DOC removals at high intensity. UV_{254} removals were high in contrast to DOC removals. As mentioned before, UV irradiation changes the MW distribution of NOM and after changes hydrophopic characteristics of NOM increased and adsorbed to MF membrane surface. This increased the UV_{254} removal efficiency. Pressure increase for the TiO_2 adsorption in the absence of UV irradiation was higher than all experiments even for the experiment performed without UV/TiO_2. This may be due to the compact cake layer of TiO_2 on MF membrane surface which resulted high pressure increase. Although the pressure increase was high for MF membrane, better performances were obtained for DOC and UV_{254} removal efficiencies due to the adsorption on the membrane.

3.1.3. Continuous and intermittent application of UVirradiation

In this set of experiments, the effects of UV irradiation time on membrane fouling as well as DOC and UV_{254} absorbance removal efficiencies were investigated. Intermittent practices were performed by use of a mechanical timer in two ways, 15 min. on –15 min. off, 15 min. on –30 min. off. Fig. 6 illustrates the pressure increase for these different UV durations. As it can be seen from the results, continuous UV application indicated the most favored scheme regarding the membrane fouling. Characteristics of organic matter

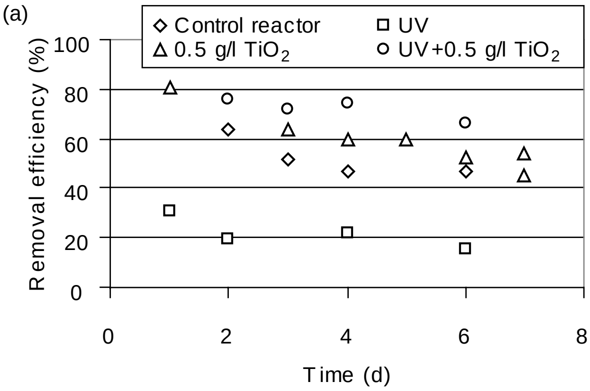

Fig. 5. Removal efficiencies of (a) DOC and (b) UV_{254} for UV irradiation, TiO_2 adsorption and UV/TiO_2.

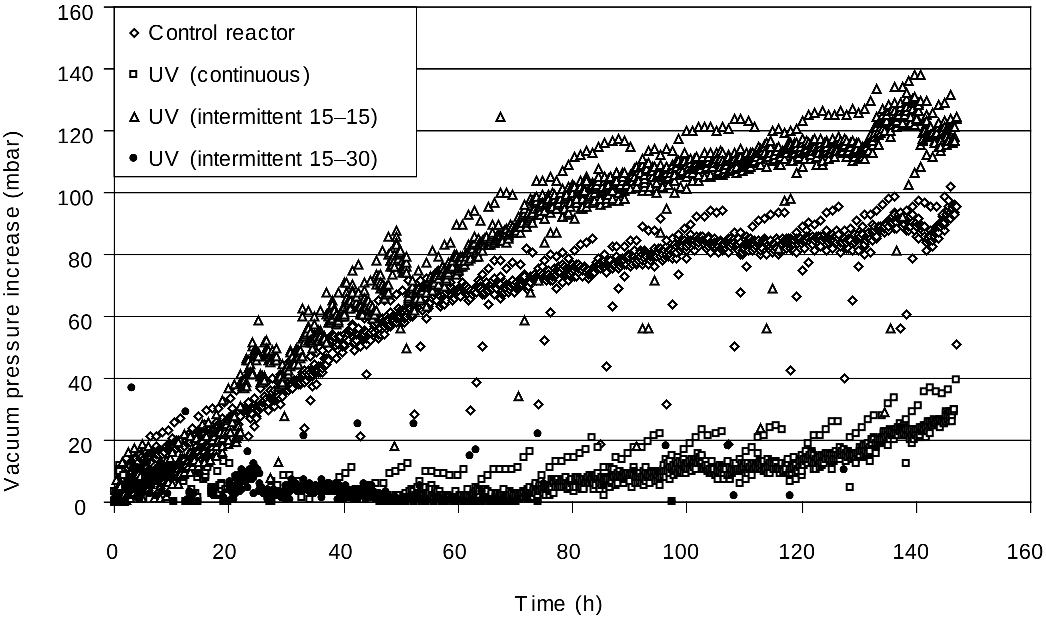

Fig. 6. Vacuum pressure increase at Continuous/Intermittent application of UV irradiation.

change during UV irradiation and small molecular weight organics are generated. As this process is proceeded, the NOM molecular weight distribution continued shifting towards lower molecular weight. Studies showed that larger NOM molecules cause more serious membrane fouling [13]. During continuous application of UV, homogenous organic matter characteristics were applied to membranes and low molecular weight NOM were generated and this caused a slight increase in pressure. However, organic matter characteristics were not homogenous with intermittent application of UV. During UV application, organic matter was degraded and small organics were created and adsorbed to TiO_2. This caused low pressure increase. However, changes of organic matter characteristics stopped with UV off and high molecular weight organics caused high pressure increase. That is why intermittent UV application did not show better performance. During the period when UV light was not applied a higher pressure increase was observed.

DOC of synthetically prepared raw water was around 1.5 mg/L. It was found that the permeate values for continuous UV application, 15 min. on –15 min. off intermittent application and 15 min. on –30 min. off intermittent application were 0.4, 0.5 and 0.7 mg/L respectively (Fig. 7). Although the permeate concentrations of both continuous and intermittent (15 min. on –15 min. off) runs were not far from each other, continuous UV application was thought to be the most appropriate case in terms of pressure increase.

3.1.4. Effect of initial NOM concentration

Three different initial NOM concentrations (1.5, 3 and 5 mg DOC/L) were studied under continuous UV irradiation and 0.5 g/L TiO_2 concentration. Figure 8

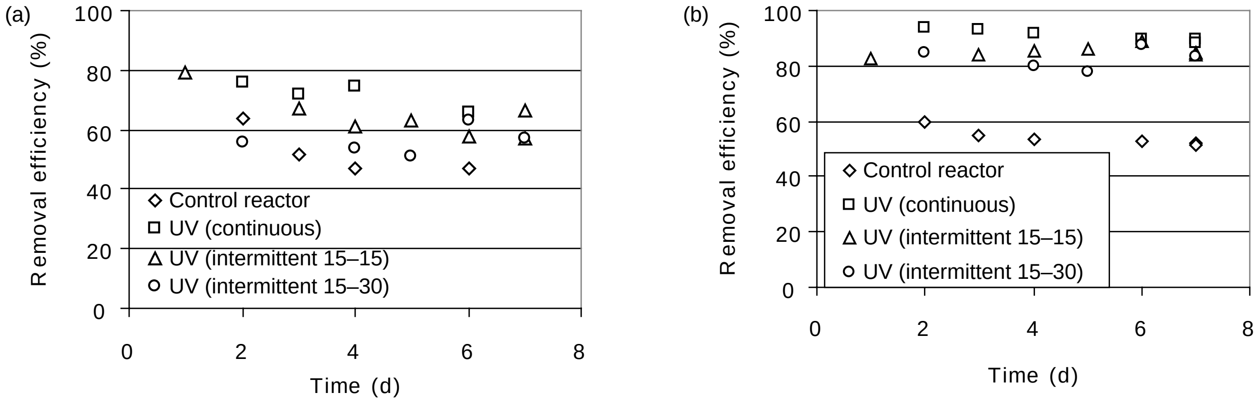

Fig. 7. Removal efficiencies of (a) DOC and (b) UV_{254} for at Continuous/Intermittent application of UV irradiation.

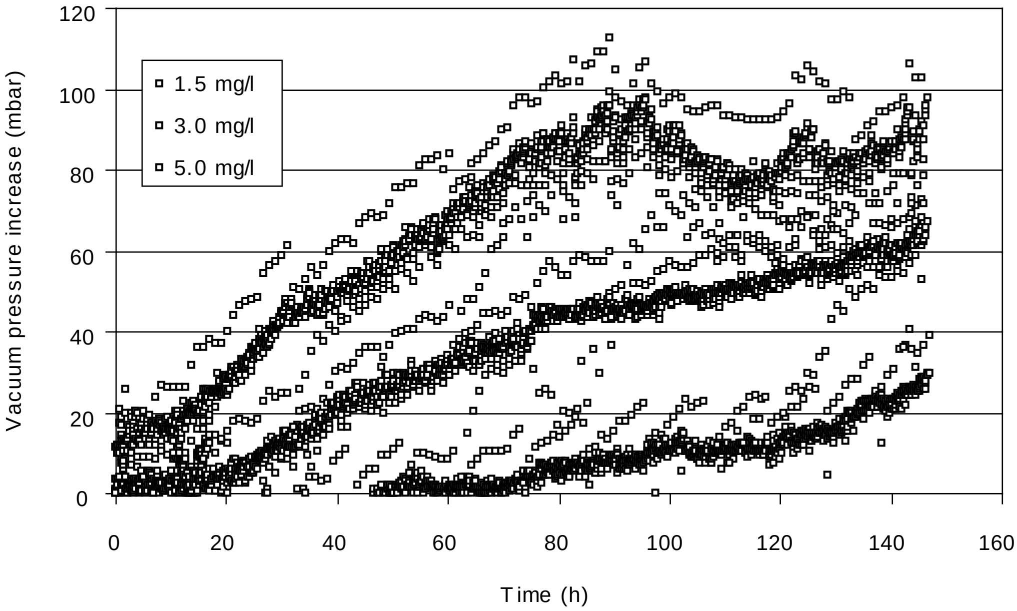

Fig. 8. Vacuum pressure increase at different initial NOM concentration.

shows the pressure increase as a function of time. The lowest pressure increase was observed with 1.5 mg DOC/L NOM concentration as expected. This was due to the formation of a thinner cake layer on the membrane surface at low organic matter content. The behavior of the same amount of UV irradiation and TiO_2 concentration at different organic matter contents were different. While low organic matter concentrations caused the lowest pressure increase, DOC and UV_{254} absorbance removal efficiencies decreased with increasing initial NOM concentrations. DOC removal efficiencies were around 70% for 1.5 and 3 mg/L NOM concentrations whereas approximately 65% DOC removal efficiency was observed for 5 mg/L NOM as shown in Fig. 9. UV_{254} absorbance removal efficiencies were about 90, 85 and 80% for 1.5, 3 and 5 mg/L NOM concentrations, respectively. Similar results were obtained in the literature [13]. The increase of the reaction rate constant at low DOC concentrations was attributed to larger contribution of TiO_2 adsorption to overall NOM removal [13].

3.2. Experiments with natural raw water

Two experiments have been performed to compare the photochatalytic oxidation effect on natural water. The experiments were performed with and without UV/TiO_2 pretreatment before submerged MF membrane. UV irradiation was applied continuously while 0.5 g/L of TiO_2 catalyst was used at the same time. Figure 10 shows the pressure increase as a function of time for raw water. As expected, UV/TiO_2 pretreatment showed better performance by means of permeate vacuum pressure increase.

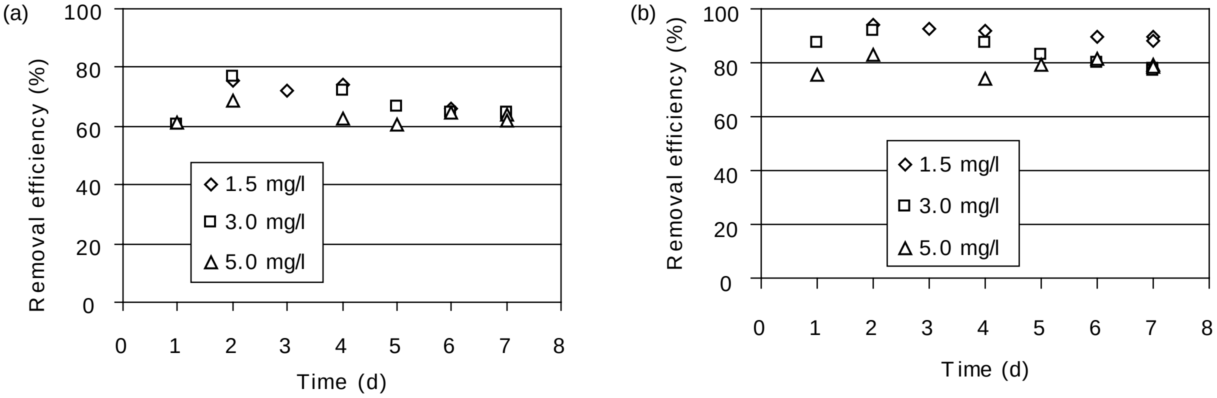

Fig. 9. Removal efficiencies of (a) DOC and (b) UV_{254} for at different initial NOM concentration.

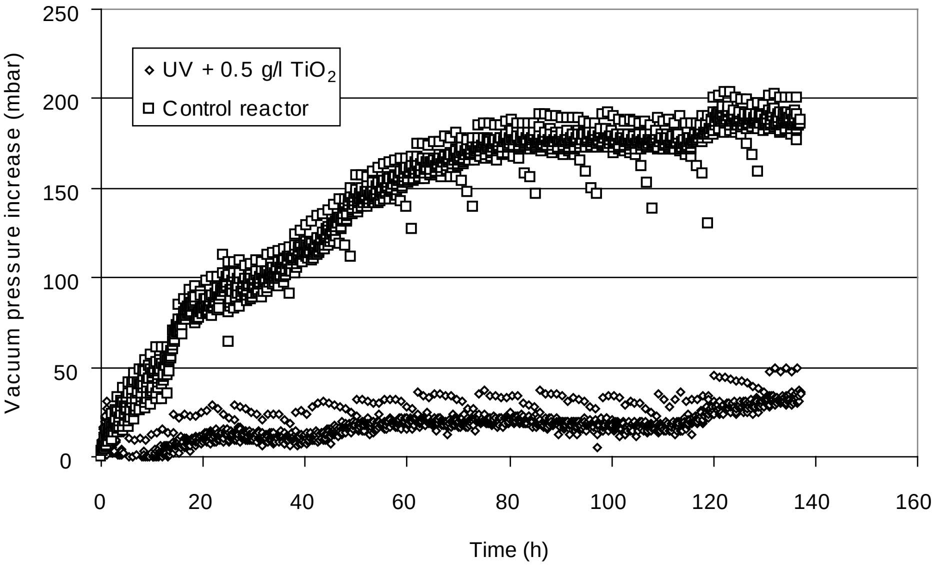

Fig. 10. Vacuum pressure increase for raw water.

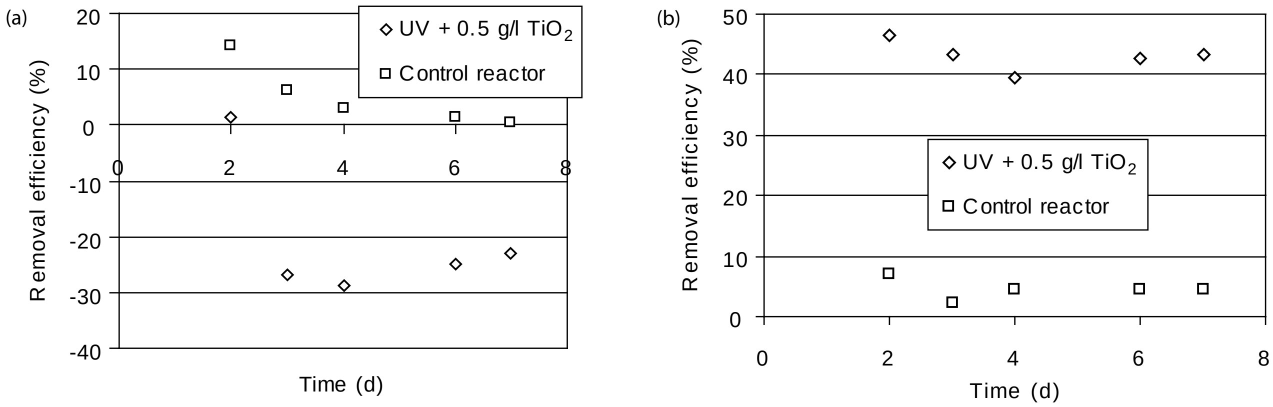

Fig. 11. Removal efficiencies of (a) DOC and (b) UV_{254} for raw water.

As explained in the experiments for synthetic water, high molecular weight organics caused high pressure increase without UV/TiO_2 pretreatment. Pressure increase was higher for raw water compared to synthetic water. This can be explained with the characteristics of organics in raw water. Only humic acid was used during synthetic experiments. However, there were different types of organics in raw water which might have caused more pressure increase in the permeate line. It can be also concluded that pressure increase reached to a plateau after 3 days similar to synthetic experiments. Removal efficiencies for DOC and UV_{254} are shown in Fig. 11. Photochatalytic degradation of organics with UV/TiO_2 increased the UV_{254} removal efficiency. However, DOC removal efficiency decreased and negative efficiencies were obtained which may be due to the excessive concentration increase in the reactor after UV irradiation.

4. Conclusions

It is shown in this research that photochatalytic oxidation with UV/TiO_2 can be a promising method to decrease the pressure increase and to obtain high quality permeate. Pressure increase decreased with increasing TiO_2 concentrations due to the increase in the adsorption capacity of TiO_2. Additionally, DOC and UV_{254} removals were high at high TiO_2 concentrations. A sudden decrease in DOC concentration was observed after addition of TiO_2 at the beginning of the experiment. This also affected the membrane permeate quality parameters. However, continuous application of TiO_2 did not give better results than sudden application. Pretreatment with UV irradiation in the absence of TiO_2 or TiO_2 adsorption in the absence of UV irradiation do not show better performance than UV/TiO_2 pretreatment. Although different UV durations for intermittent applications do not have a significant effect in terms of pressure increase and permeate water quality, it is clearly seen that continuous UV radiation gave the lowest pressure increase. The behavior of the same amount of UV irradiation and TiO_2 concentration at different organic matter contents were different. Low organic matter concentrations caused the lowest pressure increase. Pressure increase is higher for raw water compared to synthetic water which may be due to the complex nature of raw water, thus the pressure increase in the permeate line is higher. Additionally, pressure increase reaches to a plateau after 3 days in synthetic and raw water experiments.

Acknowledgements

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Reactor for Potable Water Treatment Hybrid Photocatalysis/ Submerged Microfiltration Membrane System for Drinking Water Treatment, Desalination and Water Treatment (*Accepted*).

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