Journal of Photochemistry and Photobiology A: Chemistry 216 (2010) 215–220

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Photocatalytic degradation of seawater organic matter using a submerged membrane reactor

Min-Jin Kim, Kwang-Ho Choo*, Hak-Soon Park

Department of Environmental Engineering, Kyungpook National University, 1370 Sankyeok-Dong, Buk-Gu, Daegu 702-701, Republic of Korea

ARTICLE INFO

Article history:
Available online 19 August 2010

Keywords:
Photocatalysis
Membrane reactor
Fouling
Desalination
Seawater
Chloride

ABSTRACT

A TiO_2 based advanced oxidation process is expected to degrade organic matter in seawater and thereby fouling would be mitigated in the membrane reactor. The effects of seawater sources on photocatalytic microfiltration treatment were investigated with respect to the removal of particulate and organic matter, as well as the control of membrane permeability. The TiO_2 mediated photocatalysis of seawater organic matter (SOM) was compared with that of natural organic matter (NOM) present in fresh water. The photocatalytic degradation of SOM was marginal, but it was enhanced significantly when sea salts were removed by electrodialysis. It revealed that the SOM photocatalysis was governed not by the molecular structure of SOM itself, but by the presence of ionic species in the seawater. To identify the ions responsible for the considerably reduced SOM photocatalysis, some major ionic species selected were dosed to desalted seawater. It was thus found that chloride ions were serving as a scavenger of photoinduced strong oxidizing radicals (e.g., hydroxyl or superoxide radicals), although they may contribute to the partial oxidization and chlorination of SOM molecules. The alteration of SOM molecular structures before and after the photocatalysis was confirmed by means of fluorescence spectroscopy. The X-ray fluorescence of TiO_2 surfaces showed that no significant adhesion of chloride ions onto the TiO_2 surface occurred during SOM photocatalysis.

1. Introduction

A sustainable water supply is one of the most important global issues, due to water scarcity and contamination concerns [1]. There are several alternative water resources available, such as wastewater reuse and seawater desalination, which have been more affordable and viable, particularly in arid regions across the world. Seawater reverse osmosis (SWRO) membrane filtration is considered as a promising technology for seawater desalination, but membrane fouling, which was caused by organic matter deposition as well as inorganic precipitation and microbial growth [2–5], was the major hurdle for the extensive use of SWRO processes [6,7].

There are various methods available to control reverse osmosis (RO) fouling. The addition of chelating agents can prevent the precipitation of inorganic salts. Dosing disinfectants (e.g., Cl_2) inhibits microbial growth (i.e., biofouling) on the membrane surface, although chlorine may damage the polyamide RO membranes significantly and thereby should be degraded before contact with the RO membrane. Natural organic matter (NOM) in seawater, which may deposit on the membrane surface and thus stimulate biofouling, should be removed in advance. NOM fouling is also the main issue in membrane processes for drinking water treatment [8,9]. In addition, NOM molecules including humic and fulvic acids generate disinfection byproducts (DBPs) during chlorination in the water treatment. Thus, activated carbon adsorbents (e.g., powdered activated carbon) and inorganic coagulants (e.g., alum or $FeCl_3$) have been synergistically used to sequester NOM that is known to be the potential membrane foulant as well as DBP precursors [10–12].

Recently, advanced oxidation processes (AOPs) have been applied for the abatement and mineralization of NOM as well as hazardous and toxic pollutants in water [13–15]. TiO_2 mediated photocatalysis was able to decompose toxins and NOM present in surface water and wastewater [16–19]. Especially, NOM fouling was mitigated substantially using a hybridized photocatalysis/membrane reactor, due to the adsorption and degradation of NOM onto TiO_2 particles, although the photocatalyzed NOM was not degraded as well as the original NOM. Nevertheless, there have been few reports on the photocatalysis of seawater organic matter (SOM), where the properties of organic matter and background water constituents are significantly different from those of surface water or wastewater.

Therefore, the focus of this study was primarily to investigate the removal of SOM using a TiO_2 mediated photocatalytic membrane reactor (PMR), prior to the RO filtration, while comparing it with the degradation efficiency of NOM in surface water (e.g., lake water). Additional foci were given to evaluate any influence

---

* Corresponding author. Tel.: +82 53 950 7585; fax: +82 53 950 6579.
E-mail address: chookh@knu.ac.kr (K.-H. Choo).

1010-6030/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2010.08.011

Table 1
Qualities of seawater sources used.

Parameter	Pohang seawater	Masan seawater
pH	8.1	8.2
Conductivity (mS/cm)	46.2	50.9
TOC (mg/L)	0.198	2.03
Salinity (‰)	29.2	33.1
UV_{254} (cm^{-1})	0.019	0.035
Na^+ (mg/L)	6680	14,740
Ca^{2+} (mg/L)	308	550
K^+ (mg/L)	301	451
Mg^{2+} (mg/L)	1010	2085
B (mg/L)	3.26	4.39
Silt density index (SDI_5)	2.73	>20

and interference of sea salts on the photocatalysis of SOM and to identify the substances that may act as an inhibitor in SOM photocatalysis. Various salts, such as $NaHCO_3$, NaCl, KCl, $NaNO_3$, KNO_3, and Na_2SO_4, were added to desalted seawater in order to assess the effect of each individual salt on SOM photocatalysis.

2. Materials and methods

2.1. Seawater sources

The two seawater sources tested in this study were collected in the eastern (City of Pohang) and southern (City of Masan) coasts of the Korea peninsula. The seawater samples were shipped to the laboratory and stored in a refrigerator at 4 °C. The water samples were equilibrated at room temperature for a couple of hours before use. The key characteristics of both seawater samples are given in Table 1. For the comparison of photocatalytic NOM degradation, Mooncheon Lake (Daegu, Korea) water was also used, after filtering through a 0.45-μm membrane filter to remove colloidal particles in the water. The key characteristics of the Mooncheon Lake water were as follows: pH 7.98; UV_{254}, 0.072 cm^{-1}; TOC, 4.91 mg/L; conductivity, 0.2 mS/cm. Desalted seawater samples with a conductivity of 25 and 1.0 mS/cm were also prepared by the electrodialysis of Masan seawater. $NaHCO_3$ was added to the desalted 1.0-mS/cm seawater to make up the alkalinity, while five different salts, such as NaCl, KCl, $NaNO_3$, KNO_3, and Na_2SO_4, were added to make up the lost conductivity when needed.

2.2. PMR operation

The laboratory-scale PMR used in this work, which consists of suspended photocatalysts and 0.4-μm submerged hollow fiber membranes (KMS, Korea), is shown in Fig. 1. An 8-W black light blue (BLB) UV lamp (TL8W/08, Hansung, Korea) with a maximum wavelength of 360 nm was placed in the center of the reactor for the activation of the TiO_2 particles. The reactor with a working volume of 800 mL was designed to operate either in batch or in continuous modes. 1.0 g/L of TiO_2 particles (P25, Degussa) was added to the reactor filled with seawater and the mixture was well agitated at 300 rpm during the PMR experiments. The key water characteristics, such as total organic carbon (TOC) concentration and UV absorbance at 254 nm, were monitored to evaluate the SOM degradation efficiency during the TiO_2 mediated PMR treatment. Submerged membrane filtration was performed at a constant flux mode of 50 L/m^2-h and the variation of transmembrane pressure was monitored to check the fouling behavior.

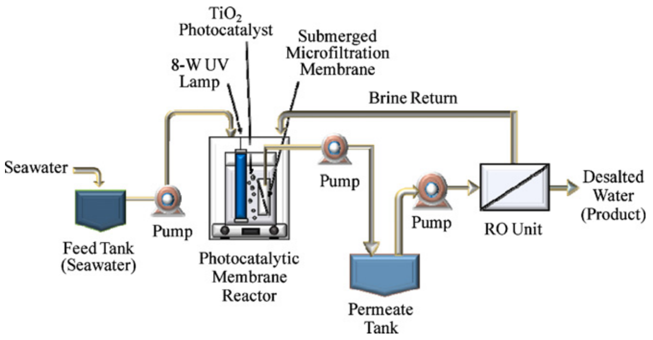

Fig. 1. A depiction of the laboratory-scale photocatalytic membrane reactor followed by RO for seawater desalination.

2.3. Analytical methods

To characterize the quality of feed and treated waters, such as metals and organic contents, an inductively coupled plasma atomic emission spectrometer (Optima 2100 DV, Perkin Elmer, USA) and a TOC analyzer (TOC-V CPH, Shimadzu, Japan) were used. A Hach 4200U UV/VIS spectrophotometer was used to determine the UV absorbance at 254 nm. The solution pH was measured using a calibrated portable pH meter (pH 330i, WTW, Germany) and the conductivity was measured by a conductivity meter (cond 340i, WTW, Germany). Fluorescence measurements were taken on a high sensitivity fluorescence spectrometer (FP6300, Jasco, Japan) at excitation and emission slit widths of 5 nm. Fluorescence spectra were obtained by measuring the emission spectra in the range from 290 nm to 700 nm at the excitation wavelength of 270 nm, while filtering the Raman peaks near 550 nm. Fourier transform infrared (FTIR) spectra were recorded on an FTIR spectrometer (IR Presige-21, Shimadzu, Japan). An X-ray fluorescence (XRF) spectrometer (PW2400, Philips, Netherlands) was used to characterize the photocatalyst surface.

3. Results and discussion

3.1. Particulate matter removal and fouling control by PMR

To begin with, the removal of particulate matter from the two seawater sources during PMR treatment was examined and is displayed in Fig. 2. The turbidity levels of the membrane permeate decreased immediately to approximately 0.15 and 0.6 NTU for both the Pohang and Masan seawater sources, respectively, when the PMR started operating, and then were maintained at a nearly constant value during the remainder (240 min) of the PMR operation. In addition, the transmembrane pressure of the PMR remained very stable at 6.5 and 4.0 kPa (Fig. 3). These results showed that the PMR

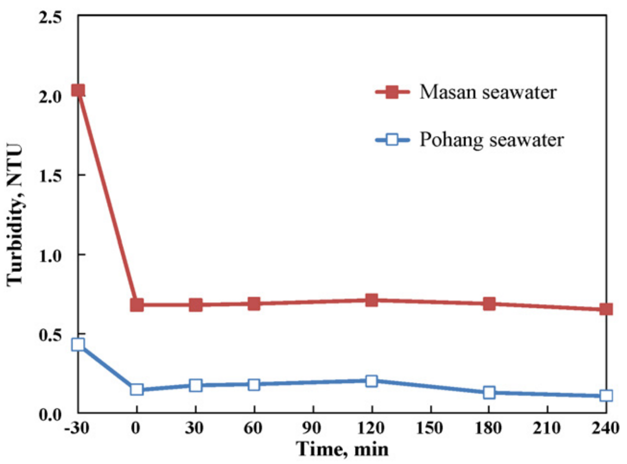

Fig. 2. The variation of permeate turbidity with time in PMR. Photocatalysis started at the time of 0 min, while only mixing was done during the time between −30 and 0 min.

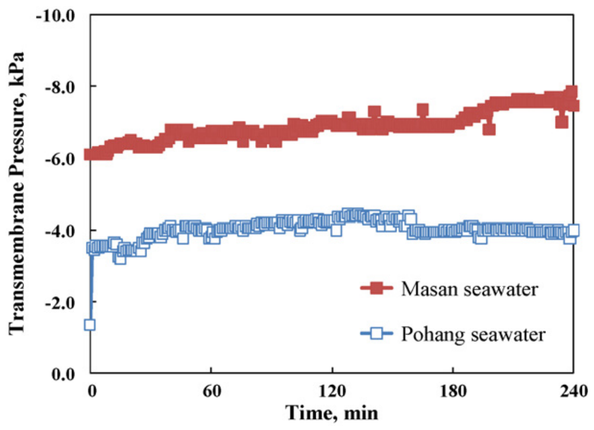

Fig. 3. The variation of membrane permeability using seawater in PMR.

treatment was able to remove particles from seawater effectively without any significant sign of membrane fouling.

3.2. Evaluation of the photocatalysis of NOM and SOM

The SOM degradation efficiency was monitored during the TiO_2 mediated PMR treatment of Pohang and Masan seawater. Fig. 4 shows the variation of TOC concentration and UV_{254} absorbance of permeate with time in the PMR treatment. Unexpectedly, the TOC level remained unchanged for both seawaters during the 240-min reaction, although approximately 60% of the UV_{254} absorbance of Masan seawater was removed. Since the UV_{254} absorbance is a surrogate parameter to assess the content of aromatic moieties in NOM molecules, the above results revealed that SOM was partially oxidized by photocatalysis, but not mineralized at all. Regarding the removal of NOM in the surface water, a control test with Mooncheon Lake water was conducted with the same PMR under the same hydraulic and photocatalytic operating conditions, and the results are shown in Fig. 5. Substantial removals (>80%) of TOC and UV_{254} absorbance were achieved within 240 min of reaction time, which was considerably different from the results of Fig. 4.

Thus, the following two hypotheses were raised to answer why SOM was not photocatalytically mineralized: (1) the chemical structure of SOM molecules is different from fresh water NOM being less amenable to photocatalysis; (2) background seawater constituents, such as sea salts, may interfere with SOM photocatalysis. Detailed investigations on which factor was responsible for the inhibited SOM photocatalysis were conducted and discussed in the subsequent section.

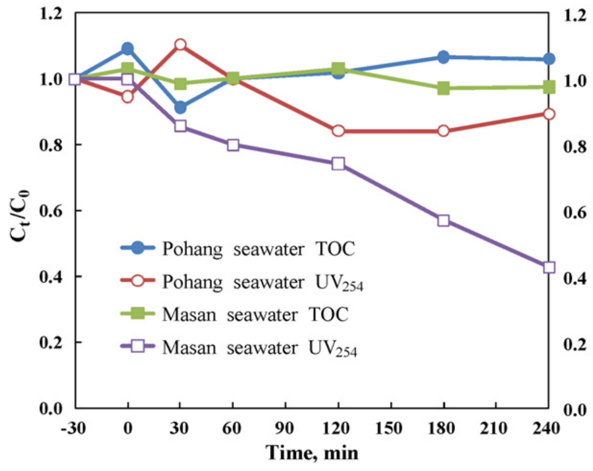

Fig. 4. The variation of TOC concentration and UV_{254} absorbance with reaction time in PMR treatment of seawater. C_0 and C_t represent the TOC concentration at the time of 0 min and t, respectively, while A_0 and A_t represent the UV absorbance at the time 0 min and t, respectively.

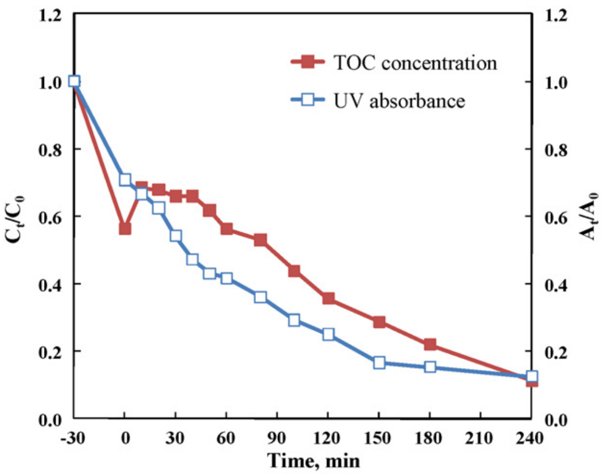

Fig. 5. Photocatalytic degradation of NOM from Mooncheon Lake water.

3.3. Effects of sea salts and alkalinity on SOM photocatalysis

To evaluate the effect of sea salts on the photocatalysis of SOM during PMR treatment, seawater was first desalted using an electrodialysis system while maintaining the organic matter content in the same level. Fig. 6 shows the variation of TOC and UV_{254} absorbance with time after the conductivity level of Masan seawater was reduced to 1.0 mS/cm by electrodialysis. It was found that PMR was able to degrade a substantial amount of SOM at lower conductivities, i.e., approximately 80% of TOC was removed within 240 min when desalted. The lower the water conductivity, the greater the SOM removal efficiency was. Additional characterization of SOM before and after photocatalytic treatment was carried out via fluorescence measurements (Fig. 7). The fluorescence spectra revealed that the photocatalysis of SOM molecules shifted the emission peak maxima toward a shorter wavelength, even though they were not mineralized in the presence of a large amount of sea salts. Particularly, the photocatalysis of the desalted seawater sample caused a substantial increase in fluorescence intensity at ~325 nm. These results indicated that SOM molecules underwent a disintegration of aromatic rings or conversion to smaller fragments [20,21]. This coincided with the UV_{254} absorbance data of decreased aromaticity of SOM after photocatalysis (see Figs. 4–6). FTIR spectra showed the presence of C=O stretching bands (~1650 cm^{-1}) corresponding to carboxyl groups in SOM, but there were insignificant changes before and after the photocatalysis (data not shown). The above results implied that background seawater constituents (e.g., salts) played a key role in obstructing the photocatalytic degradation of SOM.

Since it has been known that carbonate species in water, such as CO_3^{2-} or HCO_3^-, may act as a scavenger of OH radical [22], the alkalinity effect on SOM photocatalysis was examined (Fig. 8). For this experiment, seawater was first electrodialyzed to 1.0 mS/cm in conductivity and then its alkalinity was re-adjusted to the original level of 150 mg/L as $CaCO_3$. With the alkalinity amendment, the TOC removal efficiency decreased by 13% as compared to that of desalted water with a conductivity of 1.0 mS/cm and no alkalinity, which was not considered that significant. Hence, it was thought that the existence of carbonate species was not the main cause for the significantly reduced photocatalysis of SOM with the original seawater.

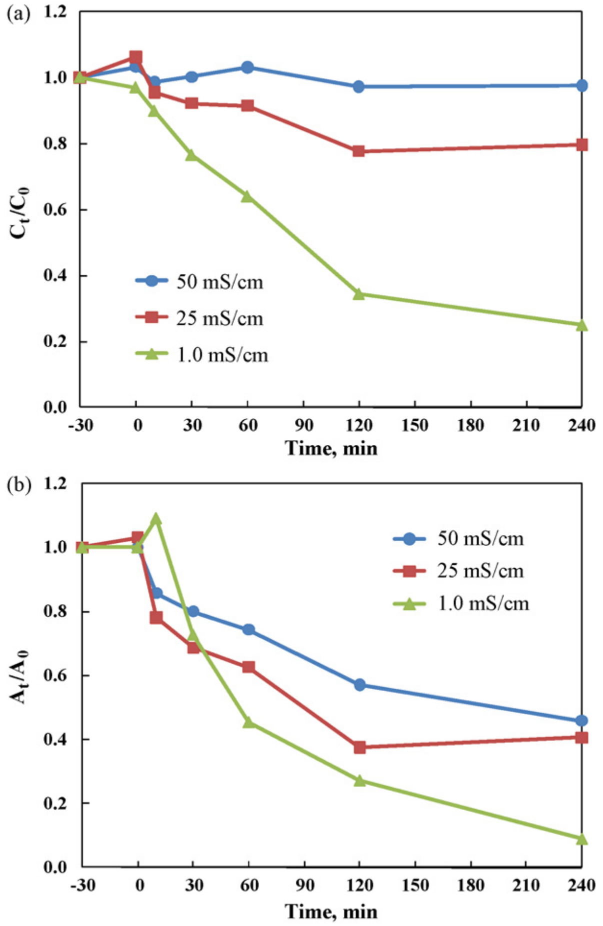

Fig. 6. The effects of sea salt levels on the photocatalysis of Masan seawater: (a) TOC; (b) UV_{254} absorbance. Seawater was desalted by electrodialysis while maintaining the organic matter content in the same level.

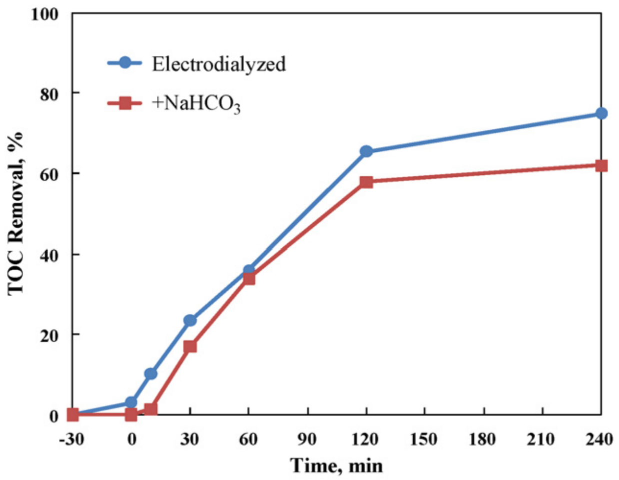

Fig. 8. The effects of alkalinity on the photocatalysis of Masan seawater. Seawater was first electrodialyzed to 1.0 mS/cm and then its alkalinity was re-adjusted to the original level of 150 mg/L as $CaCO_3$ using $NaHCO_3$.

3.4. Identification of interfering ionic species and role of chloride ions

In order to identify the interfering ionic species with SOM photocatalysis, five different salts, such as NaCl, KCl, $NaNO_3$, KNO_3, and Na_2SO_4, were added to the desalted 1.0-mS/cm seawater while raising the water conductivity to the original level of 50 mS/cm. Since some anions exist in natural water, such as chloride and nitrate, can disturb photocatalytic degradation reactions for organic compounds [23], the ionic effects on SOM photocatalytic degradation were investigated (Fig. 9). Although nitrate and sulfate ions affected the SOM photocatalysis efficiency slightly, depending on cations, and chloride ions had the greatest impact on it. With chloride ions added, the TOC removal efficiency was below 10% after 240-min photocatalysis.

Although chloride ions had a negative effect on the photocatalysis of various compounds in previous reports as well as in our study [24–27], there have been some contradictory findings that the photolytic reaction to decompose organic matter was not influenced by chlorine ions [28]. To confirm the chloride ion effect in this study, another photocatalysis experiment, after eliminating chloride ions by the addition of excess $AgNO_3$ in advance, was conducted (data not shown). Substantial TOC removal (>50%) was still achieved, which supported the fact that chloride was the major species that inhibited SOM photocatalysis.

In addition, the variation of chloride ion concentration with time during the PMR treatment was monitored and is shown in Fig. 10. The concentration of chlorine ions in the seawater decreased by approximately 2 mM during photocatalysis, which corresponds to a significant reduction of chloride ions. The disappearance of chloride

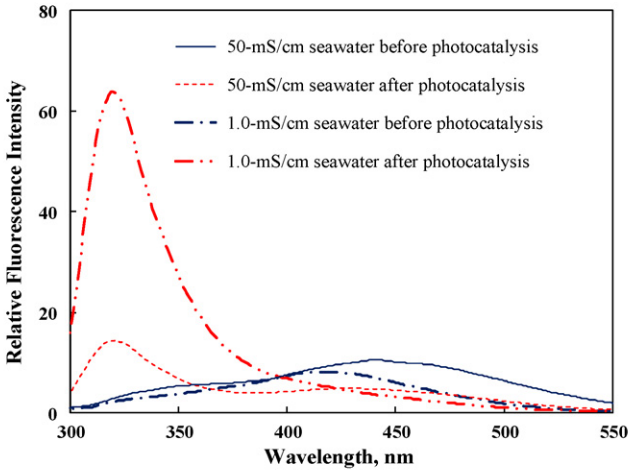

Fig. 7. The variation of fluorescence emission spectra before and after the 240-min photocatalysis of 50- and 1.0-mS/cm seawater samples.

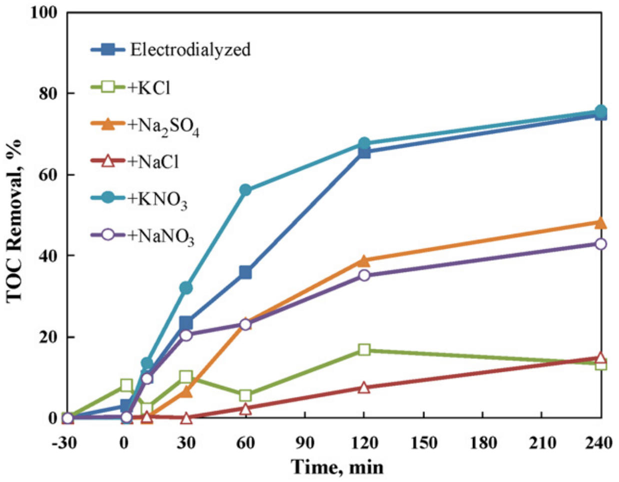

Fig. 9. TOC removal efficiencies of seawater samples electrodialyzed and modified with dosing different types of salts.

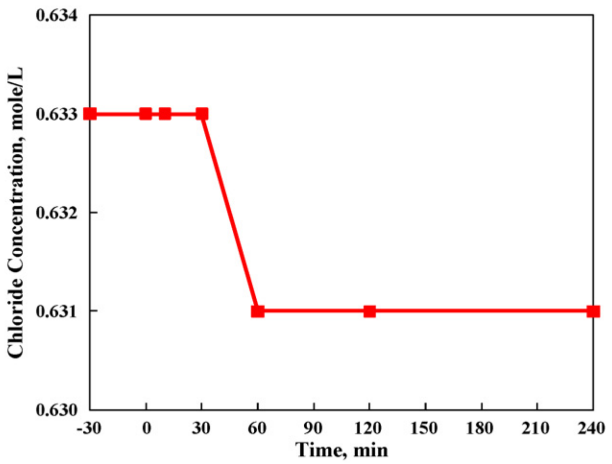

Fig. 10. Monitoring of chloride ions during seawater photocatalysis.

Table 2
The XRF analysis of the surface of TiO_2 photocatalysts.

Compound	Concentration (%)
SiO_2	<0.001
P_2O_5	<0.001
SO_3	<0.001
Cl	<0.001
K_2O	<0.001
CaO	0.323
TiO_2	99.5
Fe_2O_3	<0.001
CuO	<0.001
ZnO	0.2
SrO	<0.001
Rh	<0.001

ions could be explained as follows. Chloride ions may attach to the surface of the TiO_2 particles while covering the active reaction sites, but the XRF analysis exhibited no adhesion of chloride ions on the TiO_2 surface during SOM photocatalysis (Table 2). In addition, used and fresh TiO_2 particles showed the same TOC removal efficiency of desalted water (data not shown). Rather, chlorine ions may serve as a scavenger to $^{\bullet}OH$ radicals while hindering the enhanced oxidation of SOM. Possible scavenging of such radical reactions by chloride ions during SOM photocatalysis is illustrated in Fig. 11. Valence band holes and $^{\bullet}OH$ radicals should competitively participate in the oxidation process in the presence of chloride ions. Chlorine radical anions, preferentially produced by the transformation of chloride ions on the TiO_2 surface, could be primarily involved in the oxidative chlorination of SOM molecules. It is possible that they can partially oxidize the organics, even though their oxidizing power is less than that of the $^{\bullet}OH$ radicals. This reaction might have caused the reduction of chloride ions and UV absorbance as well as the blue-shift of the fluorescence during SOM photocatalysis.

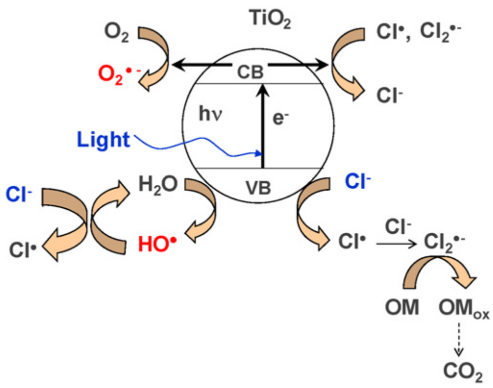

Fig. 11. An illustration of possible scavenging reactions of radicals by Cl^- ions during seawater photocatalysis. OH radicals and valence band holes can oxidize OM, but were not presented here. CB, VB, and OM stand for conduction band, valence band, and organic matter, respectively.

4. Conclusions

The present study investigated photocatalytic membrane reactor treatment of seawater with respect to SOM removal efficiency and fouling control. The turbidity removal was significant and stable without any sign of membrane fouling. Although TiO_2 mediated photocatalysis achieved a substantial degradation of NOM present in fresh water (80% of lake NOM was removed within 4 hours), but unexpectedly, no SOM was decomposed by the same system. To figure out this discrepancy in photocatalysis between NOM and SOM, the salt level of seawater was altered by electrodialysis and the effects on SOM photocatalysis were examined. When the seawater conductivity was reduced down to <1.0 mS/cm, the SOM removal efficiency was improved substantially, almost as high as that of NOM in the lake water (~80% TOC was removed). It was believed that ionic species in seawater might interfere with SOM photocatalysis. However, the fluorescence spectra revealed that SOM molecules were attacked photocatalytically even in the presence of sea salts, though not mineralized. To identify what ionic species act as an inhibitor on photocatalysis, five different salts, such as NaCl, KCl, $NaNO_3$, KNO_3, and Na_2SO_4, were added to the desalted seawater while re-adjusting the water sample's conductivity to the same level as the original seawater (i.e., ~50 mS/cm). When the photocatalytic degradation efficiency of SOM was evaluated with those water samples, chloride-containing water samples had a very low SOM removal efficiency (<10%). Consequently, it could be contemplated that chloride ions in seawater were responsible for scavenging photoinduced radicals (e.g., hydroxyl or superoxide radicals) from the TiO_2 surface, limiting the destruction of SOM molecules by photocatalysis.

Acknowledgements

This research was supported by a grant (R-01-2007-000-20690-0) from the National Research Foundation of Korea, as well as a grant (Code No. C106A1520001-06A085500125) from the Plant Technology Advancement Program funded by the Ministry of Land, Transport, and Maritime Affairs of the Korean Government.

References

[1] P.K.J. Robertson, Semiconductor photocatalysis: an environmentally acceptable alternative production technique and effluent treatment process, J. Clean. Prod. 4 (1996) 203–212.
[2] G. Pearce, Introduction to membranes: water and wastewater—RO pre-treatment, Filtr. Sep. 44 (2007) 30–33.
[3] G.K. Pearce, The case for UF/MF pretreatment to RO in seawater applications, Desalination 203 (2007) 286–295.
[4] G.K. Pearce, UF/MF pre-treatment to RO in seawater and wastewater reuse applications: a comparison of energy costs, Desalination 222 (2008) 66–73.
[5] S.A. Avlonitis, K. Kouroumbas, N. Vlachakis, Energy consumption and membrane replacement cost for seawater RO desalination plants, Desalination 157 (2003) 151–158.
[6] A.V.R. Reddy, J.J. Trivedi, C.V. Devmurari, D.J. Mohan, A.P.R.P. Singh, S.V. Joshi, P.K. Ghosh, Fouling resistant membranes in desalination and water recovery, Desalination 183 (2005) 301–306.
[7] Y. Zhao, L. Song, S.L. Ong, Fouling of RO membranes by effluent organic matter (EfOM): relating major components of EfOM to their characteristic fouling behaviors, J. Membr. Sci. 349 (2010) 75–82.
[8] J.H. Lee, B.C. Lee, J.S. Ra, J.W. Cho, I.S. Kim, N.I. Chang, H.K. Kim, S.D. Kim, Comparison of the removal efficiency of endocrine disrupting compounds in pilot scale sewage treatment processes, Chemosphere 71 (2008) 1582–1592.

[9] F. Knops, S.V. Hoof, H. Futselaar, L. Broens, Economic evaluation of a new ultrafiltration membrane for pretreatment of seawater reverse osmosis, Desalination 203 (2007) 300–306.

[10] C.H. Park, S.W. Hong, T.H. Chung, Y.S. Choi, Performance evaluation of pretreatment processes in integrated membrane system for wastewater reuse, Desalination 250 (2010) 673–676.

[11] H.K. Shon, S. Vigneswaran, I.S. Kim, J. Cho, H.H. Ngo, Effect of pretreatment on the fouling of membranes: application in biologically treated sewage effluent, J. Membr. Sci. 234 (2004) 111–120.

[12] R. Fabris, E.K. Lee, C.W.K. Chow, V. Chen, M. Drikas, Pre-treatments to reduce fouling of low pressure micro-filtration (MF) membranes, J. Membr. Sci. 289 (2007) 231–240.

[13] A. Kraft, M. Stadelmann, M. Blaschke, Anodic oxidation with doped diamond electrodes: a new advanced oxidation process, J. Hazard. Mater. 103 (2003) 247–261.

[14] J. Bacardit, J. Stotzner, E. Chamarro, S. Esplugas, Effect of salinity on the photo-Fenton process, Ind. Eng. Chem. Res. 46 (2007) 7615–7619.

[15] K. Ayoub, E.D.V. Hullebusch, M. Cassir, A. Bermond, Application of advanced oxidation processes for TNT removal: a review, J. Hazard. Mater. 178 (2010) 10–28.

[16] H.K. Shon, S. Phuntsho, S. Vigneswaran, Effect of photocatalysis on the membrane hybrid system for wastewater treatment, Desalination 225 (2008) 235–248.

[17] K.H. Choo, R. Tao, M.J. Kim, Use of a photocatalytic membrane reactor for the removal of natural organic matter in water: effect of photoinduced desorption and ferrihydrite adsorption, J. Membr. Sci. 322 (2008) 368–374.

[18] S. Liu, M. Lim, R. Fabris, C. Chow, M. Drikas, R. Amal, TiO_2 photocatalysis of natural organic matter in surface water: impact on trihalomethane and haloacetic acid formation potential, Environ. Sci. Technol. 42 (2008) 6218–6223.

[19] P. Yao, K.H. Choo, M.H. Kim, A hybridized photocatalysis-microfiltration system with iron oxide-coated membranes for the removal of natural organic matter in water treatment: effects of iron oxide layers and colloids, Water Res. 43 (2009) 4238–4248.

[20] G.V. Korshin, M.U. Kumke, C.W. Li, F.H. Frimmel, Influence of chlorination on chromophores and fluorophores in humic substances, Environ. Sci. Technol. 33 (1999) 1207–1212.

[21] J. Swietlik, E. Sikorska, Application of fluorescence spectroscopy in the studies of natural organic matter fractions reactivity with chlorine dioxide and ozone, Water Res. 38 (2004) 3791–3799.

[22] T. Hisanaga, K. Harada, K. Tanaka, Photocatalytic degradation of organochlorine compounds in suspended TiO_2, J. Photochem. Photobiol. A: Chem. 54 (1990) 113–118.

[23] H.Y. Chen, O. Zahraa, M. Bouchy, Inhibition of the adsorption and photocatalytic degradation of an organic contaminant in an aqueous suspension of TiO_2 by inorganic ions, J. Photochem. Photobiol. A: Chem. 108 (1997) 37–44.

[24] C. Guillard, H. Lachheb, A. Houas, Influence of chemical structure of dyes, of pH and of inorganic salts on their photocatalytic degradation by TiO_2 comparison of the efficiency of powder and supported TiO_2, J. Photochem. Photobiol. A: Chem. 158 (2003) 27–36.

[25] M. Abdullah, G.K.C. Low, R.W. Matthews, Effects of common inorganic anions on rates of photocatalytic oxidation of organic carbon over illuminated titanium dioxide, J. Phys. Chem. A 94 (1990) 6820–6825.

[26] P.K. Surolia, R.J. Tayade, R.V. Jasra, Effect of anions on the photocatalytic activity of Fe(III) salts impregnated TiO_2, Ind. Eng. Chem. Res. 46 (2007) 6196–6203.

[27] R.A. Burns, J.C. Crittenden, D.W. Hand, Effect of inorganic ions in heterogeneous photocatalysis of TCE, J. Environ. Eng.-ASCE 125 (1999) 77–85.

[28] S.Y. Yang, Y.X. Chen, L.P. Lou, X.N. Wu, Involvement of chloride anion in photocatalytic process, J. Environ. Sci. 17 (2005) 761–765.