Application of hybrid photocatalysis systems coupled with flocculation and adsorption to biologically treated sewage effluent for organic removal

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Abstract–The application of a photocatalysis hybrid system coupled with flocculation and adsorption in treating biologically treated sewage effluent (BTSE) was investigated. The removal of organic matter was studied in terms of dissolved organic matter (DOC), removal of hydrophobic (HP), transphilic (TP) and hydrophilic (HL) fractions, and molecular weight (MW) distribution. The photooxidation removed the majority of MW (263, 580, 865, and 43109 daltons) within the first 30 minutes of operation. The removal of MW range of organic matter of 330 daltons was low. DOC removal of HP and TP was high (80%). DOC removal from HL fraction was, however, minimum. The photocatalytic system with simultaneous PAC adsorption and $FeCl_3$ flocculation removed the effluent organic matter (EfOM) up to 90%. Therefore, photocatalysis with the ferric chloride ($FeCl_3$) flocculation and PAC adsorption hybrid system can be a possible option in the removal of DOC from BTSE for water reuse.

Key words: Adsorption, Flocculation, Hydrophobic, Hydrophilic, Molecular Weight Distribution, Photocatalysis, Transphilic, Wastewater

INTRODUCTION

Water requirements are increasing with population growth and industrialization. Reuse of wastewater after treatment will help to maintain environmental quality and to relieve the unrelenting pressure on conventional natural freshwater sources. Although the effluent from the secondary and tertiary wastewater treatment can be discharged into waterways, it cannot be used for reuse purposes without further treatment [1]. Thus, an advanced treatment technology is required to remove various organic matters, pathogenic microorganisms and persistent organic pollutants (POPs) in wastewater. Photocatalysis is one of the attractive processes for degrading POPs from biologically treated sewage effluent (BTSE). Photocatalytic reactions allow, in many cases, a complete degradation of organic pollutants into very small and harmless species without the use of any chemicals. This avoids sludge production and its disposal [2,3]. Titanium dioxide (TiO_2) catalyzed photocatalysis is broadly used because of its capability in removing a wide range of pollutants. The photochemical stability, low toxicity and low cost are the other advantages [4-8].

The efficiency of photocatalysis can be improved by collecting pollutant in the solution to the surface of TiO_2. Adsorbents such as powdered activated carbon (PAC), silica, zeolite and so on, are used to promote the adsorption. It is well known that PAC can be very efficient when it is mixed with TiO_2 in photocatalytic processes [4]. Arana et al. [4] observed that i) the combination of PAC and TiO_2 resulted in fast decantability in comparison with that of TiO_2 alone, ii) a TiO_2 particle distribution on the PAC surface yielded in a homogeneous particle size distribution, and iii) the rate of organic removal

by the PAC and TiO_2 was six times higher than that with TiO_2 alone.

When $FeCl_3$ flocculation is coupled with photocatalysis, the photocatalytic reaction is enhanced. In the photo-Fenton process with ferric (Fe^{3+}) ions under UV radiation, the super-oxide change and pH affect the organic activation in the degradation of organic matter with ferric ions. The photo-Fenton reaction produces the hydroxyl radical with a metal to ligand charge transfer. Many studies have found that photo-Fenton's systems are useful in treating a variety of contaminants including aromatic and aliphatic organic compounds [4,9,10]. Shon et al. [11] found that a photocatalytic reaction caused a forward and reverse reaction in treating organic matter with synthetic wastewater. They reported that PAC adsorption and $FeCl_3$ flocculation removed the forward and reverse reaction.

Most of the work done so far has been concentrated on the effect of photocatalysis on organic removal (only in terms of DOC, BOD and COD). It is important to study the nature of organic matter removed by this process in order to optimize this process in the removal of EfOM. This study concentrates on studying the removal in terms of different fractions (HP, TP and HL). In addition, in order to investigate the synergetic effect of flocculant, adsorption and photocatalysis, it is necessary to study the removal of organic matter of different MW ranges. Hence, this study experimentally evaluated the advantages of the chemical coupling of photocatalytic reaction with $FeCl_3$ flocculation and powdered activated carbon (PAC) adsorption.

EXPERIMENTAL

1. Biologically Treated Sewage Effluent (BTSE)

The characteristics of the BTSE used are presented in Table 1. The study was conducted with BTSE drawn from a Gwangju sewage treatment plant, Korea. The wastewater treatment is a medium-

Table 1. Characterization of biologically treated sewage effluent used

TOC (mg/L)	BOD$_5$ (mg/L)	pH	SS (mg/L)	TN (mg/L)	TP (mg/L)	Conductivity (μS/cm)
6.5-10.4	9.4-18	6.8-7.5	3.5-5.0	23.2-40	2.2-5	200-584

Table 2. Characteristics of powdered activated carbon (PAC) used in this study (James Cumming & Sons Pty Ltd., Australia)

Specification	PAC-WB
Structure	Porous
Iodine number	900 mg g^{-1} min^{-1}
Ash content	6% max.
Moisture content	5% max.
Bulk density	290-390 kg m^{-3}
Surface area	882 m^2 g^{-1}
Nominal size	80% min finer than 75 micron
Type	Wood based
Mean pore diameter	3.061 nm
Micropore volumn	0.34 cm^3 g^{-1}
Mean diameter	19.71 μm
Product code	MD3545WB powder

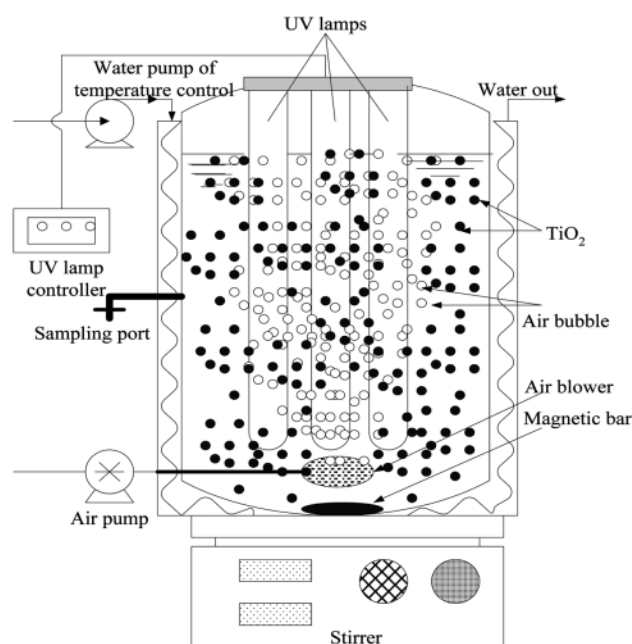**Table 3. Characteristics of P25 Degussa photocatalytic powdered used**

Specification	P25 Degussa TiO$_2$
Structure	Non-porous
Components	65% anatase, 25% rutile, 0.2% SiO$_2$, 0.3% Al$_2$O$_3$, 0.3% HCl, 0.01% Fe$_2$O$_3$
Average aggregate particle diameter	Non-porous
Primary crystal size	3 μm
Mean pore diameter	6.9 nm
Band gap	3.03 (from 500 to 300 nm) with UV-Vis
Apparent density	130 kg m^{-3}
Surface area	42.32±0.18 m^2 g^{-1}
Type	Powdered
Product code	Degussa P25, Frankfurt am Main, Germany

Fig. 1. Schematic of the photocatalytic reactor.

sized activated sludge unit (25,000 m^3/d). The hydraulic retention time and the sludge age were 6 h and about 8 days, respectively.

2. FeCl$_3$ Flocculation

Ferric chloride (FeCl$_3$), which was used as flocculant, was chosen in these experiments as it has a good capability in removing both colloidal and dissolved organic matters. Flocculation was used as a pretreatment to photocatalysis. The BTSE was placed in one liter containers, where known amounts of ferric chloride were added. The samples were then stirred rapidly for 1 minute at 100 rpm, followed by 20 minutes of slow mixing at 30 rpm, and 30 minutes of settling. The supernatant was taken and analyzed for DOC to determine the optimum FeCl$_3$ dose.

3. PAC Adsorption

PAC was placed in one liter BTSE and was stirred at 100 rpm and at 25 °C for one hour. The characteristics of PAC used are given in Table 2. The supernatant collected after one hour underwent photocatalysis. Some experiments were also conducted with simultaneous addition of PAC and TiO$_2$ in the photocatalytic reactor.

4. Photocatalytic Degradation

Photocatalysis experiments were conducted with powdered P25 Degussa TiO$_2$ particle as catalyst [12-14] (Table 3). Photoreactor used for the degradation runs consisted of a batch reactor with different UV lamps, air blower, and magnetic bar (Fig. 1). The total surface area of all three UV lamps was 537 cm^2. The volume of the reactor was 1.5 L. Air sparging was provided to supply oxygen into the reactor (5 VVM-air volume/solution volume/minute). The circulation of tap water around the reactor controlled the temperature at 25 °C.

5. Analytical Methods to Measure Organic Matter

5-1. Dissolved Organic Carbon (DOC)

DOC was measured by using the TOC analyzer. All samples were filtered through 0.45 μm membrane prior to the DOC measurement.

5-2. Fractionation of Effluent Organic Matter (EfOM) into Hydrophobic and Hydrophilic Fractions

XAD-8 and XAD-4 resins were used for fractionating EfOM into HP EfOM (XAD-8 adsorbable; mostly HP acids with some HP neutrals) and TP EfOM (XAD-4 adsorbable; HL bases and neutrals) components. The remaining fraction escaping the XAD-4 is the HL component. The EfOM adsorbed on the XAD-8/4 was eluted by using 0.1 N NaOH solution. The details on the ion-exchange columns and fractionation methods are described elsewhere [15,16]. The percentages of HP, TP and HL fractions in the BTSE used in this study were 25.3%, 15.9% and 58.8%, respectively. These samples were taken during the summer season (22-27 °C). The HL fraction was the main component in the BTSE. This result is in agreement with the study of Imai et al. [17]. However, Shon et al. [1]

observed different results during winter and summer seasons. HP fraction was found to be highest (HP (50.6%)>HL (32.4%)>TP (17.1%)) for the samples taken during the winter season (5-10 °C). Thus, the wastewater characteristics vary from season to season. The isolated fractions were concentrated in a freeze dryer (ilShin Lab Co. Ltd., South Korea). The initial concentration of each fraction was adjusted to a DOC concentration of 6.5 mg/L, which was equivalent to that of BTSE. The adjustment was done for uniformity reasons and for comparison of results with different processes. The initial conductivity of BTSE used in this study was about 250 μS/cm. When isolating using XAD-8/4 resin, different fractions were required with the addition of HCl and NaOH which resulted in high conductivity. Also, the fractions isolated were concentrated in a freeze dryer up to the initial concentration of BTSE alone. As such, the fractions from BTSE significantly increased the ionic strength. Furthermore, pH of different fractions was adjusted to pH 7 with HCl and NaOH so that this also increased the conductivity. In order for all the fractions to have a same conductivity of 15 mS/cm, a predetermined quantity of NaCl was added.

5-3. Molecular Weight (MW) Distribution

The BTSE after each treatment was subjected to MW distribution measurement. High pressure size exclusion chromatography (HPSEC, Shimadzu, Corp., Japan) with an SEC column (Protein-pak 125, Waters, Milford, USA) was used to determine the MW distributions of EfOM. Standards of MW of various polystyrene sulfonates (PSS: 210, 1800, 4600, 8000, and 18000 daltons) were used to calibrate the equipment. The details on the measurement methodology are given elsewhere [18].

RESULTS AND DISCUSSION

1. Effect of UV Light Intensity on Photodegradation

A detailed study was undertaken with photocatalysis with BTSE. The effect of UV lamp intensity was studied by using 8 W UV-C (approximately 253 nm), 15 W UV-C (approximately 235 nm) and 15 W UV-A (approximately 315-400 nm) (Fig. 2). The DOC removal was 70% after 3-hour operation when 15 W UV-C was used.
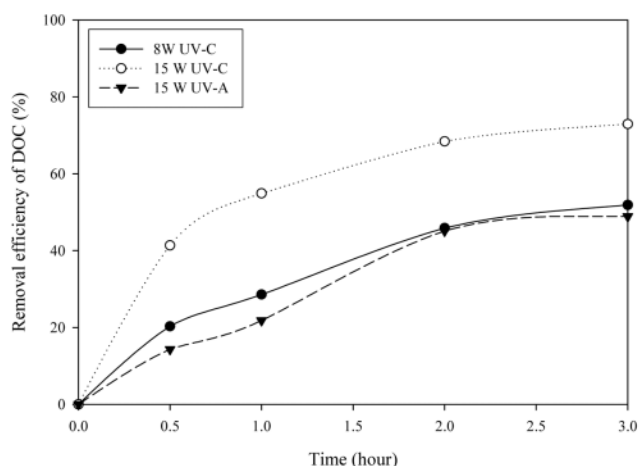

Fig. 2. DOC removal at different UV intensities (initial DOC concentration=6.5 mg/L; TiO$_2$ concentration=2 g/L; air=25 L/min).
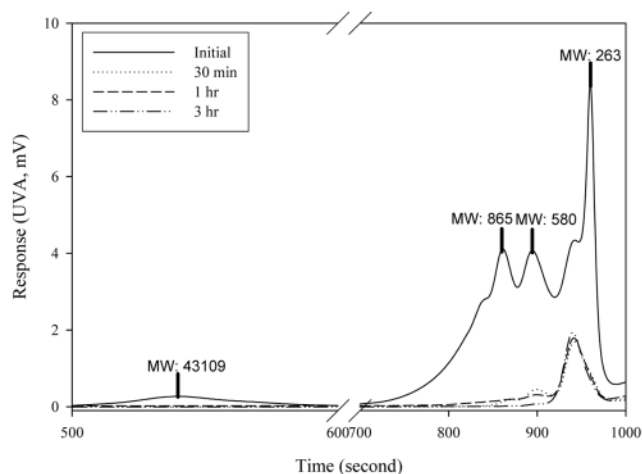
Fig. 3. MW distribution of EfOM at different UV intensities (initial DOC concentration=6.5 mg/L; TiO$_2$ concentration=2 g/L; air=25 L/min).

However, the use of 15 W UV-A resulted in only 40% removal. This may have been because the wavelength of 315-400 nm was not appropriate for the degradation of the EfOM. As expected, the 15 W UV-C gave rise to a better removal than the 8 W UV-C. The higher the light intensity, the higher is the DOC removal. In the subsequent experiments, a UV-C lamp with 15 W was used. Fig. 3 presents the MW distribution of EfOM. The photooxidation with UV-C 15 W lamp and 2 g/L of TiO$_2$ removed the majority of MW (263 daltons, 580, 865, and 43109) within the first 30 minutes of operation.

2. Effect of Fractions in Photodegradation

The hydrophobic (HP), transphilic (TP) and hydrophilic (HL) compounds were isolated from BTSE to investigate the effect of EfOM removal from each fraction during the photocatalytic reaction (Fig. 4). DOC removal was high (80%) for HP and TP components. DOC removal from HL fraction was, however, minimum, suggesting that the HL fraction may be the rate limiting fraction in photocatalytic degradation.

Figs. 4(b), 4(c) and 4(d) present the MW distribution of HP, TP and HL fractions before and after these fractions had undergone photocatalysis. MW distribution of the HP fraction included all the MWs as shown in Fig. 4(b) for BTSE (260 daltons, 330, 580, 870, and 43110). Photocatalytic degradation with the HP fraction removed the majority of large MW (43110 daltons) within 30 minutes. The EfOM corresponding to MW of 865 daltons was partially removed after this HP fraction underwent a photooxidation of 1 hour. A wide range of MW in the TP fraction was also partially removed during the photocatalysis (Fig. 4(c)). However, the HL fraction exhibited poor removal (Fig. 4(d)). The smallest MW (260 daltons) portion seemed to be a rate limiting MW in the HL fraction.

3. Effect of Simultaneous FeCl$_3$ and TiO$_2$ Addition in Photocatalysis

The effect of simultaneous FeCl$_3$ and TiO$_2$ additions in photocatalytic degradation of EfOM was studied to investigate the synergistic effect of FeCl$_3$ in TiO$_2$ photo-oxidation (Fig. 5). The combined addition of TiO$_2$ and FeCl$_3$ removed the EfOM by up to 90%. Fig. 5(b) presents the MW distribution of EfOM. The EfOM of MW of 330 daltons was removed to a least amount.
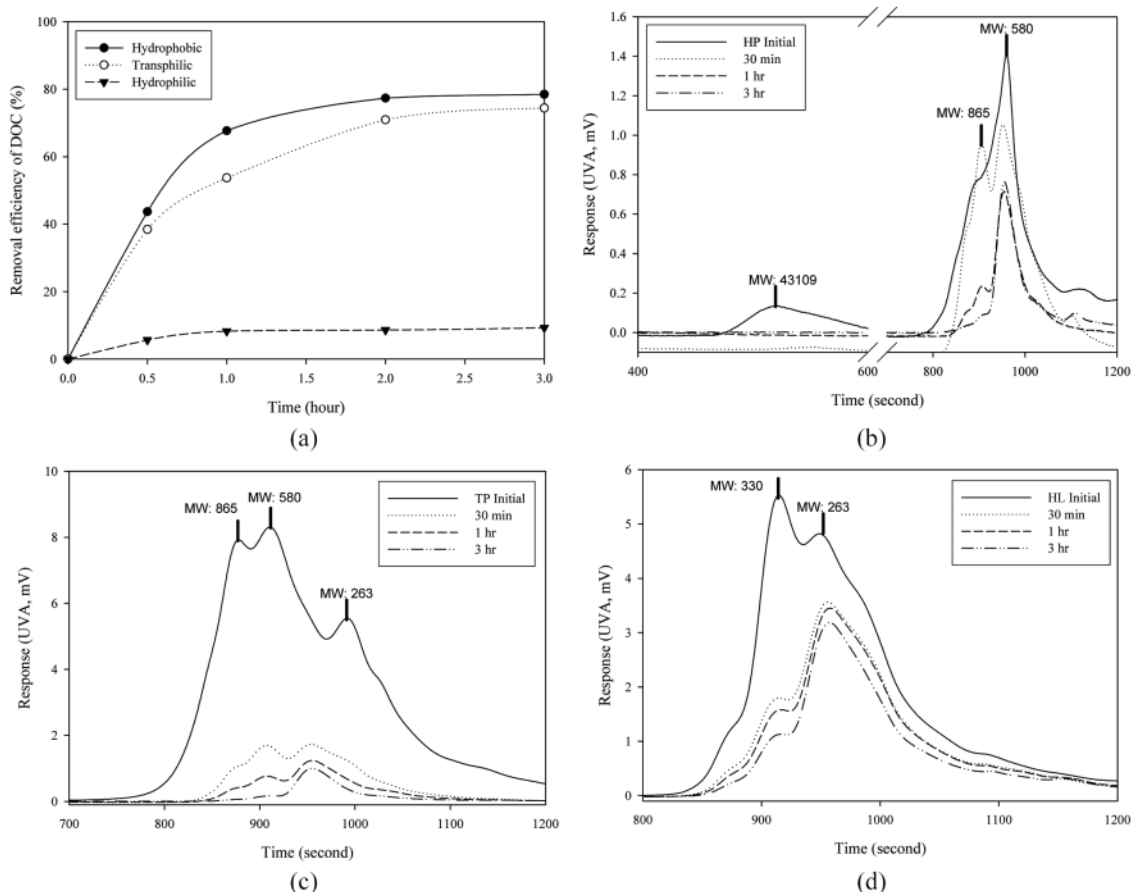
Fig. 4. (a) DOC removal and MW distribution of different fractions of EfOM by photocatalysis with (b) HP, (c) TP, and (d) HL fractions (initial DOC concentration=6.5 mg/L; TiO$_2$ concentration=2 g/L; air=5 VVM; UV intensity=UV-C 15 W).
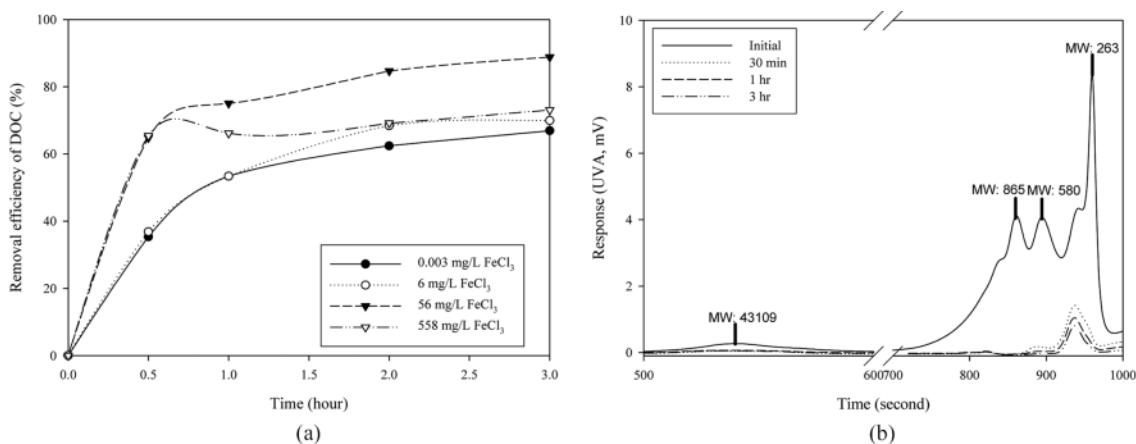

Fig. 5. (a) DOC removal and (b) MW distribution after simultaneous FeCl$_3$ and TiO$_2$ additions in the photocatalysis system (initial DOC concentration=6.5 mg/L; TiO$_2$ concentration=2 g/L; air=5 VVM; UV intensity=UV-C 15 W; (b) corresponds to 56 mg/L addition).

4. Effect of FeCl$_3$ Flocculation Followed by Photocatalysis

The effect of FeCl$_3$ flocculation followed by photocatalytic degradation was investigated in terms of DOC removal (Fig. 6(a)). When the BTSE was flocculated with 69 mg/L of FeCl$_3$, the DOC removal was up to 55%. A hybrid process with FeCl$_3$ flocculation (69 mg/L) followed by photocatalysis indicated the highest DOC removal by up to 92.1%. This removal was similar to that with nanofiltration

[19]. The flocculation-photocatalysis hybrid system could therefore be an alternative effective way to remove EfOM from BTSE.

The MW distribution curve (Fig. 6(b)) shows minimum removal of the MW fraction of 330 daltons. The flocculation followed by photocatalysis showed high removal for other MW ranges of EfOM. This trend of MW distribution was similar with those observed in nanofiltration membrane effluents [19].
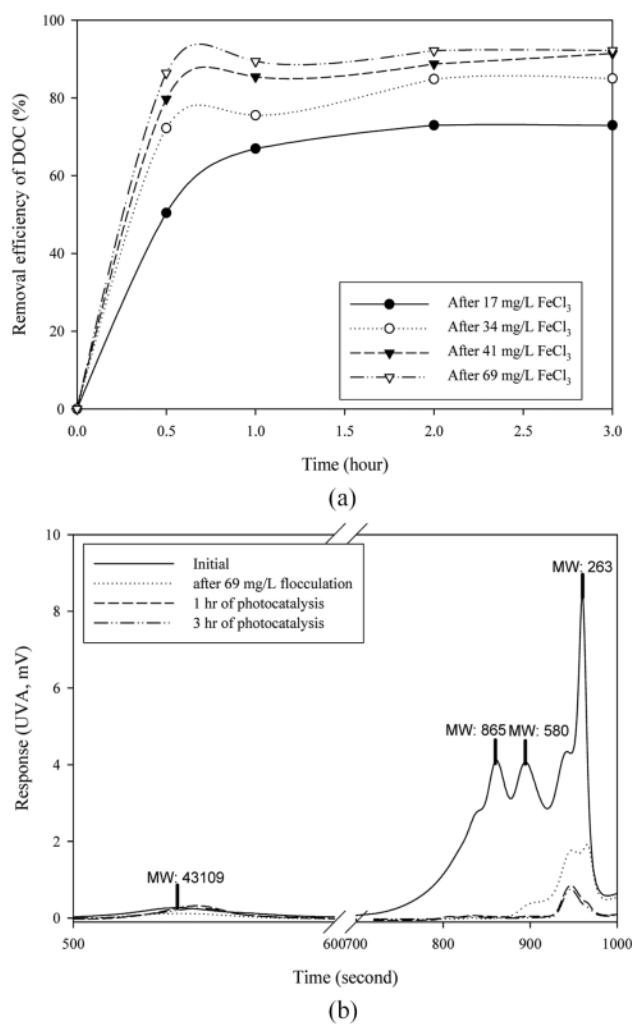
Fig. 6. (a) DOC removal and (b) MW distribution with FeCl₃ floc-
culation (69 mg/L) followed by photocatalysis (initial DOC
concentration=6.5 mg/L; TiO₂ concentration=2 g/L; air=5
VVM).

Fig. 7. DOC removal for (a) simultaneous PAC addition and (b)
PAC adsorption followed by photocatalysis (initial DOC
concentration=6.5 mg/L; TiO₂ concentration=2 g/L; air=
5 VVM).

5. Effect of PAC Adsorption as a Pretreatment to TiO₂ Photocatalysis

The effect of (i) PAC adsorption as a pretreatment to TiO₂ photocatalysis and (ii) simultaneous addition of PAC with TiO₂ in the photocatalysis was investigated (Fig. 7). The EfOM removal was increased from 52% with photocatalysis alone to 77.5% with TiO₂ photocatalysis with simultaneous PAC addition at 0.5 g/L (Fig. 7(a)). This increase of DOC removal is probably due to the adsorption of small MW organics by PAC. The non-porous TiO₂ adsorb the large MW and PAC removes the small MW. As the photocatalytic reaction proceeded, the large MW compounds were photodegraded into small MW compounds which were then adsorbed by PAC. However, when PAC was added at high concentration, the DOC removal was decreased and this may be due to the interference of the passage of UV light through the BTSE solution. Fig. 7(b) represents the effect of pretreatment of PAC adsorption on photocatalysis. The results suggest that PAC adsorption followed by photocatalysis is also effective in improving the DOC removal.

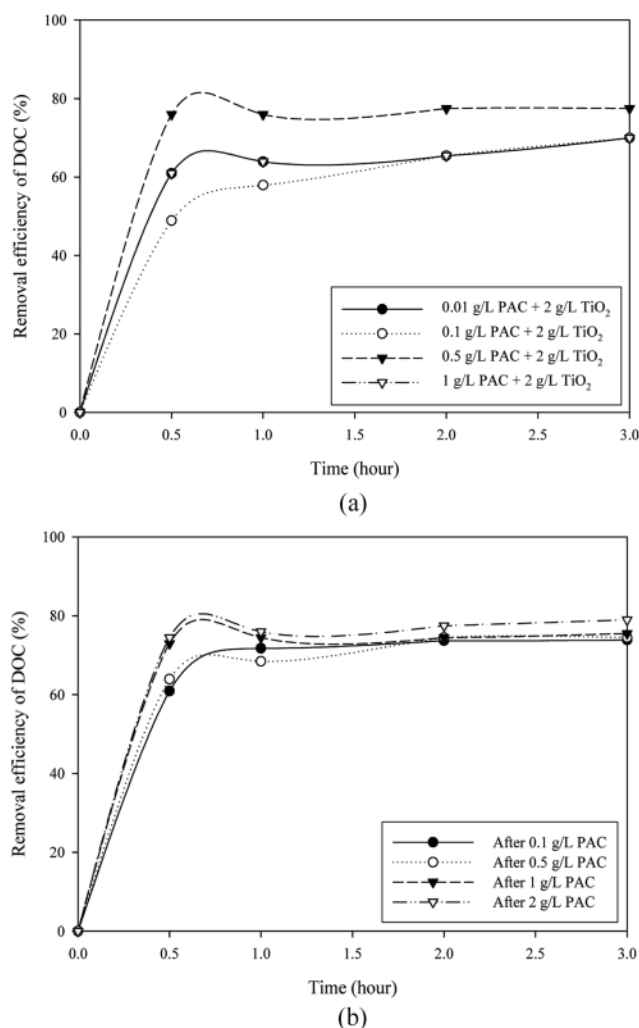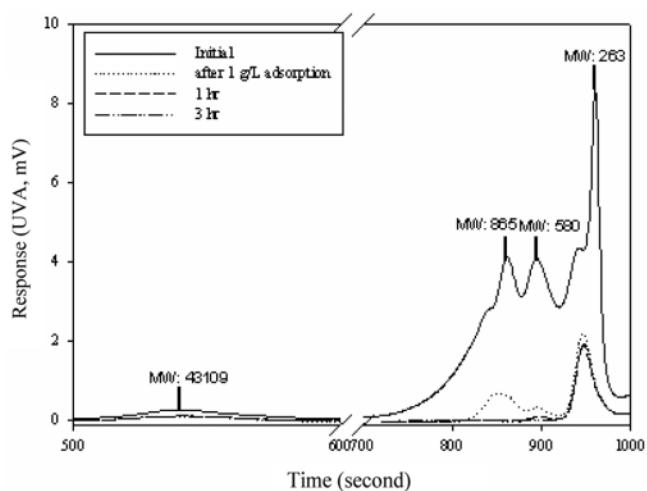Fig. 8 presents the MW distribution of the effluent obtained from

Fig. 8. MW distribution of EfOM with PAC adsorption followed
by photocatalysis (initial DOC concentration=6.5 mg/L;
TiO₂ concentration=2 g/L; 5 VVM).

the process of PAC adsorption followed by photocatalysis. 1 g/L of PAC adsorption followed by photocatalysis removed practically all ranges of MW of EfOM in BTSE. The removal response of compounds in the range of 300 to 900 daltons was in the order of 530 daltons<870 daltons<330 daltons (Fig. 8). The same trend of MW distribution was also observed with effluent from nanofiltration [19].

CONCLUSIONS

The effect of the photocatalysis hybrid system with flocculation and adsorption was studied when it was coupled with flocculation and adsorption. The effect was studied in terms of removal of DOC from fractions and different MW ranges of EfOM. The results led to the following conclusions:

1. The amount of EfOM remaining after PAC adsorption followed by photocatalysis followed the following order: 530 daltons< 865 daltons<330 daltons. This suggests that after PAC adsorption, the photocatalytic reaction is more favorable in removing 530 daltons more than large MW (of 43100 daltons). The removal of compound of 330 daltons was the least.

2. The removal of HP and TP compounds was up to 80% of DOC during the photocatalysis; however, the HL removal was low, suggesting that HL may be the rate-limiting compounds when this process is used to treat BTSE.

3. Both hybrid systems ((i) with simultaneous PAC adsorption and TiO_2 photocatalysis and (ii) $FeCl_3$ flocculation followed by TiO_2 photocatalysis) removed the EfOM by up to 90%. The majority of the MW portions were removed. The removal of MW of the organic matter of 330 daltons was the lowest.

The removal efficiency was similar to that obtained with a nanofilter. Thus, the photocatalysis with the $FeCl_3$ flocculation and PAC adsorption hybrid system can be an alternative and cost-effective option in the removal of DOC from BTSE.

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REFERENCES

1. H. K. Shon, S. Vigneswaran, I. S. Kim, J. Cho and H. H. Ngo, *Water Res.*, **38**, 1933 (2004).
2. G. Sagawe, R. J. Brandi, D. Bahnemann and A. E. Cassano, *Chem. Eng. Sci.*, **58**, 2587 (2003).
3. R. Molinari, M. Borgese, E. Drioli, L. Palmisano and M. Schiavello, *Catal. Today*, **75**, 77 (2002).
4. J. Arana, J. A. H. Melian, J. M. D. Rodriguez, O. G. Diaz, A. Viera, J. P. Pena, P. M. M. Sosa and V. E. Jimenez, *Catal. Today*, **76**, 279 (2002).
5. M. C. Blount, D. H. Kim and J. L. Falconer, *Environ. Sci. Technol.*, **35**, 2988 (2001).
6. Y. Xiaoli, S. Huixiang and W. Dahui, *Korean J. Chem. Eng.*, **20**, 679 (2003).
7. H. J. Lee, D. W. Kang, J. Chi and D. H. Lee, *Korean J. Chem. Eng.*, **20**, 503 (2003).
8. R. Thiruvenkatachari, T. O. Kwon and I. S. Moon, *Korean J. Chem. Eng.*, **22**, 938 (2005).
9. M. C. Lu, G. D. Roam, J. N. Chen and C. P. Huang, *Water Sci. Technol.*, **30**, 29 (1994).
10. R. A. Doong, R. A. Maithreepala and S. M. Chang, *Water Sci. Technol.*, **42**, 253 (2000).
11. H. K. Shon, S. Vigneswaran, H. H. Ngo and J.-H. Kim, *Water Res.*, **39**, 2549 (2005).
12. J. Kleine, K. V. Peinemann, C. Schuster and H. J. Warnecke, *Chem. Eng. Sci.*, **57**, 1661 (2002).
13. R. Molinari, C. Grande, E. Drioli, L. Palmisano and M. Schiavello, *Catal. Today*, **69**, 273 (2001).
14. R. Al-Rasheed and D. J. Cardin, *Chemosphere*, **51**, 925 (2003).
15. J. Cho, G. Amy, J. Pelligrino and Y. Yoon, *Desal.*, **118**, 101 (1998).
16. Y. Yoon, G. Amy, J. Cho and N. Her, *Desal.*, **173**, 209 (2005).
17. A. Imai, T. Fukushima, K. Matsushige, Y. H. Kim and K. Choi, *Water Res.*, **36**, 859 (2002).
18. N. G. Her, G. Amy, D. Foss, J. Cho, Y. Yoon and P. Kosenka, *Environ. Sci. Technol.*, **36**, 1069 (2002).
19. H. K. Shon, S. Vigneswaran and S. A. Snyder, *Crit. Rev. Env. Sci. Tec.*, **36**, 327 (2006).