

Removal of color substances using photocatalytic oxidation for membrane filtration processes

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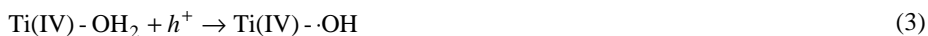
Abstract This study aims to remove the color substances, which normally cause difficulties in membrane filtration processes due to fouling using heterogeneous UV/TiO₂/H₂O₂ reactor. It is confirmed that the technique used in this study was effective to remove TOC at 38% and color₄₀₀ at 89% within 150-min irradiation. The experiment results showed that low concentrations of hydrogen peroxide dosage (less than 0.016 M) to UV/TiO₂ system accelerated the TOC and Color₄₀₀ removal rate from 9% to 38% and 40% to 89% respectively, while over-dosage made this positive effect decline. The humic acid solution treated by photo catalytic oxidation in UV/TiO₂/H₂O₂ reactor did not change the zeta potential on membrane surface and membrane rejection rate.

Keywords Humic acid; hydrogen peroxide; UV; titanium dioxide; membrane filtration

Introduction

Humic acid is condensed, refractive mixture of high molecular weight aromatic organic acids and is usually present in water, especially in biologically treated wastewater, as color substances. Safe and cost effectively removal of colored substances from wastewater is a significant problem for the wastewater recycling and reuse industries. Traditional methods for recycling and reuse of wastewater consist of various combinations of biological, chemical and physical methods including activated sludge, chlorination, ozonation, coagulation, adsorption and membrane filtration. These treatment methods mainly transfer the pollutants from wastewater to solid waste which needs further safer disposal. Chemical oxidation by ozone and chlorine is effective (Arai *et al.*, 1986), but the expensive cost of ozonation processes and chlorination by products such as carcinogens etc. restrict the technology to be widely used in industries for recycling and reuse of wastewater as potable water (Kou, 1992).

Recently, photo catalytic oxidation processes have been actively investigated. These processes are based on the generation of very active hydroxyl radicals ($\cdot\text{OH}$), which attract organic compounds and initiate a series of oxidative reactions and ultimately lead to the complete mineralization of the color substances to H₂O and CO₂ or biodegradable material (Li *et al.*, 1997). The titanium dioxide (TiO₂) irradiation (Serpone, 1994) generates these radicals ($\cdot\text{OH}$):



Studies using photo catalytic oxidation processes to further reduce color and total organic carbon (TOC) in wastewater have been reported intensively (Li *et al.*, 1996; Tang *et al.*, 1997). The literature shows that the use of a photo catalytic oxidation process in the presence of TiO₂ can decolorize many different types of dye chemicals, which could be an

effective alternative for further polishing the biologically treated dyeing effluents (Li *et al.*, 1997). In order to reduce the membrane fouling problem, the present study was undertaken to investigate the potential of using TiO_2 and H_2O_2 photooxidation process to remove the color substances in water prior to membrane water purification. It was carried out with a view to design a simple and economical UV/ TiO_2 / H_2O_2 reactor which could be applied into membrane filtration processes as fouling prevention technique.

Experimental and methodology

UVA-915 UV Multi-Purpose Cabinet was provided by Ultra-Lum, Singapore as shown in Figure 1. The cabinet was fitted with nine 15 W low-pressure mercury UV lamps and several magnetic stirrers. The UV lamps had a major emission at 253.7 nm and allowed a total of 135 W that may be applied in the photocatalytic oxidation reaction. As photocatalyst, titanium dioxide was completely mixed and suspended in the beakers to conduct UV/ TiO_2 and UV/ TiO_2 / H_2O_2 reaction.

Titanium dioxide P-25 used in this study was kindly supplied by Degussa, Frankfurt, Germany. It has the BET surface area $50 \pm 15 \text{ m}^2/\text{g}$, average size of 21 nm and mainly anatase in crystal form. Hydrogen peroxide (30% w/w) was obtained by Fisher ChemAlert. All the other chemicals were reagent grade.

Humic acid was obtained from Fluka Chemical. The concentration of humic acid used in this experiment was 32.13 TOC mg/L. Humic acid solutions were prepared according to the methods described by Urano *et al.*, (1983). The solution of humic acid was filtered through 0.45 μm membrane filter before use.

UV light intensity was measured by using the method described by Murov *et al.* (1993). In this method, four reactors were located at different positions in the cabinet and potassium ferrioxalate was added in the reactors to act as chemical actinometry. The absorbency of chemical actinometry plotted versus different irradiation time, an approximately linear relationship can be obtained. According to the slopes of the linear relationship, the incident light intensities were then calculated.

Total organic carbon in the sample was analyzed with a Shimadzu TOC Analyzer (TOC 5000). Optical absorption spectra on humic acid were determined by a Perkin Elmer Lambda Bio 20 spectrophotometer. The absorbency at 400 nm was selected for quantitative analysis of color. Hydrogen peroxide concentration was determined based on the method which Klassen *et al.* (1994) proposed. ES20 flat RO membrane was used in this study and kindly supplied by Nitto Denko Company, Singapore. Zeta potential of membrane was measured by an Electrokinetic Analyzer, Model PAAR EKA and made by Brookhaven Instruments Corp, USA. The electrolyte was 900 mL 1.0mM NaCl solution. Mass balance was account for all samples taken from reactor. All experimental results presented in this paper were carried out at pH 7.0.

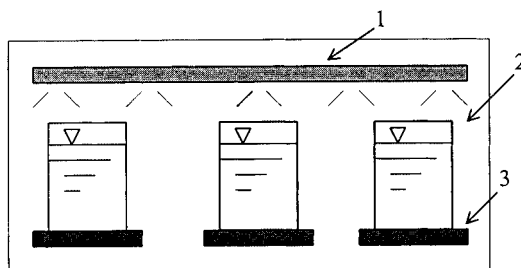


Figure 1 Schematic diagram of the completely mixed batch photoreactor system 1: UV lamp, 2: Beaker, 3: Magnetic stirrer

Results and discussion

Effect of UV light intensity

UV light intensity is a major parameter, which affects the photo catalytic oxidation rate in UV/TiO₂ process. Theoretically, the higher the UV light intensity, the faster the formation of ·OH free radical, which leads to the higher oxidative reaction (degradation) of humic acid. Figure 2 and 3 show the results of the degradation of humic acid for Color₄₀₀ and TOC respectively at different UV illumination time. It was obvious that more UV energy consumed per unit volume, the faster the removal of color and TOC. The decolorization was influenced by UV light intensity with removal rate from 40% to 54% within 150 minutes. However, the TOC removal rate was found from 9% to 19% within 150-min UV illumination time. It is clear that the decompositions of TOC were significantly affected by UV light intensity.

According to Herrmann *et al.* (1983), the TiO₂ photo catalyzed reaction follows Langmuir–Hinshelwood model.

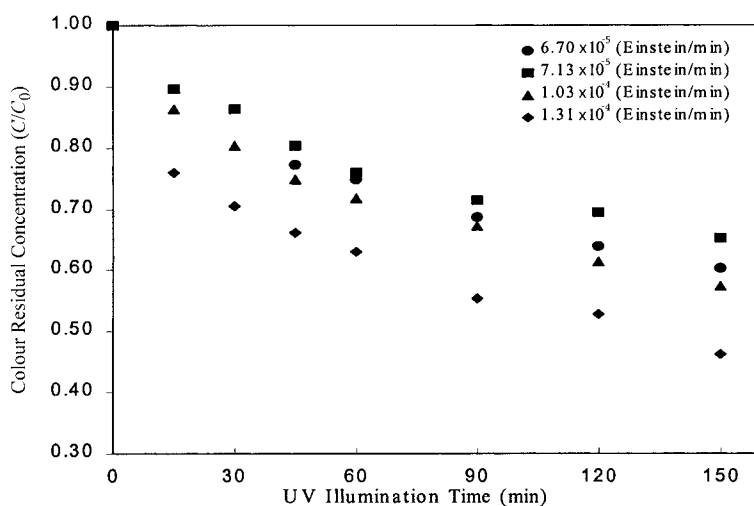


Figure 2 The effect of UV light intensity on color in UV/TiO₂ reactor. TiO₂ concentration was 0.3 g/L. UV wavelength was 253.7 nm. The concentration of humic acid was 32.13 TOC mg/L. pH was 7.0. Temperature was 25°C

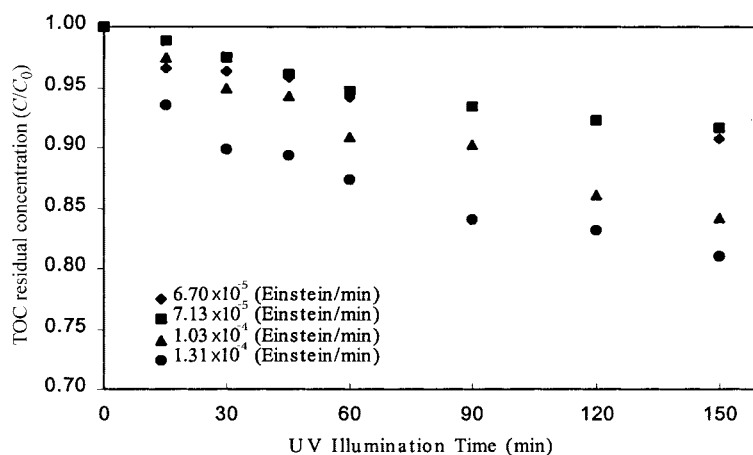


Figure 3 The effect of UV light intensity on TOC removal in UV/TiO₂ reactor. TiO₂ concentration was 0.3 g/L. UV wavelength was 253.7 nm. The concentration of humic acid was 32.1 TOC mg/L. pH was 7.0. Temperature was 25°C

$$r = -\frac{dc}{dt} = K \cdot r \frac{K_a C}{1 + K_a C}$$

This equation can be simplified into

$$\ln \frac{C_0}{C} = K \cdot r \cdot K_a \cdot t = k' t$$

where: C_0 is initial concentration, C is the concentration at time t , t is photocatalytic reaction time, k' is pseudo first-order rate constant.

To investigate the reaction rate affected by the incident light intensity, a set of tests was carried out in the UV/TiO₂ reactor. Figure 4 shows degradation of humic acid in UV/TiO₂ reactor under different UV light intensities. It is clear that an approximately linear relationship can be obtained from this study. It indicates that reaction rate constant for photocatalytic oxidation of humic acid followed the pseudo first-order kinetics. This phenomenon indicates that light intensity is one of the most important scale-up parameters of UV/TiO₂ process and that it linearly affects the reaction rate constant. From the experimental results, the reaction rates in terms of TOC, Color₄₀₀ and UV₂₅₄ were proportional to the UV light intensity from 6.703×10^{-5} to 1.314×10^{-4} Einstein/min respectively.

Typical rate constants between hydroxyl radicals and organic substances are in the range of 10^8 – 10^{10} M⁻¹.S⁻¹ (Farhataziz *et al.*, 1977). This means photooxidation of typical organic substances will be practical, even if the steady-state concentration of ·OH radicals in only 10^{-10} – 10^{-12} (William *et al.*, 1989).

Effect of hydrogen peroxide

Photocatalytic oxidation of humic acid of 32.13 mg/L TOC for TOC and Color₄₀₀ removal has been studied at nine different hydrogen peroxide concentrations. Figure 5 shows the degradation of humic acid in the presence of hydrogen peroxide for TOC and Color₄₀₀ removal respectively.

It is indicated that with increasing the initial concentration of hydrogen peroxide, the degradation of humic acid first increased greatly and reached a maximum beyond which they appeared to decline at high hydrogen peroxide dosage. A similar result was also reported by Bekbölet *et al.* (1996). Another phenomenon was that in the range of the experiment, over dosage of hydrogen peroxide also had a positive effect on UV/TiO₂ system compared to that of no H₂O₂ dosage. Compare with the UV/TiO₂ system, it was also found that adding H₂O₂ in UV/TiO₂ system can accelerate the TOC and color removal rate. It is

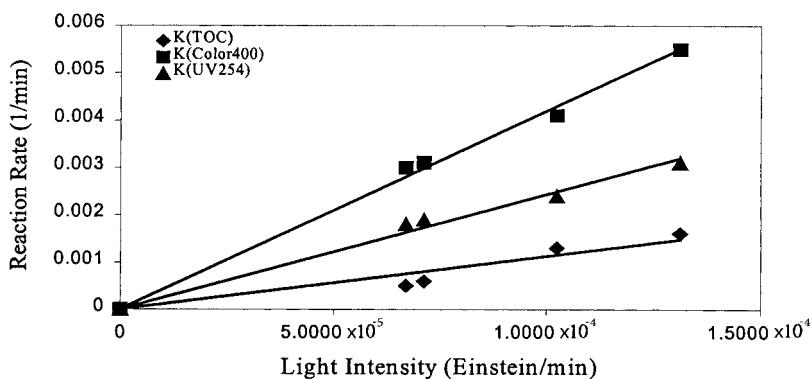


Figure 4 Pseudo first order reaction rate constant versus UV light intensity in UV/TiO₂ heterogeneous reactor. Humic acid concentration was 32.13 mg/L TOC. TiO₂ concentration was 0.3 g/L and pH was 7.0. Temperature was 25°C

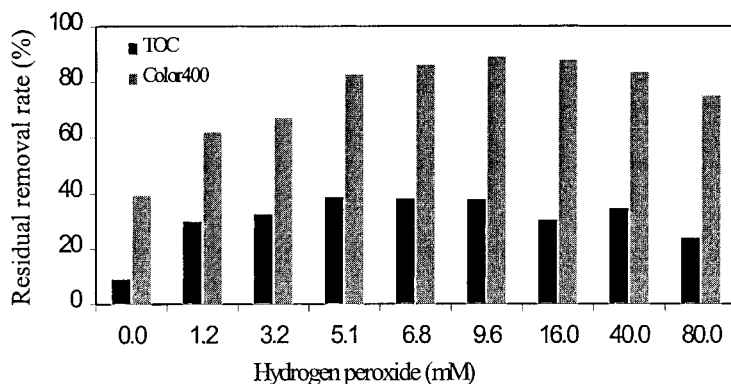
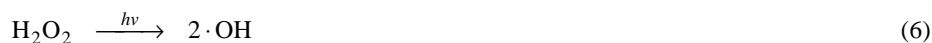


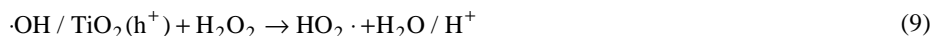
Figure 5 The removal rate of photocatalytic oxidation at different hydrogen peroxide dosage. The concentration of humic acid was 32.13 mg/L TOC. TiO_2 concentration was 0.3 g/L. Light intensity was 6.703×10^{-5} Einstein/min and pH was 7.0. Reaction time was 150 min. Temperature was 25°C

clear that low concentrations of hydrogen peroxide dosage (less than 0.016 M) to UV/ TiO_2 system accelerated the TOC and color₄₀₀ removal rate from 9% to 38% and 40% to 89% respectively. Make a comparison of UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$ and UV/ H_2O_2 systems, under the same UV light intensity (6.703×10^{-5} Einstein/min) and the same H_2O_2 dosage (5.1 mM), the reaction rates for UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$ system were 0.0034 min^{-1} , 0.0118 min^{-1} and 0.0057 min^{-1} in terms of TOC, Color₄₀₀ and UV₂₅₄ respectively, while for UV/ H_2O_2 system, the reaction rates were 0.0019 min^{-1} , 0.0029 min^{-1} and 0.0021 min^{-1} respectively. This comparison reveals that the reaction in UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$ system was much faster than that in UV/ H_2O_2 system.

Wolfrum and Ollis (1994) gave quite a comprehensive review of studies, which concerned the effects of adding hydrogen peroxide to photocatalytic oxidation of various organics. Among these studies, some got positive effects and others on the contrary. In fact, two different mechanisms influenced the character of this effect. The first mechanism is positive acceleration. This means that the dosage of hydrogen peroxide provided additional source of hydroxyl radicals and oxygen.



The second mechanism is negative acceleration. This means that hydrogen peroxide scavenges both hydroxyl radicals and photogenerated holes:



In addition, in the presence of excess O_2 , the semiconductor surface may become highly hydroxylated (Pozzo *et al.*, 1997) to the point of inhibiting the adsorption of humic acid, and thus slows down the reaction rate. This effect was also referred by Lea *et al.* (1998) in the study of photodegradation of sodium dodecyl sulphate.

The effect of adding hydrogen peroxide to photocatalytic system depended on these two mechanisms. In this study, when the concentration of hydrogen peroxide was low, the first mechanism dominated the positive effect. However, when the concentration of hydrogen peroxide was over the maximum level, the second mechanism became pre-eminent and

made the reaction rate decline. In practice, this principle may be used to design TiO_2/UV reactor. If dosing hydrogen peroxide can give a positive effect, hydrogen peroxide should be added slowly and continuously to the photocatalytic oxidation system in order to maintain the concentration of hydrogen peroxide at a relatively low level. This measure may minimize the scavenging effect of hydrogen peroxide and accelerate the reaction. In addition, it may also save the dosage of hydrogen peroxide.

Effect of photocatalytic oxidation on RO membrane filtration processes

It was obvious that the more concentration of humic acids in feed water, the faster the fouling of membranes. Hence, the comparison was made under the same concentration of TOC in two kinds of feed water. One was original humic acid solution made by humic acid directly at concentration 6.45 TOC mg/L. The other solution was treated by photo catalytic oxidation process to reduce the humic acid concentration to 6.41 TOC mg/L from 31.3 TOC mg/L. ES20 flat RO membrane was used to remove TOC in two kinds of feed water for 300 minutes, their comparison results were listed in Table 1.

It is clear that the treated humic acid has the similar zeta potential as pure water and original humic acid solution. TOC removal rate for both pretreated and non-pretreated humic acid was similar. It is usually regarded that humic acid will be broken into small molecular compounds through photo degradation and this may lead to the declination of organic rejection rate of membranes. However, the experimental results indicated that humic acid solution pretreated by photo catalytic oxidation process had no effect on RO membrane filtration processes. The main reason of the results may be explained that humic acid is a kind of complicated high molecular weight compound and it is very difficult to be completely mineralized. So it is suggested that the refractory part of humic acid that resists oxidation may be high molecule weighted. Thus it can be rejected by ES20 RO membrane mostly. On the other hand, the negative charged character of ES20 membrane might also be beneficial for the removal of humic acid, because humic acid colloidal is also negatively charged. The results in Table 1 indicate that photo catalytic oxidation technology can be used as pretreatment technology to remove the TOC and color prior to membrane filtration processes without changing the behavior of membrane filtration processes.

Conclusions

In the presence of H_2O_2 , the photo catalytic oxidation of humic acid solutions in TiO_2 suspended solution was successful to remove TOC at 38% and Color_{400} at 89% within 150-min irradiation. The experimental results indicated that photo catalytic oxidation rate constant was proportional to the incident light intensity. The effect of dosing hydrogen peroxide to the photocatalytic oxidation system was also investigated. The experiment results showed those low concentrations of hydrogen peroxide dosage (less than 0.016 M) to UV/ TiO_2 system accelerated the reaction rate greatly, while over dosage made this positive effect declined. Even at the over dosage of hydrogen peroxide, it also had positive effect

Table 1 The comparison of the effect of photooxidative pretreatment to RO membrane (Driven pressure was 0.55Mpa. Recycling flow rate was 1.44 L/min, pH was 7.0. Temperature was 25°C.)

Feed water type	Ultra pure water	Pretreated by photooxidation	Original humic acid solution
TOC of feed water (mg/L)	0.00	6.41	6.45
TOC of permeate (mg/L)	0.00	1.60	1.68
TOC removal rate	\	75%	74%
Permeate flux (mL/hr)	159.4	143.2	155.4
Zeta potential of membrane at pH7 (mV)	-29.0	-26.5	-29.1

compared to no dosage of hydrogen peroxide. The humic acid solution treated by photocatalytic oxidation in UV/TiO₂/H₂O₂ reactor did not change the behaviors of membrane filtration processes. The parameters found in this study can be used in a scale-up to the commercial reactor for pretreatment of biologically treated effluent prior to membrane filtration processes.

Acknowledgements

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