

# A new submerged membrane photocatalysis reactor (SMPR) for fulvic acid removal using a nano-structured photocatalyst

Jianfeng Fu<sup>a,\*</sup>, Min Ji<sup>a,1</sup>, Zheng Wang<sup>b,c</sup>, Luonan Jin<sup>a</sup>, Dingnian An<sup>a</sup>

<sup>a</sup> School of Environmental Science and Engineering, Tianjin University, Weijin Road 92, Nankai District, Tianjin 300072, China

<sup>b</sup> School of Environmental and Municipal Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

<sup>c</sup> School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

Received 19 May 2005; received in revised form 9 September 2005; accepted 20 September 2005

Available online 2 November 2005

## Abstract

The study focuses on the degradation of fulvic acid by nano-structured TiO<sub>2</sub> in a submerged membrane photocatalysis reactor (SMPR). It has been demonstrated that the composite TiO<sub>2</sub> photocatalyst could be automatically settled due to its gravity and then be easily separated by MF membrane. In addition, it was more efficient to maintain high flux of membranes than that of commercial TiO<sub>2</sub> P25. The paper describes the effects of operational parameters on the photocatalytic degradation of fulvic acid in SMPR. It was found that the photocatalyst at 0.5 g/L and airflow at 0.06 m<sup>3</sup>/h were the optimal condition for the removal of fulvic acid (FA) and the FA degradation rate was higher at acidic condition than that at alkaline media. In order to compare the effects of different filtration duration on permeate flux rate of MF, P25 powder and nano-structured TiO<sub>2</sub> were employed. According to the experiments, the permeate flux rate of MF is improved and thus the membrane fouling phenomenon is reduced with the addition of nano-structured TiO<sub>2</sub> catalyst. Therefore, the submerged membrane photocatalysis reactor can be potentially applied in photocatalytic oxidation process during drinking water treatment.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Fulvic acid; Microfiltration membrane; Nano-structured TiO<sub>2</sub>; Photocatalytic oxidation; Reactor

## 1. Introduction

Natural organic matter (NOM) is widely distributed in soil, natural water, and sediments and consisted of a mixture of the decomposition products of plant and animal residues [1]. The main components of NOM are humic acid (HA) and fulvic acid (FA). In water purification, the disinfection by-products (DBPs) like trihalomethanes (THMs) were formed from chlorination of drinking water containing NOM [2,3]. In Tianjin, it has been reported that more than 70% of NOM in surface waters was fulvic acid, representing a major fraction of NOM [4]. Consequently control of fulvic acid plays an important role in treating the surface water. Some studies have reported that NOM with fulvic acids is difficult to remove by the conventional treatment processes. In general, the removal efficiency of TOC in con-

ventional drinking water treatment processes is only 10–50% [5].

TiO<sub>2</sub>-mediated photocatalytic oxidation (PCO) has been the focus of numerous investigations in recent years. In particular, owing to the formation of hydroxyl radicals ( $\bullet$ OH), PCO shows an extraordinarily oxidizing power in the reaction mixture and can thus mineralize a myriad of undesirable organic matters to CO<sub>2</sub>, H<sub>2</sub>O and inorganic constituents [6]. The catalyst can be applied in the form of powder suspended in a slurry or it can be immobilized on various supporting medium, such as glass, quartz or stainless steel [7,8]. Each configuration has its advantages and disadvantages. In case of catalyst fixed onto a supporting material, a drawback is mass transfer limitations of pollutants to the surface of the photocatalyst. When a suspension of catalyst is used the photocatalytic degradation efficiency is high. However, the catalyst particles have to be separated from treated water after detoxification.

A very promising method for solving the above-mentioned problems is coupling the photocatalysis and membrane techniques. The membrane would play both the role of a simple

\* Corresponding author. Tel.: +86 22 27404005; fax: +86 22 27406057.

E-mail addresses: fjf.tju@126.com (J. Fu), jimin@tju.edu.cn (M. Ji).

<sup>1</sup> Tel.: +86 22 27404005; fax: +86 22 27406057.

barrier for the catalyst and of a selective barrier for the molecules to be degraded [9]. Molinari et al. [9] immobilized P25 photocatalyst on different flat polymeric membranes, but the membranes were slightly damaged by UV irradiation depending on the membrane materials. Other researchers also tried to use a batch-recirculated slurry photoreactor associated with a hollow fiber ultrafiltration membrane unit for the degradation of humic acid [10]. The photocatalyst described in the literature was fine powder TiO<sub>2</sub> P25 photocatalyst. The major problems with application of powder catalyst are greater membrane flux decline and membrane fouling. In fact, it is reported that TiO<sub>2</sub> particles in suspension have a better efficiency than that in immobilized form [11].

In this study, a submerged membrane photocatalysis reactor (SMPR) was designed for degradation of fulvic acid by using novel nano-structured TiO<sub>2</sub>/silica gel photocatalyst. The synthesized TiO<sub>2</sub>/silica gel catalyst particles with an average size of 50 μm were small enough for suspension to bubble air through and to stir. On the other hand, the particles in the suspension were big enough to settle while having the TiO<sub>2</sub> with high activity. Thus, it could be easily separated, recovered and reused by microfiltration separation process. More significantly, it was efficient to maintain high flux of membranes. This paper presented the experimental investigation on the possibility of coupling photocatalysis and membrane for degradation of fulvic acid in aqueous solution. The effects of the operational parameters including TiO<sub>2</sub> loading (0–0.6 mg/L), pH (3.4–10.3), airflow (0.01–0.09 m<sup>3</sup>/h) were investigated. The possibility of using novel TiO<sub>2</sub> for the prevention of MF membrane fouling for water purification was tested as well.

## 2. Experiments

### 2.1. Materials

The nano-structured TiO<sub>2</sub>/silica gel photocatalyst employed in this study was obtained from Kunland University, Australia, with a BET surface area of 250 m<sup>2</sup>/g and an average particle size of 50 μm. Titanium dioxide P25 (Degussa, Germany), mainly anatase (ca. 70%) under the shape of non-porous polyhedral particles of ca. 30 nm mean size with a surface area of 50 m<sup>2</sup>/g. Fulvic acids were provided by Beijing Chem. Corp. The concentration of FA used in the experiment was 11.95 TOC mg/L. The microfiltration membrane module made of polyvinylidene (PVDF) hollow fiber membranes with a pore size of 0.2 μm and a filtration area of 0.2 m<sup>2</sup> was provided by Mo Tian Mo Corp., Tianjin. The pH of the solutions was adjusted by the addition of either H<sub>2</sub>SO<sub>4</sub> or NaOH. All reagents utilized were of analytical purity.

### 2.2. Photoreactor

The SMPR process, shown in Fig. 1, was designed and conducted in a laboratory-scale. The reactor was made of plexiglass with a working volume of 3200 cm<sup>3</sup>. A light tight baffle separated the reactor into two parts: the photocatalytic oxidation zone and the membrane separation zone, which were connected by a bottom flow channel and an overflow channel. The low pressure UV lamp (11 W, Philip) emitting a wavelength of predominantly 253.7 nm was suspended vertically inside the quartz glass cylinder in the middle of the photocatalytic zone. Air was supplied from a porous titanium plate directly below the membrane

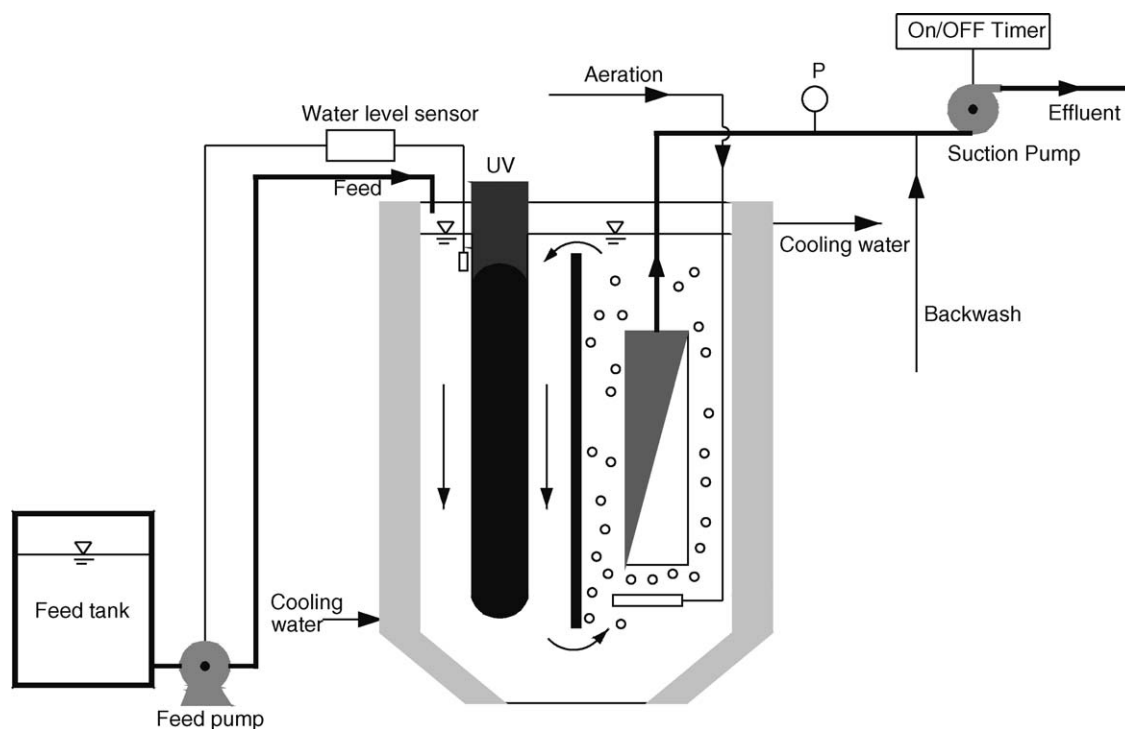


Fig. 1. Schematic diagram of the SMPR system.

module in order to provide dissolved oxygen for photoreaction, fluidize the TiO<sub>2</sub> particles and create sufficient turbulence along the membrane surface. The reaction temperature was maintained at about 20 °C with the aid of recirculation cooling water. A negligible change of reaction volume was observed due to evaporation of water when turning on the lamp. The filtration was continuously obtained by using a suction pump. A water level sensor was used to maintain a constant level in the reactor. After each run of experiments the membrane was cleaned by gas back-flushing followed by tap water backflushing. Additionally, the exterior wall of the reactor was covered with a reflecting aluminum foil to improve the efficiency of UV utilization.

### 2.3. Analytical methods

The total organic carbon was analyzed with TOC-5000A (Shimadzu, Japan). The pH was measured by a HACA digital pH-meter (model pHs-3C). The light intensity was measured by a UV Irradiance Meter (Model UV-A).

## 3. Results and discussion

### 3.1. Effects of TiO<sub>2</sub> concentration

Photocatalyst concentration is a major parameter, which affects the photocatalytic oxidation rate. In order to avoid the use of excess catalyst it is necessary to find out the optimum loading for efficient removal of FA. According to Herrmann et al. [12], the TiO<sub>2</sub> photocatalytic reaction follows the first-order kinetic model. The effect of catalyst concentration on TOC removal of FA was investigated from 0 to 0.6 g/L at pH 5.33. HRT was fixed at 248 min.

Fig. 2 shows the patterns of reaction rate of FA degradation during the SMPR process performance under different TiO<sub>2</sub> concentrations. It is clear from Fig. 2 that degradation reaction of FA also follows the pseudo first-order kinetics, and the reaction rate increases with the concentration of TiO<sub>2</sub>. In the case of

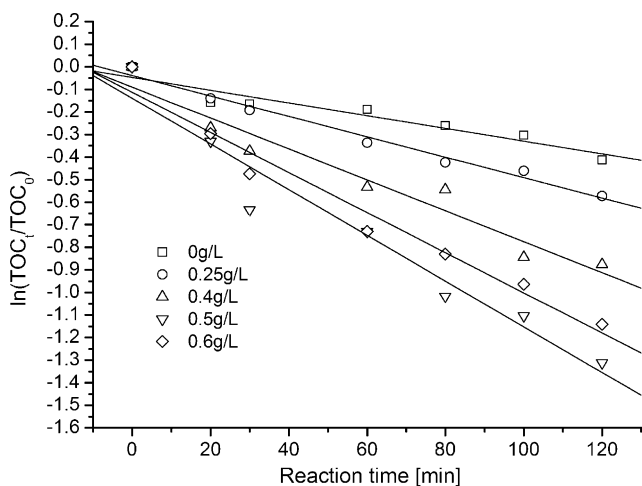


Fig. 2. Kinetic effect of TiO<sub>2</sub> concentration on photocatalytic oxidation of FA (TOC<sub>0</sub> = 11.95 mg/L, airflow = 0.06 m<sup>3</sup>/h, I = 0.75 mW/cm<sup>2</sup>, pH 6.5, HRT = 248 min).

reaction rate, the highest value was observed for catalyst concentration equal to 0.5 g/L. When the catalyst concentration of 0.6 g/L was applied, reaction rate of FA degradation decreased slightly. The observed decrease of reaction rate was probably due to the following reasons: as the catalyst concentration increases, the number of photons absorbed and the number of FA molecules adsorbed increase because of an increase in the number of catalyst particles. At a certain level, the number of available substrate molecules is insufficient for adsorption by the increased number of TiO<sub>2</sub> particles. At the same time, due to an increase in the turbidity of the suspension, there is a decrease in UV light penetration as a result of increased scattering effect and hence the photoactivated volume of suspension decreases. Therefore above a certain level, additional particles are not involved in catalyst activity.

On the basis of the experiments discussed above, a catalyst concentration of 0.5 g/L was chosen as the optimum one for this hybrid process.

### 3.2. Effects of pH on FA oxidation

In the photocatalytic system, pH value is an important parameter for determining the properties of both the solid catalyst and the solute molecules. As a result, pH can influence both photocatalytic reactions and the rate of adsorption on the TiO<sub>2</sub> surface. In this experiment, the initial TOC concentration of FA was 11.95 mg/L and the TiO<sub>2</sub> loading was 0.5 g/L. The pH was adjusted by H<sub>2</sub>SO<sub>4</sub> and NaOH. Results of the experiments at pH 3.4, 6.5, 8.2, and 10.3, respectively, in the form of kinetic curves are presented in Fig. 3. The results indicated that pH value had a significant effect and at low pH values photodegradation rates were quite high. Degradation rate for FA increased rapidly with a decrease of pH value.

The overall photoreaction can be described as follows [13]:

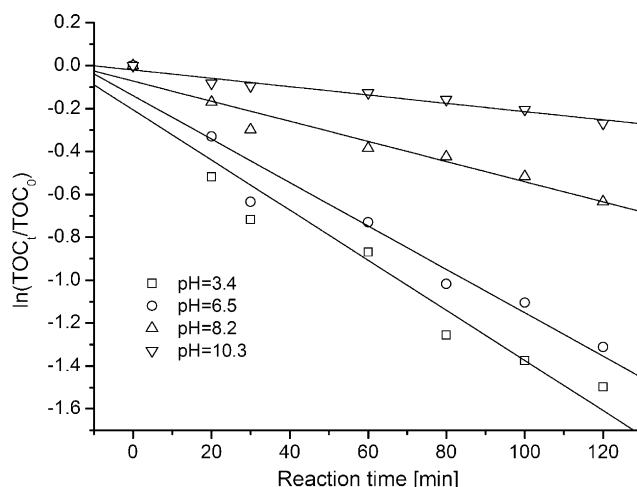
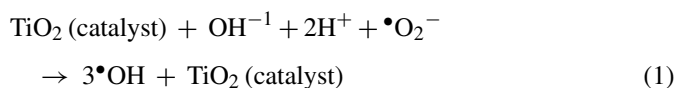


Fig. 3. Kinetic effect of pH value on photocatalytic oxidation of FA (TOC<sub>0</sub> = 11.95 mg/L, airflow = 0.06 m<sup>3</sup>/h, I = 0.75 mW/cm<sup>2</sup>, HRT = 248 min).

Equilibrium constant  $K_e$  is written as Eq. (2)

$$K_e = [\bullet\text{OH}]^3 / ([\text{OH}^-][\text{H}^+]^2[\bullet\text{O}_2^-]) \quad (2)$$

Since  $[\text{OH}^-][\text{H}^+] = K_w = 1 \times 10^{-14}$ , Eq. (2) can be rewritten as

$$[\bullet\text{OH}]^3 = K_e K_w [\text{H}^+][\bullet\text{O}_2^-] \quad (3)$$

The concentration of  $[\bullet\text{OH}]$  increases with concentration of  $[\text{H}^+]$  in the acidic region. Thus, the photodegradation rate constant of FA is more rapidly at pH 3.4 than that at pH 10.3. However, since hydrogen concentration is too high in the strong acidic region [14], Eqs. (1)–(3) may be accepted in explaining the effect of pH on the photodegradation of FA below pH 4.

### 3.3. Effects of airflow

In general, a bubble column reactor with a porous plate distributor can offer best gas–liquid mass transfer efficiency [15]. In view of this consideration, a special kind of porous titanium plate was used as a gas distributor in this study. During the experiment, many thinly distributed air-bubbles with a size of about 1 mm are generated, which was beneficial to mass transfer and oxygen dissolving. It is well known that oxygen plays a vital role in the photocatalytic reaction and provides dual functions. One is to supply essential oxygen to capture photogenerated electrons, reducing the recombination of photogenerated electron and hole [16] (Eq. (4)), and the other is to agitate the solution in order to speed up mass transfer



The relationship between airflow and the reaction rate of photocatalytic degradation of FA was illustrated in Fig. 4. It is easy to see that the rate constant increases considerably from 0.01 to 0.09  $\text{m}^3/\text{h}$  with airflow, but exhibits a maximum at approximately 0.06  $\text{m}^3/\text{h}$  and then decreases slightly after the maximum point. This is possibly due to the fact that the adsorption reaction of FA onto the catalyst could be considerably slowed down

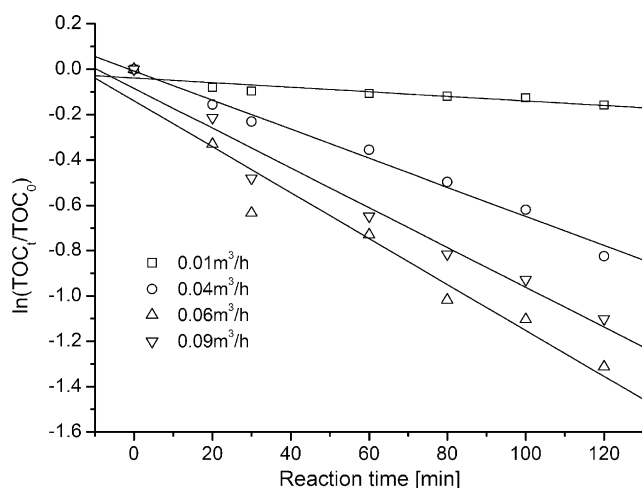


Fig. 4. Kinetic effect of airflow on photocatalytic oxidation of FA ( $\text{TOC}_0 = 11.95 \text{ mg/L}$ ,  $I = 0.75 \text{ mW/cm}^2$ , pH 6.5, catalyst = 0.5 g/L, HRT = 248 min).

when more air is sparged into the reactor. In addition, the capturing effect of molecular oxygen to photogenerated electrons could be greatly reduced because large airflow was not favorable to the adsorption of air onto photocatalyst. It is also observed that the required air volume is approximately 0.014  $\text{m}^3$  when TOC concentration of FA reduces from 11.95 to 3.218 mg/L in 120 min.

### 3.4. MF membrane performance

In order to determine the effect of the presence of this spherical ball-shaped photocatalyst on MF process performance, especially on the permeate flux, investigations using catalyst suspension were performed. The TMP was remained on a constant value (0.005 MPa) during the whole process.

The experimental results indicated that the spherical ball-shaped photocatalyst played an influential role on the specific permeate rate. Fig. 5 shows the comparative results obtained with powder P25 and nano-structured  $\text{TiO}_2$  photocatalyst at 0.5 g/L during MF process. It is evident from the MF membrane performance that when nano-structured  $\text{TiO}_2$  photocatalyst is mixed with FA solution, the permeate flux of MF is improved. With the addition of P25, the permeate flux rate is 25.2  $\text{L/h m}^2$  at the filtration duration of 200 min while the permeate flux rate is 48  $\text{L/h m}^2$  with the addition of nano-structured  $\text{TiO}_2$  photocatalyst. Permeate flux decreases a bit slightly and then reaches the steady value when the filtration duration is beyond 200 min. Clearly, the spherical ball-shaped  $\text{TiO}_2$  photocatalyst improves the service life of the MF membrane by reducing fouling on the membrane surface. Moreover, unlike P25 the spherical ball-shaped catalyst particle will not easily deposit internally, which eventually will not cause pore closure. It was noted that the lower concentration of fulvic acid used in this study did lead to less fouling.

On the basis of the experiment, it was found that the MF membrane in the SMPR can solve the difficulty of photocatalyst separation from water. In addition, the fouling problem on filtration membrane was reduced when nano-structured  $\text{TiO}_2$  is used.

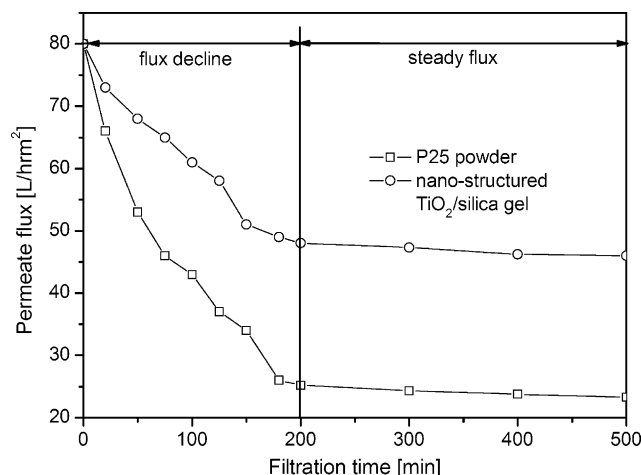


Fig. 5. Effects of different catalyst on permeate flux ( $\text{TOC}_0 = 11.95 \text{ mg/L}$ , pH 6.5, airflow = 0.06  $\text{m}^3/\text{h}$ ,  $I = 0.75 \text{ mW/cm}^2$ , TMP = 0.005 MPa).

#### 4. Conclusions

The SMPR system for advanced photooxidation process with nano-structured TiO<sub>2</sub> catalyst has been preliminarily developed in this study. Experimental results indicate that an optimum catalyst loading is to be 0.5 g/L. Degradation of FA is more effective in acidic conditions at airflow of 0.06 m<sup>3</sup>/h. High conversion of reactants can be achieved at pH 3.4 in 2 h irradiation. This nano-structured TiO<sub>2</sub> photocatalyst has potential application because it has a larger particle size than P25 and can be easily separated and reused by membrane separation. The addition of nano-structured TiO<sub>2</sub> in the reactor resulted in an increase of permeate flux rate in comparison with TiO<sub>2</sub> P25 powder. For this reason the addition of nano-structured TiO<sub>2</sub> provides great potential reduction of fouling problems on the membrane surface. The hybrid process coupling the photocatalysis and MF is a novel method in removal of organic compounds. However, in order to select the best process conditions and to reveal the mechanism of FA photodegradation in such a reactor further extensive investigations are highly desirable.

#### Acknowledgements

The work described in this paper was fully supported by a grant from the Corporation Foundation of Tianjin University and Nankai University, China. The authors sincerely thanks Dr. Yaqian ZHAO of University College Dublin for his help in English language expression.

#### References

- [1] H. Degaard, B. Eikebrokk, R. Storhaug, Processes for the removal of humic substances from water—overview based on Norwegian experiences, *Wat. Sci. Technol.* 40 (9) (1999) 37–46.

- [2] A.A. Stevens, C.J. Slocum, Chlorination of organics in drinking water, *J. Am. Water Works Assoc.* 68 (1976) 615–623.
- [3] T.J. Casey, K.H. Chua, Aspects of THM formation in drinking water, *J. Water Supply Res. Technol.* 46 (1) (1997) 31–32.
- [4] An Ding Nian, Organic matter on ultra water and prevention technology, *Technol. Water Treatment* 1 (1982) 7–11.
- [5] J.G. Jacangelo, J. DeMarco, D.M. Owen, S.J. Randtke, Selected process for removing NOM, *J. AWWA* 87 (1) (1995) 64–77.
- [6] E.C. Butler, A.P. Davis, Photocatalytic oxidation in aqueous titanium dioxide suspensions: the influence of dissolved transition metals, *J. Photochem. Photobiol. A: Chem.* 70 (1993) 273–283.
- [7] V. Loddò, G. Marci, L. Palmisano, A. Sclafani, Preparation and characterization of Al<sub>2</sub>O<sub>3</sub> supported TiO<sub>2</sub> catalysts employed for 4-nitrophenol photodegradation in aqueous medium, *Mater. Chem. Phys.* 53 (3) (1998) 217–224.
- [8] G.P. Lepore, L. Persaud, C.H. Langford, Supporting titanium dioxide photocatalysts on silica gel and hydrophobically modified silica gel, *J. Photochem. A: Chem.* 98 (1–2) (1996) 103–111.
- [9] R. Molinari, M. Mungari, E. Drioli, Study on a photocatalytic membrane reactor for water purification, *Catal. Today* 55 (2000) 71–78.
- [10] S.H. Lee, K.H. Choo, C.H. Lee, Use of ultrafiltration membrane for the separation of TiO<sub>2</sub> photocatalysts in drinking water treatment, *Ind. Eng. Chem. Res.* 40 (2001) 1712–1719.
- [11] D. Robert, A. Gauthier, Prospects for a supported photocatalyst in the detoxification of drinking water, *Water Qual. Int.* 11–12 (1998) 27–35.
- [12] J.M. Herrmann, M.N. Mozzanega, P. Pichat, Oxidation of oxalic acid in aqueous suspensions of semiconductors illuminated with UV or visible light, *J. Photochem.* 22 (4) (1983) 333–343.
- [13] O. Legrini, E. Oliveros, A.M. Braun, Photochemical process for water treatment, *Chem. Rev.* 93 (1993) 671–698.
- [14] M.S. Kim, J.G. Chung, A study on the adsorption characteristics of orthophosphates on rutile-type titanium dioxide in aqueous solutions, *J. Colloid. Interf. Sci.* 233 (2001) 31–37.
- [15] I.Z. Shirgaonkar, A.B. Pandit, Sonophotocatalytic destruction of aqueous solution of 2,4,6-trichlorophenol, *Ultrason. Sonochem.* 5 (1998) 53–61.
- [16] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, *Chem. Res.* 93 (1993) 341–357.