Desalination and Water Treatment
www.deswater.com

21 (2010) 303–307
September

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doi: 10.5004/dwt.2010.1620

A new microfiltration photocatalytic reactor for DDT removal

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Received 4 November 2009; accepted 8 March 2010

ABSTRACT

In this paper, a process combining stainless steel membrane and UV/TiO_2 is developed to degrade DDT in water. The photocatalyst TiO_2 was deposited on a kind of glass cenospheres whose diameters ranged from 20 to 200 μm, so they could be kept in the reactor by microfiltration membrane. The influence of different variables (TiO_2 concentration, radiation) on the reaction rate was tested. According to the experiment, the removal was mainly caused by adsorption during the early stages of the reaction and mainly by UV/TiO_2 degradation in the later stages. Three sample solutions with DDT concentrations: $C_0 = 30$, 40 and 50 μg/L, were treated in the reactor and the removal rate of DDT was found to be 98.3%, 97.8% and 97.6%, respectively. Adequate dosage of the catalyst increased the generation rate of electron/hole pairs which promoted the formation of OH radicals for enhancing photodegradation.

Keywords: Drinking water; Stainless steel membrane; Persistent organic pollutants

1. Introduction

DDT[(1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane)] is one of the 12 persistent organic pollutants urgently needed to be eliminated because they are characterized by a high solubility in greases. Although the use of some chloroorganic insecticides in agriculture was banned in most countries in the last century, thousands of tons of obsolete pesticide deposits in farms and other places have been jeopardizing the environment [1–3]. The level of DDT is regarded as one of the non-regular indices in the newly issued drinking water standards in China. Several methods can be applied to remove DDT from water, these include membrane filtration [4], activated-carbon absorption [5] or Fenton oxidation [6]. However, they only transfer DDT from one phase to another, rather than chemically destructing the toxic compound.

Titanium dioxide, TiO_2, has been used as photocatalyst in numerous researches [7,8] since TiO_2 surface under UV-irradiation can generate highly oxidative electrical holes to decompose various aqueous organic compounds, particularly at ambient temperature and pressure conditions. In the beginning of the experiment, TiO_2 powder was directly added to water without reclamation [9–11]. In subsequent tests however, membrane was used for reclaiming TiO_2 powder [12,13] or immobilized TiO_2 on fixed media, such as optical fiber [14], rotating disc [15], and corrugated plate [16]. Although membrane can retain TiO_2 powder in reactor, frequent backwashing is required, otherwise membrane fouling may occur. In addition, the reduction in the efficiency in immobilized mode pose a problem in designing proper reactor system. Stainless steel membrane has been used in many researches for the purpose of separation [17,18].

In this study, we developed a new membrane photocatalytic reactor for DDT removal in water. The

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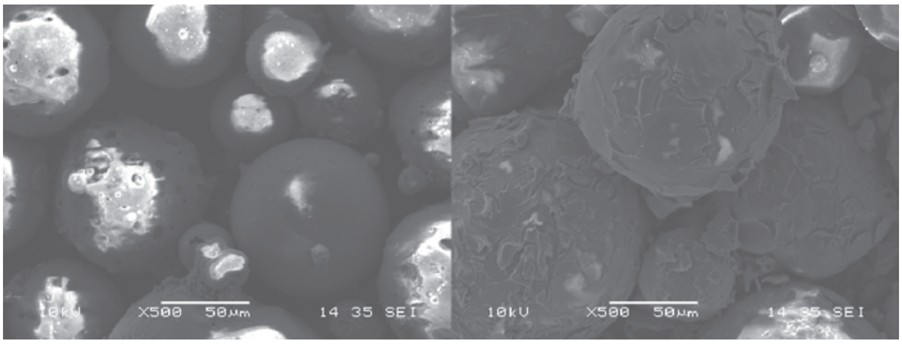

(a) Cenospheres (b) Coated with TiO_2 film

Fig. 1. Cenospheres before and after being coated with TiO_2 film.

reactor is combined with immobilized TiO_2 and stainless steel microfiltration.

2. Experimental

2.1 Materials

The photocatalyst was made by means of sol–gel [5], and all the chemicals were at least the ACS grade, supplied by Sinopharm Chemical Reagent Co., Ltd. With isopropyl alcohol (IPA) as a solvent of titanium tetra-butoxide and HNO_3 as a catalyst, TiO_2 sol was prepared by the partial hydrolysis and polycondensation with water. The molar ratio of titanium tetra-butoxide and water was 1:1. The mixture was vigorously stirred with magnetic stirrer for 2 h. The solution was tinged with transparent yellowish and kept for 24 h until film deposition.

The source water was prepared from distilled water spiked with DDT standard sample. The pH of the DDT-containing water was around 7.5 and was unchanged during the reaction. Since DDT is insoluble in water and easily adsorbed by solid powder, the cenospheres are put into the reactor in the absence of UV and stirred for 2 h before the experiment.

The substrate for depositing TiO_2 thin films was a sort of glass cenospheres generally used as an additive for engineering plastic. The density of the cenospheres was 0.6–0.8 g/cm^3 with diameters ranging from 20 to 200 µm. The average specific surface area of the glass cenosphere was 1.9 m^2/g. Until film deposition, the cenospheres were blended with water in the volume ratio of 1:3, stirred for 24 h and then selected by flotation. The selected cenospheres were put into above sol solution and then stirred for 30 min before being separated with filter paper. Films so obtained were first dried at 100°C and then annealed at various temperatures from 200 to 550°C for 1 h in muffle furnace. After being coated with TiO_2 film, the true density of the cenospheres was changed to 0.8–0.9 g/cm^3 (Fig. 1).

The stainless steel membrane was purchased from Hyflux Company, Shanghai and the membrane pore size was 0.1 µm in average.

2.2. Analytical methods

During photodegradation DDT is measured by a Gas Chromatographer (Shimadzu GC-2010) with a HP-5 fused silica capillary column (30 m × 0.32 mm I.D., film thickness of 0.25 µm) [19]. Residual pollutants in water were extracted with n-hexane and one microlitre aliquot of extraction was analyzed. The injector temperature was set to 250°C. The ECD was maintained at 300°C. The temperature of GC oven was programmed as follows: 100°C, isothermal for 2 min, then it was raised by 20°C/min to 250°C and held at 250°C for 10 min.

2.3 Reactors and procedure

A schematic representation of the geometry of the photocatalytic reactor is shown in Fig. 2. The reactor is composed of a water box, UV lamps, cenospheres coated with photocatalyst and stainless steel membrane that prevents fine cenospheres from escaping. The diameters of pores in the membrane were about 0.1 µm. In static state, the cenospheres can be floated on water. Bubblers fixed at the bottom of the reactor aerate to ensure a well-mixed condition in the reaction zone. Furthermore, the fed bubbles suspended the cenospheres to provide a good mass transfer condition for the reaction and prevent them from adhering to the surface of membrane. Each UV lamp was installed in a two-tier quartz casing, and cooling water passed through the casing to maintain the reaction temperature. Before filling water in the reactor, UV light

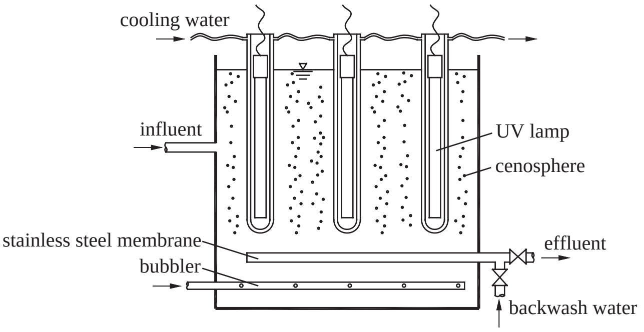

Fig. 2. UV/TiO_2 and stainless steel microfiltration combined reactor.

intensity at the quartz casing surface was tested with cooling water passing through the casing.

3. Results and discussion

3.1. The adsorption of DDT by cenospheres

DDT adsorption from water by cenospheres was determined by measuring DDT remaining in solution. In the test, the concentration of cenospheres was 2 g/L while the concentration of DDT in raw water samples were 31.2, 52.5 and 80.1 μg/L, respectively. The reactor was run in dark condition and the results indicate that the adsorption was almost complete during the first 10 min of the experiment as illustrated by Fig. 3. In order to detect the removal effect of DDT by photocatalytic reaction, water was sampled after the first and subsequent 10 min for all the tests.

3.2. The contributing factors towards DDT removal

Three initial concentrations of DDT solution ($C_0 = 30$ μg/L, 40 μg/L, 50 μg/L) were treated in the reactor. C_p represents the concentration of DDT in water samples and the removal rate can be defined as $(C_0 - C_p)/C_0$, After 70 min of irradiation in the presence of TiO_2 deposited on the cenospheres, the removal rate of DDT was 98.3%, 97.8% and 97.6%, respectively.

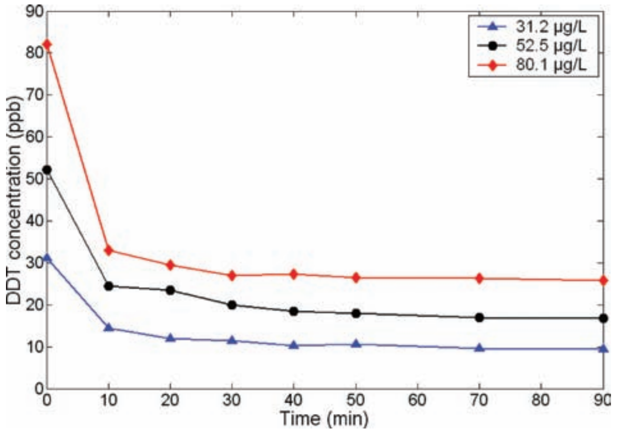

Fig. 3. Adsorption of DDT by cenospheres at different initial concentrations.

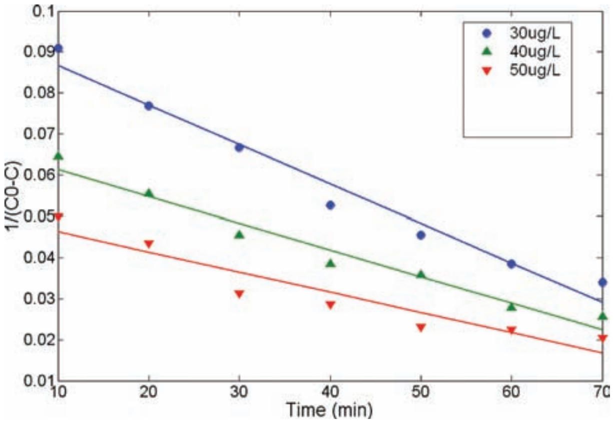

Fig. 4. Relation between $1/(C_0 - C)$ and time.

It can be seen from Fig. 4 that $1/(C_0 - C)$ is in linear relation with time, so this phenomenon is illustrated well in second-order kinetics:

$$r = kC_p^2, \tag{1}$$

where r represents the reaction rate of DDT degradation, μg/L.min; k is the second-order degradation constant of the main compound (DDT), L/μg.min.

On condition that the reaction zone is mixed completely and the power of UV is not changing, there are mainly two factors related to k: UV light intensity and photocatalyst concentration [20]. So k is the function of I and C_c as in Eq. (2):

$$k = f(I, C_c), \tag{2}$$

where I represents the light intensity, μW/cm^2; and C_c represents the photocatalyst concentration of the reactor, g/L.

3.2.1. The effect of UV light intensity on k

The influence of the UV light intensity on the degradation of DDT was investigated by using different power of 254-nm lamp. The power of the lamp was varied from 8 to 32 W while other reaction conditions were kept constant.

According to the result (Fig. 5), it was found that UV light intensity has significant effect on the rate of photocatalytic degradation of DDT. The stronger the UV light intensity, the deeper the penetration of UV light into the catalyst. Since the concentration of photocatalyst was kept constant, the reaction rate was

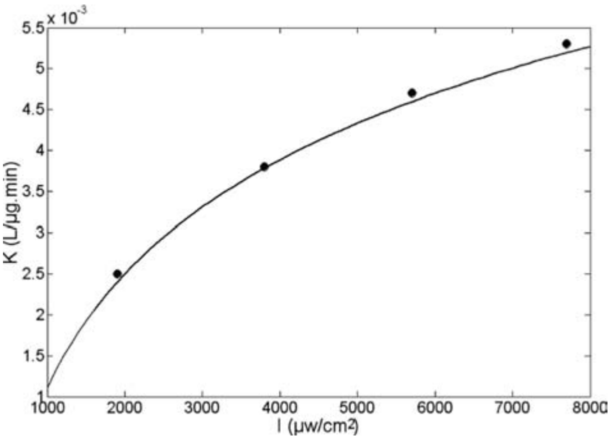

Fig. 5. Relation between k and total UV light intensity ($C_c = 2$ g/L; air flow = 0.5 L/L.min).

not proportional to the light intensity at high intensity level.

3.2.2. *The effect of C_c on k*

The effect of C_c on k is shown in Fig. 6. It shows that more DDT was removed with the increase of cenospheres concentration which led to an increase in the number of reaction sites and thus the quantity of hydroxyl radicals produced. A further increase in catalyst loading may cause opacity and light scattering and thus decrease in the passage of irradiation through the solution. Therefore, the degradation rate was not linear with respect to the concentration of cenospheres.

3.3. *The fouling of stainless membrane*

By keeping the water level of the box and the valve of effluent unchanged during the test, the flux of effluent along time is as shown in Fig. 7. Though the value decreased during the whole process, the slope was very small. The reasons can be attributed to following: the first reason is that, the treatment sample was prepared from distilled water. As such, it was clean and difficult to be fouled. Secondly, the mixing effect from air made the water to be in a fluidized state, which kept cenospheres and some other granules from adhering on the membrane. Finally, there was little catalyst powder casted from cenospheres, which also kept the water clean.

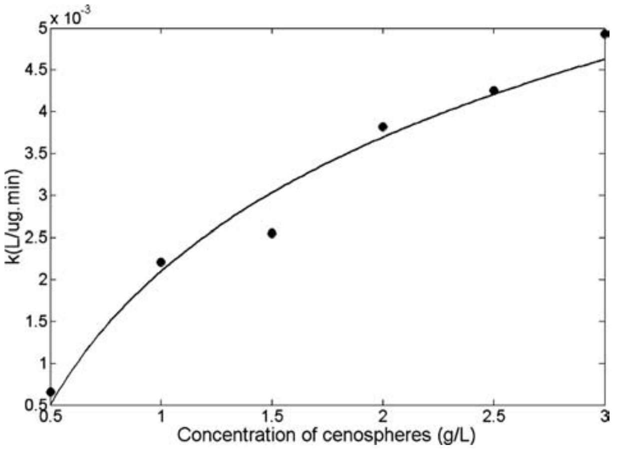

Fig. 6. Effect of the concentration of cenospheres on DDT removal (UV light intensity = 1,200 μw/cm^2).

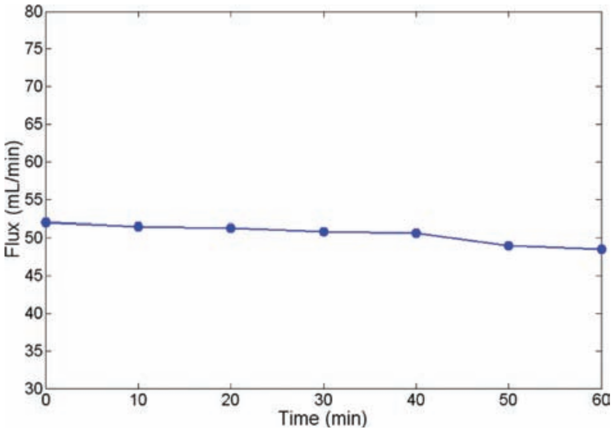

Fig. 7. Change of flux with time during the test.

4. Conclusion

During the process of catalytic oxidation of DDT, the active surface area of the catalyst is very important. At the same time one has to consider the catalyst stability, recovery and reuse since it is expensive and can cause solid pollution if disposed arbitrarily. In the experiment, the photocatalyst TiO_2 was deposited on a kind of glass cenospheres whose diameters ranged from 20 to 200 μm. Stainless steel membrane was used to ensure the photocatalysts remained within the reactor during the treatment. With high TiO_2 specific surface area and good mass transfer efficiency, the reactor was effective to remove DDT in water. Within an appropriate range, higher photocatalyst concentration led to higher reaction efficiency. However, excessive photocatalyst may cause opacity and light scattering and thus decrease in the passage of irradiation through the solution. The reactor is suitable for treating water with refractory organic matter but without turbidity.

Acknowledgement

This work was kindly supported by the following: the National Natural Science Foundation of China, (Project 50808134), the Chinese National Eleven Five-Year Scientific and Technical Support Plans (No. 2006BAJ08B02 and 2006BAJ08B06), the Chinese State Key Laboratory of Pollution Control and Resource Reuse; (No. PCRRY08002) and the Chinese National Major Project of Science & Technology Ministry (Grant No.2008ZX07421-002).

Reference

[1] L.K. Thetwar, P.K. Sarway, S. Gupta, M.R. Augar, R.C. Tandon and H.S. Dewangan, Concentration, distribution of DDT and Malathion in soil water, plant and fishes in Rajnandgaon, India. Asian J. Chem., 19 (2007) 1562–1564.

[2] T. Satapanajaru, P. Anurakpongsatorn and P. Pengthamkeerati, Remediation of DDT-contaminated water and soil by using pretreated iron byproducts from the automotive industry. J. Environ. Sci. Health Part B – Pest. Food Contam.Agric. Wastes, 41 (2006) 1291–1303.

[3] K. Feng, B.Y. Yu, D.M. Ge, M.H. Wong, X.C. Wang and Z. H Cao, Organo-chlorine pesticide (DDT and HCH) residues in the Taihu Lake Region and its movement in soil-water system I. Field survey of DDT and HCH residues in ecosystem of the region, Chemosphere, 50 (2003) 683–687.

[4] B.O. Yoon, S. Koyanagi, T. Asano, M. Hara and A. Higuchi, Removal of endocrine disruptors by selective sorption method using polydimethylsiloxane membranes. J. Membr. Sci., 213 (2003) 137–144.

[5] D. Di Claudio, A.R. Phani and S. Santucci, Enhanced optical properties of sol-gel derived TiO2 films using microwave irradiation, Opt. Mater., 30 (2007) 279–284.

[6] R. Boussahel, D. Harik, M. Mammar and S. Lamara-Mohamed, Degradation of obsolete DDT by Fenton oxidation with zerovalent iron, Desalination, 206 (2007) 369–372.

[7] M.C. Vincent-Vela, E. Bergantinos-Rodriguez, S. Alvarez-Blanco, et al. An approach to heoretical prediction of permeate flux decline in ultrafiltration, Desalination Water Treat., 10 (2009) 134–138.

[8] M.C. Vincent-Vela, S. Alvarez-Blanco, J. Lora-Garcia, et al., Prediction of ultrafiltration permeate flux decline by means of a shear induced diffusion model with empirical estimation of the gel layer concentration, Desalination Water Treat., 10 (2009) 139–143.

[9] A.P. Toor, A. Verma, C.K. Jotshi, P.K. Bajpai and V. Singh, Photocatalytic degradation of Direct Yellow 12 dye using UV/TiO2 in a shallow pond slurry reactor, Dyes Pig., 68 (2006) 53–60.

[10] F. Shiraishi, M. Nagano and S.P. Wang, Characterization of a photocatalytic reaction in a continuous-flow recirculation reactor system, J. Chem. Technol. Biotechnol., 81 (2006) 1039–1048.

[11] W.L. Kostedt, et al., Magnetically agitated photocatalytic reactor for photocatalytic oxidation of aqueous phase organic pollutants, Environ. Sci. Technol., 39 (2005) 8052–8056.

[12] R. Molinari, et al., Photocatalytic degradation of dyes by using a membrane reactor. Chem. Eng. Process., 43 (2004) 1103–1114.

[13] J.F. Fu, et al., Kinetics of aqueous photocatalytic oxidation of fulvic acids in a photocatalysis-ultrafiltration reactor (PUR), Sep. Purif. Technol., 50 (2006) 107–113.

[14] H.F. Lin and K.T. Valsaraj, An optical fiber monolith reactor for photocatalytic wastewater treatment. AICHE J., 52 (2006) 2271–2280.

[15] L.F. Zhang, W.A. Anderson, and Z.S.J. Zhang, Development and modeling of a rotating disc photocatalytic reactor for wastewater treatment. Chem. Eng. J., 121 (2006) 125–134.

[16] H.L. Shang, Z.S. Zhang, and W.A. Anderson, Nonuniform radiation modeling of a corrugated plate photocatalytic reactor, AICHE J., 51 (2005) 2024–2033.

[17] A. Brunetti, G. Barbieri, E. Drioli, K.-H. Lee, B.-K. Sea and D.-W. Lee, Porous stainless steel supported silica membrane for WGS reaction, Desalination, 200 (2006) 681–683.

[18] L.M. Zhao and W.S. Xia, Stainless steel membrane UF coupled with NF process for the recovery of sodium hydroxide from alkaline wastewater in chitin processing, Desalination, 249 (2009)774–780.

[19] S.J. Jang, M.S. Kim and B.W. Kim, Photodegradation of DDT with the photodeposited ferric ion on the TiO$_2$ film, Water Res., 39 (2005) 2178–2188.

[20] N. Daneshvar, M. Rabbani, N. Modirshahla, M.A. Behnajady, Kinetic modeling of photocatalytic degradation of Acid Red 27 in UV/TiO$_2$ process, J. Photochem. Photobiol. A: Chem., 68 (2004) 39–45.