Journal of Zhejiang University SCIENCE A
ISSN 1673-565X (Print); ISSN 1862-1775 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
E-mail: jzus@zju.edu.cn

Novel photocatalytic reactor for degradation of DDT in water and its optimization model*

Wei-hai PANG[1], Nai-yun GAO[†‡1], Yang DENG[2], Yu-lin TANG[1]
([1]*State Key Laboratory of Pollution Control and Resources Reuse, Tongji University, Shanghai 200092, China*)
([2]*Department of Civil Engineering and Surveying, University of Puerto Rico at Mayaguez, Mayaguez, PR 00681, USA*)
[†]E-mail: gaonaiyun@sina.com

Received June 7, 2008; Revision accepted Oct. 13, 2008; Crosschecked Feb. 26, 2009

Abstract: A novel photocatalytic reactor was developed to remove (1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane) (DDT) from water. In the reactor, a cenosphere was used to support TiO_2 film made by means of sol-gel. Because the cenospheres were coated with TiO_2, their specific gravity was slightly increased from the original 0.6~0.8 to 0.8~0.9, so that they were able to be suspended in water. With the mixed operation of a bubbler, the water in the reactor was in a well-fluidized state. The bottom of the reactor is a sand filter bed, which can be used to prevent the photocatalyst from being lost. A mathematical model of the reactor has been developed in the two primary influential factors: ultraviolet (UV) light intensity and photocatalyst concentration. With such a model, the reactor can be designed more reasonably.

Key words: Photocatalytic reactor, Persistent organic pollutants (POPs), Reactor model
doi:10.1631/jzus.A0820501 **Document code:** A **CLC number:** X703.3

INTRODUCTION

DDT [(1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane)] was designated by the World Health Organization (WHO) as one of the 12 persistent organic pollutants (POPs) urgently needed to be eliminated because they are characterized by a high solubility in greases, which involves an accumulation in fat tissues of the living organisms. Although the use of some chloro-organic insecticides in agriculture was banned in most countries in the last 20 years of the last century, thousands of tons of obsolete pesticide deposits in farms and other places have been jeopardizing the environment (Feng *et al*., 2003; Satapanajaru *et al*., 2006; Thetwar *et al*., 2007). High DDT concentration was observed in the air over Taihu Lake, a lake near Shanghai, China, which is the water supply source for several nearby cities (Qiu *et al*., 2005). The level of DDT is also regarded as one of the non-regular indices in the newly issued drinking water standard in China. Several methods are able to remove DDT in water, such as membrane filtration (Yoon *et al*., 2003), solvent sublation (Sahle-Demessie and Richardson, 2000), activated-carbon absorption (Di Claudio *et al*., 2007). However, they only transfer DDT from one phase to another, rather than chemically destruct the toxic compound. The Fenton process has been reported to effectively remove DDT (Dalla Villa and Nogueira Pupo, 2006; Boussahel *et al*., 2007), but it appears not to be suitable for drinking water treatment for some reasons. For example, the optimal pH for the Fenton process is typically between 3.0 and 4.0 (Mosteo *et al*., 2007).

Titanium dioxide, TiO_2, has been used as photocatalyst in numerous researches since TiO_2 surface under ultraviolet (UV)-irradiation can generate highly oxidative electrical holes to decompose various aqueous organic compounds, particularly at ambient temperature and pressure conditions.

---

‡ Corresponding author

* Project supported by the National Science and Technology Support Program of China (No. 2006BAJ08B06) and the Major Projects on Control and Rectification of Water Body Pollution by Ministry of Environmental Protection (No. 2008ZX07421-002), China

Typically, photocatalytic reactors are divided into four categories: (1) Directly adding TiO_2 powder to water, without the reclamation of TiO_2 (Kostedt *et al.*, 2005; Shiraishi *et al.*, 2006; Toor *et al.*, 2006); (2) Reclaiming TiO_2 powder by membrane (Molinari *et al.*, 2004; Fu *et al.*, 2006); (3) Immobilized TiO_2 on fixed media, such as optical fiber (Lin and Valsaraj, 2006), rotating disc (Zhang *et al.*, 2006), and corrugated plate (Shang *et al.*, 2005); (4) Fluidized bed (Qiu and Zheng, 2007). Generally, TiO_2 is difficult to reclaim. Although the membrane can retain the catalyst in reactor, frequent backwashing is required, otherwise membrane fouling may occur. Fixing the catalyst on the substrate can avoid TiO_2 reclamation, but the treatment efficiency is not satisfactory in this type of reactor. In a TiO_2 fluidized bed, immobilized TiO_2 readily detaches from media due to the fluid shear force and particle friction.

Though the process of photocatalysed oxidation of the industrial effluent looks very effective, the scale-up is a major difficulty in its implementation. In addition, the recovery of the catalyst in the slurry mode of operation and a reduction in efficiency in the immobilized mode pose a problem in designing a proper reactor system. In this study, we developed a new photocatalytic reactor for DDT removal in tap water. The reaction model is put forward and tested through experiment.

The main objectives in this paper are: (1) Establishing a degradation model for the new photocatalytic reactor; (2) On the basis of the model, finding out the way to achieve the optimized design of the reactor.

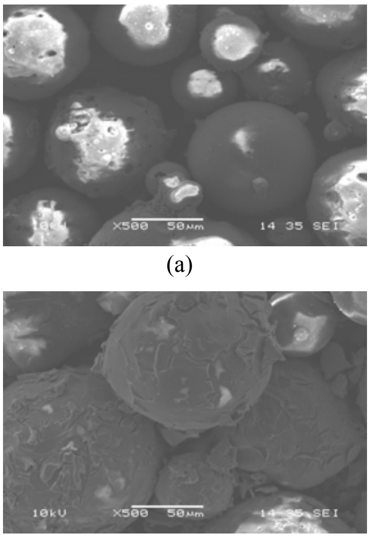
EXPERIMENTAL

Materials

The photocatalyst was made by means of sol-gel (Di Claudio *et al.*, 2007), and all the chemicals were at least the analytical reagent grade, and purchased from Sinopharm Chemical Reagent Co., Ltd, China. 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 with tap water spiked with DDT standard sample. The tap water quality parameters were as follows: dissolved organic carbon (DOC) 4.61~7.02 mg/L, turbidity 0.10~0.45 NTU, conductivity 606~720 μS/cm. The pH of the DDT-containing water was around 7.5 and was unchanged during the reaction. Since DDT is insoluble in water and is easy to be 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 purchased from a company in Shanghai and they were 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 (Fig.1). 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 and stirred for 24 h, and then they are selected by flotation. The selected cenospheres are put into the above sol solution and stirred for 30 min, and then they are separated with filter paper. Films so obtained are first dried at 100 °C and then annealed at various temperatures from 200 to 550 °C (10 °C /min) for 1 h in muffle furnace. After being coated with TiO_2 film, the true density of the cenospheres is changed to 0.8~0.9 g/cm^3.



(a)

(b)

Fig.1 Cenospheres before (a) and after (b) coated with TiO_2 film

Analytical methods

DDT during the photodegradation was measured by a gas Chromatographer (GC) (Shimadzu GC-2010, Japan) with an HP-5 fused silica capillary column (30 m×0.32 mm inner diameter (ID), film thickness of 0.25 μm) (Jang *et al.*, 2005). 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 Electronic Capture Detector (ECD) was maintained at 300 °C. The temperature of GC oven was programmed as follows: 100 °C, isothermal for 2 min, then the temperature was raised at 20 °C/min to 250 °C and held at 250 °C for 10 min.

Reactors and procedure

A schematic representation of the geometry of the photocatalytic reactor is shown in Fig.2. The reactor is composed of two parts: the upper is the reaction zone where aqueous pollutants are degraded by UV light in the presence of photocatalyst; and the bottom is the sand filter, which prevents fine cenospheres from escaping. The diameters of the sand are from 0.5 to 1 mm. In static state, the cenospheres can be floated on water. Bubblers fixed at the middle of the reactor aerate to ensure a well-mixed condition in the reaction zone. Furthermore, the bubbles suspended the cenospheres to provide a good mass transfer condition for the reaction. Each UV lamp was installed in a two-tier quartz casing, and cooling water passed through in the casing to maintain the reaction temperature. When the head loss of the filtration is more than 50 cm, backwash was started up. Usually 2 min of backwashing is enough for the sand filter to resume its function.

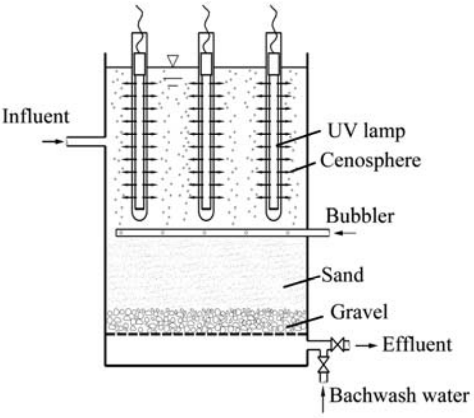


Fig.2 Cenosphere photocatalyst reactor

RESULTS AND DISCUSSION

Adsorption of DDT by cenospheres

DDT adsorption from water by cenospheres was determined in a parallel test by measuring DDT remaining in solution. In the test, DDT concentration of raw water was 30 μg/L; one reactor was run with UV and the other was in dark conditions. The result indicated that the adsorption was almost completed during the first 10 min of experiment. In order to detect the removal effect of DDT by photocatalytic reaction, water was sampled after the first 10 min in the following tests.

Kinetic model for DDT removal

Three concentrations of DDT solution (C_0=49, 40, and 30 μg/L) are 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 is 59.2%, 55.0% and 83.3%, respectively. It can be seen from Fig.3 that $1/(C_0-C)$ is in linear relation with time, so this phenomenon is illustrated well in the 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).

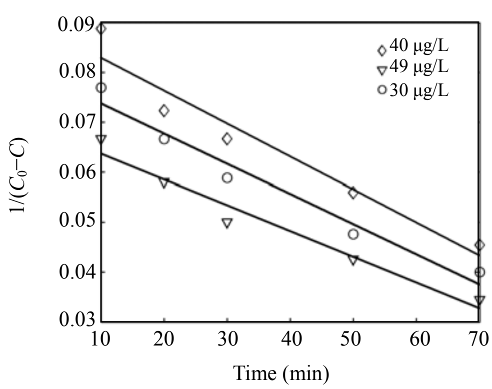


Fig.3 Relation between $1/(C_0-C)$ and time

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 (Daneshvar *et al.*, 2004). So k is the function of I and C_c:

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

where I represents the light intensity, L/(μg·min), and C_c represents the photocatalyst concentration of the reactor, g/L. In order to determine the effect of I and C_c on k, every factor related to I and C_c was studied separately.

Effect of *I* on *k*

The influence of the UV light intensity on the degradation of DDT was investigated using different power of 254-nm lamp. The power of the lamp was ranging from 8 to 32 W and other reaction conditions kept unchanged. As shown in Fig.4, k linearly increased from 1.59×10^{-3} to 5.19×10^{-3} L/(μg·min) with the UV light intensity changing. The mathematical relation is shown as:

$$k=0.0024\ln I-0.0169. \tag{3}$$

According to the result (Fig.4), it was found that UV light intensity has significant effect on the rate of photocatalytic degradation of DDT and the rate of degradation is a nonlinear function of the light intensity. The stronger the UV light intensity, the deeper the penetration of UV light into the catalyst. Since the concentration of photocatalyst was kept the same, the reaction rate was not proportional to the light intensity at high intensity level.

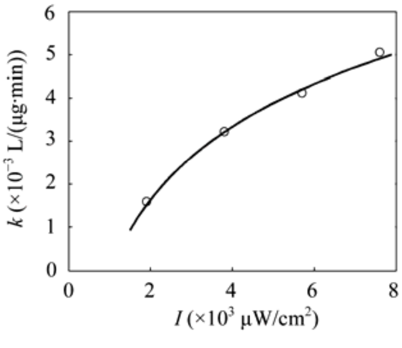


Fig.4 Relation between k and total UV lamps power p (C_c=2 g/L; air flow rate=0.5 L/(L·min))

Effect of C_c on *k*

The effect of C_c on k was shown in Fig.5. Apparently, k increased obviously with the increasing C_c, with a mathematical equation as:

$$k=0.0023\ln C_c+0.0055. \tag{4}$$

Fig.5 shows that more DDT was removed with the increase of cenospheres concentration that 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. According to Eqs.(3) and (4), k can be expressed as:

$$k=k_a\times(0.0024\ln I-0.0169)\times(0.0023\ln C_c+0.0055), \tag{5}$$

where k_a is the accommodation coefficient. In order to establish a degradation model, the UV light intensity distribution and other influential factors on it should be analyzed.

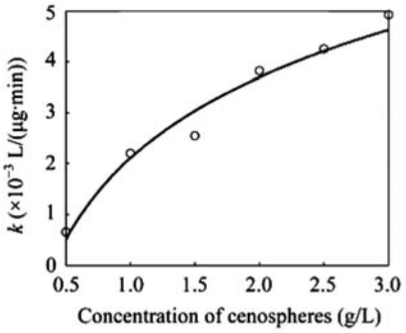


Fig.5 Effect of the concentration of cenospheres on DDT removal (UV light intensity=1200 μW/cm²; air flow rate=0.3 L/(L·min))

UV light intensity distribution

UV light intensity is generally attenuated while passing through media, such as water. 2D and 3D UV light intensity distributions of a 12 W lamp in distilled water are shown in Figs.6a and 6b, respectively. The UV lamp was placed at the point (x=0, y=0) with a starting intensity of about 2000 μW/cm². The UV intensity was significantly decreased to 646 μW/cm² at the point 4 cm away (68% loss), and to 200 μW/cm² at 20 cm away (90% loss). The relation between UV light intensity and the distance was fitted to Eq.(6):

$$I=0.9966I_0D_i^{-0.8227}, \tag{6}$$

where D_i represents the distance from UV lamp to the detecting point, cm; I_0 represents the UV light intensity on the surface of the lamp, μW/cm^2.

It is found that the UV intensity at any point decreases in proportion to the distance from the point to the lamp. In order to keep the UV intensity relatively homogeneous in the whole reaction zone, it is best to place the UV lamps closer to the water.

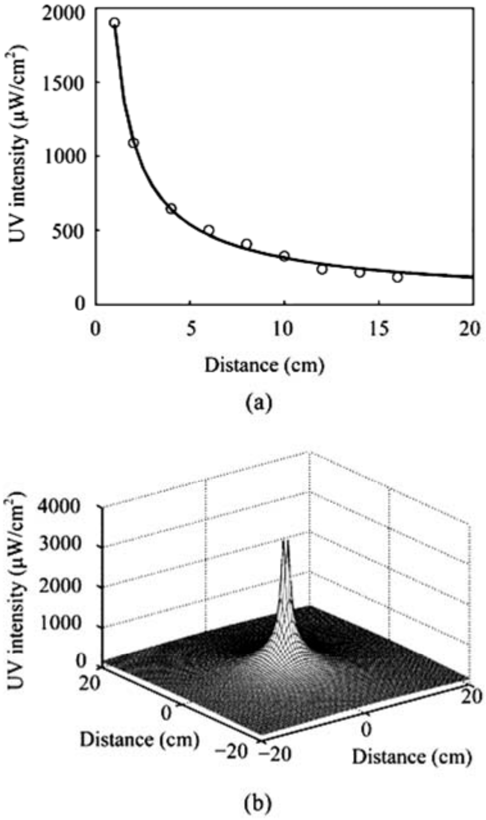


Fig.6 UV light intensity distribution. (a) 2D; (b) 3D

Effect of air flow rate on UV intensity

Air bubbles were used to ensure a well-mixed condition, but they might prevent the UV light from penetrating. The effect of air flow rate on the UV light intensity at different locations is shown in Fig.7. Of interest, UV light intensity slightly decreased with the increasing air-flow rate at any particular location. The trend appeared to be linear described as:

$$I=1.9517I_0-Q_a^{-0.8506}, \tag{7}$$

where Q_a represents the air flow rate, L/(L·min).

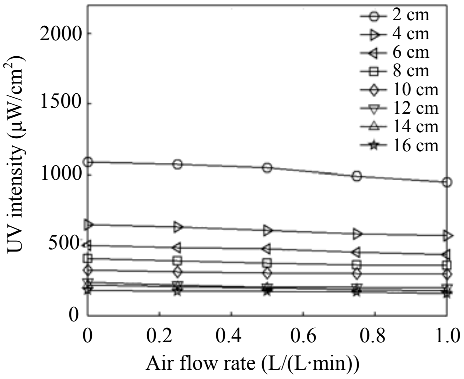


Fig.7 Effect of air flow rate on UV light intensity

Effect of the concentration of cenospheres on UV light intensity

When the water was bubbled or blended by a mixer, all of the cenospheres coated with TiO_2 film were suspended within the reactor, which could prevent UV light from penetrating. Thus, the concentration of the cenospheres influenced the degree of the UV light passing through. The relation between the concentration of the cenospheres and the UV light intensity at different locations (4, 6, 10, 14 cm away from the lamp) is shown in Fig.8. These curves in Fig.8 were fit for Eq.(8):

$$I=0.833I_0\exp(-1.3805C_c). \tag{8}$$

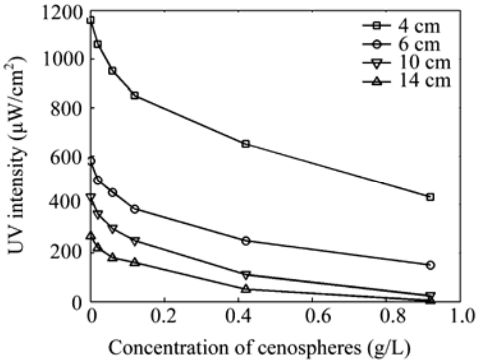


Fig.8 Relation between concentration of cenospheres and the UV light intensity

REACTING MODEL FOR CENOSPHERES PHOTOCATALYST REACTOR

Reacting model

Based on the above analysis, the reaction model of the cenospheres photocatalyst reactor was recomposed as:

$$r = k_a \times \left[0.0024 \times \ln\left(I_0 \times 0.9966 D_i^{-0.8227} \times 1.9517 \times Q_a^{-0.8506} \times 0.833 \exp\left(-1.3805 C_c\right)\right) - 0.0169 \right] \times \left(0.0023 \ln C_c + 0.0055\right) \times C_p^{2}. \quad (9)$$

For a reactor, the concentration of the pollution is usually uncertain and is changing during the process of treatment. Q_a was decided by the least airflow for all the cenospheres in the state of fluidization. Since the UV lamp that provides energy is usually a linear light source, the space where light fills in is a column (Fig.9). The radius of the column R is from the UV lamp to the point that UV light can reach. The reaction rate r_t in the whole reaction zone can be expressed as:

$$\begin{aligned} r_t &= \int_0^l \int_0^{2\pi} \int_0^R r r_e \mathrm{d}r_e \mathrm{d}\theta \mathrm{d}z \\ &= \pi l k_a (0.0023 \ln C_c + 0.0055) \times [(0.0012 \ln I_0 \\ &\quad -0.00102 \ln Q_a - 0.00166 C_c - 0.00787) R^2 \\ &\quad -0.000987 R \ln R + 0.000494 R] \times C_p^2, \end{aligned} \quad (10)$$

where r is the reaction rate at a specific point and r_e is the radius of polar coordinate.

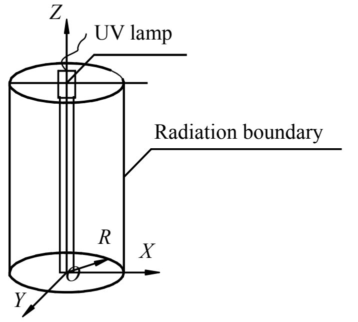


Fig.9 UV lamp light integral domain

For a specific UV lamp, R will be reduced with the increase of the cenospheres concentration. By experiment the relation between R and the cenospheres concentration is expressed as:

$$R = -6.01 \ln C_c + 13.594. \quad (11)$$

Comparison of model with experimental results

Experiments were performed to test the effectiveness of the model at different cenospheres concentration and the result is shown in Fig.10. It is clear that, under Q_a=0.3 L/(L·min), I_0=2000 μW/cm^2, with increasing concentration of cenospheres (less than 0.4 g/L), the organic destruction rate is increased. This is predictable because the higher the photocatalyst concentration, the more OH radicals are produced. However, further increase in concentration of cenospheres can reduce the reaction rate. The results can be attributed to a reduction of the UV light attenuated toward the reaction zone and leading to a lesser fraction of photocatalytic activation, which means that the photocatalyst has an optimum concentration during the process of the treatment.

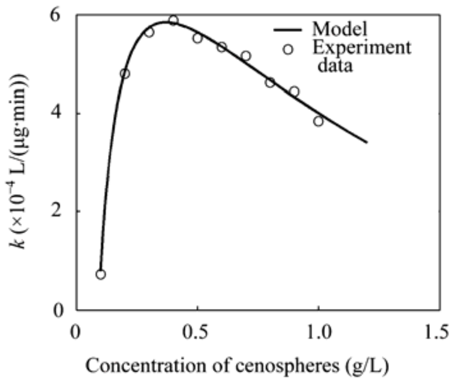


Fig.10 Effect of cenospheres concentration on *k* in the whole reactor

CONCLUSION

During the process of catalytic oxidation of the 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. This method ensured that 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.

A mathematical model was provided for scale-up and design of these types of photoreactors. The model was compared to the experimental results and was found to fit the experimental results satisfactorily within the ranges of the parameters investigated. 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 optimum concentration of the catalyst can be calculated with the model developed. The model provides a simple solution to develop photocatalytic oxidation technology for water treatment and purification.

References

Boussahel, R., Harik, D., Mammar, M., Lamara-Mohamedl, S., 2007. Degradation of obsolete DDT by Fenton oxidation with zero-valent iron. *Desalination*, **206**(1-3):369-372. [doi:10.1016/j.desal.2006.04.059]

Dalla Villa, R., Nogueira Pupo, R.F., 2006. Oxidation of p,p′-DDT and p,p′-DDE in highly and long-term contaminated soil using Fenton reaction in a slurry system. *Science of the Total Environment*, **371**(1-3):11-18. [doi:10.1016/j.scitotenv.2006.05.010]

Daneshvar, N., Rabbani, M., Modirshahla, N., Behnajady, M.A., 2004. Kinetic modeling of photocatalytic degradation of Acid Red 27 in UV/TiO_2 process. *Journal of Photochemistry and Photobiology A Chemistry*, **168**(1-2):39-45. [doi:10.1016/j.jphotochem.2004.05.011]

Di Claudio, D., Phani, A.R., Santucci, S., 2007. Enhanced optical properties of sol-gel derived TiO_2 films using microwave irradiation. *Optical Materials*, **30**(2):279-284. [doi:10.1016/j.optmat.2006.10.032]

Feng, K., Yu, B.Y., Ge, D.M., Wong, M.H., Wang, X.C., Cao, Z.H., 2003. 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**(6):683-687. [doi:10.1016/S0045-6535(02)00204-7]

Fu, J.F., Ji, M., Zhao, Y.Q., Wang, L.Z., 2006. Kinetics of aqueous photocatalytic oxidation of fulvic acids in a photocatalysis-ultrafiltration reactor (PUR). *Separation and Purification Technology*, **50**(1):107-113. [doi:10.1016/j.seppur.2005.11.017]

Jang, S.J., Kim, M.S., Kim, B.W., 2005. Photodegradation of DDT with the photodeposited ferric ion on the TiO_2 film. *Water Research*, **39**(10):2178-2188. [doi:10.1016/j.watres.2005.03.028]

Kostedt, W.L., Drwiega, J., Mazyck, D.W., Lee, S.W., Sigmund, W., Wu, C.Y., Chadik, P., 2005. Magnetically agitated photocatalytic reactor for photocatalytic oxidation of aqueous phase organic pollutants. *Environmental Science & Technology*, **39**(20):8052-8056. [doi:10.1021/es0508121]

Lin, H.F., Valsaraj, K.T., 2006. An optical fiber monolith reactor for photocatalytic wastewater treatment. *AIChE Journal*, **52**(6):2271-2280. [doi:10.1002/aic.10823]

Molinari, R., Pirillo, F., Falco, M., Loddo, V., Palmisano, L., 2004. Photocatalytic degradation of dyes by using a membrane reactor. *Chemical Engineering and Processing*, **43**(9):1103-1114. [doi:10.1016/j.cep.2004.01.008]

Mosteo, R., Ormad, M.P., Ovelleiro, J.L., 2007. Photo-Fenton processes assisted by solar light used as preliminary step to biological treatment applied to winery wastewaters. *Water Science and Technology*, **56**(2):89-94. [doi:10.2166/wst.2007.476]

Qiu, W., Zheng, Y., 2007. A comprehensive assessment of supported titania photocatalysts in a fluidized bed photoreactor: Photocatalytic activity and adherence stability. *Applied Catalysis B: Environmental*, **71**(3-4):151-162. [doi:10.1016/j.apcatb.2006.08.021]

Qiu, X.H., Zhu, T., Yao, B., Hu, J.X., Hu, S.W., 2005. Contribution of dicofol to the current DDT pollution in China. *Environmental Science & Technology*, **39**(12):4385-4390. [doi:10.1021/es050342a]

Sahle-Demessie, E., Richardson, T., 2000. Cleaning up pesticide contaminated soils: Comparing effectiveness of supercritical fluid extraction with solvent extraction and low temperature thermal desorption. *Environmental Technology*, **21**(4):447-456. [doi:10.1080/09593332108618106]

Satapanajaru, T., Anurakpongsatorn, P., Pengthamkeerati, P., 2006. Remediation of DDT-contaminated water and soil by using pretreated iron byproducts from the automotive industry. *Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes*, **41**(8):1291-1303. [doi:10.1080/03601230600963888]

Shang, H.L., Zhang, Z.S., Anderson, W.A., 2005. Nonuniform radiation modeling of a corrugated plate photocatalytic reactor. *AIChE Journal*, **51**(7):2024-2033. [doi:10.1002/aic.10440]

Shiraishi, F., Nagano, M., Wang, S.P., 2006. Characterization of a photocatalytic reaction in a continuous-flow recirculation reactor system. *Journal of Chemical Technology and Biotechnology*, **81**(6):1039-1048. [doi:10.1002/jctb.1526]

Thetwar, L.K., Sarway, P.K., Gupta, S., Augar, M.R., Tandon, R.C., Dewangan, H.S., Tripathi, N.K., 2007. Concentration, distribution of DDT and Malathion in soil water, plant and fishes in Rajnandgaon, India. *Asian Journal of Chemistry*, **19**(2):1562-1564.

Toor, A.P., Verma, A., Jotshi, C.K., Bajpai, P.K., Singh, V., 2006. Photocatalytic degradation of Direct Yellow 12 dye using UV/TiO_2 in a shallow pond slurry reactor. *Dyes and Pigments*, **68**(1):53-60. [doi:10.1016/j.dyepig.2004.12.009]

Yoon, B.O., Koyanagi, S., Asano, T., Hara, M., Higuchi, A., 2003. Removal of endocrine disruptors by selective sorption method using polydimethylsiloxane membranes. *Journal of Membrane Science*, **213**(1-2):137-144. [doi:10.1016/S0376-7388(02)00520-3]

Zhang, L.F., Anderson, W.A., Zhang, Z.S.J., 2006. Development and modeling of a rotating disc photocatalytic reactor for wastewater treatment. *Chemical Engineering Journal*, **121**(2-3):125-134. [doi:10.1016/j.cej.2006.05.011]