Int. J. Mar. Sci. Eng., 1(1), 23-28, Autumn 2011

Photocatalytic Degradation of Diazinon From Marine Source Using TiO_2/SiO_2 Thin Layer Coated on Glass

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Received 11 August 2011; revised 28 August 2011; accepted 30 August 2011

ABSTRACT: TiO_2 photo catalyst was prepared in presence of nano SiO_2 and Hydroxy Propyl Cellulose (HPC) by sol gel method with Titanium Tetra IsoproPoxide (TTIP) as titanium precursor. Additional effect of HPC in preparation of nano catalyst, and photo catalyst properties measured and characterized by FT-IR, FT-Raman and SEM. The catalyst size and structural properties of the film were determined by X-Ray Diffraction (XRD). The nano particles of TiO_2/SiO_2 with HPC contained anatase phase in advance. The surface area measured by the Brunauer, Emmett and Teller (BET) method. Presences of Ti and Si in the nano structure were confirmed by Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray (EDX) spectroscopy. Photo catalyst properties of TiO_2/SiO_2 examined at first for decomposition of Methyl Red as azo dye, and then for degradation of 5ppm diazinon solution as an organo phosphorous insecticide pollutant in marine source, (Caspian Sea water). Concentration of diazinon during of degradation by TiO_2/SiO_2 photo catalyst was monitored by UV-Vis spectrophotometery. The insecticide degradation occurred within 105 min of photocatalytic treatment.

Key words: *Photocatalytic Degradation, Thin Film, TiO2/SiO2, HPC, Diazinon, Methyl Red, Caspian Sea Water*

INTRODUCTION

In the face of global water scarcity, there is an urgent need to prevent contamination of available water resources from various type pollutants such as pesticides, of which, a wide variety of them are introduced into the water system from various sources, such as industrial effluent, agricultural runoff and chemical deposits. Their toxicity, stability to natural decomposition and persistence in the environment has been the cause of much concern to societies and regulation authorities around the world (Sakes et al., 2005). One strategy is effective treatment of pesticide-contaminated wastewater at the generator level or before final disposal (Echavia et al., 2009). TiO2 mediated semiconductor photo catalysis is gaining more importance due to its high production of hydroxyl radicals, inexpensive, non-toxic, abundantly available and especially stable under solar irradiation. However, there are some drawbacks like fast recombination of photo-induced electrons and holes that results in limited photocatalytic performance. Also, phase separation of titania particles after reaction is laborious. These problems have motivated to design and prepare efficient photocatalytic materials (Noorjahan et al., 2004; Wang et al., 2006; Wu et al., 2006). In recent years, there has been a growing interest in the use of thin, transparent TiO2 film for generating a self-cleaning surface (Abroomand Azar et al., 2011). It has been observed that the addition of SiO2 to TiO2 films not only permits an increase of in-time persistence of the photo-induced super-hydrophilicity (Guan et al., 2003), but also creates an extremely large surface area (Enomoto et al., 2002). HPC is a well-known dispersant used for preventing agglomeration of titania powder (Kusabe et al., 2007). Therefore, it is used to prepare mesoporous TiO2 thin

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films.

Diazinon,(O,O-diethylO-[2-isopropyl-6-methylpyrimidin-4-yl] thiophosphate), a phosphorothioate commercially introduced in 1952 is used as an insecticide for different types of cultivation such as fruit trees, rice, sugarcane, corn, tobacco and horticultural plants because of its inhibition of the acetylcholinesterase of most kinds of insects (Zhang and Pehkonen et al., 1999). It is classified by the World Health Organization (WHO) as "moderately hazardous" class II (Shemer and Linden, 2006) with an LC50 in killifish (48h) of 4.4mgl^{-1} (Zhang and Pehkonen et al., 1999). Fatal human doses were found to be in the range from 90 to 444mgkg^{-1} (Shemer and Linden, 2006). Toxic effects of diazinon are attributed to its inhibition of the enzyme acetylcholinesterase (Kouloumbos et al., 2003). Diazinon is relatively water soluble, moderately mobile and persistent in soil, hence, it is of concern for groundwater and surface derived drinking water. Diazinon has a vapor pressure of 1.4×10^{-4} mmHg at 20°C, which would indicate that it would not easily volatilize from water and soil (Howard, 1991).

The aim of present work is to study the photocatalytic activity of prepared mesoporous TiO_2/SiO_2 thin film. For this purpose, the HPC synthesized TiO_2/SiO_2 thin films were prepared by sol gel method and examined as photo catalyst for UV-induced photocatalytic degradation of diazinon as model of organic compound in Sea water.

MATERIALS AND METHODS

1. Materials

TTIP and SiO2 colloidal solution were obtained from Aldrich Chemical Co. (USA). HNO_3, HPC, and NaOH are all analytical reagents and were obtained from Merck Co. (Germany). Diazinon, an insecticide was purchased from chem-service (USA). Caspian Sea water was used during the study.

2. Preparation of HPC synthesized TiO_2/SiO_2 thin films

The solution was prepared based on the method of (Kusabe et al., 2007), and the difference was the addition of SiO_2 to the solution. TTIP in a molar ratio 1:125 was dissolved and stirred vigorously in ethanol with amount of 4.5×10^{-3}g.g$^{-1}_{sol}$ HPC. Further, another mixture of ethanol, HNO_3, deionized water, SiO_2, with a molar ratio of ethanol:HNO_3:H_2O:SiO_2 = 35:0.42:1:0.38 respectively was dropped wise with vigorous stirring. The obtained colloidal suspension aged for 72h. Afterwards, the glass sheets (25.4 × 76.2mm, 1mm Thick) were coated three times by dip-coating method and calcined in Carbolite furnace at a certain temperature (500°C for 5h) to produce the thin films.

3. Detection Method

To identify the crystal structure of the photo catalyst, the glass films were characterized by XRD (SCIFERT-3003 PTS X-ray diffractometer). The specific surface area of the catalyst was determined by BET method (Jw-k surface area and pore size distribution analyzer equipment, Beijing JWGB Sci. and Tech.). Texture, morphology, and particle size of the films were observed by SEM-XL30 equipped with EDX spectroscopy. Thermo Nicolet Nexus 870 FT-IR and Thermo Nicolet 960 FT-Raman both from USA were used for recording FT-IR and FT-Raman spectra of the photo catalyst sample.

4. Photocatalysis

At first, for finding the power of the photo catalyst in degradation of organo pollutants, a 5ppm azo dye, Methyl Red (MR), dissolved in deionized water at neutral pH was examined during photo degradation. For this purpose the solution was set in the vicinity of the glass thin films under 25W UV-Vis irradiation mercury lamp (OSRAM), which was put in center of a batch photoreactor. The reaction temperature was kept at 25°C by cooling water jacket. The MR concentration change was determined by UV-Vis (Varian) Cary 300 spectrophotometer at λ=433nm. As shown in Fig. 1. MR was degraded in presence of TiO_2/SiO_2 glass thin films within 240min. Due to photocatalytic degradation of the insecticide, the Sea water solution, pH value was adjusted at neutral level using dilute NaOH and H_2SO_4. Other conditions were kept as before. Concentration of the insecticide in each degraded sample was recorded using UV-Vis spectrophotometer, at λ=247nm of diazinon.

RESULTS AND DISCUSSION

Catalyst Characterization

The crystal size and structure of the films were examined by XRD. According to the Debye–Scherrer equation: $D = k(\lambda/(\beta \cos\theta))$ where k is a constant equal to 0.89, λ the X-ray wavelength equal to 0.154056 nm, β the full width at half maximum and θ is the half diffraction angle (Liu et al., 2011). The average particle size of prepared TiO_2/SiO_2 thin film is about 34 nm. The XRD pattern in Fig. 2 for HPC container sample, possess 14% of Rutile phase, 22% of Brookite

phase, and 64% of anatase phase. Furthermore, the formation of the anatase structure was confirmed by the Raman spectroscopy, which showed almost all of the expected anatase vibrational modes (Rengaraj et al., 2007). As shown in Fig. 3, the peaks observed at around 144, 398, 517 and 639 cm^{-1} would be attributed to the anatase phase of TiO2. Consequently, it provides strong evidence of presence the anatase phase in the structure in advance. Fig. 4 shows the FT-IR spectrum of the sample in the wave range number 400 - 4000 cm^{-1}. A pick appearance in 3000-3600 cm^{-1} absorption band is OH stretching vibration of surface hydroxyl group due to use of ethanol during the synthesis. Besides, the absorption band observed around 1630 cm-1 is stretching mode of physically hydroxyl group adsorption (Sojić et al., 2010). The absorption peak at 620 cm^{-1} is assigned to Ti-O-Ti stretching motion. The peak at 1120 cm^{-1} is assigned to asymmetric stretching vibration of the Ti-O bands. Due to asymmetric vibration of Si-O-Si bond in unit of SiO2 matrix the peak at the range 1080 cm^{-1} is appeared, however the peak at 791 cm^{-1} delivered the symmetric Si-O-Si stretching vibration bond. The peak at 960 cm^{-1} was corresponded to Si-O-Ti vibration due to involving a Ti atom bonded to a SiO_4 tetrahedron unit (Abroomand Azar et al., 2011; Zou and Gao et al., 2011). In Fig. 5 the SEM image, shows particle size uniformity and less agglomeration with the presence of additive besides, EDX image in Fig. 6 confirms the presence of Ti and Si in the sample. Results indicate the specific surface area of prepared thin film TiO_2/SiO_2 in presence of HPC is 115m^2 g^{-1}.

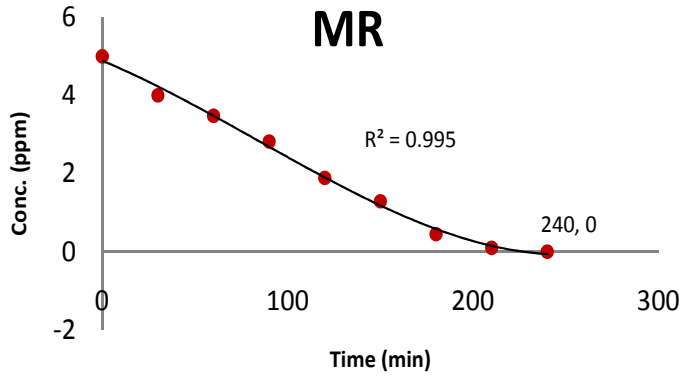

Fig. 1: Effect of UV-Vis light on photocatalytic degradation of diazinon in Sea water. (Ci = 5ppm; pH= 7; T = 25°C)

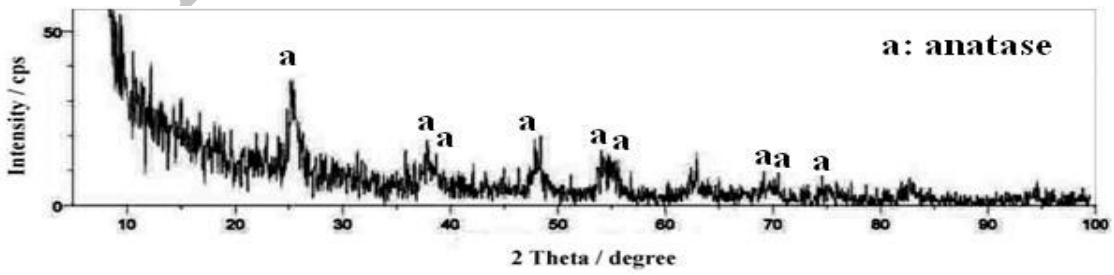

Fig. 2: XRD pattern of TiO_2/SiO_2 thin film sample

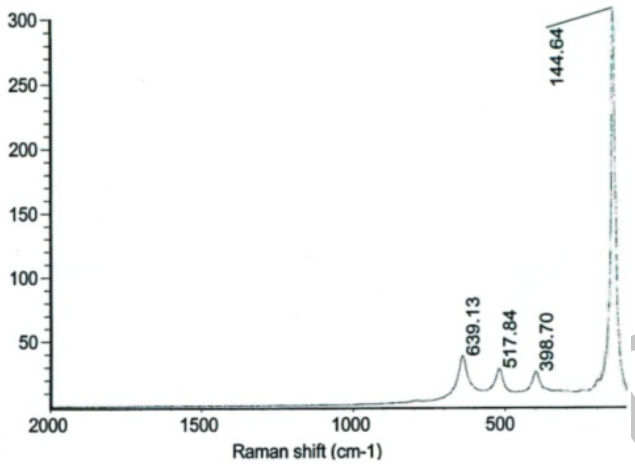

Fig. 3: FT-Raman spectrum of TiO_2/SiO_2 sample

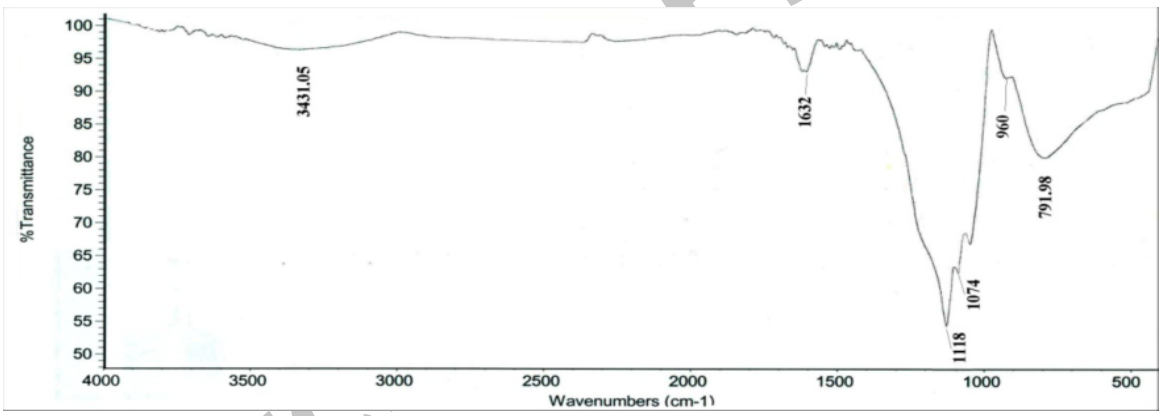

Fig. 4: FT-IR spectrum of TiO_2/SiO_2 sample

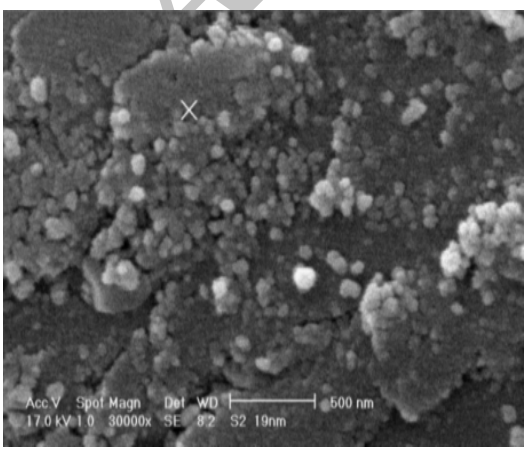

Fig. 5: SEM image of TiO_2/SiO_2 thin film sample

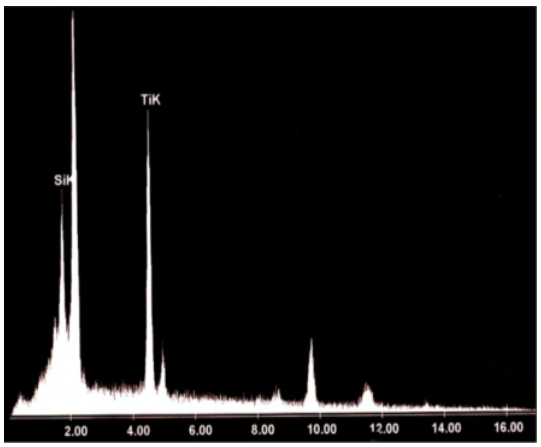

Fig. 6: EDX image of TiO_2/SiO_2 thin film sample

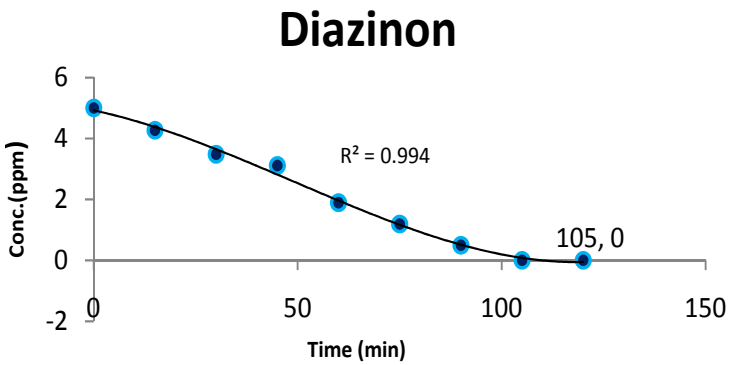

Fig. 7: Effect of UV-Vis light on photocatalytic degradation of diazinon in Sea water. (C_i = 5ppm; pH= 7; T = 25°C)

2. Photocatalytic degradation of diazinon

Fig. 7 is the UV-Vis diagram degradation of 5ppm diazinon in Sea water, with presence of TiO_2/ SiO_2 synthesized with HPC coated on glass films. It shows fast degradation within 105 min in presence of diazinon. When initial concentration increase, more organic substances are adsorbed on the surface of TiO_2/ SiO_2 thin films. Therefore, there are only a fewer active sites for adsorption of hydroxyl ions so the generation of hydroxyl radicals will be reduced. Further, as the concentration of an insecticide solution increase, the photons get intercepted before they can reach the catalyst surface, hence the adsorption of photons by the catalyst decreases, and consequently the degradation percent is reduced (Daneshvar et al., 2003; Shankar et al., 2004).

CONCLUSION

Diazinon, an organophosphorous insecticide, in Sea water was easily degraded by the UV light in presence of nano composite TiO_2/SiO_2 thin film synthesized by sol-gel method. For increasing surface area in production process in sol gel step, HPC added as emulsifier for stabilization of gel phase. Control process in calcination step is very important in photocatalyst activity. Photodegradation of diazinon performed fast when the optimization of condition in product accomplished.

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How to cite this article: (Harvard style)

Aberoomand Azar, P.; Moradi, Sh.; Piramoon, Sh.; Mashinchian Moradi, A., (2011). Photocatalytic Degradation of Diazinon From Marine Source Using TiO2/SiO2 Thin Layer Coated on Glass. Int. J. Mar. Sci. Eng., 1(1), 23-28.