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Photo catalytic degradation of pesticides in immobilized bead photo reactor under solar irradiation

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Abstract

The discharge of wastewaters containing pesticides from industries, agricultural applications and surface run off are toxic, which is one of the major cause of water pollution and is responsible for a variety of adverse environmental impacts. *Heterogeneous photo catalysis* has proved to be an effective treatment method for removal of toxic pollutants from industrial wastewaters owing to its ability to convert them in to innocuous end products such as CO_2, H_2O and mineral acids. The photo catalytic degradation of three pesticides, widely used in India, viz., Monocrotophos (MCP), Endosulfan (ES) and Chlorpyriphos (CPS) was studied in sunlight using Immobilized Bead Photo Reactor (IBPR) under solar radiation. TiO_2 coated on the polymeric bead was characterized using SEM, XRD, UV–Vis spectrophotometer and FT-IR. Batch degradation of pesticides were studied to establish the photo catalytic activity of immobilized beads under solar irradiation.

Keywords: Immobilized bead photo reactor; Solar radiation; Pesticides; Photo catalytic degradation

1. Introduction

Large scale, indiscriminate use of pesticides to accelerate food production, particularly in developing countries, has resulted in pesticide contamination of natural waters which is posing serious threats to environment in many parts of the world. The concentrations of organo phosphorus pesticides have exceeded frequently the maximum contamination level in surface water and ground water. Heterogeneous photo catalytic oxidation with TiO_2 as photo catalyst is emerging as an attractive technique for pesticide removal. Many efforts have been taken to improve the photo catalytic activity of TiO_2 to increase the photo catalytic activity by improving the illumination and oxygenation processes.

Chaudhuri et al. (2013) studied the degradation of pesticide chlorothalonil using visible light responsive photocatalyst, ferrioxalate and H_2O_2 under solar irradiation using response surface methodology. They found out the optimum operating conditions such as H_2O_2/COD molar ratio, H_2O_2/Fe^{3+} molar ratio, $H_2O_2/C_2H_2O_4$ molar ratio, reaction time, pH, COD, NH_3-N, and TOC removal. The biodegradability (BOD_5/COD ratio) of the mixture was improved from zero to 0.42. Photo catalytic degradation of Isoproturon pesticide by C, N and S Doped TiO_2 (TCNS) was studied by Reddy et al. (2010). They reported that TCNS photo catalysts showed higher photo catalytic

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activity under solar light irradiation due to inhibition of charge carrier recombination process, synergetic effects of red shift in the absorption edge and higher surface area. Yaroshenko et al. (2007) identified a new method for production of composites constituted by expanded graphite, amorphous carbon and titanium dioxide. They formed a floating photo catalyst and used it for water treatment to remove organic contaminants.

Floatable photo catalysts are especially interesting for solar remediation of non-stirred and non-oxygenated reservoirs since the process maximizes the optimization of illumination and oxygenation, which results in higher rates of radical formation and oxidation efficiencies. Literature review shows that only few studies have been published on floating photo catalyst using TiO_2 and exfoliated graphite (Lev et al., 1997), TiO_2 supported on SiO_2 hollow glass micro beads (Yao and Chen, 2005), natural porous pumice (Inagki et al., 2004), TiO_2 hollow microspheres (Lee et al., 2007) and TiO_2 grafted on grafted polystyrene beads (Lago and Magalhaes, 2009). However, in all these studies preparation of catalyst is a very expensive and complex using titanium precursor, which produces TiO_2 phase mixtures with low photo catalytic activity. Photo catalytic degradation of organo phosphorus (OP) pesticides in aqueous titanium dioxide suspension has been reported (Chen et al., 1999; Konstantinou and Sakellarides, 2001). Chen and Gengyu (2005) studied the photo catalytic degradation of organo phosphorus pesticides using floating photocatalyst $TiO_2 \cdot SiO_2$ hollow glass beads using sol–gel method.

In the present study, photo catalytic degradation of three pesticides, widely used in India, viz., Monocrotophos (MCP), Endosulfan (ES) and Chlorpyriphos (CPS), was investigated using a suspension of polymeric beads coated with TiO_2 under solar irradiation. Batch degradation experiments were carried out in well stirred glass beakers exposed to sunlight at initial concentrations of pesticides ranging from 5 to 50 mg/l and at a catalyst loading of 2 g of TiO_2 coated on 200 g of beads. Experiments were performed during daytime (10 am–4 pm). Samples were collected from the beaker at specific time intervals and analyzed in HPLC.

2. Materials

2.1. Chemicals

Titanium dioxide photocatalyst employed was CDH (technical grade), TiO_2 pure anatase, BET surface area 15 m^2/g (CDH, India). Technical grade pesticide Endosulfan (E.I.D. Parry's pesticide division, Ranipet), Monocrotophos and Chlorpyrifos were got from (Sreeram Pesticides division, Pudukottai). All other chemicals used in the experiments were of reagent grade. Adjustment of pH of the pesticide solutions prior to degradation was carried out with 1 M sodium hydroxide (NaOH) or 0.5 M sulfuric acid (H_2SO_4). Acetonitrile and milli-Q were used as HPLC grade (Ranbaxy chemicals, India).

3. Methods

3.1. Experimental methods

3.1.1. Photo catalyst immobilization

Commercially available polystyrene beads (6 mm) were first washed with distilled water and dried. A thick suspension of the catalyst was prepared by sonicating a slurry of TiO_2 (10 g/l) for 15 min using ultrasonic probe (20 kHz). The dried beads were first coated with a thin film of silicon based commercial adhesive and immediately mixed thoroughly with the TiO_2 slurry. The coated beads were then dried in an oven for one hour. The dried beads were stirred in 500 ml of water in a beaker to remove any loosely bound TiO_2.

3.1.2. Experimental setup

3.1.2.1. Batch degradation studies using floating immobilized beads under solar irradiation. Batch experiments were conducted to study the feasibility of photo catalytic degradation of pesticides using immobilized beads. About 200 g of beads were added to 500 ml of pesticide solution of different concentrations in 1 l beakers. The solution was stirred using a magnetic stirrer and exposed to solar radiation from 9 am to 4 pm. To study the effect of aeration air was bubbled through diffusers using air pumps. The effect of photolysis was measured without addition of beads and aeration. In all experiments samples were collected and analyzed for residual pesticide by HPLC.

3.2. Analytical methods

3.2.1. Estimation of concentration of pesticide

Concentration of residual pesticide in the samples was analyzed by gradient HPLC method (Jasco Pu-2089 plus, Japan) with PDA detector using Agilent Eclipse PAH 5 μm Column of dimension 10×150 mm. Acetonitrile and water (low conductivity) in the ratio of 70:30 was used as mobile phase at a flow rate of 1 ml min^{-1}. The pesticide concentration was determined by measuring area of the peak corresponding to the absorbance of samples and reading the concentration from a standard calibration.

3.2.2. Characterization of TiO_2 coating

The surface morphology was characterized by scanning electron microscopy (HR SEM-EDAX) with Secondary Electron and Back Scattered Electron detectors. Partially split piece of TiO_2 coated polymeric beads were used and images were captured at different magnification. The images obtained were analyzed with the image processing software (Meazure) for thickness measurement. The samples of TiO_2 coatings for XRD, FTIR and UV–Vis spectrophotometer analysis were removed from the coated bead surface before and after treatment of pesticides. XRD measurements of TiO_2 coating were carried out using a diffractometer (Shimadzu, Japan) equipped with a monochromator and using a Cu Ká radiation. FTIR (Fourier