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Photocatalytic degradation of dimethoate using LbL fabricated TiO_2/polymer hybrid films

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ABSTRACT

Degradation of dimethoate under UV irradiation using TiO_2/polymer films prepared by the layer-by-layer (LbL) method was investigated. The thin films were fabricated on glass slides and the surface morphology and roughness of the thin films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). The effect of lamp intensity, catalyst loading in the layers, number of bilayers, pH and initial dimethoate concentration on the degradation of dimethoate was systematically studied. The degradation was monitored using high performance liquid chromatography (HPLC) analysis and total organic carbon (TOC) measurements as a function of irradiation time, to see the change in concentration of dimethoate and mineralization, respectively. Complete degradation of dimethoate was achieved under TiO_2 optimum loading of 4 g/L at an UV irradiation time of 180 min. Increase in the lamp intensity, catalyst loading and number of bilayers increased the rate of degradation. At a pH of 4.62, complete degradation of dimethoate was observed. The degradation efficiency decreased with increase in initial dimethoate concentration. The degradation byproducts were analyzed and confirmed by gas chromatography–mass spectra (GC–MS). Toxicity of the irradiated samples was measured using the luminescence of bacteria *Vibrio fischeri* after 30 min of incubation and the results showed more toxicity than the parent compound. Catalyst reusability studies revealed that the fabricated thin films could be repeatedly used for up to ten times without affecting the photocatalytic activity of the films. The findings of the present study are very useful for the treatment of wastewaters contaminated with pesticides.

1. Introduction

In the last two decades, organophosphorous pesticides have been extensively used worldwide in agriculture as an alternative to organochlorides. Dimethoate is a systemic organophosphorous pesticide that is widely used to kill mites and insects on contact. In India, it is one of the commonly used pesticides besides monocrotophos, phorate, phosphamidon and methyl parathion [1]. It is considered as 'moderately hazardous, class II' compound by World Health Organization (WHO) and the maximum permissible limit of dimethoate in drinking waters is 0.006 mg/L [2]. Considering the toxicity of this compound, there is an urgent need to develop an effective treatment method to remove the compound from water.

A review on organophosphorous pesticides and the breakdown products, which are stated to be very harmful and toxic when compared to the parent chemical, discusses their fate in the aquatic environment via several processes [3]. Conventional methods for the removal of pesticides from wastewaters include adsorption [4], ozonation [5], reverse osmosis [6], nanofiltration [7], etc. These methods, however, possess certain limitations, like-ozone has relatively low solubility and stability in water. Also the cost of production of ozone is very high [8]. Whereas, a competitive adsorption of natural organic matter (NOM) reduces the efficiency of the carbon filters and therefore limits its usage [9]. Hence, in order to protect the environment and to meet the stringent enforcement regulations, many researchers are developing effective, reliable and economical way for pesticide-containing water treatment system. Owing to the non-biodegradable nature of these pollutants, the chemical oxidation or biological treatment methods are not effective as these are unable to mineralize all organic substances [10].

Advanced oxidation process (AOP's), like photocatalysis using semiconductor catalyst such as TiO_2, has gained interest of researchers recently due to its ability to destruct organic compounds [11]. TiO_2 is widely used as a photocatalyst because of its availability, stability, low cost, and favorable band gap energy [12].

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Several studies on the photocatalytic degradation of dimethoate in aqueous solutions using nanosized TiO_2 have been reported in literature [13,14]. The degradation products as well as reaction pathways have also been evaluated [14–17]. However, it is known that any wastewater purification process using catalyst in its suspended form posses several disadvantages related to filtration and reuse of the catalyst. As a result, processes employing catalyst in suspension form directly incurs high treatment costs making such process economically unviable [18]. These problems can be overcome by immobilizing TiO_2 particles as thin films on some substrates.

Catalyst can be immobilized with various techniques such as dip coating, sol–gel synthesis, chemical vapor deposition method, spin coating, sputtering technique, layer-by-layer (LbL) assembly multilayer technique, etc. [19–24]. The photocatalytic degradation of organophosphorus pesticides: dichlorvos, monocrotophos, phorate and parathion using TiO_2 thin films was studied [25]. Till date, very few studies reported the photodegradation of dimethoate using TiO_2 thin films [26–28]. These studies used the sol–gel method to immobilize TiO_2 and the substrates used were silica gel particles and PVF films in comparison to our study that is based on electrostatic interactions. Also, most of the fabricating methods need either high temperatures (as in CVD) or post treatment (as in sol–gel synthesis) of the coated samples. On the other hand, the LbL method makes use of biodegradable or biocompatible polymers and one can achieve controlled thickness without the use of expensive equipment. Further the deposition of particles is independent of size or shape of substrate and is very environment friendly. The LbL fabricated thin films showed to possess a great potential for the degradation of chemical contaminants [29]. The significance of LbL method for the photodegradation of Rhodamine B, in terms of using a strong polyelectrolyte system such as PSS/TiO_2, its stability and applicability, compared to other fabrication methods were reported in detail in our previous study [29].

In the present study, the photocatalytic degradation of dimethoate with LbL immobilized commercial Degussa Aeroxide TiO_2 P25 catalyst on a glass substrate is investigated. To our knowledge, there are no reports on the photocatalytic degradation of dimethoate with the catalyst immobilized by LbL technique. The effect of various operating parameters like lamp intensity, catalyst loading, number of bilayers, pH and initial dimethoate concentration on degradation has been investigated. The degradation products were identified by GC–MS and the treated solutions were tested for their toxicity. In addition, the present study highlights the reusability of the catalyst to see its performance efficiency in degrading dimethoate.

2. Experimental

2.1. Materials

Dimethoate (*O*,*O*-dimethyl *S*-[2-(methylamino)-2-oxoethyl] phosphorodithioate) technical grade (90% pure), was supplied by Hyderabad Chemicals Limited, Hyderabad, India. Commercial Degussa Aeroxide P25 TiO_2 (80% of anatase and 20% of rutile, average particle size: 21 nm, specific surface area: $50 \pm 15\,m^2/g$) (Degussa AG, Germany) was used as the photocatalyst. Poly(styrene sulfonate) sodium salt (PSS, MW = 70,000 g/mol) (Sigma–Aldrich, USA) and poly (allylamine hydrochloride) (PAH, MW = 70,000 g/mol) (Sigma–Aldrich, USA) were used for thin film preparation. Microscopic glass slides (25.4 mm × 63.5 mm) were used as substrates for the film deposition. Millipore water (resistivity: 18 MΩ) was used throughout the work. Sulfuric acid, ascorbic acid, ammonium molybdate and potassium antimonyl tartarate used for the preparation of combined reagent and all other chemicals used in the present work were of AR grade. Stock solution of 1000 ppm dimethoate was prepared and refrigerated at 4 °C. HPLC-graded organic solvents were used for HPLC analysis.

2.2. Apparatus

The catalyst was characterized by X-ray diffraction (X'Pert Pro, PANalytical instruments). A T60U Spectrophotometer (PG Instruments Ltd., UK) was used for the analysis of the samples. The surface morphology of the thin films was examined using a field emission scanning electron microscope (FEI-SIRION, Eindhoven, The Netherlands). AFM images were obtained using a MFP-3D-SA atomic force microscope (Asylum Research, USA). HPLC analysis was performed using a Hewlett Packard/Agilent 1100 series HPLC analyzer. Total organic carbon (TOC) was measured using a Multi N/C® 3100 TOC analyzer (Germany). The GC–MS analysis was performed using a Shimadzu QP5050A analyzer. The toxicity tests were conducted using a LUMISTox Dr Lange Analyzer.

2.3. Photocatalytic reactor

The photoreactor consists of a jacketed quartz tube with dimensions of 3.4 cm inner diameter, 4 cm outer diameter, and 21 cm length and the reaction vessel was a 100 mL beaker (Qualigens, Mumbai, India). The UV source used in this study was a 125 W and 400 W mercury vapor lamp. The outer glass shell was removed and placed inside the quartz tube for use. The ballast and capacitor were connected in series with the lamp to avoid fluctuations in the input power supply. Submersible water pump was used to circulate water through the jacket of the quartz tube to avoid heating caused by dissipative loss of UV light. The reactant solution was taken in the reaction vessel and placed 10 cm away from the quartz tube. The whole reactor setup was enclosed in a wooden box. The schematic of photoreactor set up is shown in Fig. 1.

2.4. Experimental procedure

The catalyst was immobilized on clean glass slides by LbL technique. The polyelectrolyte solutions, PSS and PAH each of concentration 1 g/L, and the TiO_2 solution were prepared in deionized (DI) water. For immobilizing the substrates using LbL technique, glass slides and silicon wafers were first cleaned by sonicating for

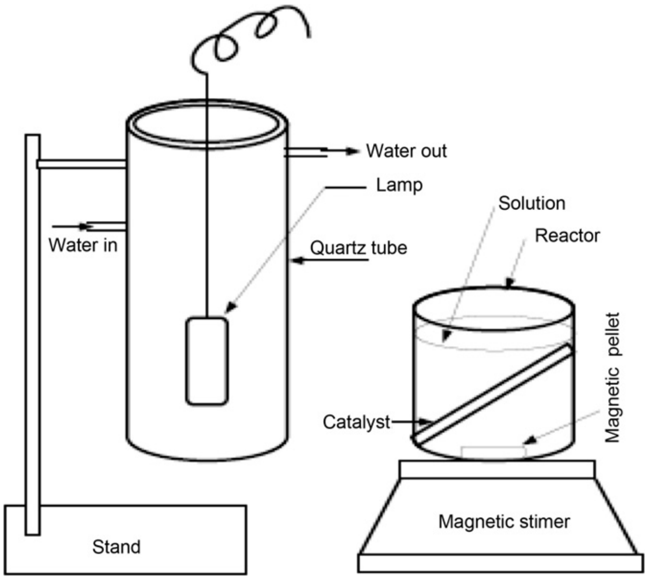

Fig. 1. The schematic of photoreactor set up.