Photocatalytic degradation of dimethoate using LbL fabricated TiO$_2$/polymer hybrid films

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ARTICLE INFO

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.

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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].

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
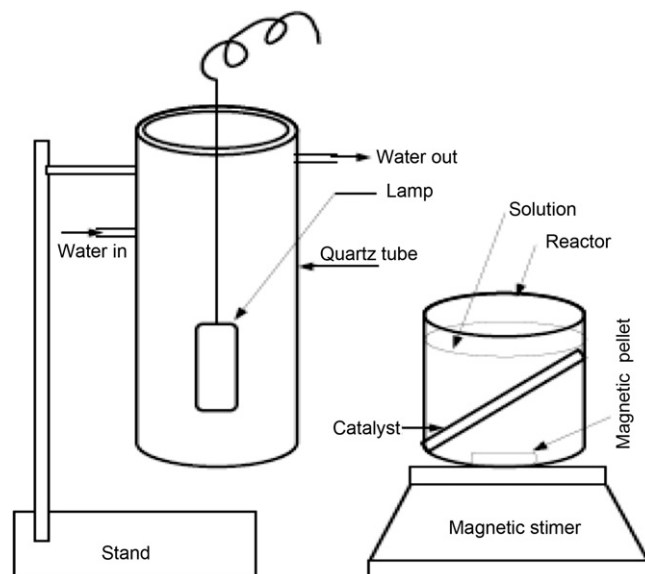

Fig. 1. The schematic of photoreactor set up.

10 min in a solution containing 2:1(v/v) ratio of iso-propanol and water mixture. PSS and PAH each of concentration 1 g/L in DI water were prepared and adjusted to the desired pH. Water pH for rinsing purpose was adjusted to that of the polyelectrolytes and TiO$_2$. To deposit TiO$_2$ on glass substrates and silicon wafers, a colloidal solution of TiO$_2$ was made in DI water and pH was adjusted such that it was stable during deposition and at the same time it had the desired charge to be suitable for LbL technique. Initially, one precursor monolayer of PAH was deposited by immersing the substrates in a solution of PAH for 15 min to reverse the charge on the substrate followed again by rinsing with water for 3 min. The alternate multilayers layers of PSS/TiO$_2$ were then assembled by repeatedly immersing the substrates in PSS and TiO$_2$ solutions. The final layer was TiO$_2$ in all the experiments. In all the catalyst immobilization experiments TiO$_2$, PAH and PSS were deposited at pH 2.5. In our previous work using the LbL-TiO$_2$ thin films for the photodegradation of Rhodamine B [29], we showed the effectiveness of LbL method in comparison to methods like drop casting and spin coating in terms of catalyst immobilization and photodegradation. The SEM images of the catalysts prepared by these three methods are shown in supplementary information (Fig. SI 1).

Dimethoate solution (100 mL of 10 ppm, pH 4.62, unless otherwise stated) with appropriate amount of catalyst deposited on the slides was taken in the reaction vessel. The immobilized catalyst slides were placed vertically in the solution along the sides of the beaker. The solution was stirred continuously using a magnetic stirrer for the complete mixing of catalyst and the solution during the course of reaction. Before starting the degradation experiment, the catalyst-dimethoate solution was stirred for 60 min in dark to establish the adsorption–desorption equilibrium. The concentration of dimethoate solution after the adsorption–desorption equilibrium was analyzed by HPLC (SI Fig. SI 2). It was observed that the concentration of dimethoate after 60 min was same as the initial concentration and was not affected. Hence, further experiments to establish adsorption–desorption equilibrium were performed for 30 min in dark. At regular irradiation time intervals, 2 mL of the sample was collected for HPLC and UV–vis spectrophotometer analysis. The combined reagent was added to the samples analyzed using UV–vis spectrophotometer. Stoichiometrically, degradation of each mole of dimethoate releases one mole of phosphate. Therefore, the concentration of dimethoate degraded was indirectly calculated from the phosphate remaining, using the standard phosphate calibration curve. In order to check the reproducibility of results, all the degradation experiments were repeated at least 2 times and the experimental error was found to be within 5%. The percentage of dimethoate remaining in the solution was calculated from the following expression:

$$\%\text{dimethoate remaining} = \frac{C_t}{C_0} \times 100$$

and $C_t = C_0 - P_t$; where C_t is the concentration of dimethoate remaining at time t, P_t is the amount of phosphate present after time t and C_0 is the original concentration of dimethoate.

2.4.1. GC–MS analysis

The GC–MS analysis of dimethoate samples was performed using a Shimadzu QP5050A attached with Shimadzu GC-17A with a split injector. The GC–MS was equipped with a Chrompack WCOT FS CP-Sil 5CB column of 25 m length and 0.25 i.d. Helium was used as the carrier gas (at a flow rate of 38.9 mL/min) with a column flow of 1.3 mL/min. The solution samples were filtered through a 0.45 μm filter, prior to analysis. The chromatographic conditions used for the identification of intermediates were: initial injector temperature of 250 °C with an interface temperature of 230 °C. The oven temperature was programmed from 50 °C to 250 °C at a rate of 5 °C/min. The interface temperature of the MS was set at 230 °C

and the spectrum was obtained at a scan range from *m/z* 40 to 500. The total scan time was 30 min.

2.4.2. HPLC analysis

Dimethoate concentration was analyzed using a reverse-phase liquid chromatography equipped with diode array detector (DAD) with Zorbax C8 column (250 mm × 4.6 mm, 5 μm particle size) at 25 °C, using an isocratic separation with mobile phase of water and acetonitrile (60:40, v/v) at a flow rate of 1 mL/min. At specific time intervals, samples were withdrawn from the reactor and filtered through a 0.45 μm filter prior to analysis. The injection volume was 75 μL and the detection was realized at 210 nm, which was identified on the basis of retention time comparison with authentic standard.

2.4.3. Toxicity tests

The toxicity of dimethoate samples collected before and after different irradiation time intervals were examined by means of a LUMISTox 300 luminometer (Dr Lange GmbH, Dusseldorf, Germany). The reagents and *Vibrio fischeri* NRRL-B-11177 luminescent bacteria supplied by the same manufacturer were used. The inhibition of the luminescence of bacteria *V. fischeri* after 30 min of incubation was determined. NaCl, 2 vol.% was added to all samples and the pH was adjusted to a value between 6.8 and 7.2 by addition of HCl or NaOH, respectively. After the reactivation of the liquid-dried bacteria for 15 min at 15 °C, 0.5 mL of the bacteria suspension was mixed with 0.5 mL of dimethoate samples of different irradiation times. The sample in the measuring cell was incubated for 30 min at 15 °C. The inhibition of the luminescence was measured in comparison to a blank sample of 0.5 mL NaCl (2%) solution and 0.5 mL bacteria suspension. The percentage of luminescence inhibition was calculated for each concentration relative to the control.
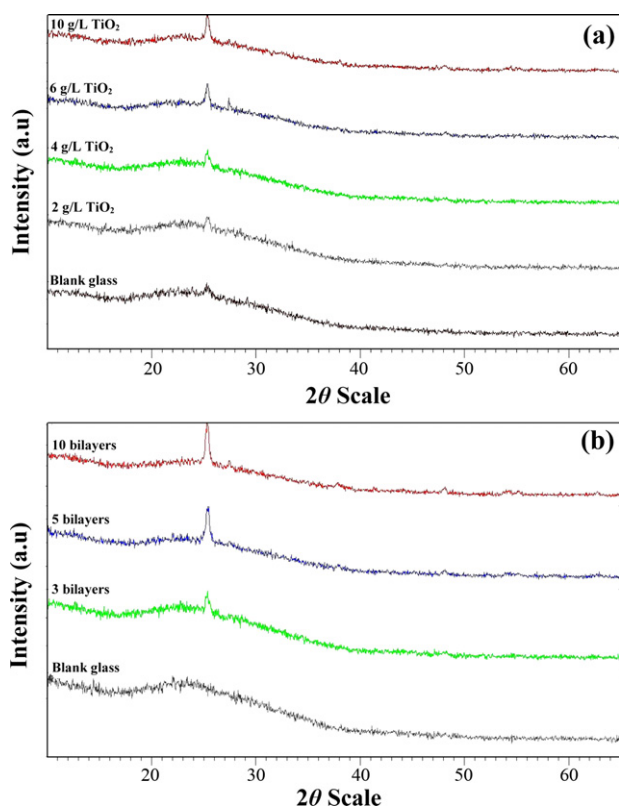
3. Results and discussion

3.1. Catalyst characterization studies

The mean crystallite size of the catalyst determined by XRD patterns using Scherrer formula is 20 ± 2 nm, which is close to the data supplied by the manufacturer. Fig. 2 shows the X-ray diffraction patterns of PSS/TiO$_2$ thin films with increase in TiO$_2$ loading (Fig. 2a) and bilayers (Fig. 2b). It was observed that the peaks corresponding to the anatase phase have appeared at $2\theta = 25.33$ in all cases. Further, the peaks were getting sharper with increase in catalyst loading and number of bilayers. But there was no remarkable difference in the peak intensity of TiO$_2$ after a loading of 4 g/L and appears to be the same with further increase in catalyst loading from 6 g/L to 10 g/L. On the other hand, with increase in number of bilayers from 1 to 10, a difference in peak intensity was noticed. This observation implies that higher intensity of TiO$_2$ peak is due to the presence of more amount of TiO$_2$ available for the degradation of dimethoate making the process favorable for degradation.

The LbL-TiO$_2$ thin films were characterized by SEM and AFM to evaluate the surface morphology and effectiveness of the multilayer assembly technique. The thickness of films with increasing number of layers 1, 3, 5 and 10 was measured from the cross sections of these films using SEM. For clear imaging, the multilayer thin films were assembled on silicon wafers at pH 2.5 using 4 g/L TiO$_2$ suspension. The thickness of the films was found to be 125 nm, 730 nm, 1.563 μm and 3.268 μm for 1-, 3-, 5- and 10-layered films respectively. Thickness of the layers is also dependent on the concentration of TiO$_2$ used. It was observed that initial layers were not uniform but as the number of layers increased, the surface of the film looks homogeneous and smooth. Interestingly, the increase in thickness for each layer was approximately linear. Fig. 3a shows

Fig. 2. XRD images of LbL-TiO$_2$ films with increase in (a) TiO$_2$ loading and (b) number of bilayers.

tional view SEM images of the PAH/(PSS/TiO$_2$)$_5$ thin film showing well-defined porous multilayers.
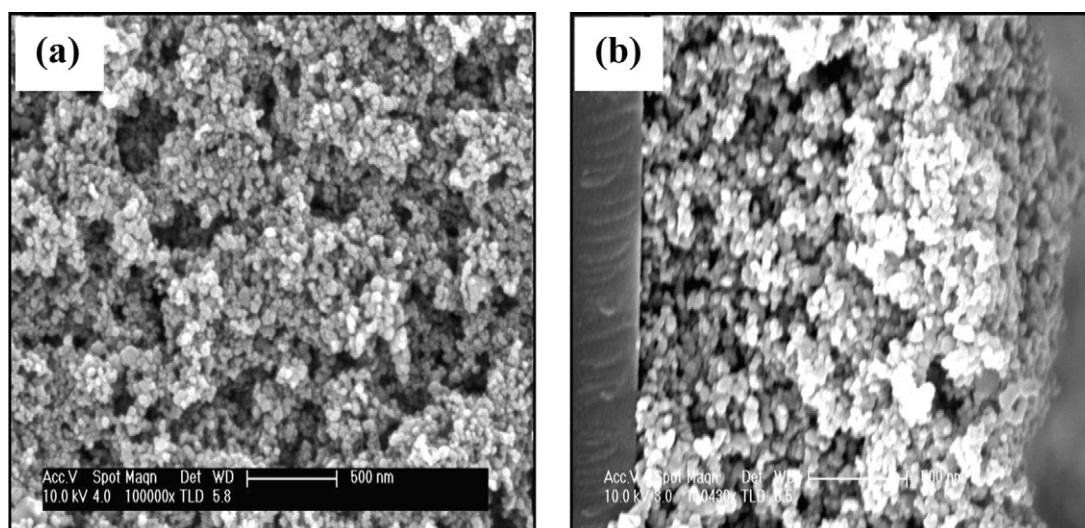
The PSS/TiO$_2$ multilayer thin films were further examined by AFM to determine the surface roughness. PAH/(PSS/TiO$_2$)$_n$ films were deposited with 1, 3 and 5 bilayers using 4 g/L TiO$_2$ and PAH, PSS concentrations of 1 g/L. Fig. 4a–c shows the 3D images for the three samples with PAH/(PSS/TiO$_2$)$_1$, PAH/(PSS/TiO$_2$)$_3$ and PAH/(PSS/TiO$_2$)$_5$, respectively. It was observed that the roughness of the films for 1, 3 and 5 bilayers were 71, 86 and 92 nm, respectively. The roughness increased with increase in the number of bilayers, which is due to the increase in the amount of TiO$_2$ deposited per each layer.

### 3.1.1. Comparison of LbL-TiO$_2$ films with other films

The ability of immobilized catalysts prepared by LbL-TiO$_2$ films in comparison with films prepared by drop casting and spin coating methods is studied. Fig. SI 1 shows the SEM images of PAH/(PSS/TiO$_2$)$_5$ deposited with TiO$_2$ loading of 4 g/L and PELs of 1 g/L each at deposition pH of 2.5. It is very clear from these images that films prepared by drop casting (Fig. SI 1a) and spin coating (Fig. SI 1b) methods do not show uniform surface morphology when compared to LbL-TiO$_2$ films (Fig. SI 1c) deposited under the same experimental conditions. It can also be seen that polyelectrolytes and TiO$_2$ are aggregated as clusters in case of films assembled using drop casting and spin coating methods. On the other hand, the SEM image of LbL-TiO$_2$ film illustrates a smooth surface morphology and a complex network of cross-linked polyelectrolytes with TiO$_2$ nanoparticles uniformly distributed in the multilayer thin films. The image also shows a high degree of porosity, which plays an important role in the photocatalytic activity, as larger surface area provides for more photocatalysis reactions to take place. The efficiency of these highly stable LbL-TiO$_2$ films in terms of photodegradation (studied in our previous paper but data not reported here) have also proven their ability to degrade the pollutant for number of cycles with the same efficiency as compared to the other two films.

3.2. Effect of lamp intensity

The effect of lamp intensity on degradation of dimethoate was studied with an UV irradiation source of 125 and 400 W lamp. Prior to the experiment, O–nitrobenzaldehyde actinometry experiment was performed to calculate the light intensity of the UV power source and the values were found to be 12 mW/cm^2 and

the top view surface morphology of a PAH/(PSS/TiO$_2$)$_5$ thin film examined by field emission scanning electron microscope. A close view surface of the film shows a flat and dense surface morphology of polyelectrolytes and uniformly distributed TiO$_2$ nanoparticles embedded in the film. The film shows sufficient porous structure to permit free diffusion of pollutant in and out of the film and these porous structures can effectively trap light into the inner layers. Also, the optical absorbance as measured by the UV–vis spectra (data not shown) increases linearly with film thickness showing that the film is accessible to light. Fig. 3b shows the cross sec-

Fig. 3. (a) Top view SEM image of PAH/(PSS/TiO$_2$)$_5$ and (b) cross sectional SEM image of PAH/(PSS/TiO$_2$)$_5$ deposited by LbL method.
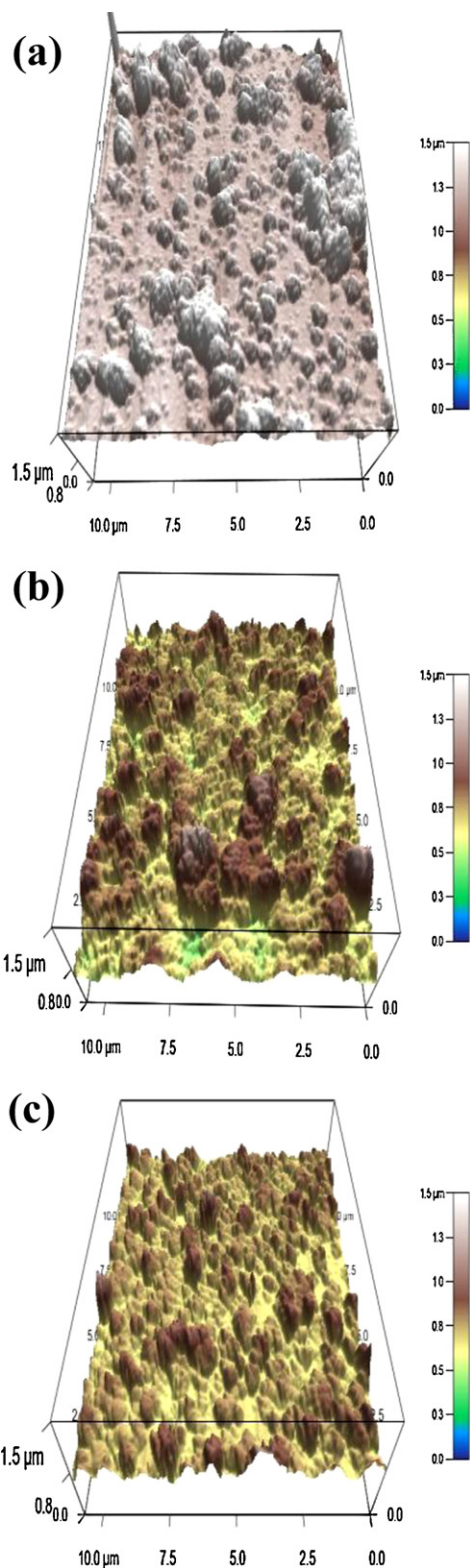
Fig. 4. AFM images of LbL-TiO$_2$ thin films with (a) 1 bilayer of PAH/(PSS/TiO$_2$)$_1$, (b) 3 bilayers of PAH/(PSS/TiO$_2$)$_3$ and (c) 5 bilayers of PAH/(PSS/TiO$_2$)$_5$.

31.6 mW/cm^2, respectively for 125 W and 400 W lamps. The experiment on effect of lamp intensity was then performed with five numbers of immobilized catalysts (PAH/(PSS/TiO$_2$)$_5$) each with a TiO$_2$ loading of 1 g/L and 2 g/L, for an irradiation time of 300 min. The results are shown in Fig. 5. It was observed that, at TiO$_2$ loading of 1 g/L and 2 g/L with 125 W lamp, the amount of dimethoate
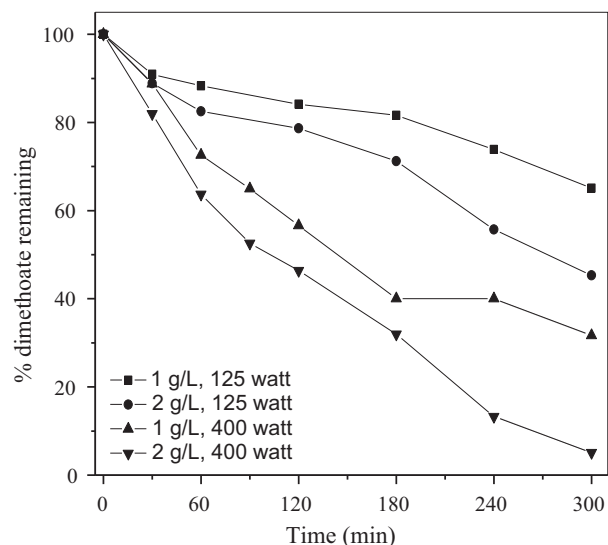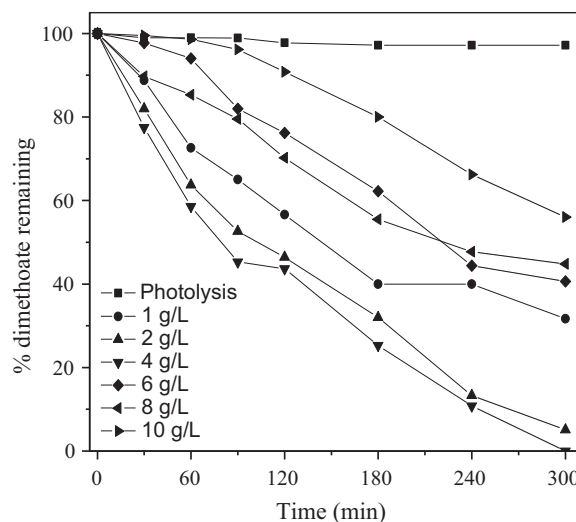

Fig. 5. Effect of lamp intensity on degradation of dimethoate. In all the experiments, 5 slides were immobilized having 5 bilayers on each.

remaining was 65% and 45%, respectively. However, under the same set of conditions with 400 W lamp, the amount of dimethoate remaining after 300 min of irradiation was 31.7% and 5.1%, respectively. With increase in lamp intensity increase in the rate of degradation was observed. This is due to the increase in number of photons generated with 400 W lamp leading to more reactive species generation and more degradation of dimethoate. The observed results are in agreement with the earlier studies [13]. Since the degradation was more effective with a 400 W lamp as compared to a 125 W lamp, further experiments were carried out with a 400 W lamp that would yield better degradation of dimethoate.

3.3. Effect of catalyst loading

The effect of catalyst loading on dimethoate degradation was studied by varying TiO$_2$ concentration from 1 g/L to 10 g/L with five slides immobilized with PAH/(PSS/TiO$_2$)$_5$ and subjecting for an irradiation time of 300 min with a 400 W lamp. The results are shown in Fig. 6. Photolysis alone (without catalyst) had no effect on degra-

Fig. 6. Effect of catalyst loading on degradation of dimethoate, with 400 W lamp. In all the experiments, 5 slides were immobilized having 5 bilayers on each.

dation. It was observed that with increase in catalyst loading, the percentage of dimethoate remaining in the solution decreased from 100% to 31.7%, 5.1% and 0%, respectively for 1 g/L, 2 g/L and 4 g/L. Complete degradation of dimethoate was achieved with a catalyst loading of 4 g/L at an irradiation time of 300 min. However, any further increase in the catalyst loading than 4 g/L reduced the rate of degradation. This indicates that optimum loading for immobilized catalyst was achieved with 4 g/L TiO_2.

The increase in percentage degradation of dimethoate with increase in TiO_2 concentration up to 4 g/L is due to the availability of more amount of catalyst for the reaction. The sudden decrease in the percentage degradation with further loading from 6 g/L to 10 g/L is attributed mainly to the light scattering effect as reported in the earlier studies [13,30]. Though the films are homogeneous, the coating becomes turbid with increase in concentration after certain number of layers. When all the dimethoate molecules are adsorbed on TiO_2, the addition of higher quantities would also have no effect on the degradation efficiency. And this is the reason why at high catalyst concentration, in spite of more amount of catalyst available for reaction, the degradation efficiency decreases due to the reduced transparency of the film which proportionately lowers the photocatalytic activity. This was also well supported by the XRD patterns of the films (Fig. 2a) where there was negligible difference in peak intensity with further increase in TiO_2 loading from 6 g/L to 10 g/L. Catalyst loading beyond this point was not significant and resulted in decreased degradation efficiency. Hence, we considered 4 g/L TiO_2 as the optimum loading concentration that would efficiently degrade dimethoate and further experiments were performed at this loading concentration. A comparison was made on the optimum amount of TiO_2 required in powder form and that for thin film deposition for the complete degradation of dimethoate. The amount of catalyst deposited by the LbL method was roughly calculated from the difference between the weight of the empty slide and the weight after 10 bilayers of TiO_2 deposition. The optimal amount of TiO_2 required in powder form as reported by Evgenidou et al. [14] and Chen et al. [13] was 0.1 g/L and 0.6 g/L for the complete degradation of a 10 ppm and 50 ppm dimethoate solution respectively. On the other hand, using the LbL technique, the average deposition of TiO_2 per each layer was ~0.33 mg and on each slide was ~3.69 mg. Hence the amount of TiO_2 required for the preparation of catalyst with 10 bilayers and 5 numbers of slides is approximately 18.45 mg, which is very less as compared to that required by the earlier researchers to achieve complete degradation of 100 mL of 10 ppm dimethoate solution. Further, the catalyst can be reused several times with the same efficiency.

3.4. Effect of number of bilayers

Fig. 7 shows the effect of number of bilayers on degradation of dimethoate. Experiments were carried out by varying the bilayers from 1 to 10, at an optimum catalyst loading of 4 g/L and at a lamp intensity of 400 W. It was observed that with PAH/(PSS/TiO_2)₁, the amount of dimethoate remaining in the solution was 22.5% for the irradiation time of 300 min. On the other hand, when the number of bilayers was increased from 1 to 5, the amount of dimethoate remaining decreased from 22.5% to 19.6% and 0% with 3 and 5 bilayers, respectively. Further, when the bilayers were increased to 10, it was observed that dimethoate was completely degraded within 180 min.

Increase in dimethoate degradation with increase in the number of bilayers can be attributed mainly to two reasons – the first being more amount of catalyst deposited per each layer, i.e., as the number of layers increase, more TiO_2 gets immobilized in the multilayers which in turn increases the degradation efficiency due to more catalyst available for reaction. The second is the porous structure of the film (as evident from the SEM images Fig. 3a and b where
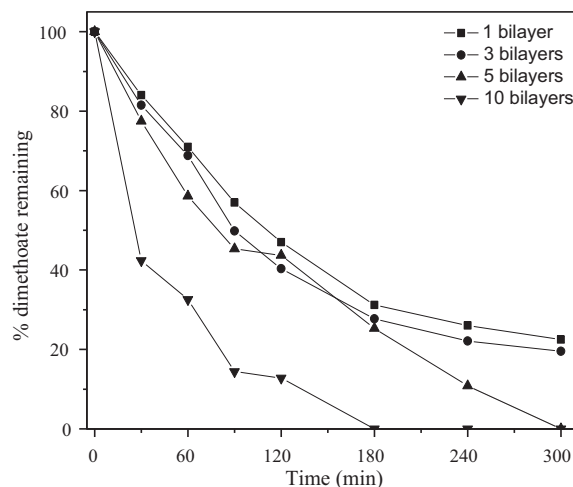

Fig. 7. Effect of bilayers on the degradation of dimethoate at an optimum catalyst loading of 4 g/L and with 400 W lamp. In all the experiments, 5 slides were immobilized having 5 bilayers on each.

the growth of the films is uniform), which allows the free diffusion of dimethoate molecules in and out of the layers promoting enhanced degradation efficiency. This observation is consistent to our previous study where we proved that the degradation is not only carried out by TiO_2 on the outermost layer but also by the inner layers [29]. This result is also supported by the explanation given by Andrea Malagutti et al. [31] that, in films with higher number of layers, the electron recombination process becomes slower because electrons have to diffuse in to the inner layers and interact before returning to the surface of the semiconductor owing to a greater density of holes at the surface leading to higher photocatalytic activity as compared to films with less number of layers. Further, the investigations made by Chen et al. [13] and Evgenidou et al. [14] on the degradation of dimethoate stated that the addition of oxidants like H_2O_2 and $K_2S_2O_8$ to the pesticide solutions improved the photodegradation rate. On the contrary, in our study, the increase in number of bilayers had a significant effect on enhancing the degradation efficiency of dimethoate, which proportionately reduced the UV irradiation time. In comparison to the earlier reported methods this is much safer in terms of environmental perspectives since new compounds are not introduced in to the system.

3.5. Effect of pH

The effect of pH on degradation of dimethoate was studied by varying the pH from 2.0 to 10.0. The catalyst was immobilized at an optimum loading (4 g/L) on 5 slides with 10 bilayers and the experiment was carried out for 180 min. The natural pH of dimethoate was observed to be 4.62. To carry out the experiments, the initial pH of the dimethoate solution was adjusted (using 0.1 M of HCl or NaOH) along with the immobilized catalyst to cover both the acidic and basic regions. Fig. 8 shows the effect of pH on the degradation of dimethoate. It was observed that pH had a very significant effect on dimethoate degradation. For an acidic pH of 2.0, the amount of dimethoate remaining in the solution was 27.1%, after 180 min of photocatalysis. Increasing the initial pH values of 4.62, a complete degradation was observed. However, further increase in the initial pH values to 6, 8 and 10 resulted in decreased degradation. At a pH of 10, the least degradation was observed and 60% of the dimethoate was remained in the solution. Thus from the results obtained, it can be concluded that a better degradation can be achieved at natural pH of the dimethoate solution.

The dependency of dimethoate degradation on pH values is attributed to the surface charge interactions between dimethoate
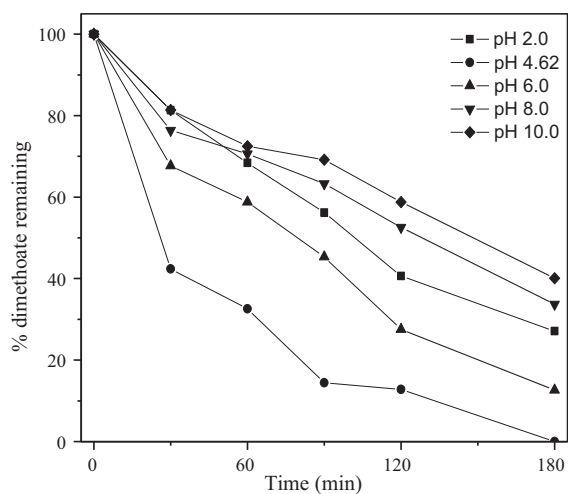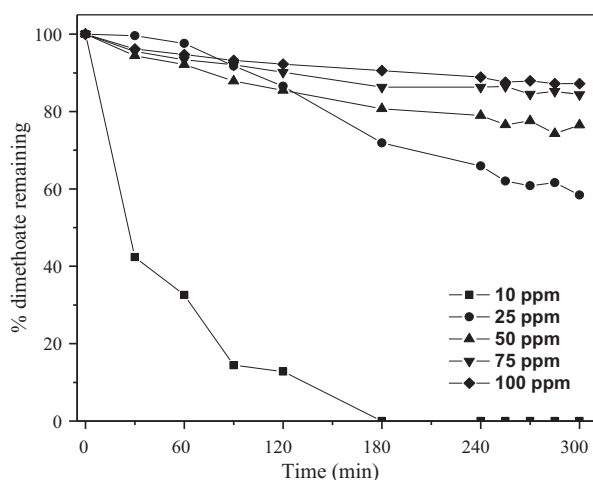
Fig. 8. Effect of pH on the degradation of dimethoate at an optimum catalyst loading of 4 g/L and with 400 W lamp. In all the experiments, 5 slides were immobilized having 10 bilayers on each.

and TiO$_2$. The point of zero charge (pzc) of commercial TiO$_2$ catalyst is around 6.0, below this pzc, the catalyst surface is positively charged and above it is negatively charged. The maximum degradation around pzc of TiO$_2$ at higher pH values has been reported by Evgenidou et al. [14]. Other reason is that hydroxyl ions with elevated concentration would scavenge photogenerated holes, which yield highly oxidative •OH species through interaction with H$^+$ ions. At lower pH, the degradation results from photogenerated holes whose oxidizing ability is less as compared to that of •OH species [13]. Hence the degradation efficiency of dimethoate is less at low pH values than at higher pH.

3.6. Effect of initial dimethoate concentration

The effect of initial dimethoate concentration on the degradation of dimethoate was studied by varying the initial concentration between 10 and 100 ppm, at optimum catalyst loading of 4 g/L TiO$_2$ (pH 4.62) with PAH/(PSS/TiO$_2$)$_{10}$ for an irradiation time of 300 min. The results are shown in Fig. 9. Complete degradation of dimethoate was observed at 10 ppm within 180 min of exposure. With increase in the initial concentration of dimethoate from 10 ppm to 100 ppm, the degradation reduced and the percentage

Fig. 9. Effect of initial dimethoate concentration (pH 4.62) on the photocatalytic degradation at an optimum catalyst loading of 4 g/L and with 400 W lamp. In all the experiments, 5 slides were immobilized having 10 bilayers on each.

of dimethoate remaining in the solution drastically increased from 0% to 87.21%, respectively for an irradiation time of 300 min.

When the initial dimethoate concentration was increased from 10 ppm to 100 ppm, the catalyst loading, light intensity and illumination time were held constant. Moreover the available reaction sites are also constant. Therefore the free radicals formed on the catalyst surface might not be sufficient enough to degrade the pollutant molecules on the surface of the catalyst resulting in decreased degradation efficiency. From the previous studies, it is evident that the photocatalytic degradation reaction of the organophosphorus pesticides occurs on the surface of TiO$_2$ in trapped holes and generation of reactive species play an important role in efficient degradation of pollutants. The contaminants cannot be degraded unless they are adsorbed on the surface of TiO$_2$. Since other parameters like light intensity and illumination time are constant, as the initial concentration increases, more and more organic substances are adsorbed on the surface of the TiO$_2$, but the free radicals formed on the surface of TiO$_2$ will be constant. Hence the relative number of free radicals attacking the organophosphorus compounds decreases thereby decreasing the degradation efficiency [25]. Similarly, phosphate concentration increases with increase in initial concentration of dimethoate to a certain extent but remains constant when the surface concentration of dimethoate reaches a steady state. Therefore the availability of total adsorption sites is the dominating factor which results in different degradation efficiencies between low and high concentrations [13]. However, the present study shows that dimethoate concentrations of ≤10 ppm could be effectively degraded.

3.7. GC–MS and HPLC data

The degradation byproducts of dimethoate were analyzed and confirmed by GC–MS. Table 1 shows the GC–MS data of dimethoate with respect to retention time. The data of dimethoate degradation intermediates was obtained after 180 min of UV irradiation (spectra not shown). Eight degradation products were identified that matched with the data reported earlier [15–17]. The first compound identified was N-methyl-2-sulfanylacetamide by a peak at m/z = 105 and the characteristic ions at m/z = 71 and m/z = 57 which matched with the data reported by Evgenidou et al. [16]. The second compound was identified as O,S,S-trimethyl phosphorothioate which exhibited a peak at m/z = 156 [16]. The third compound was identified as 2-S-methyl-(N-methyl)acetamide and it exhibits ions at m/z = 119 that correspond to the molecular ion [M]+ and the characteristic ions m/z = 73 and m/z = 58. In addition, this compound was also detected as by-product of dimethoate thermal decomposition [16,17]. Compound 4 was identified as O,O,S-trimethyl thiophosphorothioate [16] with a peak at m/z = 172. This product has also been identified as an intermediate during thermal decomposition [17]. Compound 5 exhibits a peak at m/z = 151 which corresponds to the molecular ion [M]+ and the characteristic ions m/z = 105, m/z = 73 and m/z = 58 [16]. The sixth compound which exhibited a peak at m/z = 182 was identified as O,O,S-trimethyl thiophosphorodithioate, a product obtained during the thermal decomposition of dimethoate [17]. Compound 7 is identified as omethoate which gives a characteristic rearrangement ion peak at m/z = 156 and compound 8 was identified as 1,2-bis(acetyl-N-methyl-)methane disulfide that exhibited a peak at m/z = 206, which corresponds to the molecular ion [M]+. A detailed explanation of the characteristic ions of these compounds has been given by Evgenidou et al. [16].

The concentration of dimethoate was also determined using HPLC (SI Fig. SI 2) and observations are made from the changes in dimethoate parent signal at retention time (R$_t$) of 6.04. When experiments with dimethoate solution along with the catalyst were performed in dark for 60 min, there was no change in the signal at all. After irradiating with UV, there was a decrease in the parent

Table 1
GC–MS data of dimethoate degradation products with retention times and characteristic ions.

| Degradation products	R_t (min)	Characteristic ions (m/z)
N-methyl-2-sulfanylacetamide	8.7	105, 71, 57
O,S,S-trimethyl phosphorothioate	9.3	156, 141, 126, 110, 95, 79
2-S-methyl-(N-methyl)acetamide	12.5	119, 73, 62, 58
O,O,S-trimethyl thiophosphorothioate	14.6	172, 125, 95, 57
O,O,S-trimethyl thiophosphoro-dithioate	20.7	182
Omethoate	23.7	213, 156, 141, 126, 110, 79, 58
Dimethoate	28.2	229, 143, 125, 93, 87
1,2-Bis(acetyl-N-methyl-) methane disulfide	30.41	206, 105, 73, 58

signal with increase in time. At the end of 180 min of exposure to UV irradiation, the signal became totally flay indicating that dimethoate is completely removed from the solution and at the same time new peaks were detected with increasing intensities indicating the formation of new intermediates during the course of reaction.

3.8. Mineralization studies

Complete mineralization of organic compounds is of great significance in wastewater treatment. Hence TOC measurements were carried out to determine the extent of mineralization and the results are shown in Fig. 10. It was expected that total mineralization of the compound would be achieved within 180 min due to the total disappearance of dimethoate peak (as determined by HPLC) at this irradiation time. On the contrary, the TOC removal efficiency at 180 min was 21%. The irradiation time was further extended to 300 min in order to achieve complete mineralization but TOC removal at this stage was only 50%. The rate of TOC removal was very slow which might be due to the presence of more stable intermediates produced during the course of degradation. Similar trend of results was reported by Evgenidou et al. [14] where comparison of the TOC removal of dimethoate with TiO$_2$ alone and with the addition of H$_2$O$_2$ was made. They were able to achieve 59% TOC removal with TiO$_2$ alone and 100% with TiO$_2$–H$_2$O$_2$ system.

3.9. Toxicity tests using V. fischeri

The treated dimethoate solutions were also tested for their toxicity. When complete mineralization is not achieved even after 300 min, it is obvious that the final products could be more toxic than the parent compounds. Hence toxicity measurements were performed for the treated solutions. The toxicity of the samples collected was measured using the LUMIStox luminometer. The results
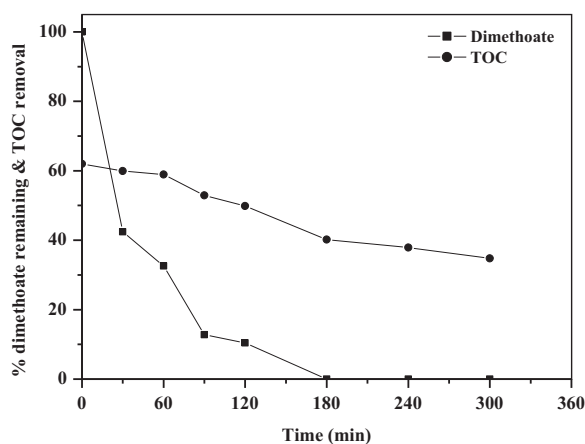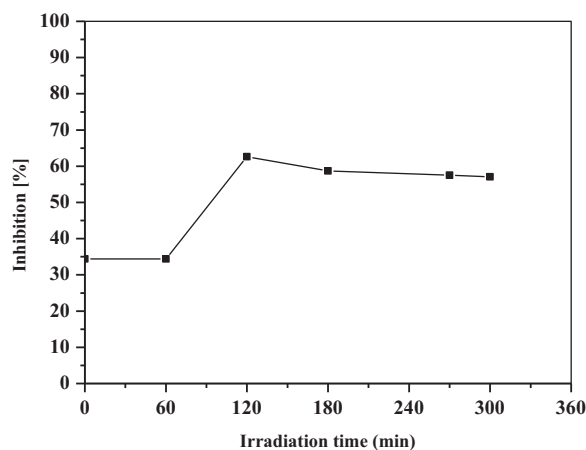
obtained are presented in Fig. 11. Initially, there was an increase in toxicity from 34% to 62% after 120 min of irradiation. When the samples were further irradiated till 300 min, only a slight decrease (<8%) in toxicity was observed (54%). These results can be related to the TOC measurements where, TOC removal decreased in the initial stages but appears to be more or less the same with increase in irradiation time. Similarly there was not much effect on the reduction of toxicity also. The intermediates obtained during the degradation of dimethoate were already discussed under GC–MS analysis stating that the intermediates produced during the course of reaction are more toxic than the parent compound especially omethoate, one of the main degradation products, is proved to be more toxic than dimethoate. Complete mineralization and total reduction in toxicity can be achieved in the presence of an oxidant as reported by Evgenidou et al. [14,16].

3.10. Catalyst reusability

The amount of dimethoate left in the solution after each cycle of catalyst reuse. Experiments were performed with 4 g/L TiO$_2$ (pH 4.62) with PAH/(PSS/TiO$_2$)$_{10}$ for an irradiation time of 180 min for 10 cycles. To compare the dimethoate degradation efficiency, after the first cycle of reaction the degraded dimethoate solution was removed and a fresh solution (10 ppm) of dimethoate was placed in the beaker without removing the catalysts. The same procedure was repeated for nine more cycles. Samples were collected at the end of each cycle and analyzed to see the percentage degradation of the dimethoate in 180 min. The results after each cycle showed complete degradation of dimethoate by reusing the immobilized slides. The results indicate that there was no alteration in the surface characteristics of LbL-TiO$_2$ thin films even after several repeated uses indicating its stability and thus retaining the same photocatalytic activity after several cycles of operation. These

Fig. 10. Mineralization studies of dimethoate. Immobilized catalysts with TiO$_2$ loading of 4 g/L, 5 slides with 10 bilayers were used. The UV irradiation source was 400 W lamp.

Fig. 11. Measurement of toxicity of dimethoate toxicity using *Vibrio fischeri*. Immobilized catalysts with TiO$_2$ loading of 4 g/L, 5 slides with 10 bilayers were used. The UV irradiation source was 400 W lamp.

studies are very important for any wastewater treatment system in terms of economic perspectives.

Although the degradation of dimethoate with TiO_2 in powder form was extensively studied by previous researchers [13–16], none of these studies focused on the reusability of the catalyst. Complete degradation was achieved but there are some drawbacks associated with the use TiO_2 in powder form. One major concern is the difficulty in separating the TiO_2 powder from water after the completion of the reaction. In this case a centrifugation step is definitely required to recover the catalyst for further use which might lead to the loss of catalyst during the process and practically not feasible to scale up the process. On the other hand, with the solutions treated using LbL-TiO_2 films, the final solution is absolutely clean and free of any suspended nanoparticles that can be safely discharged to the environment. For real time applications this method can be used for continuous systems thus making it an option for scale up.

4. Conclusions

The present study deals with the application of LbL-TiO_2 thin films for the photocatalytic degradation of dimethoate in presence of UV irradiation. Complete degradation of 10 ppm dimethoate at an optimum loading of 4 g/L TiO_2 was achieved. Increase in number of bilayers increased the degradation with a reduction in UV illumination time to 180 min. pH had a significant effect on degradation and at pH 4.62, maximum degradation was observed. The degradation rates reduced with increase in the initial dimethoate concentration. The GC–MS analysis confirmed complete degradation. Though complete removal of dimethoate was achieved within 180 min, mineralization of dimethoate was only 50% after an irradiation time of 300 min. The toxicity increased during the course of the reaction due to the presence of stable intermediates. Hence future studies will be focused on this aspect by bringing some modifications in the system like irradiating for a longer time or increasing the number of bilayers. Though the illumination time is longer as compared to that used in suspension form, it is apparent that the reaction time can be reduced with increase in number of bilayers. Further, the main advantage of LbL technique is its applicability to any kind of shape and substrate which makes an attractive option for scale up. The immobilized catalyst has advantages such as catalyst reusability, solution free of TiO_2 after the completion of reaction, etc. This technique is a worthwhile endeavor and a new approach that alleviates all the drawbacks associated with TiO_2 in suspension form and can be successfully applied to continuous systems with significant savings in terms of TiO_2 and polymer requirement. The results obtained can be applied for the treatment of industrial wastewaters and others contaminated with pesticides.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.08.030.

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