



An efficient and novel porous nanosilica supported TiO₂ photocatalyst for pesticide degradation using solar light

Mangalampalli V. Phanikrishna Sharma, Gullapelli Sadanandam, Ajjarapu Ratnamala, Valluri Durga Kumari, Machiraju Subrahmanyam*

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology (IICT), Tarnaka, Hyderabad, Andhra Pradesh 500607, India

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ABSTRACT

A latex polymer of styrene–acrylic acid emulsion is used as a template for the synthesis of novel porous nanosilica (PNS) material. TiO₂ is dispersed over PNS by solid state dispersion and the composite materials are characterized by XRD, nitrogen adsorption–desorption isotherms, SEM and TEM measurements. The photocatalytic activities of the composite TiO₂/PNS catalysts are evaluated for degradation of isoproturon pesticide in water with different parameters under solar light. Furthermore, commercial pesticide solutions containing imidacloprid and phosphamidon were also degraded successfully with the composite system using the same developed conditions for isoproturon degradation. The 5 wt% TiO₂/PNS is found to be active in the present investigation.

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1. Introduction

Pesticides are frequently occurring in water bodies by their extensive use for pest control in the agricultural practices [1]. Numerous studies demonstrated that heterogeneous photocatalysis is an effective process for degradation of pesticides in wastewater [2–4]. TiO₂ mediated semiconductor photocatalysis 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. To overcome these problems, TiO₂ is immobilized on materials like electron acceptors and adsorbents that provide good dispersion of TiO₂ on their surface. The high adsorption capacity of the support helps in pooling the pollutants to the vicinity of TiO₂ surface [5–7]. In this regard, mesoporous nanomaterials have attracted greater attention. Nano-structured inorganic materials showed fascinating applications due to unique and useful electronic, optical and magnetic properties [8].

Isoproturon (*N,N*-dimethyl-*N*-[4-(1-methylethyl) phenyl] urea, WHO hazardous class III) is a herbicide. It is mainly used for the control of annual grasses and many broad leaved weeds in the cereals and wheat crops [9,10]. Parra et al. [11] reported its non-biodegradability. Imidacloprid (1[(6-chloro-3-pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine, WHO hazardous class II) is a systemic, chloro-nicotinyl insecticide for the control of sucking insects. Phosphamidon (2-chloro-2-diethylcarbamoyl-1-methylvinyl dimethyl phosphate, WHO hazardous class Ia) is a noncumulative systemic organophosphorous pesticide with a broad spectrum of activity. All the three pesticides (Fig. 1) are potential water contaminants and are highly toxic to aquatic environment due to their high solubility [12,13].

The present investigation aims synthesis of novel porous nanosilica (PNS) material and it is used as a support for TiO₂ to increase its efficiency in treating pesticide containing aqueous solutions. We have proposed a novel route to prepare porous silica nano-materials using latex polymers of styrene–acrylic acid emulsion as a template. Different TiO₂ loadings are immobilized over PNS and their photocatalytic investigations are carried out. Initially, Isoproturon is used as a model compound to establish the photocatalytic degradation conditions over the composite photocatalysts under solar light in aqueous suspensions. Later, the studies are extended to commercial pesticide formulations of imidacloprid and phosphomidon in order to know the extent of degradation efficiency of the combine catalyst system with the established conditions arrived for isoproturon.

* Corresponding author. Tel.: +91 40 27193165; fax: +91 40 27160921.
E-mail address: subrahmanyam@iict.res.in (M. Subrahmanyam).

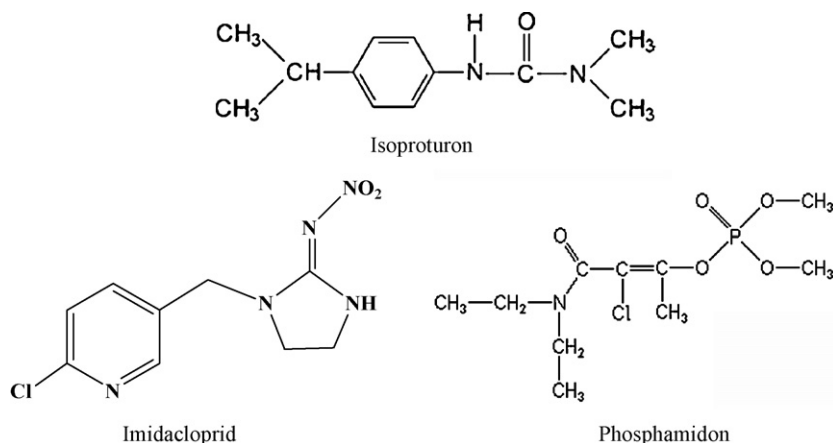


Fig. 1. Molecular structures of pesticides.

2. Experimental

2.1. Materials and methods

All chemicals in the present investigation are used as such without further purification. Isoproturon (>99% pure, Technical) is obtained from Rhône-Poulenc Agrochimie, France. The commercial formulations, mida (Imidacloprid, 17.8 SL), sumidon (Phosphomidon, 40 SL) were purchased in the local market. Polyvinyl alcohol, potassium persulphate, sodium metabisulphate, sodium fluoride were from Loba Chemie pvt. Ltd. Styrene, butyl acrylate, acrylic acid, tetraethylammoniumhydroxide (TEAOH), tetraethylorthosilicate (TEOS) were obtained from Aldrich chemicals and titanium dioxide P25 (Anatase 80%, rutile 20%, surface area $50 \text{ m}^2 \text{ g}^{-1}$ and particle size 27 nm) is from Degussa Corporation, Germany. All the solutions were prepared with deionized water (resistivity $18 \text{ M}\Omega \text{ cm}$ –DOC $< 0.1 \text{ mg C l}^{-1}$) obtained using a Millipore device (Milli-Q).

2.2. Preparation of PNS and TiO_2/PNS composites

2.2.1. Preparation of PNS

The styrene–acrylic acid emulsion is prepared by emulsion polymerization technique. The synthesis is carried out in a four-neck glass reactor equipped with a glass stirrer, condenser and a gas inlet into which pure N_2 gas was passed gradually and all this equipment is kept in a water bath at 70°C . In a kettle, 20 g of non-ionic emulsifier (nonyl-phenol-ethyleneoxide condensates) SE-305 is added and then 10% aqueous sol of polyvinyl alcohol is added followed by the addition of redox catalysts potassium persulphate (4% aqueous solution) and sodium metabisulphate (4% aqueous solution) 50 ml of each one after the other in five equal lots. Monomer mixture (styrene 200 g + acrylic acid 100 g) is then added by delayed addition technique over a period of 4 h under continuous stirring. After complete addition, the mixture is continuously stirred for another 1 h for complete polymerization. The bluish white colored emulsion contains 45% of solids suspended in water containing 52% of styrene, 46% butyl acrylate, 1.6% acrylic acid with 52.4% aromaticity ($T_g = 31^\circ\text{C}$).

PNS material is prepared using the latex polymer of styrene–acrylic acid as a template (structure directing agent for silica). Salt mediated synthesis is used for PNS preparation, in which sodium fluoride (3.0 g), polymer (9.2 g) were dissolved by mixing them in 50 ml of deionized water in a beaker at room temperature. After complete dissolution of the above mixture, 15 g of the silica precursor TEOS, 9 ml of TEAOH were added under vigorous stirring, after which the stirring rate was lowered. The precipitation started

almost immediately after addition of TEOS. This mixture was continuously stirred for 6 h and it was transferred into an autoclave and cooked at 100°C for 24 h. The product was filtered and washed with water and calcined at 500°C for 6 h. Thus the technique of organic and inorganic hybrid precursors used for the preparation resulted to a porous nano silica material.

2.2.2. Preparation of TiO_2/PNS composites

TiO_2/PNS catalysts are prepared by solid state dispersion (SSD) method [4]. The required amount of 1, 5 and 10 wt% TiO_2 is admixed with PNS in absolute ethanol and is thoroughly mixed. This solid material is calcined at 450°C for 5 h.

2.3. Characterization

TiO_2 supported catalysts are characterized by X-Ray Diffraction (XRD), nitrogen adsorption–desorption isotherms, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) techniques. The low angle XRD patterns were recorded on a Philips PW 1840 powder diffractometer using Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) from $2\theta = 0.5$ – 5.0° and high angle from Siemens D-5000 using Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) from $2\theta = 5$ – 50° . The surface properties of fresh and used samples were measured by N_2 adsorption in Autosorb 1C Quantachrome physical adsorption apparatus. The specific surface area and pore volume were calculated applying BET and Barrett–Joyner–Halenda (BJH) numerical integration methods respectively. The BJH desorption model was used to calculate the pore size distribution of the samples [14]. For SEM analysis the sample was mounted on an aluminum support using a double adhesive tape coated with gold in HUS-SGB vacuum coating unit and is observed in Hitachi S-520 SEM unit. The TEM analysis is carried out on TECHNAI F12 Philips unit operated at 80 kV with a filament current of 27 mA.

2.4. Photocatalytic experiments

Pesticide solutions are prepared by dissolving required amounts in deionized water by continuous stirring. Prior to the start of light experiments, dark (adsorption) experiments are carried out for 60 min under continuous stirring for better adsorption of the pesticides on to the surface of catalyst. For solar experiments, pesticide solution of 50 ml is taken in an open glass reactor with a known amount of the catalyst. The slurry solution is continuously stirred in a shaking unit at 120 rpm and is illuminated under bright solar light. Distilled water is added at regular intervals to avoid concentration changes due to evaporation with the help of markings present on the reactor. All solar experiments (intensity of $\sim 75 \text{ mW cm}^{-2}$

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