



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

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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.

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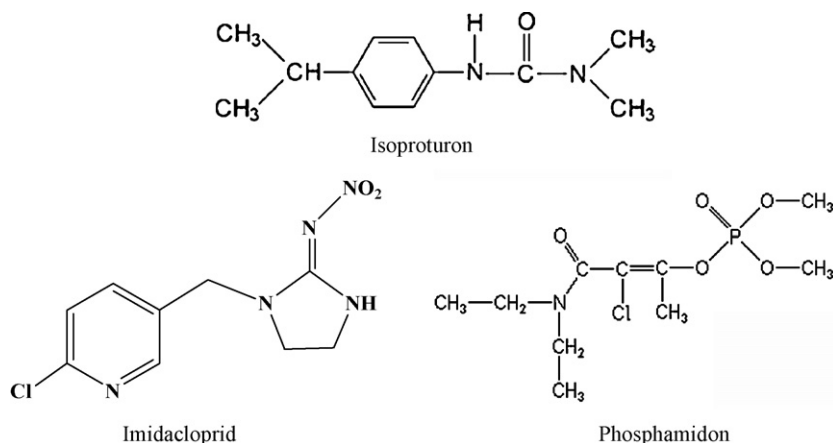


Fig. 1. Molecular structures of pesticides.

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 $18 \text{ M}\Omega \text{ cm} - \text{DOC} < 0.1 \text{ mg C l}^{-1}$) 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 $2\theta = 0.5\text{--}5.0^\circ$ and high angle from Siemens D-5000 using Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) from $2\theta = 5\text{--}50^\circ$. 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 $\sim 75 \text{ mW cm}^{-2}$

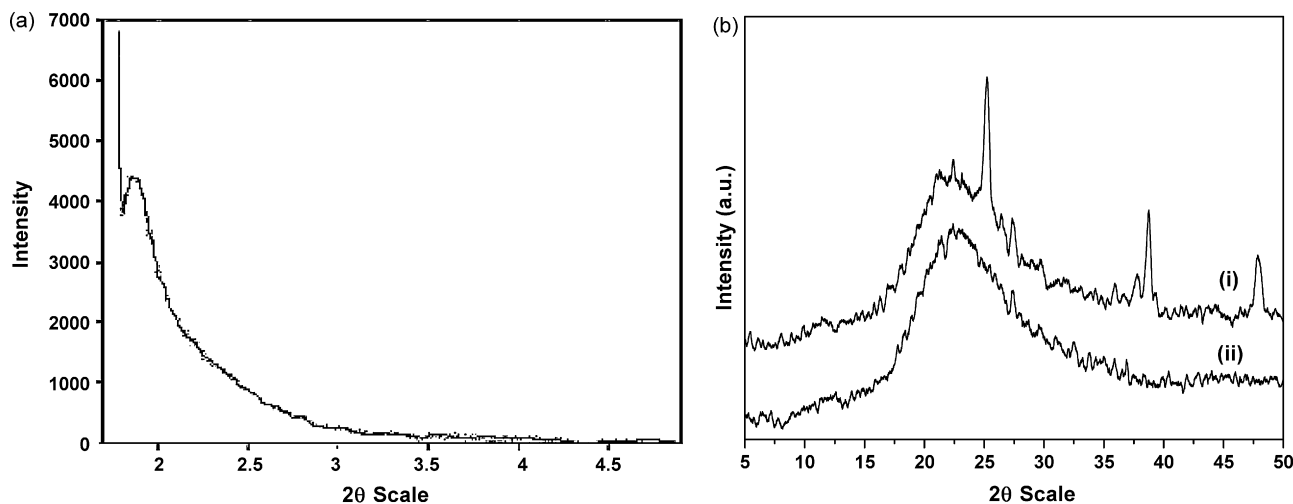


Fig. 2. (a) Low angle XRD pattern of PNS. (b) High angle XRD pattern of (i) PNS, (ii) 5 wt% TiO₂/PNS.

and temperature of $\sim 38^\circ\text{C}$) are carried out between 11.00 a.m. to 3.00 p.m. in May and June 2007 at Hyderabad, India.

2.5. Analyses

The degradation of respective pesticide is monitored by Shimadzu 10AvP HPLC using C-18 phenomenex reverse phase column with acetonitrile/water mobile phase of ratio 50:50 (v:v) % at a flow rate of 1 ml min^{-1} . The wavelength of UV detector of HPLC is set at 254 nm for isoproturon, 235 nm for phosphamidon and 275 nm for imidacloprid samples. The samples collected from solar experiments at regular intervals are filtered through micro syringe filters ($0.2\ \mu\text{m}$).

3. Results and discussion

3.1. Characterization

A typical low angle XRD pattern of PNS material is provided in Fig. 2a. It shows a clear inference peak corresponds to the presence of mesoporous material with a pore structure lacking the long range order [15]. Fig. 2b shows the high angle XRD patterns of PNS and TiO₂/PNS samples. It is indicating clearly that PNS material is very amorphous in nature and TiO₂ supported over PNS material is clearly showing the presence of dispersed titania peaks ($d = 3.5, 1.89$ and 1.69) in the graph.

Fig. 3 shows N₂ adsorption/desorption isotherms of PNS material. The adsorption isotherm shows a steep increase in the adsorbed amount of N₂ below the relative pressure $P/P_0 = 0.1$. These are type IV isotherms, characteristic of mesoporous materials with a lagging loop [16,17] indicating that capillary cohesion and evaporation occurred at different pressures. Fig. 3 (inset) is the pore size distribution curve of BJH model in which the pore diameter distributes from 0.2 to 100 Å with an average diameter of 64 Å and maxima of pore diameter is at 20 Å.

The specific surface area of PNS is $153\text{ m}^2\text{ g}^{-1}$ whereas 5 wt% TiO₂/PNS is having $115\text{ m}^2\text{ g}^{-1}$ only. The decrease in surface area with TiO₂ loading is due to the dispersion of TiO₂ particles over surface of the support.

The morphology of PNS and 5 wt% TiO₂/PNS catalysts are investigated by SEM and TEM techniques and the respective micrographs are presented in Fig. 4. The general morphology of nanoporous silica material showed that spherical aggregates of variable size and these are not providing a clear morphology. The morphology of TiO₂ loaded over silica material is similar to that of support and is not

showing clearly titania crystallites. This indicates the formation of fine particles and dispersion of TiO₂ over the support. The TEM photograph of PNS is showing porous nature with hexagonal structure of the particles of about 100–200 nm range and TiO₂ supported catalysts are having 80–100 nm. The reduction in particle size after loading with TiO₂ may be because of the crushed silica particles during grinding in SSD method and thus TiO₂ particles are finely dispersed over the support.

3.2. Photocatalytic activity

Initially, the adsorption capacities of PNS and TiO₂/PNS combines towards isoproturon are carried out in dark. The maximum adsorption equilibrium is reached within 60 min over all the systems. This period is considered as optimum time for adsorption equilibrium and is used for all other experiments. PNS has maximum adsorption capacity of $\sim 15\%$ and 10–15% adsorption is noticed for all supported systems whereas for TiO₂ it is 2% only (Fig. 5). The photolysis experiment is carried out for the photo-stability of the pollutant in solar light. There is a $\sim 2\%$ disappearance of isoproturon observed in 6 h duration. In the light experiment with PNS, there is no further degradation (i.e. after adsorption) which confirms that PNS acts only as a support but not as a photocatalyst.

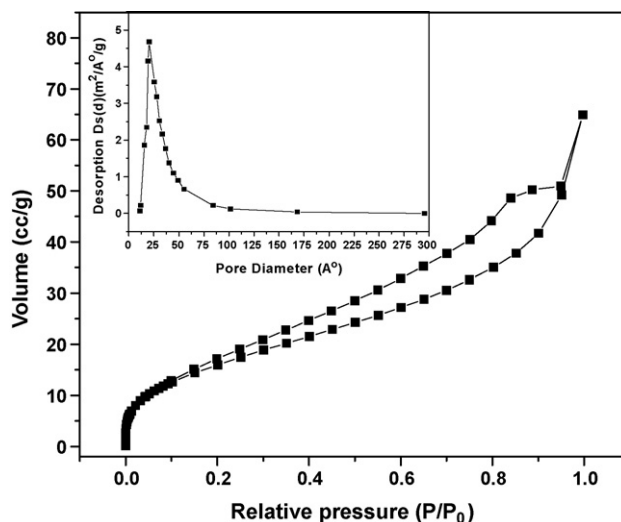


Fig. 3. Nitrogen adsorption/desorption isotherms of PNS and (inset) pore size distribution graph.

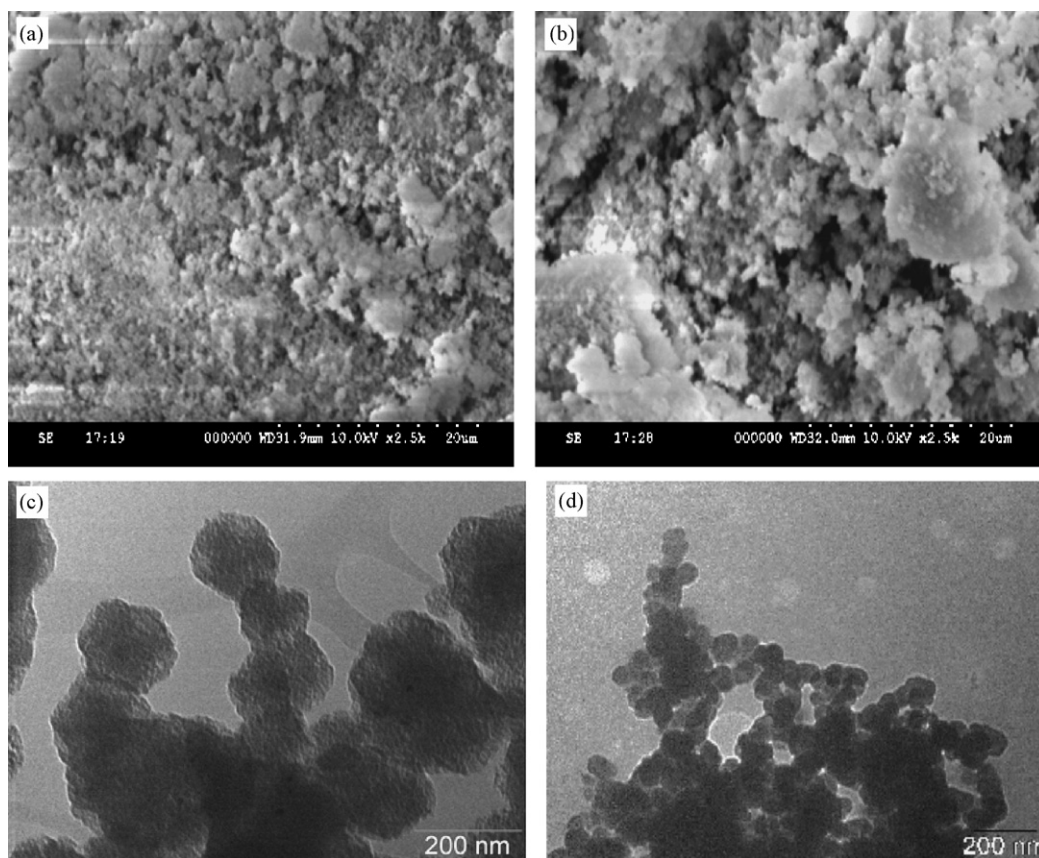


Fig. 4. (a) SEM photographs of (i) PNS, (ii) 5 wt%TiO₂/PNS. (b) TEM photographs of (i) PNS, (ii) 5 wt%TiO₂/PNS.

3.2.1. Effect of TiO₂ loading on PNS

The TiO₂ loading over PNS support affects the photocatalytic activity for degradation of the pollutant. There is a need for optimization of TiO₂ loading over the support. Photocatalytic degradation of isoproturon is monitored with TiO₂ 1, 5 and 10 wt% loadings over PNS taking 1.0 g l⁻¹ of the catalyst in 50 ml of isoproturon containing solution (Fig. 5). The photocatalytic activity increases with increasing TiO₂ from 1 to 5 wt% and there is not much increase in degradation rate with 10 wt% loading. Among all the studied catalysts, 5 wt% TiO₂ over PNS seems to be an efficient

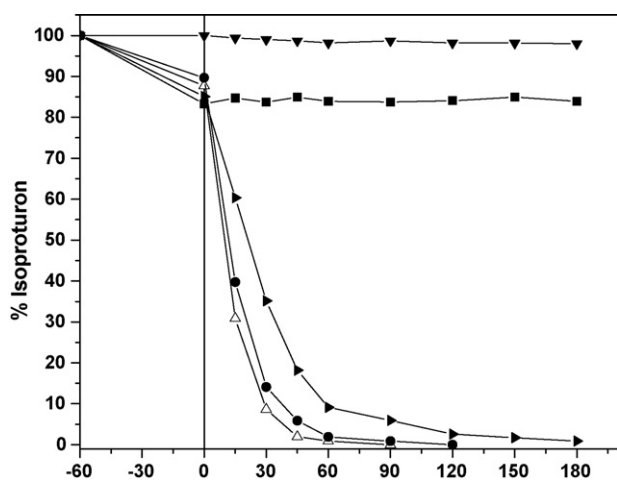


Fig. 5. Solar photocatalytic isoproturon degradation (▼) Photolysis and TiO₂ (wt%) (■) 0, (▸) 1, (△) 5 and (●) 10 supported over PNS. (Experimental conditions: C₀ = 1.14 × 10⁻⁴ M; pH 7; catalyst amount = 1.0 g l⁻¹.)

photocatalyst for the degradation of isoproturon i.e., complete disappearance of isoproturon is found within 90 min. The reasons for loss in activity at higher TiO₂ loading are poor adsorption capacity of the support due to its pore blockage by titania, turbidity of the solution that blocks penetration of light into the solution, faster recombination of the electrons and holes of excited TiO₂ particles which are not close to the support surface resulting lower degradation rates. In view of this, the TiO₂ loading is required to be optimized without affecting the adsorption capacity of the support and also keeping the original activity of TiO₂ in order to have an effective synergism.

3.2.2. Activity comparison of TiO₂ and 5 wt% TiO₂/PNS

The amount of TiO₂ available over 5 wt% TiO₂ supported system is considered for the activity evaluation. It is observed that TiO₂ supported system shows higher rate of degradation than bare TiO₂ (Fig. 6). This is due to synergistic effect resulted by adsorption of isoproturon over porous material, which is facilitating the degradation without affecting the photocatalytic properties of TiO₂. The good dispersion of photoactive TiO₂ leads the presence of more number of active sites near the adsorbed isoproturon molecules resulting faster degradation rates. Thus, comparison studies proved the beneficial effect of the support during isoproturon degradation activity.

3.2.3. Effect of substrate concentration

The effect of substrate concentration is an important parameter for photocatalytic degradation activity over a known catalyst amount. The 7.28 × 10⁻⁵, 1.14 × 10⁻⁴ and 2.42 × 10⁻⁴ M concentrations of isoproturon are studied over 5 wt% TiO₂/PNS catalyst with 1.0 g l⁻¹ catalyst amount. It is seen from Fig. 7a, a slight difference in degradation rate over titania supported catalyst for

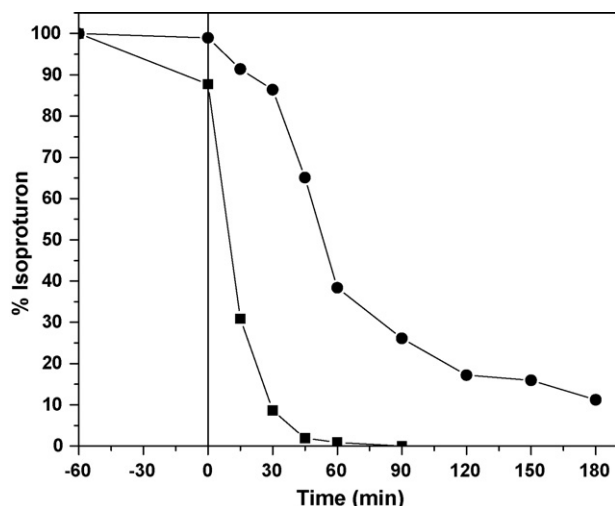


Fig. 6. Solar photocatalytic isoproturon degradation activity comparison over (●) TiO₂ and (■) 5 wt% TiO₂/PNS. (Experimental conditions: C₀ = 1.14 × 10⁻⁴ M; pH 7; catalyst amount = 1.0 g l⁻¹.)

7.28 × 10⁻⁵, 1.14 × 10⁻⁴ M concentrations are observed compared to 2.42 × 10⁻⁴ M. This indicates, at higher concentrations produced OH radicals by the catalyst are not sufficient to degrade the pollutant molecules which are adsorbed or near to the catalyst surface. Hence, 1.14 × 10⁻⁴ M solution is chosen for the degradation as there is an equilibrium between adsorption of reactant molecules and the generation of OH radicals from the active sites.

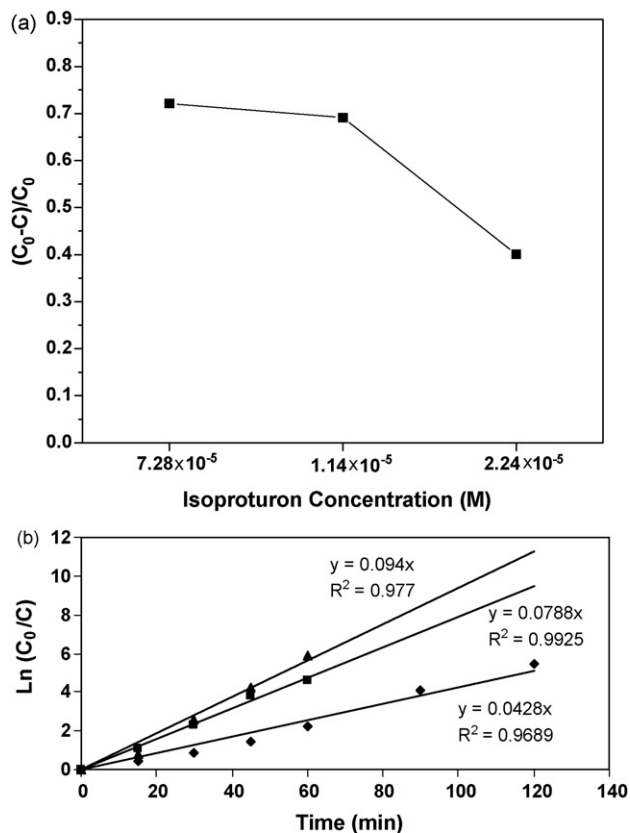


Fig. 7. Photocatalytic isoproturon degradation efficiency after 15 min of illumination over 5 wt% TiO₂/PNS. (a) Effect of initial concentration (Experimental conditions: pH 7; catalyst amount = 1.0 g l⁻¹). (b) Kinetics of isoproturon degradation at (▲) 7.28 × 10⁻⁵, (■) 1.14 × 10⁻⁴ and (◆) 2.42 × 10⁻⁴ M concentrations over 5 wt% TiO₂/PNS.

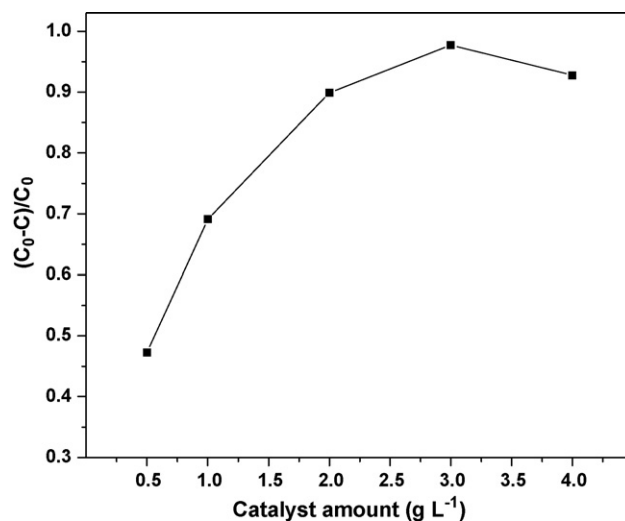


Fig. 8. Effect of catalyst amount on photocatalytic isoproturon degradation efficiency after 15 min of illumination over 5 wt% TiO₂/PNS. (Experimental conditions: C₀ = 1.14 × 10⁻⁴ M; pH 7.)

The kinetic results presented in Fig. 7b are showing that increase in isoproturon concentration decreases the degradation rate and the rate constant 'k' decreases with increase of the initial isoproturon concentrations. Similar results are reported for the photocatalytic oxidation of other pesticides [18]. The influence of initial concentration of isoproturon on the photocatalytic degradation rate found to be pseudo-first order kinetics. The apparent rate constant for the degradation of isoproturon (1.14 × 10⁻⁴ M) over 5 wt% TiO₂/PNS catalyst is 0.0788 min⁻¹ (r² = 0.993). In the present investigation, 1.14 × 10⁻⁴ M concentration is found to be optimum for degradation of isoproturon.

3.2.4. Effect of catalyst amount

The catalyst amounts 0.5, 1.0, 2.0, 3.0 and 4.0 g l⁻¹ of 5 wt% TiO₂/PNS are investigated for effective isoproturon degradation (Fig. 8). It is observed that, increasing 0.5–3.0 g l⁻¹, the photocatalytic activity is increased and at higher amounts the activity trend is not encouraging. At higher amount, the catalyst may be obstructing the light path into solution due to the turbidity which inturn

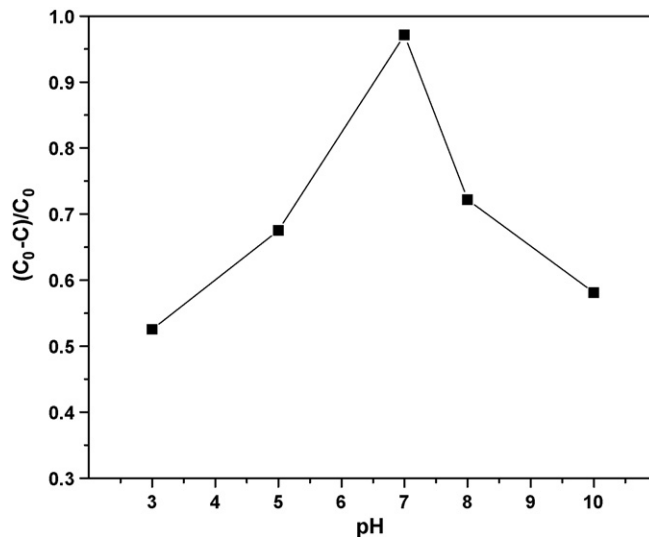


Fig. 9. Effect of pH on photocatalytic isoproturon degradation efficiency after 15 min of illumination over 5 wt% TiO₂/PNS. (Experimental conditions: C₀ = 1.14 × 10⁻⁴ M; catalyst amount = 3.0 g l⁻¹.)

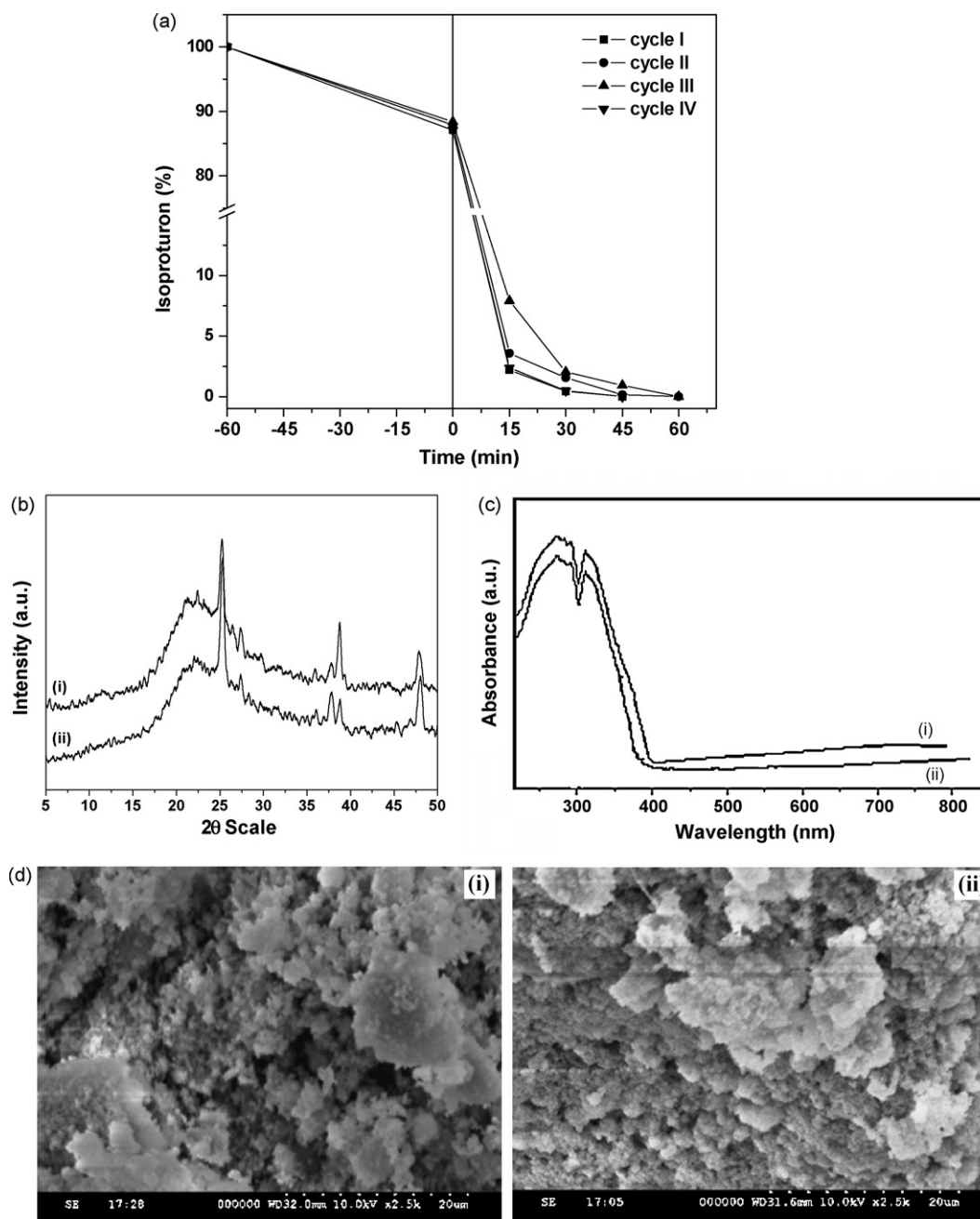


Fig. 10. Isoproturon degradation over 5 wt% TiO₂/PNS catalyst. (a) Recycling activity studies. (Experimental conditions: $C_0 = 1.14 \times 10^{-4}$ M; pH 7; catalyst amount = 3.0 g l^{-1} .) Characterization of (i) Fresh and (ii) Used (after 4th cycle) catalysts by (b) XRD patterns, (c) UV-vis DRS spectra and (d) SEM photographs.

reducing the formation of OH radicals. In the present study, 3.0 g l^{-1} is found to be the optimum catalyst amount for efficient degradation of isoproturon.

3.2.5. Effect of pH

The effect of pH is an important parameter because it commands the surface charge properties of the catalyst and therefore the adsorption of the pollutant. The pH studies at 3–10 are carried over 5 wt% TiO₂/PNS using 3.0 g l^{-1} of 1.14×10^{-4} M isoproturon solution. The adsorption capacity of the catalyst in different pH ranges is not much affected due to the non-ionic nature of isoproturon. The results depicted in Fig. 9 are showing that at neutral pH, the rate of degradation is faster compared to acidic or basic medium. This may be due to the non-ionic nature of isoproturon. In basic

medium, there is a slight increase in degradation rate is observed when compared to the acidic medium. This may be because, the OH radicals are mainly attacking methyl groups and the hydroxylation of aromatic ring is clearly unfavored with decrease in pH [19], whereas in basic medium the hydroxylation of aromatic ring is favored but not the methyl groups. In neutral medium, the OH radicals attack both on the aromatic ring and on the methyl groups. This cumulative affect results a maximum degradation rate of the pollutant.

3.2.6. Catalyst recycling studies

To evaluate stability/activity of the catalyst for photocatalytic degradation, the recycling studies are conducted over 5 wt% TiO₂/PNS using 3.0 g l^{-1} catalyst and the results are provided in

Fig. 10a. After completion of the 1st cycle within 45 min, the catalyst is recovered, dried and is reused as such (without any calcination) for the 2nd and 3rd cycles. The catalyst has taken slightly more time (60 min) for degradation in comparison to the 1st cycle and a slight decrease in the adsorption property of the catalyst is noted by subsequent run cycles. The differences in rates are due to the accumulated organic intermediates in the cavities and on the surface of the porous material support, affecting the adsorption in turn reducing the activity. This is confirmed by calcining the 3rd cycle used sample at 450 °C for 3 h and reused for the 4th cycle activity. The original activity of the catalyst for degradation is restored. This indicates that calcination of the used catalyst is necessary in order to regain the activity. Furthermore, this is substantiated by comparison of the surface characterization studies like XRD, UV–Vis DRS and SEM techniques on the fresh and 4th cycle used samples (Fig. 10b–d). There is a slight intensity decrease in the 4th cycle used sample in XRD pattern but its overall spectra remained unchanged in comparison to the original. The band gap as well as wavelength excitations are not having any changes in the UV–Vis DRS spectra of the fresh and used catalysts. From SEM photographs, it is clear that the surface morphology is not changed much and it indicates that catalyst is intact even after the 4th cycle. Thus, all these studies prove that the catalyst is reusable for number of cycles without any loss in activity and stable for longer life.

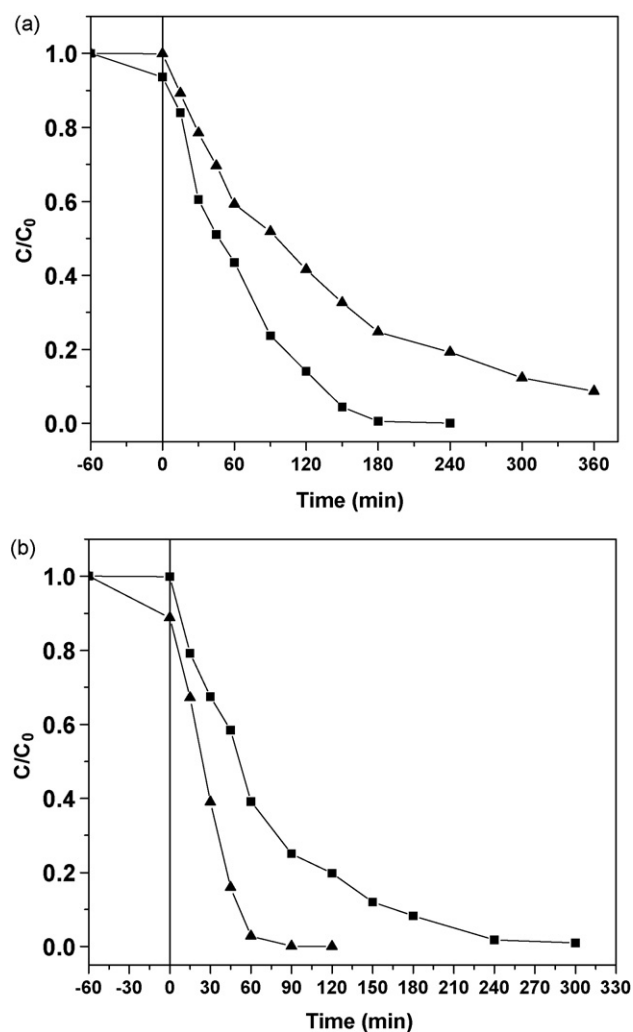


Fig. 11. Solar photocatalytic degradation of (a) imidacloprid over (▲) TiO₂ and (■) 5 wt% TiO₂/PNS and (b) phosphamidon over (■) TiO₂ and (▲) 5 wt% TiO₂/PNS. (Experimental conditions: $C_0 = 50$ ppm; pH 7; catalyst amount = 3.0 g l⁻¹.)

3.3. Photocatalytic degradations of commercial pesticides

The investigations are extended to commercial pesticide solutions, after obtaining the optimum parameters during photocatalytic degradation of model compound isoproturon. The commercial pesticide solutions not only contain active pesticide ingredient but also have some additives to enhance the solubility of the pesticides in water and/or to stabilize the mixture (emulsion) and/or to improve the efficiency of the pesticides for increasing the assimilation by the plants or the insects towards specific targets [20].

The two commercial pesticide solutions i.e., imidacloprid and phosphamidon are tested for their photocatalytic degradation. Photolytic and catalytic destruction of these technical compounds are studied earlier by many researchers under UV and solar light illumination [13,21–28]. The present commercial pesticide investigations are made with 50 ppm concentration. Photocatalytic experiments are carried out over 5 wt% TiO₂/PNS catalyst of 3.0 g l⁻¹ amount with 50 ml of solution at neutral pH. Before photocatalytic experiments, the dark adsorption experiments are carried over the catalyst and is found to be 9% for imidacloprid and 12% for phosphamidon. For TiO₂ only 1–2% adsorption is observed for these pesticides. The photocatalytic activity of the supported TiO₂ is compared with bare TiO₂ powder equivalent to the amount present over surface of the support. It is observed that complete degradation of imidacloprid takes nearly 240 min, whereas phosphamidon has 120 min as shown in Fig. 11a and b. The present combine catalyst is much efficient to degrade both the pesticides compared to bare TiO₂. Thus, it is proved that 5 wt% TiO₂/PNS catalyst is found to be very efficient to degrade the pesticides in wastewater.

4. Conclusions

The present investigation demonstrates preparation of a novel PNS system and its role as a support for immobilization of TiO₂ during photocatalytic pesticide degradations. The results conclude that 5 wt% TiO₂ supported on PNS is an efficient catalyst for the photocatalytic degradation of pesticides. The adsorption and delocalization capacity of the support plays a key role to enhance degradation rates. The substrate concentration of 1.14×10^{-4} M, catalyst amount 3 g l⁻¹ and neutral pH are found to be favorable for higher degradation rates of isoproturon. The catalyst activity is found to be sustainable even after the 4th cycle (as evidenced by XRD, SEM and UV–Vis DRS techniques). The commercial pesticide solutions containing imidacloprid and phosphamidon are also successfully degraded using 5 wt% TiO₂/PNS combine within the established conditions.

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