

Photocatalytic Degradation of Isoproturon Pesticide on C, N and S Doped TiO₂

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Abstract

TiO₂ doped with C, N and S (TCNS photocatalyst) was prepared by hydrolysis process using titanium isopropoxide and thiourea. The prepared samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photo electron spectroscopy (XPS), BET surface area, FTIR and diffuse reflectance spectra (DRS). The results showed that the prepared catalysts are anatase type and nanosized particles. The catalysts exhibited stronger absorption in the visible light region with a red shift in the adsorption edge. The photocatalytic activity of TCNS photocatalysts was evaluated by the photocatalytic degradation of isoproturon pesticide in aqueous solution. In the present study the maximum activity was achieved for TCNS5 catalyst at neutral pH with 1 g L⁻¹ catalyst amount and at 1.14 x 10⁻⁴ M concentration of the pesticide solution. The TCNS photocatalysts showed higher photocatalytic activity under solar light irradiation. This is attributed to the synergetic effects of red shift in the absorption edge, higher surface area and the inhibition of charge carrier recombination process.

Keywords: Isoproturon, Pesticide Degradation, C, N and S Doped TiO₂, Visible Light Active Catalysts

1. Introduction

Organic compounds are widely used in industry and in daily life, have become common pollutants in water bodies. As they are known to be noxious and carcinogenic, an effective and economic treatment for eliminating the organic pollutants in water has been found to be an urgent demand. The treatment of water contaminated with recalcitrant compounds is an important task to attend every country in the world. To attain the standards, there is a need for new treatment. It is very much important that the treatment should be safe and economically feasible. The wastewater purification technologies are classified as physical, biological, and chemical methods. All the above processes are having some flaws during their usage. The limitations include relative slow degradation, incomplete transformations and their inability to cover many organic compounds that do not occur naturally. Several chemical processes which use oxidizing agents such as ozone, hydrogen peroxide, H₂O₂/UV, H₂O₂/ozone/UV etc. have been carried out to mineralize many synthetic organic chemicals. Sometimes interme-

diates formed are more hazardous than the parent compound. Therefore, alternative technologies are in demand for development to treat recalcitrant compounds in wastewater effluents. Photocatalytic process has been found to be very active in the treatment of wastewaters for the mineralization of broad range of organic pollutants. Thus, heterogeneous mediated photocatalysis treatment technique gained noteworthy importance for the treatment of wastewaters.

Semiconductor mediated photocatalytic oxidation of water pollutants offers a facile and cheap method. Among various oxide semiconductor photocatalysts, TiO₂ has proved to be the most suitable catalyst for wide spread environmental applications because of its biological and chemical inertness, strong oxidizing power, non toxicity, long term stability against photo and chemical corrosion [1,2]. However, its applications seems to be limited by several factors, among which the most restrictive one is the need of using an UV wavelength of < 387 nm, as excitation source due to its wide band gap (3.2 eV), and this energy radiation availability is less than 5 % in solar light.

Several works reported that doping TiO_2 with anions such as carbon, nitrogen, sulphur, boron and fluorine shifts the optical absorption edge of TiO_2 towards lower energy, there by increasing the photocatalytic activity in visible light region [3–9]. The preparation of doped TiO_2 resulting in a desired band gap narrowing and an enhancement in the photocatalytic activity under visible light.

In earlier reported studies, N doping of TiO_2 is achieved by different methods such as sputtering of TiO_2 in a gas mixture followed by annealing at higher temperatures [3], treating anatase TiO_2 powders in an NH_3/Ar atmosphere [10], solution based methods like precipitation [11,12], sol-gel [13,14], solvothermal [15], hydrothermal processes [16] and direct oxidation of the dopant containing titanium precursors at appropriate temperatures [17]. In our earlier studies, we have concentrated on degradation of isoproturon using TiO_2 supported over various zeolites. The main idea of using Zeolite support for TiO_2 is to enhance the adsorption capacity of the pollutant over the combine photo catalyst systems [18–20]. In the present case the main focus is on shifting the absorption edge of TiO_2 to visible light region by introducing C, N and S into the TiO_2 lattice structure. The present results obtained provides a simple route for the preparation of C, N and S doped TiO_2 with enhanced photocatalytic activity under visible light irradiation for isoproturon pesticide degradation.

2. Experimental Details

2.1. Materials and Methods

All the chemicals in the present work are of analytical grade and used as such without further purification. Isoproturon (IPU) (>99% pure, Technical grade) was obtained from Rhône-Poulenc Agrochemie, France and titanium isopropoxide was from Sigma-Aldrich chemie GmbH, Germany. HCl, NaOH and acetonitrile were obtained from Ranbaxy Limited, India. All the solutions were prepared with deionized water obtained using a Millipore device (Milli-Q).

2.2. Preparation of C, N and S Doped TiO_2 Photocatalyst

C, N and S doped TiO_2 photocatalyst was prepared by a simple hydrolysis process using titanium isopropoxide as the precursor for titanium and thiourea as the source for carbon, nitrogen and sulphur [26,34]. In a typical preparation, 10 mL of titanium isopropoxide solution was mixed with 30 mL of isopropyl alcohol solution. This solution was added drop wise to 20 mL deionized water containing in a 250 mL beaker. The solution was thoroughly mixed using a magnetic stirrer for 4 h. To this solution, required amount of thiourea, dissolved in 5 mL

deionized water was added. The mixture was stirred for 6 h and dried in oven at 80°C for 12 h. The solid product formed was further calcined at 400°C temperature for 6 h in air to get C, N, and S doped TiO_2 photocatalyst. The weight (%) of thiourea doped TiO_2 was controlled at 0, 1, 3, 5, 10 and 15 wt% and the samples obtained were labeled as TCNS0, TCNS1, TCNS3, TCNS5, TCNS10 and TCNS15 respectively.

2.3. Characterization

The catalysts were characterized by various techniques like XRD, XPS, FTIR, SEM, BET surface area and UV-Vis DRS. The XRD of catalysts were obtained by Siemens D 5000 using Ni Filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) from $2\theta = 1-60^\circ$. XPS spectra were recorded on a KRATOS AXIS 165 equipped with Mg K α radiation (1253.6 eV) at 75 W apparatus using Mg K α anode and a hemispherical analyzer, connected to a five channel detector. The C 1s line at 284.6 eV was used as an internal standard for the correction of binding energies. The Fourier transform-infra red spectra (FTIR) were recorded on a Nicolet 740 FTIR spectrometer (USA) using KBr self-supported pellet technique. The SEM analysis samples were mounted on an aluminum support using a double adhesive tape coated with gold and observed in Hitachi S-520 SEM unit. BET data was generated on (Auto Chem) Micro Maritics 2910 instrument. UV-Vis diffused reflectance spectra (UV-Vis DRS) was from UV-Vis Cintra 10e spectrometer.

2.4. Photocatalytic Experiments

IPU solution (0.114 mM) was freshly prepared by dissolving in double distilled water. All the photocatalytic experiments were carried out at same concentration until unless stated. The pH of the solution was adjusted with HCl and NaOH. Prior to light experiments, dark (adsorption) experiments were carried out for better adsorption of the herbicide on the catalyst. For solar experiments, isoproturon solution of 50 mL was taken in an open glass reactor with known amount of the catalyst. The solution was illuminated under bright solar light. Distilled water was added periodically to avoid concentration changes due to evaporation. The solar experiments were carried out during 10.00 A.M. to 3.00 P.M. in May and June 2009 at Hyderabad.

2.5. Analyses

The IPU degradation was monitored by Shimadzu SPD-20A HPLC using C-18 phenomenex reverse phase column with acetonitrile/water (50/50 v/v %) as mobile phase at a flow rate of 1 mL min^{-1} . The samples were collected at regular intervals, filtered through Millipore

micro syringe filters (0.2 μm).

3. Results and Discussion

3.1. Characterization

3.1.1. XRD

To investigate the phase structure of the prepared samples XRD was used and the results are shown in **Figure 1**. It can be seen that TCNS exhibits only the characteristic peaks of anatase (major peaks at 25.41° , 38° , 48° , 55°) and no rutile phase is observed. The results are in good agreement with earlier studies [21]. By applying Debye-Scherrer equation, the average particle size of the TCNS catalysts is found to be about 3.8 to 5.8 nm. It can be inferred that the ratio of thiourea to titania slightly influence the crystallization of the mesoporous titania. Also the peak intensity of anatase decreases and the catalyst becomes more amorphous. It might be due to the fact that the doped nonmetals can hinder the phase transition (anatase to rutile) and restricts the crystal growth. It is noteworthy that, even the doped samples exhibit typical structure of TiO_2 crystal without any detectable dopant related peaks. This may be caused by the lower concentration of the doped species, and moreover, the limited dopants may have moved into either the interstitial positions or the substitutional sites of the TiO_2 crystal structure [22,23].

3.1.2. XPS

To investigate the chemical states of the possible dopants incorporated into TiO_2 , $\text{Ti}2p$, $\text{O}1s$, $\text{C}1s$, $\text{N}1s$, and $\text{S}2p$ binding energies are studied by measuring the XPS spectra. The results are shown in **Figure 2**.

The high resolution spectra of $\text{Ti}2p_{3/2}$ and $\text{Ti}2p_{1/2}$ core levels are given in the **Figure 2(a)**. The binding energy for the $\text{Ti}2p_{3/2}$ and $\text{Ti}2p_{1/2}$ core level peaks for TCNS0 appeared at 458.8 and 464.5 eV respectively which are attributed to O-Ti-O linkages in TiO_2 . $\text{Ti}2p_{3/2}$ and $\text{Ti}2p_{1/2}$ core level peaks for TCNS5 are observed at 458.4 and 464.1 eV with a decrease in the binding energy value compared to TiO_2 indicating that the TiO_2 lattice is considerably modified due to C, N and S doping [24].

The chemical environment of carbon is investigated by the XPS of $\text{C}1s$ core levels as shown in the **Figure 2(b)**. Three peaks are observed for the $\text{C}1s$ at 284.6, 286.2 and 288.8 eV. The first peak observed at 284.6 eV is assigned to elemental carbon present on the surface, which is also in agreement with the reported studies [25]. The second and third peaks at 286.2, 288.8 eV are attributed to C-O and C=O bonds respectively [21,26].

The high resolution XPS spectra of $\text{N}1s$ core level is shown in **Figure 2(c)**. Generally, $\text{N}1s$ core level in N doped TiO_2 shows binding energies around 369-397.5

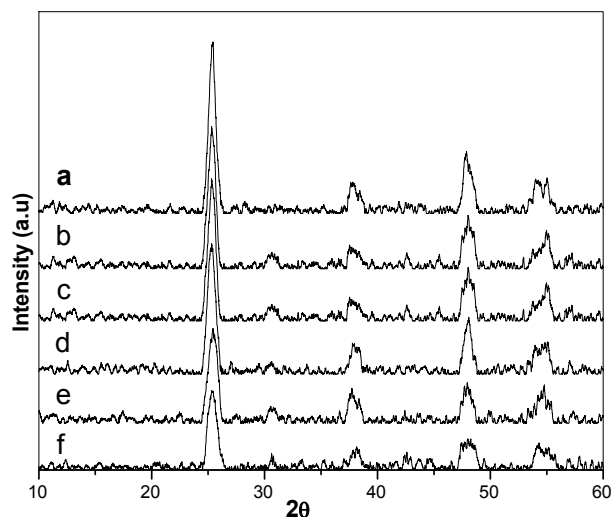


Figure 1. XRD patterns of TCNS catalysts: (a) TCNS0, (b) TCNS1, (c) TCNS3, (d) TCNS5, (e) TCNS10, (f) TCNS15.

eV that are attributed to substitutionally doped N into the TiO_2 lattice or β nitrogen [3,27]. $\text{N}1s$ peaks, with high intensity observed at and above 400 eV are assigned to NO , N_2O , NO_2^- , NO_3^- . Sakthivel *et al.* [28] observed an intense peak at 400.1 eV that was assigned to hyponitrile species and concluded that the higher binding energy is due to the lower valence state of N in N doped TiO_2 . Many researches pointed out that intense peak at 400 eV are due to oxidized nitrogen like Ti-O-N or Ti-N-O linkages. Dong *et al.* [26] observed three peaks of $\text{N}1s$ at 397.8, 399.9 and 401.9 eV and has attributed to N-Ti-N, O-Ti-N and Ti-N-O linkage respectively. Recently, Gopinath observed $\text{N}1s$ binding energy at 401.3 eV and claimed the presence of Ti-N-O linkage on the surface of N doped TiO_2 nano particles [29]. **Figure 2(c)** shows the $\text{N}1s$ spectra of TCNS5 catalyst and three peaks are observed at 397.8, 399.9 and 401.2 eV. Taking the literature support, here in the present investigation, the first peak at 397.8 eV is attributed to N-Ti-N linkages and the second and third peaks at 399.9 and 401.2 eV are ascribed to O-Ti-N, Ti-N-O linkages in the TiO_2 lattice respectively.

The $\text{O}1s$ spectra of TCNS0 and TCNS5 are shown in **Figure 2(d)**. The $\text{O}1s$ peak for TCNS0 is observed at 529.7 and 531.6 eV. The corresponding values are 530.2 and 531.7 eV for the TCNS5 sample. The first peak is mainly attributed to the O-Ti-O linkage in the TiO_2 lattice, and the second peak is closely related to the hydroxyl groups (-OH) resulting mainly from chemisorbed water. It can be seen that the content of surface hydroxyl groups is much higher in the TCNS5 sample than in the TCNS0 sample. The increase in surface hydroxyl content is advantageous for trapping more photogenerated holes and thus preventing electron-hole recombination [26].

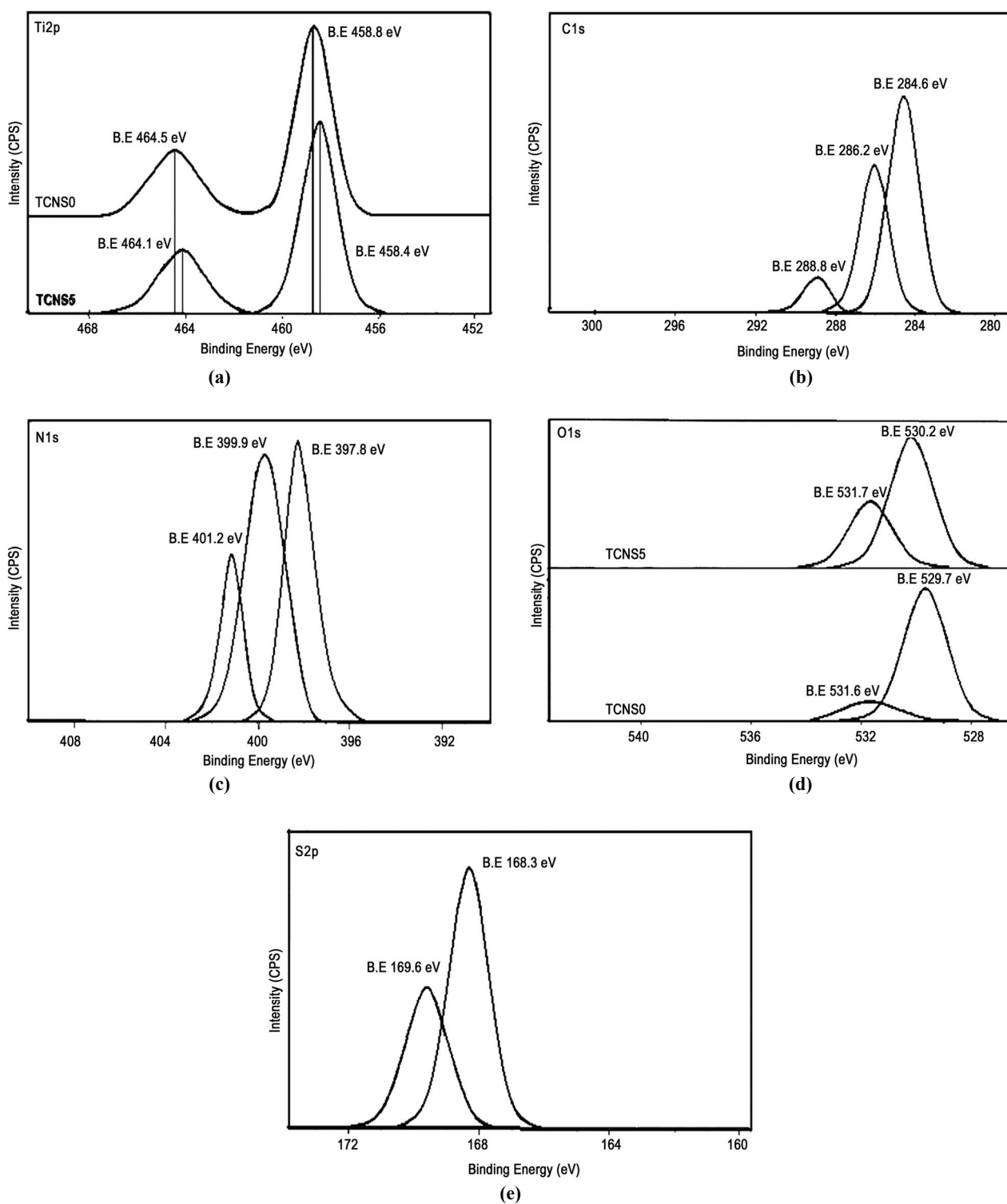


Figure 2. High resolution XPS of TCNS5 catalyst: (a)Ti2p, (b)C1s, (c)N1s, (d)O1s, (e)S2p.

S2p XPS spectra for TCNS5 are shown as **Figure 2(e)**. The oxidation state of the S-dopant is dependent on the preparation routes and sulfur precursors. Previous studies

have reported that if thiourea was used, the substitution of Ti^{4+} by S^{6+} would be more favorable than replacing O^{2-} with S^{2-} [4]. S2p spectra can be resolved into four

peaks, $S2p_{1/2}^{6+}$, $S2p_{3/2}^{6+}$, $S2p_{1/2}^{4+}$ and $S2p_{3/2}^{4+}$. The **Figure 2(e)** shows two peaks at 168.3 and 169.6 eV corresponding to $S2p_{3/2}^{6+}$, $S2p_{1/2}^{6+}$ binding energies [30]. It is clear from the figure that S was doped mainly as S^{6+} and not S^{4+} or S^{2-} peaks. The sulfur doping further can be substantiated by the decrease in binding energies of the $Ti2p_{1/2}$ and $Ti2p_{3/2}$ of TCNS5 sample compared to the binding energies $Ti2p_{1/2}$ and $Ti2p_{3/2}$ of the TCNS0 sample respectively (**Figure 2(a)**). This may be caused due to the difference of ionization energy of Ti and S. Therefore, it could be concluded that the lattice titanium sites of TiO_2 were substituted by S^{6+} and formed as a new band energy structure.

3.1.3. FTIR Spectra

Figure 3 shows the FTIR spectra of TCNS0 and TCNS5 catalysts calcined at 400 °C. The absorption bands 2800–3500 cm^{-1} , 1600–1680 cm^{-1} are assigned to the stretching vibration and bending vibration of the hydroxyl group respectively present on the surface of TiO_2 catalyst [31,32]. The presence of surface hydroxyl groups are substantiated by XPS of O1s spectra (**Figure 2(d)**). The band around 1730 cm^{-1} is attributed to carbonyl group and bands at 1130, 1040 cm^{-1} are corresponding to nitrite and hyponitrite groups present in TCNS5 and they are absent in TCNS0 which shows successful doping of nitrogen into the lattice of TiO_2 [33,34]. No peak corresponding to NH_4^+ absence (3189 and 1400 cm^{-1}) shows that N is present only in the form of nitrite and hyponitrite species [32].

3.1.4. SEM

The surface morphology of TCNS photocatalyst is studied by scanning electron microscopy and the micrographs are presented in **Figure (4)**. The samples appeared are agglomeration of smaller particles. From this image, we can see that the surface is rough and large number of pores found to be seen. SEM images for the undoped (TCNS0) and CNS-doped (TCNS5) shows that

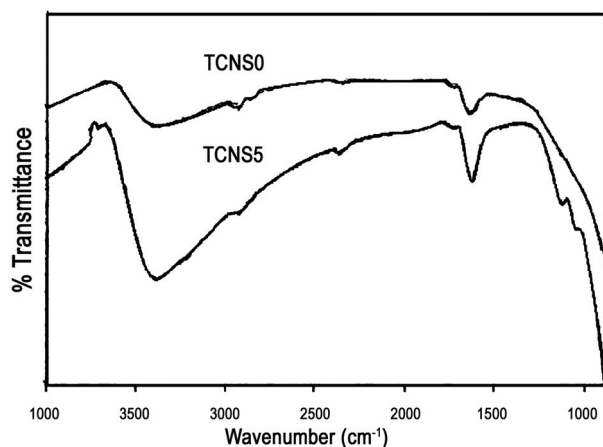


Figure 3. FTIR spectra of TCNS catalysts.

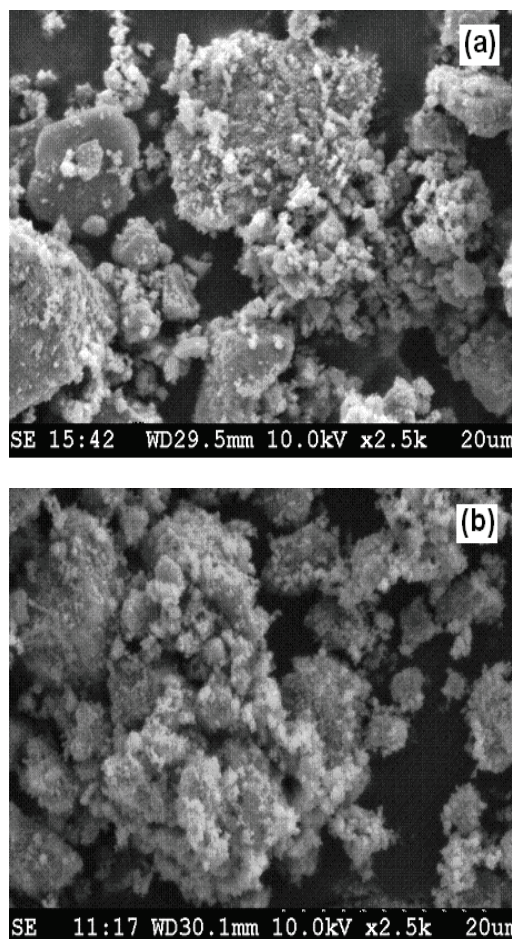


Figure 4. SEM images of (a) TCNS0 and (b) TCNS5 catalysts.

the particle morphology seems to be as spherical in both the images and there is no considerable change in morphology of both. The photograph of thiourea doped TiO_2 (TCNS5) sample is exhibiting well-dispersed crystals and the particle is homogeneous with the formation of fine and well dispersed particles.

3.1.5. UV-VIS DRS

The UV-Vis diffuse reflectance spectra (DRS) of TCNS catalysts are shown in **Figure 5**. It is seen from **Figure 5(a)** that the undoped TiO_2 nano catalyst (TCNS0) showed strong absorption band around 380 nm in the ultraviolet region. But, TCNS sample is showing absorbance at 400–470 nm with red shift (about 100 nm) towards visible region. This shift in the absorption edge decreases the direct band gap of TCNS catalyst compared to undoped TiO_2 (TCNS0) and this may be due to the insertion of C, N and S into the TiO_2 lattice [13,25,35]. Furthermore, the red shift in the DRS band increases with the increase in doped elements content into TiO_2 lattice. Band gap energy (E_g value) of all the catalysts is estimated from the plot of absorbance versus photon energy ($h\nu$). The

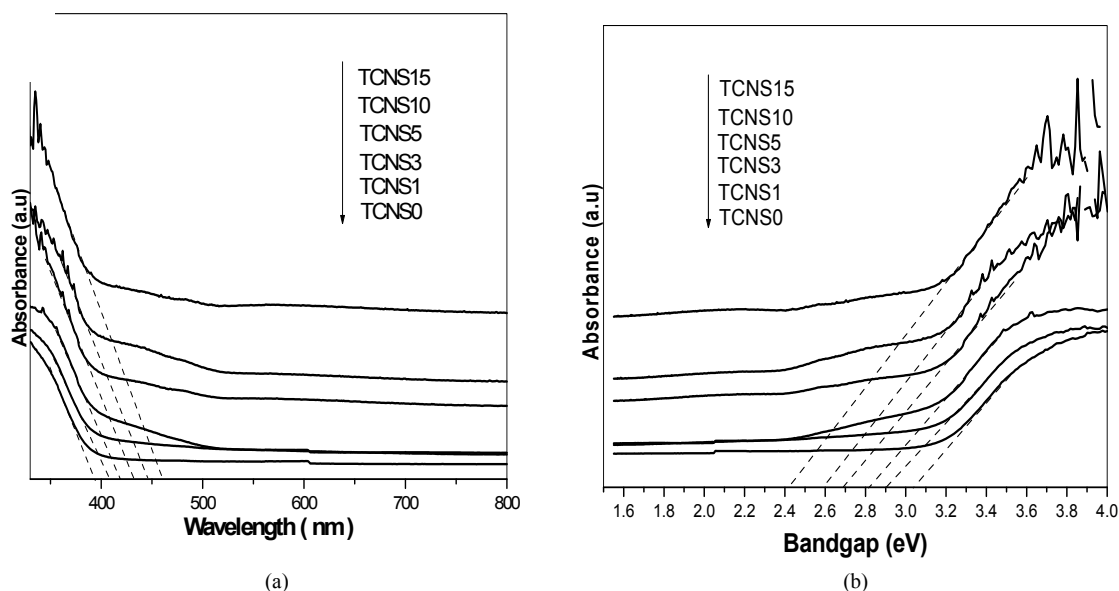


Figure 5. UV-Vis diffusion reflectance spectra of TCNS catalysts. (a) Absorbance versus Wavelength; (b) Absorbance versus Bandgap.

absorbance is extrapolated to get the bandgap energy for the TCNS catalyst with good approximation as observed in **Figure 5(b)**. The estimated bandgap energies of TCNS0, TCNS1, TCNS3, TCNS5, TCNS10 and TCNS15 are 3.05, 2.91, 2.82, 2.7, 2.6 and 2.41 respectively. From the DRS results, it is clear that the C, N and S doping can shift the absorption edge of TiO_2 to the visible range and reduce the band gap, which is beneficial for improving the photo absorption and ultimately photo catalytic performance of TiO_2 .

3.1.6. BET Surface Area

The surface area of TCNS catalysts calcined at 400°C is shown in **Table 1**. The TCNS catalysts are showing high surface area. The high surface area of the prepared catalysts is due to nanosize of the particles. It is also observed that the surface area of the catalysts increases with the increase in the ratio of thiourea to TiO_2 . This can be attributed to decreasing of the crystallite sizes, as discussed in XRD analysis.

3.2. Photocatalytic Activity

3.2.1. Adsorption Studies

Prior to photocatalytic experiments adsorption and photolysis studies are carried out. The isoproturon solution was kept in dark without catalyst for 10 days and no degradation is observed. Fifty milligrams of the catalyst in 50 mL of isoproturon (1.14×10^{-4} M) solution is allowed under stirring in dark. Aliquots were withdrawn at regular intervals and the change in isoproturon concentration is monitored by HPLC. Maximum adsorption is

reached within 30 min for all the catalysts prepared. This illustrates the establishment of adsorption equilibrium as 30 min and is chosen as the optimum equilibrium time for all the future experiments. The photolysis (without catalyst) experiment is carried out under the solar light taking 50 mL of isoproturon solution in glass reactor and only 2–4 % of degradation is observed after 10 h of solar irradiation.

3.2.2. Determination of Thiourea Loading over TiO_2

To compare the photocatalytic activity of the as-prepared samples, photocatalytic degradation of isoproturon under solar light irradiation is performed. All the studies are carried out at 1 g L^{-1} catalyst amount in 1.14×10^{-4} M isoproturon solution. The photocatalytic activity of TCNS catalysts under solar light irradiation is shown in **Figure 6**. Among all the catalysts prepared, TCNS5 is showing better photocatalytic activity and complete degradation. The visible light activity of the samples has increased gradually with the increasing amount of dopant and it reaches optimum at 5 wt % loading (TCNS5) and further increase results an activity decrease gradually.

Table 1. BET surface area and particle size of the TCNS catalysts.

Catalyst	Particle size by XRD (nm)	BET surface area (m^2/g)
TCNS0	5.8	80.53
TCNS1	5.2	82.47
TCNS3	5.1	83.97
TCNS5	4.6	89.14
TCNS10	4.2	92.98
TCNS15	3.8	124.28

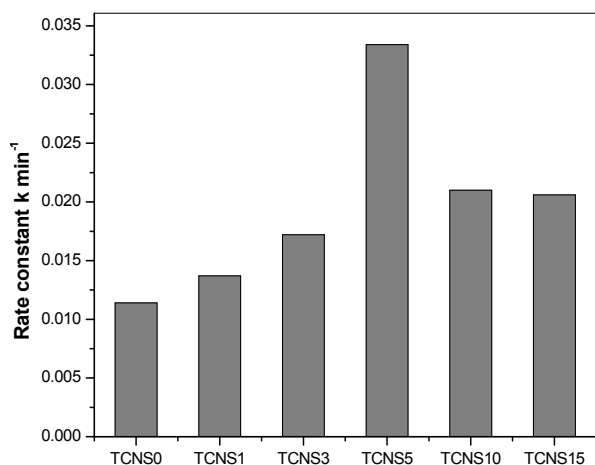


Figure 6. Photocatalytic activity of C, N and S doped TiO₂ for the degradation of isoproturon aqueous solution (1.14×10^{-4} M) under solar-light irradiation.

The different samples photo catalytic activity can be attributed to the following factors. It is known that the doping of C, N and S elements in titania brings visible light absorption photocatalytic activity of titania. It can be seen from the DRS spectra that C, N, and S doping resulted in an intense increase in absorption in the visible light region and a red shift in the absorption edge of the titania (**Figure 5(a)**). The band-gap narrowing of titania by C, N, S doping lead to enhanced photocatalytic activity of the titania under visible light. Because the prepared doped samples can be activated by visible light, thus more electrons and holes can be generated and participate in the photocatalytic redox reactions [21]. All together, the C, N, and S doped samples show much higher photocatalytic activity than undoped titania. But we can also see that at higher loadings photocatalytic activity of TCNS samples has decreased though they show more red shift in the absorption edge. It might be due to the fact that, the excess dopant acts as recombination centers which facilitates electron-hole recombination thus lowering the activity. So, the photocatalytic activity is depressed to a certain extent. To conclude, the higher activity of the TCNS5 sample can be ascribed to the high surface area, strong adsorption in visible region and lower recombination of electron-hole pair due to high concentration of surface hydroxyl groups (**Figure 2(d)**) which can trap the photo generated holes and thus decreasing the electron hole recombination process [26].

3.2.3. Effect of Substrate Concentration

The effect of substrate concentration is an important parameter for photocatalytic degradation activity over known catalyst amount. The 7.28×10^{-5} , 1.14×10^{-4} and 2.42×10^{-4} M concentrations of isoproturon are studied over TCNS5 catalyst with 1.0 g L^{-1} catalyst amount. It is seen from **Figure 7** a slight difference in degradation rate

over titania supported catalyst for 7.28×10^{-5} , 1.14×10^{-4} M concentrations are observed compared to 2.42×10^{-4} M. This indicates, at higher concentrations OH radicals produced 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 solutions 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.

3.2.4. Effect of Catalyst Amount

The catalyst amounts 0.5 , 1.0 and 2.0 g L^{-1} of TCNS5 are investigated for effective isoproturon degradation (**Figure 8**). It is observed that, increasing amounts 0.5 – 1.0 g L^{-1} , the photocatalytic activity has increased and at the higher amounts the activity trend is not encouraging. This is due to the higher amounts of the catalyst makes the solution turbid which obstructs the light path into the solution and inturn reducing the formation of OH radicals. In the present study, 1.0 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 TCNS5 catalyst using 1.0 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 **Figure 9** are showing that at neutral pH, the rate of degradation is faster compared to acidic or basic medium [36]. This may be due to the non-ionic nature of isoproturon. In basic medium, there is a slight increase in degradation rate and is observed when compared to the acidic medium. This may be because, the OH radicals are mainly attacking methyl groups

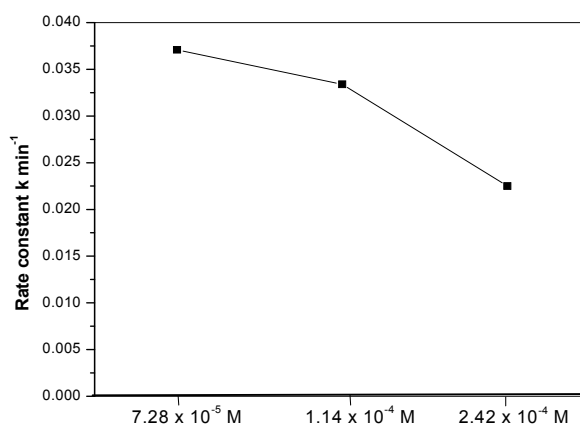


Figure 7. Effect of initial concentration on the rate of solar photocatalytic degradation of isoproturon over TCNS5.

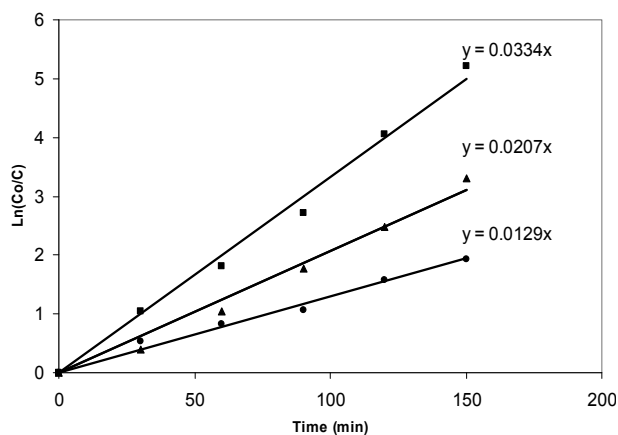


Figure 8. Effect of catalyst amount on photocatalytic degradation of isoproturon over TCNS5 catalyst under solar light irradiation: 0.5 g L⁻¹ (●), 1 g L⁻¹ (■) and 2 g L⁻¹ (▲).

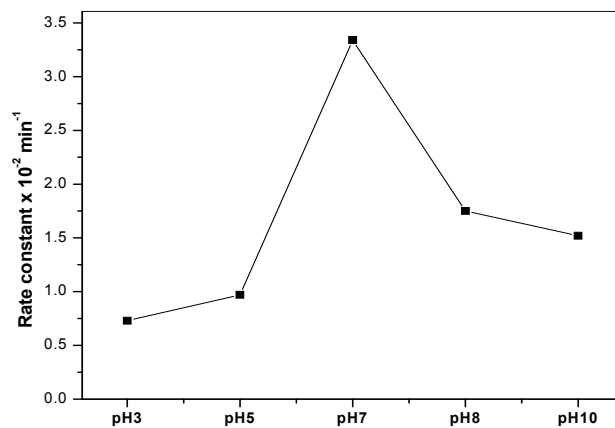
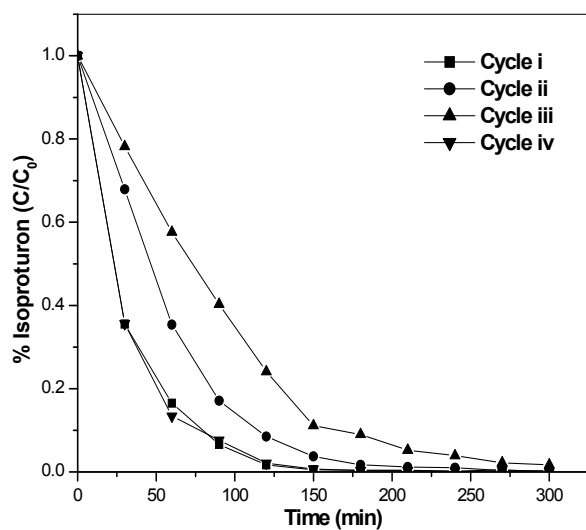
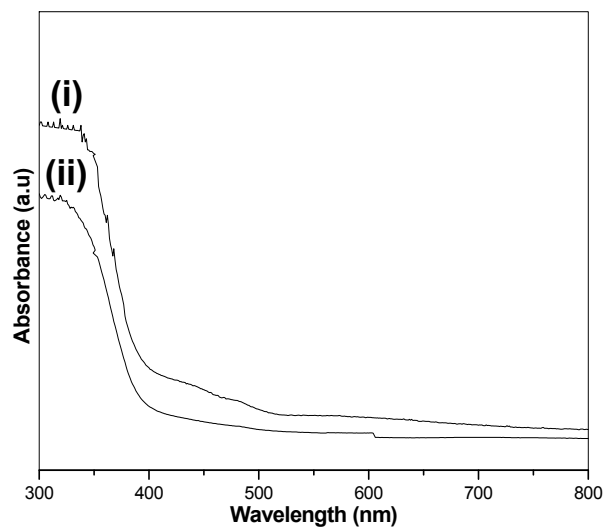


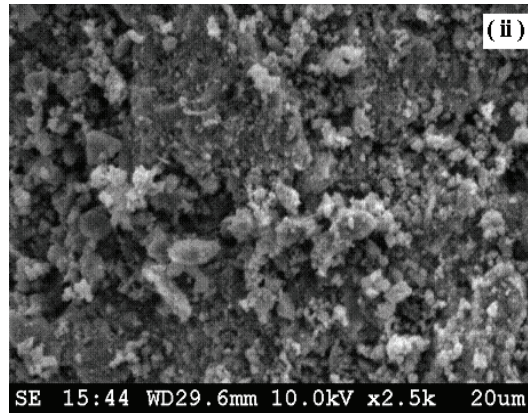
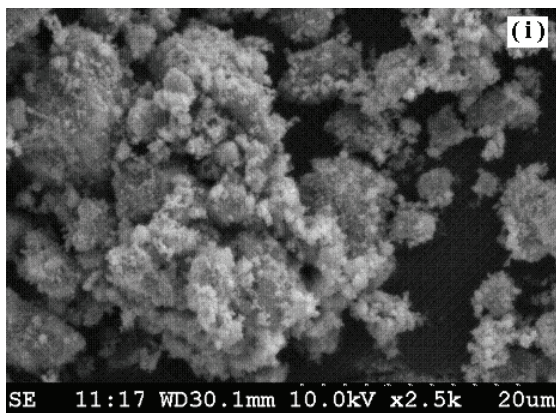
Figure 9. Effect of pH on solar photocatalytic isoproturon degradation over TCNS5. (Experimental conditions: $C_0 = 1.14 \times 10^{-4}$ M; catalyst amount = 1.0 g L⁻¹.)



(a)



(b)



(c)

Figure 10. Isoproturon degradation over TCNS5 catalyst. (a) Recycling activity studies. (Experimental conditions: $C_0 = 1.14 \times 10^{-4}$ M; pH 7; catalyst amount = 1.0 g L⁻¹.) Characterization of 1) Fresh and 2) Used (after 4th cycle) catalysts (b) UV-Vis DRS spectra and (c) SEM photographs.

and the hydroxylation of aromatic ring is clearly unfavored with decrease in pH, 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 effect results a maximum degradation rate of the pollutant [20].

3.2.6. Catalyst Recycling Studies

To evaluate stability/activity of the catalyst for photocatalytic degradation, the recycling studies are conducted over TCNS5 using 1.0 g L^{-1} catalyst and the results are provided in **Figure 10(a)**. After completion of the 1st cycle, the catalyst is recovered, dried and is reused as such (without any calcination) for the 2nd cycle, a slight decrease in the rate of degradation is observed compared to the first cycle. When same catalyst is reused without calcination for the third cycle, there is a slight decrease in degradation rate observed compared to first and second cycle. The differences in rates are due to the accumulated organic intermediates on the surface of the catalyst, affecting the adsorption in turn reducing the activity. This is confirmed by calcining the 3rd cycle used sample at 400°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 SEM and UV-Vis DRS techniques on the fresh and 4th cycle used samples **Figures 10(b)-10(c)**. 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, the above studies prove that the catalyst is reusable for number of cycles without any loss in activity and stable for longer life.

4. Conclusions

The present study demonstrates preparation of a C, N, and S doped TiO_2 photocatalyst and its role in photocatalytic pesticide degradation. The results conclude that 5 wt% thiourea doped TiO_2 (TCNS5) is an efficient catalyst for the photocatalytic degradation of isoproturon. The higher activity of TCNS5 catalyst may be due to the high surface area, lower electron-hole recombination and the stronger adsorption in visible light region. The substrate concentration of $1.14 \times 10^{-4} \text{ M}$, catalyst amounts 1 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 SEM and UV-Vis DRS techniques).

5. Acknowledgements

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