

Research Article

Photocatalytic Degradation of Organics by Using Nanocrystalline Titania

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Titanium dioxide nanoparticles were prepared by a modified sol-gel route. Titanium butoxide was used as precursor and nebulizer was used for a fine spray of particles. The prepared powders were characterized by FT-IR, SEM, XRD, and TGA-DTA methods. The results indicated that nanoparticles with small size and high surface area were synthesized. XRD result indicated that TiO₂ nanoparticles were obtained in pure anatase crystalline form with a crystallite size of 40 nm. The catalytic activity of as-synthesized nanoparticles was tested for the degradation of formic acid and toluene.

1. Introduction

The industrial growth has led to increase in the manufacture and growth of unused byproducts that cause severe environmental complications. Worldwide the researchers are working on several methodologies to overcome the issue. The use of light energy to waste mineralization is an important technique for the removal of industrial waste. TiO₂ is extremely stable, of low cost, and safe for both living and nonliving things. Hence it is considered to be an almost perfect semiconductor for photocatalysis [1–3]. Various synthesis protocols of TiO₂ nanoparticles have been reported in literatures that include hydrothermal method, solvothermal method, sol-gel route, precipitation method, and ultrasonic and microwave assisted methods. The sol-gel route is quite attractive for the preparation of nanosized TiO₂ as it offers several advantages including high chemical purity, high homogeneity, purity, and flexibility in offering dopants in high concentrations, easy processing, control on composition, and stoichiometry [4, 5].

In the presence of UV or near UV irradiation, a wide range of organic compounds can be oxidized to CO₂ and H₂O on TiO₂ catalyst surface at room temperature. The absorption of light results in the transfer of an electron from the valence band to the conduction band. This electron

transfer process generates an electron-hole pair that imparts the redox properties to TiO₂ surface. Many factors including the crystal nature and size of the photocatalyst affect the band gap value. Numerous researchers have reported the potential applications of TiO₂ nanoparticles as a photocatalyst for the degradation of various organic compounds [6, 7].

In the present work, TiO₂ nanoparticles were synthesized by a modified sol-gel route. Titanium butoxide was used as precursor and nebulizer was used for a fine spray of particles in an attempt to control particle size. The prepared powders were calcined at 550°C and characterized. The catalytic activity of as-synthesized nanoparticles was checked for the degradation of toluene and formic acid. Both formic acid and toluene were chosen as model compounds because they both degrade to simple degradation products like CO₂ and H₂O. Toluene is an important indoor and industrial pollutant. It is aromatic and hence the efficiency of our prepared photocatalyst against an aliphatic (formic acid) and an aromatic organic species (toluene) was evaluated.

2. Materials and Methods

Titanium butoxide was purchased from Sigma Aldrich. Toluene, formic acid, HCl, and butanol were purchased from RDH. X-ray diffraction spectra of the powders were

recorded at room temperature using a powder diffractometer (Jeol, Model: JDX-3523). Morphology determination was carried out with a scanning electron microscope (SEM), Jeol Jem-6480LV. The Fourier transform infrared spectrum (FT-IR) was recorded on a Midac Corporation, Model: 2000. Ultraviolet-visible spectra were performed with a Hitachi Japan, U-2800 UV-Vis spectrophotometer while TGA analysis was performed with a NETZCH, STA-449C TGA-DTA instrument.

2.1. Preparation of Titanium Dioxide (TiO_2) Nanoparticles.

A solution of titanium butoxide (2 mL, 5.86 mmol) was prepared in butanol (6 ml) in a conical flask. This solution was sprayed to a mixture of water and butanol (3 : 1) by using a nebulizer. The solution was left for stirring for 2 hours at room temperature. The pH of the solution was adjusted to 3 by using HCl (1M). The solution was aged for 24 h at room temperature and a gel was formed. The gel was washed and dried in oven at 80°C for 10 hours. A white powder was obtained and was calcined at 550°C for 4 hours in air. A fine white powder consisting of TiO_2 nanoparticles was obtained.

2.2. Photocatalytic Activity

2.2.1. Formic Acid Degradation. A small amount of TiO_2 (0.2 mg) was added in 0.1 M formic acid solution (200 ml) in a Pyrex glass beaker. The solution was held under sun light for 7 hours with occasional stirring. After certain time intervals, samples were taken out and were analyzed for total organic carbon (TOC) by titration.

2.2.2. Degradation of Toluene. In a conical flask, 100 ml of 30 ppm toluene solution was taken and 0.4 mg of prepared TiO_2 nanoparticles was added in the solution. The solution was stirred in dark for 20 min on a shaker and then exposed to sunlight for a certain period of time. Simultaneously, a blank experiment without the catalyst was carried out. At regular time intervals, a small amount of sample solution was taken out from the flask. UV-Vis absorption spectra were recorded to study the process of degradation.

In another experiment, degradation of toluene was studied under various pH values.

3. Results and Discussion

3.1. Characterization of the Photocatalyst. Figure 1 shows the FT-IR spectrum of the TiO_2 nanoparticles calcined at 550°C . An expected band between 500 and 800 cm^{-1} (Ti-O stretching) was seen which relates to the presence of Ti-O-Ti network. Two very small bands were observed at 3400 cm^{-1} and 1662 cm^{-1} that can be assigned to the stretching and bending vibration of O-H group. This shows the existence of a small amount of moisture in the sample.

FT-IR result indicates that required TiO_2 nanoparticles were successfully prepared which contain Ti-O-Ti network. No extra peak was observed which confirms the purity of our sample [8, 9].

TGA plot of the prepared TiO_2 nanoparticles is given in Figure 2. The 1st mass loss of 2% was observed below

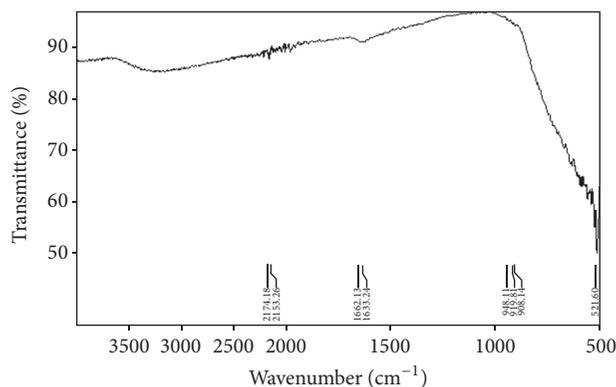


FIGURE 1: FT-IR spectrum of prepared TiO_2 nanoparticles.

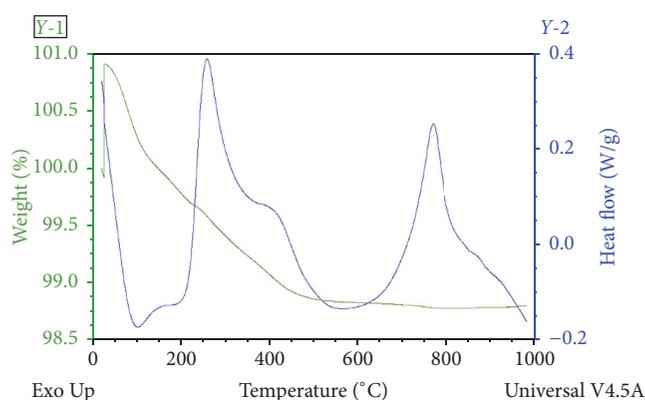


FIGURE 2: TGA plot of TiO_2 nanoparticles.

400°C and can be linked to either dehydroxylation of Ti-OH groups or to the removal of some moisture present in the sample. After that there is no further mass loss up to 1000°C which indicates good thermal stability of the prepared TiO_2 nanoparticles at high temperature.

Figures 3(a) and 3(b) display SEM images of TiO_2 nanoparticles. It is observed from the images that almost all nanoparticles are spherical. The particle size is approximately 50 nm. Only a little particle aggregation was observed in the sample. No big clusters or rocks were seen in the images [10, 11].

Figure 4 shows the XRD patterns of TiO_2 powder calcined at 550°C . A typical diffractogram corresponding to anatase crystalline phase was obtained. It is noteworthy that no extra peaks corresponding to rutile or brookite phase were observed [12, 13].

Average crystallite size of the sample was calculated by using Scherrer's equation. The result confirms that only pure titanium dioxide nanoparticles were obtained in anatase crystalline form with average crystallite size of 40 nm.

3.2. Catalytic Activity

3.2.1. Degradation of Formic Acid. Degradation rate of formic acid was estimated by measuring total organic carbon (TOC). TOC is calculated by simple titration method. After different

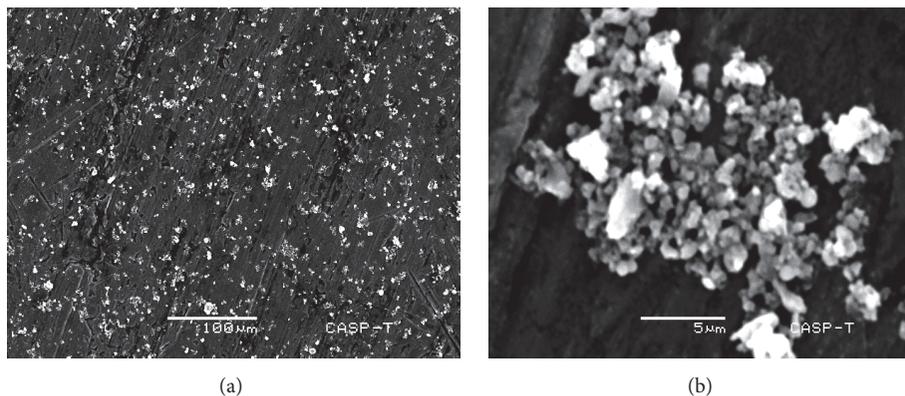
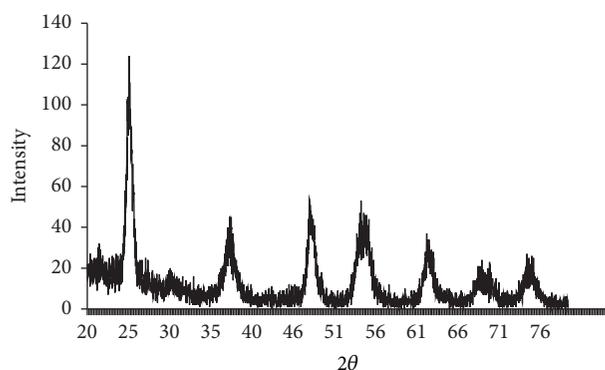
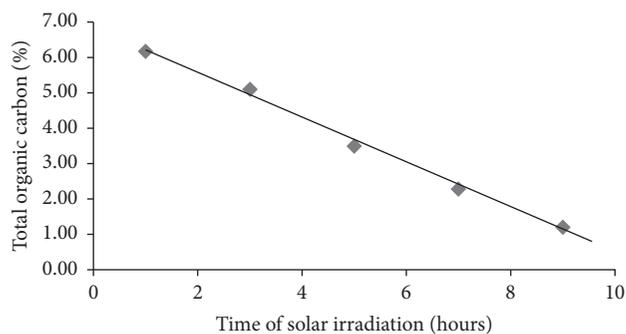
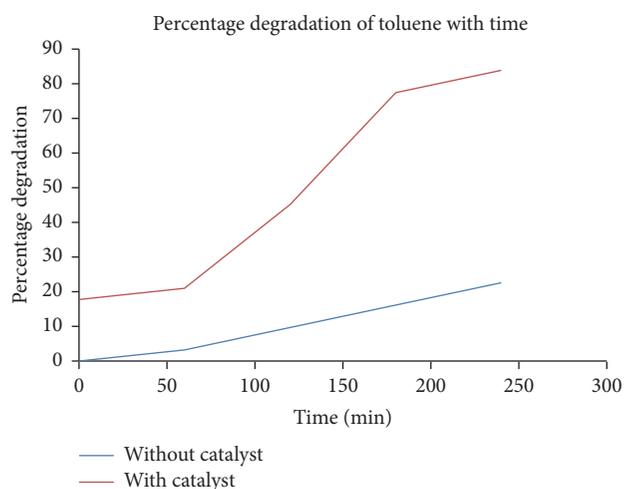
FIGURE 3: SEM images of prepared TiO₂ nanoparticles.FIGURE 4: XRD pattern of TiO₂ nanoparticles.

FIGURE 5: Degradation of formic acid under different times of solar irradiation at room temperature.

time intervals, the samples were taken from formic acid solution (under process of degradation in sunlight) and the process of titration was repeated.

TOC measurement indicates catalytic (TiO₂/UV) degradation of formic acid under sunlight after 8 hours of the reaction. TOC was transformed from 6.17% to 1.20% (Figure 5) which relates to about 80% of formic acid removal in the experiment.

FIGURE 6: Degradation of toluene after different time intervals without and with TiO₂ photocatalyst.

3.2.2. Degradation of Toluene

(1) *Effect of Time on Photocatalytic Degradation of Toluene.* The decrease in the absorbance at 244 nm wavelength, corresponding to the λ_{max} of toluene, was utilized to determine the extent of degradation of toluene. The degradation of toluene was checked after regular time intervals of 60 minutes. A blank experiment in the absence of TiO₂ was also performed to study the effect of the photocatalyst. Results show that toluene was degraded rapidly in the presence of TiO₂ photocatalyst on illumination with sunlight. In the absence of photocatalyst, however, the degradation was very slow as shown in Figure 6.

When a small amount of catalyst was added to the solution, it was noticed that the absorbance of the solution decreases, due to the adsorption of toluene molecules on the catalyst surface. When the solution was exposed to sunlight, a sharp decrease in the absorbance was observed indicating the degradation of toluene. The blank solution showed only a little change in absorbance indicating that the degradation of toluene mainly takes place due to the catalyst.

TABLE 1: Pseudo-second-order kinetic model.

Initial concentration	Without catalyst		Pseudo-2nd-order			
	q_e (min-g/mg)	K_2 (1/min)	R^2	q_e (min-g/mg)	K_2 (1/min)	R^2
30 ppm	29.440	7.990	0.9998	37.087	0.0367	0.9983

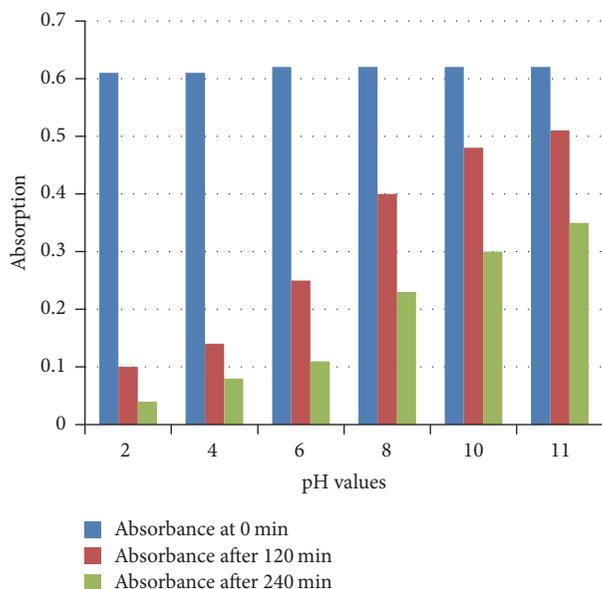


FIGURE 7: Degradation of toluene at various pH values.

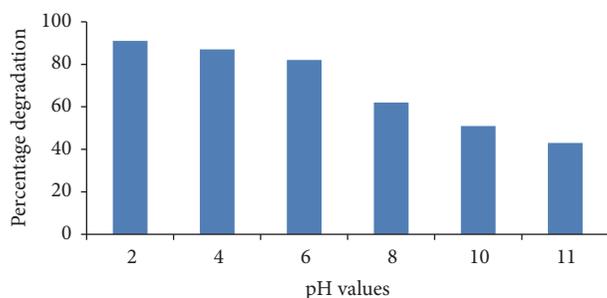


FIGURE 8: Percentage degradation of toluene at various pH values.

The results show that the prepared TiO_2 is an effective photocatalyst for the degradation of toluene. The toluene was almost completely degraded after 240 minutes of exposure of sunlight. The percentage degradation was about 83.8%. In the absence of catalyst, the rate of degradation was very slow.

(2) *Effect of pH on Degradation of Toluene.* pH plays very important role in degradation process. Different toluene solutions were prepared having the same concentration (30 ppm) but with different pH values ranging from 2 to 11. A small amount of catalyst (TiO_2 nanoparticles) was added in each solution and samples were exposed to sunlight for 240 min. A marked decrease in toluene concentration was observed after 240 min in each sample. However, the maximum degradation was observed in acidic conditions at 2 pH (Figures 7 and 8).

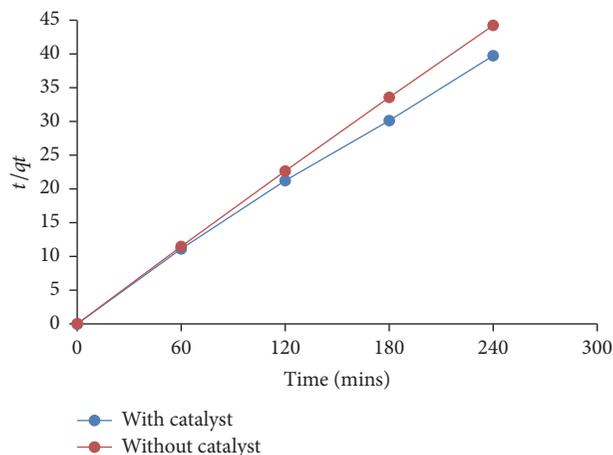


FIGURE 9: Pseudo-2nd-order kinetics.

In acidic pH, electrostatic attraction is higher between protonated catalyst surface and the adsorbed species (toluene). In contrast, in basic pH, the TiO_2 becomes negatively charged which gives rise to a coulombic repulsion between the adsorbed species and the catalyst surface preventing the adsorption of the species. Hence the high photodegradation is observed in acidic pH and a marked decrease in the degradation is observed in basic pH.

3.3. *Kinetic Study.* The kinetics for the degradation of toluene was studied by applying pseudo-first-order models. However, it was unsuccessful and then pseudo-second-order model was applied. The pseudo-second-order equation based on equilibrium adsorption is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \quad (1)$$

where k_2 (g/mg min) is the rate constant of second-order adsorption. A plot of t/q_t versus time for different initial sorbent concentration was found to be linear for the degradation of toluene onto sorbent indicating the validity of equation and is given in Figure 9. The calculated R^2 , k_2 , and q_e for pseudo-second-order kinetic model are shown in Table 1. The experimental data showed a good compliance with the pseudo-second-order equation and the correlation coefficients for the linear plots were 0.99 for all the experimental data. These results suggested that the pseudo-second-order adsorption mechanism was predominant and that the overall rate for the degradation of toluene process appeared to be controlled by chemical process involving valence forces through sharing or exchange of electrons between sorbent and adsorbate.

4. Conclusion

In summary, we have synthesized TiO₂ nanoparticles by a modified sol-gel method. Titanium butoxide was used as precursor and a novel spray technique was used to hydrolyze the precursor. The particle size of prepared TiO₂ nanoparticles was 40 nm with spherical morphology and anatase crystalline form. The catalytic activity of TiO₂ nanoparticles for the degradation of formic acid and toluene was checked after different time intervals and variable pH, under sunlight. Results concluded that the prepared TiO₂ nanoparticles are effective catalyst for degradation of both formic acid and toluene. Kinetic study shows that the degradation of toluene follows pseudo-second-order reaction mechanism.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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