Facile Construction of Sandwich-like TiO₂-ZnO-ED-HPV Composite for Photodegradation of Ciprofloxacin

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Abstract: The TiO₂-ZnO, TiO₂-ZnO-ED and TiO₂-ZnO-ED-HPV (TZEDHPV) nanocomposite were successfully prepared by simple hydrothermal process. The nanocomposite was characterized and confirmed by DRS-UV, FT-IR, XRD, SED and EDX analysis. The DRS-UV analysis of TZEDHPV nanocomposite absorption was increased with the band gap decrease of TiO₂-ZnO by the addition of heteropoly acid (HPV). The FT-IR spectra of photocatalyst, presents the characteristic bands of metal oxide, ED and HPV. SEM and EDX analysis reveals clustered microsponge-like structure of catalyst with more number of cavities. Photodegradation of ciprofloxacin (CF conc.: 40 µM), exhibited 98.20 % removal efficiency under UV light. According to the scavenger method results, O₂⁻ radical played a main role in the photocatalytic degradation.

Keywords: Ciprofloxacin, Heteropoly acid, Photodegradation, UV irradiation.

I. INTRODUCTION

Pharmaccompounds are beneficial and widely used, but their release of toxic contaminations makes the environment highly polluted [1-3]. Ciprofloxacin, a fluoroquinolone antibiotic medicine, is used for infections caused by certain bacteria. Ciprofloxacin is active against gram-negative bacteria and gram-positive bacteria and used for various infections [4-6]. Side effects of Ciprofloxacin may be serious or even cause death. Degradation of a toxic molecule is caused by the photocatalytic material by the absorption of photons, particularly of those wavelengths found in sunlight such visible light and ultraviolet light [7]. Semiconductor oxides such as titania, zinc oxide are widely used as photocatalysts for environmental remediation [8-10]. As environmental pollution exceeds the limits of natural purification, an improved advanced oxidation process has become essential for effective wastewater treatment [11-15].

Nowadays, Semiconductor photocatalysis, an advanced oxidation processes, is a ‘green approach’ for the degradation of toxic chemicals. ZnO gained much importance in photocatalytic degradation due to its advantages over other photocatalysts. The heteropoly acids with keggin structure are strongly acidic and are particularly stable when deposited on the oxide surface. Due to their solubility in polar solvents they are widely used in catalysis. Improved decomposition of organic pollutants in UV / TiO₂ activity has been reported in the presence of supported keggin-type HPAs [17]. The significant increase in reactivity was justified by the semiconductor’s ability to transfer electrons from the conduction group to the activated HPA* species. Dispersion of HPAs in solid support with high surface area is generally useful for enhancing their access to their acidic sites and increasing the photoactivation activity. In the present work, a composite catalyst using ZnO, TiO₂ ethylene diamine (ED) and heteropoly vanadate (HPV) was prepared hydrothermally and its photocatalytic activity was investigated.

II. EXPERIMENTAL SECTION

A. Materials and Methods

Ethylene diamine, ethylene glycol, ethanol, disodium hydrogen phosphate, sodium tungstate, titanium tetra isopropoxide were purchased from Himedia. High purity (>99%) ciprofloxacin was supplied by Sigma–Aldrich. UV–Visible diffused reflectance spectra (DRS-UV) of the samples were measured by Shimadzu UV-2450 UV–Visible spectrophotometer. FT-IR spectra were recorded using Shimadzu IR Tracer-100 FT-IR spectrophotometer as KBr disks. The surface morphology and size of the samples was observed by scanning electron microscopy (EVO-80, CARL ZEISS) operated at an acceleration voltage of 20 kV. The structural plane and crystallinity of the samples were studied by X-ray diffraction (XRD) studies using an XPERTPRO multipurpose X-ray diffractometer (Cu Ka radiation with a wavelength of 1.540 Å). The degradation of organic pollutants was studied using Shimadzu UV-1800 UV-visible spectrophotometer.

B. Preparation of Catalysts

Preparation of TiO₂-ZnO

Titanium tetra isopropoxide (4.5 mmol), zinc acetate (5.4 mmol) and 95% ethanol (80 mL) were mixed and the solution was 30 min sonicated. This mixed solution was poured into a 100 mL Teflon-lined autoclave at 115 °C for 24 h. The composite was filtered and...
Preparation of TiO$_2$-ZnO-ED

1 g of TiO$_2$-ZnO was dispersed in ethylene glycol (20 m) and ethylene diamine (ED) (40 mL). This mixture of compound was sonicated (30 min) and poured into a teflon-lined autoclave and maintained for 24 h in 115 °C. The black product was filtered and completely washed by ethanol solvent and pure water. The composites was dried at 60 °C in vacuum.

Preparation of HPV (TZEDHPV) nanocomposites

The following procedure is employed for synthesis HPVs grafted TiO$_2$-ZnO-ED: 0.2 g of H$_4$[PVW$_{11}$O$_{40}$]·32H$_2$O (HPV) was dissolved in 80 mL of ethanol and then 0.8 g of TiO$_2$-ZnO-ED added to it. Then, it was transferred to a teflon-lined autoclave and maintained for 24 h in 115 °C. The black product was filtered and washed several times by ethanol and deionized water and finally dried at 60 °C in vacuum.

Preparation of TiO$_2$-ZnO-ED-HPV (TZEDHPV)

C. Photodegradation of ciprofloxacin

30 mg of TZEDHPV was dispersed in 100 mL of 40 µM CF aqueous solution in 250 mL beaker. The solution was reaching the equilibrium between absorption-desorption in 30 minutes by stirring in the dark room. After stirring, the solution was irradiated by UV light in a photoreactor with eight mercury vapor lamps (8 W) set in parallel and emitting at 365 nm wavelength. 3 mL of the reaction solution was sampled with 10 min interval and centrifuged. Its absorbance was measured at 276 nm by an UV–visible spectrophotometer to monitor its concentration.

III. RESULTS AND DISCUSSIONS

A. DRS-UV analysis

The UV–vis diffuse reflectance spectra of as-prepared photocatalysts are shown in Fig. 1. The pure TiO$_2$-ZnO shows the absorption broad band at 200–350 nm, and the corresponding band gap could be estimated to be 3.60 eV. Further loading of heteropoly acid the absorption band position are slightly shifted and corresponding band gap is 3.56 eV to estimate by Tacu’s plot. The figure 1 results conclude that, the TZEDHPV photocatalyst is activated only UV irradiation by the application of photodegradation of organic pollutants.

B. FT-IR spectra

In figure 2a, the broad bands observed for TiO$_2$-ZnO at 3505 and 1604 cm$^{-1}$ confirms well that TiO$_2$-ZnO contains hydroxyl groups (OH) which give rise to stretching and bending vibrations. After the nanocomposites materials were supported on HPV (Fig. 2c), the corresponding band of W-O stretching and O-W-O deformation vibrations in tungstate groups are absorbing at 1056 and 795 cm$^{-1}$ [20].

C. XRD patterns

Fig. 3 shows the XRD patterns for the TiO$_2$, ZnO, TiO$_2$-ZnO, HPV and TZEDHPV nanocomposite materials respectively. In Fig. 3, the TiO$_2$ XRD patterns peaks at 20 values TiO$_2$ nanoparticle peaks appear at 25.13, 37.45, 47.98,
53.68, 54.98, 62.47 and 68.56 corresponding to the planes of (101), (004), (200), (105), (211), (204) and (116) were matched with the JCPDS card number 21-1272. In the XRD diffraction pattern of ZnO, the peaks at 31.54°, 34.29°, 36.10°, 47.48°, 56.63°, 62.82° and 67.78° correspond to the reflection planes of (100), (002), (101), (102), (110), (103) and (112) which may be corresponded to the hexagonal primitive structure of ZnO (JCPDS no. 89–7102) [11]. Finally, XRD pattern of TZEDHPV presence of slightly shift peaks of TiO₂, ZnO and HPV peaks. Therefore, the above results conclude that the formation of TZEDHPV nanocomposites.

D. SEM and EDX analysis

Fig. 4a and b shows SEM images of TiO₂-ZnO (different magnification) and it has a morphology of plate like structure. TiO₂-ZnO-ED-HPV material has a morphology of clustered microsponge-like structure (Fig. 4c and d). The presence of elements Ti, O, Zn, C, N, P, V and W in the catalyst was confirmed by EDX recorded from the selected area (Fig. 5). Multi-elemental EDS mapping images of Ti, O, Zn, C, N, P, V and W are shown in Fig. 6. Apparently, the corresponding C, N, P, V and W elements demonstrated bright spots corresponding to the calculated area, and illustrate the homogeneous distribution of these components.

E. Photodegradation of Ciprofloxacin

The optimized photodegradation of CF was performed under various conditions with UV light irradiation. Fig. 7a shows the degradation activity of 30 mg of various catalysts with 100 mL 2 X 10⁻⁵ CF solution. Fig. 7a results conclude that, degradation efficiency of TZEDHPV is higher than other catalysts such as, TiO₂, ZnO, TiO₂-ZnO and TZEDHPV. Based on result, the TZEDHPV photocatalyst was selected for further optimization. Fig. 7b shows the absorption spectra of an aqueous solution of CF degradation 40 µM in the presence of TZEDHPV nanocomposites (30 mg) under UV light irradiation. It can be seen that the absorption peaks corresponding to CF decrease with increase in the time and almost complete degradation of CF takes place at 120 minutes of irradiation.
30 mg of TZEDHPV nanocomposites at different irradiation times.

The efficiency of TZEDHPV dosage for the degradation of 100 mL 4 × 10⁻⁵ M CF solution is shown in Fig. 8a, which concludes that 30 mg of TZEDHPV degradation efficiency is higher than 10, 20 and 30 mg dosages. The photocatalyst presents the reactive sites directly proportional to the catalyst concentration [21, 22]. Further the amount of catalyst dosage increases with increase in reactive sites of the catalyst. At a higher dosage of catalyst reaction, the decrease in photodegradation activity is by agglomerations of catalyst particles and scattering of light by the excess particles.

The effect of initial concentration of CF from 20 to 60 µM under the photocatalytic activity of TiO₂-ZnO-ED-HPV composite (30 mg) was investigated under UV light irradiation. There is a decrease in degradation efficiency with the increase in CF concentration. At high concentrations, CF is an internal filter that excludes photons from the catalytic surface. An increasing number of CF molecules are absorbed into the surface of the catalyst, thereby reducing the rate of degradation of surface active sites.

Fig. 8. Photodegradation of CF solutions under different dosage of TZEDHPV (CF conc.: 4 × 10⁻⁵ M)

To estimate the key role of the reactive active species involved in the degradation process, triethanolamine (TEOA), p-benzoquinone (BQ) and isopropanol alcohol (IPA) were used as scavengers for holes, superoxide radicals and hydroxyl radicals respectively. In optimized photodegradation reaction by the addition of BQ decreased the photodegradation activity (Fig. 9a). These conclude that superoxide radicals play a prominent role in degradation process. The photocatalytic degradation of CF solution is also slightly decreased by the addition of TEOA and IPA indicating the involvement of holes and hydroxyl radicals in the degradation process. Since the degradation occurs mainly by superoxide radicals, the mechanism involves the photogeneration of electrons and holes on irradiation of the photocatalyst by UV light. These electrons react with oxygen forming superoxide radicals, which degrade the CF.

After end of the photodegradation process, the catalyst was removed from the solution, dried and reused for five runs. As shown in Fig. 9b, the photodegradation efficiency is slightly decreased with increasing number of runs. The TZEDHPV photocatalyst degradation efficiency is 89 % even at 5th run, which shows its stability, recyclability.

Fig. 9. a) Photodegradation of CF solution under different scavengers (CF conc.: 4 × 10⁻⁵ M; TEOA-1 mmol / BQ-0.1 mmol / IPA-0.1 mmol, irradiation time 120 min) and b) Recycle efficiency of the TZEDHPV photocatalyst.

IV. CONCLUSION

The UV light active sandwich-like composite TiO₂-ZnO-ED-HPV was synthesized by simple hydrothermal method. The XRD pattern conform the formation of TZEDHPV nanocomposites. TZEDHPV has morphology of micro-sponge clustered structure. The presence of Ti, O, Zn, C, N, P, V and W elements in the surface of the photocatalysts was clearly confirmed by EDX mapping analysis. The optimization of photodegradation efficiency of TZEDHPV carried out, the final results conclude that 40 µM CF solution was completely degraded by 30 mg of TZEDHPV. The reactive oxidative species studies reveal that the superoxide radicals play a prominent role in degradation of CF solution. The advantages of the catalyst are high degradation efficiency, low-cost, easy recovery and recyclability.

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REFERENCES


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