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Photocatalytic degradation of erythromycin under visible light by zinc phthalocyanine-modified titania nanoparticles

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ABSTRACT

Zinc phthalocyanine modified TiO_2 nanoparticles (Znpc–TiO_2) were prepared by the chemical impregnation method to improve the photocatalytic activity of TiO_2 under visible light. The prepared nanoparticles were characterized by UV–vis diffuse reflectance spectroscopy (UV–vis-DRS), X-ray powder diffraction, scanning electron microscopy transmission electron microscopy and Brunauer-Emmett-Teller. surface area analysis techniques. The photocatalytic activity of Znpc–TiO_2 was investigated for the degradation of erythromycin. The results revealed that UV–vis absorption edge of Znpc–TiO_2 is slightly shifted towards visible region and it has a higher surface area than that of TiO_2. The photocatalytic activity of Znpc–TiO_2 was superior (74.21%) than that of TiO_2 (31.57%). Besides the photocatalyst (Znpc–TiO_2) is stable and may be reused for several times.

1. Introduction

In recent years, antibiotics have been widely used in human and veterinary medicine to treat several diseases and infections. These antibiotics are released into the water bodies (ground water, surface water and drinking water) through its metabolized and non-metabolized forms. They are non-biodegradable and its presence in the environment will create antibiotic resistance bacteria [1,2]. Erythromycin (Ery) is a macrolide antibiotic that has an antimicrobial spectrum similar to or slightly wider than that of penicillin, and is often prescribed for people who have an allergy to penicillin [3]. For respiratory tract infections, it has better coverage of typical organisms, including mycoplasma and legionellosis. Although this medication is not particularly toxic, an overdose could cause diarrhea, stomach pain, upset stomach, hearing loss, dizziness, fainting, irregular heartbeat, etc.

The conventional waste water treatments are totally ineffective to treat pharmaceutical effluents. Heterogeneous photocatalysis employing TiO_2 nanoparticles has been proved as a potential, cost-effective and eco-friendly technique to degrade and mineralize the antibiotics in water [4,5]. TiO_2 is a non-hazardous, easily available, and chemically stable compound; it can be recovered and reused during photodegradation studies [6]. However, the wide band gap of TiO_2 has limited its utility under visible light (more than 45% in the solar spectrum). In this regard, several surface modification methods have been carried out to make visible light active TiO_2. The surface of TiO_2 has been modified via doping with metals (or) non-metals, sensitization with porphyrin (or) phthalocyanine and coupling with other narrow band gap semiconductors [7,8]. In our previous study, we have reported the photocatalytic activity of Hes–TiO_2 [9], AgI–ZnO [10], Bi_2O_3–ZrO_2 [11] and Cur–Ag–SnO_2 [12] towards the degradation of various organic dyes and reduction of heavy metal.

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Xekoukoulotakis [13] reported the photocatalytic decomposition of Ery using TiO_2 under UV light irradiation. However, the studies related to the visible light assisted photocatalytic activity of TiO_2 towards the degradation of antibiotics are limited. To the best of our knowledge, the photodegradation of erythromycin (Ery) using zinc phthalocyanine modified TiO_2 nanoparticles (Znpc–TiO_2) was seldom addressed. Hence, our present investigation demonstrates the synthesis, characterization and photocatalytic activity of Znpc–TiO_2 for the degradation of Ery.

2. Experimental

2.1. Materials

TiO_2-P-25 was purchased from Sigma-Aldrich and all other chemicals were purchased from Merck. The chemicals used were of analytical grade and applied without further purification. Double distilled water was used in all experiments.

2.2. Synthesis of Znpc–TiO_2

Znpc–TiO_2 was prepared by a chemical impregnation method [14] as follows: 0.003 g of Znpc and 3 g of TiO_2 were dispersed in 50 mL of $CHCl_3$ and then the suspension was stirred at room temperature for 5 h. After that the mixture was filtered, dried in an oven at 100 °C for 2 h followed by calcination at 400 °C for 3 h.

2.3. Photocatalytic experiments

Photocatalytic activity was evaluated by monitoring the degradation of Ery at pH 5 [13]. Photocatalytic experiments were performed in an immersion type photoreactor. The detailed experimental procedure was described in our previous report [12]. 300 mL aqueous solution of Ery (1×10^{-5} M) with certain amount of photocatalyst was taken in the cylindrical glass vessel of the photoreactor, which was surrounded by a circulating water jacket to cool the lamp. Air was bubbled continuously into the aliquot by an air pump in order to provide a constant source of dissolved oxygen. Prior to light irradiation, the suspension was stirred in dark for 30 min to ensure that the suspension is uniform. A 300 W Xe arc lamp with an ultraviolet ($l > 400$ nm) cut off filter was used as the visible light irradiation source. During the course of light irradiation, 5 mL aliquot was withdrawn at a regular time interval of 30 min. Then the samples were centrifuged and filtered through a Milliporefilter to remove the photocatalyst. The filtrate was analyzed using a total organic carbon (TOC) analyzer (TOC-VCSH-Shimadzu).

2.4. Characterization

The characterization techniques were similar to our previous report [11]. UV–vis diffuse reflectance spectral measurements were carried out in a JASCO V-550 double beam spectrophotometer with PMT detector equipped with an integrating sphere assembly, using BaSO4 as a reference sample. The X-ray powder diffraction patterns were measured in an X-ray diffractometer (X'PERT PRO X-RAY) using Cu Kα irradiation at 25 °C and the structural assignments were made with reference to the JCPDS powder diffraction files. The surface morphology was examined using scanning electron microscopy (SEM) (JSM 6701F—6701) in both secondary and backscattered electron modes and the elemental analysis was also detected. Transmission electron microscopy (TEM) images were taken using a TEM-TECNAI G2 model transmission electron microscope. The B.E.T surface area was measured by the ASAP 2020 volumetric adsorption analyzer (Micromeritics Instrument Corporation). pH was monitored using a EUTECH instrument pH meter.

3. Results and discussion

3.1. Characterization

3.1.1. UV–vis-DRS

The UV–vis-DRS of TiO_2 and Znpc–TiO_2 are shown in Fig. 1. It is clearly seen that the absorption edge of Znpc–TiO_2 is slightly red-shifted when compared to that of TiO_2. The observed shift may be attributed to the electron transfer process between TiO_2 and Znpc. Generally, the band gap of semiconductors is related to its range of absorption wavelength and the band gap decreases with increasing of absorption edge. The band gaps can be evaluated using Tauc approach [12]. The band gap values of TiO_2 and Znpc–TiO_2 are found to be 3.23 eV and 3.08 eV, respectively. Hence, Znpc–TiO_2 absorbs more visible light than that of TiO_2.

3.1.2. XRD

The XRD profiles of TiO_2 and Znpc–TiO_2 are shown in Fig. 2. The diffraction peaks of Znpc–TiO_2 at 2θ of 25.24, 37.86, 48.05, 53.89, 54.97, 62.62, 68.69, 70.39 and 75.13 are consistent with those of anatase phase TiO_2 (JCPDS # 21-1272) and no impurity peaks appeared. The peak intensities are slightly reduced when compared to that of TiO_2. This shows that the surface modification with Znpc did not affect the crystal phase structure of TiO_2. This is attributed to the low concentration and high dispersion of Znpc on the surface of TiO_2. The average crystallite size was measured on the basis of Debye–Scherrer equation [11]. The average crystallite size of TiO_2 and Znpc–TiO_2 is found to be 15.59 nm and 12.47 nm, respectively. There is a slight decrease in the crystallite size of TiO_2 after surface modification with Znpc. This is due to the significant interaction between Znpc and TiO_2 and this stabilizes the nanoparticles by preventing further growth of crystallization.

3.1.3. SEM, TEM and B.E.T. surface area

The morphology of Znpc–TiO_2 was analyzed by SEM and TEM. Fig. 3 shows the SEM and TEM images of Znpc–TiO_2. The synthesized nanoparticles are composed of spherical like structures, favouring for good photocatalytic activity [15]. Znpc is observed as dark spots on TiO_2. From TEM measurements, the average grain diameter of Znpc–TiO_2 is in the range of 15–20 nm. The TEM results are in good agreement with the XRD results.