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Photocatalytic ozonation of metronidazole by synthesized zinc oxide nanoparticles immobilized on montmorillonite

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ABSTRACT

Released antibiotics in the aquatic environment have undesirable biological and ecotoxicological effects. In this work, photocatalytic ozonation process was used for removal of metronidazole (MET) as commonly used antibiotic from aqueous media. ZnO nanoparticles as an effective photocatalyst were immobilized on the surface of montmorillonite (MMT). The ZnO/MMT catalyst was characterized by X-ray diffraction (XRD), N_2 adsorption/desorption, Fourier transform infrared (FT-IR), scanning electron microscope (SEM), and high resolution transmission electron microscope (HR-TEM). The ZnO/MMT activity was examined in the degradation of metronidazole under ozone bubbling and UV-A irradiation through photocatalytic ozonation process. The main influence factors on the photocatalytic ozonation activity such as ZnO/MMT dosage, pH, metronidazole initial concentration and ozone flow rate were studied. The results indicated that the MET removal efficiency was increased with increasing all the investigated factors except initial MMT concentration. The effect of organic and inorganic radical scavengers on the photocatalytic ozonation of MET was studied. Finally, several by products were identified by GC–MS analysis, which allowed to depict a possible mechanism for the MET degradation.

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1. Introduction

In the past decade production and consumption of pharmaceutical compounds have been increased across the developed world. Antibiotics are a large family of pharmaceutical compounds consumed in human and veterinary for therapeutic purposes [1]. Antibiotics are released in the aquatic environment mostly from human excretion, veterinary clinics and runoff from agricultural applications [2]. This kind of pharmaceutical compounds have antibacterial nature. Therefore, the presence of the antibiotics in water resources even at very low concentrations leads to enhancement of the bacterial resistance against antibiotics [3]. Accordingly, their presence in the aquatic environment is undesirable.

Due to antibacterial nature of antibiotics, oxidation potential of conventional biological treatments is not enough to oxidize and degrade these pharmaceutical products [2]. For example, metronidazole as one of the most frequently used compounds that encompass most gram-positive and gram-negative anaerobic bacteria and protozoans. Furthermore, this antibiotic is very stable even under UV light irradiation [4]. Accordingly, various treatment techniques and processes have been developed and used to remove these compounds from polluted sources. Among these techniques, advanced oxidation processes (AOPs) have been recognized as promising approach for complementary degradation of organic pollutants from contaminated water resources [5]. AOPs are based on the generation of highly reactive and nonselective radicals especially hydroxyl radicals, which are effective oxidant toward organic compounds.

In recent years attention has been focused on heterogeneous photocatalysis as one of the most promising AOPs. In this process, semiconductors with high photocatalytic activity such as TiO_2 and ZnO particles are irradiated by UV or visible light as energy source. This energy leads to the excitation of electrons (e^-) from valence band of semiconductor into the conduction band and development of holes (h^+) in the valence band. Reaction of h^+ with H_2O or OH^- leads to reactive radicals development [6].

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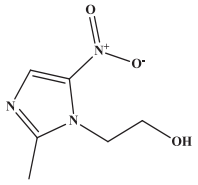
Table 1
Characteristics of the metronidazole.

Name	Chemical structure	Molecular formula	M_w (g/mol)	λ_{max} (nm)	Class
Metronidazole		$C_6H_9N_3O_3$	171.15	317	Antibiotic

Although different works have been reported to date for the use of ZnO photocatalysis for photodegradation of organic pollutants, some limitations have been recognized for this including: separation of semiconductor powders from batch slurry photoreactor and higher tendency of photo-generated $e^-/h+$ to recombine rather than contribution in the formation of reactive radicals which imposes low efficiency of photocatalytic degradation [7].

Application of ozone assisted photocatalytic degradation is one of the effective methods to overcome the mentioned limitations. O_3 molecules as a strong inorganic oxidative species can trap the photo-generated electrons and increase h^+ contribution in the formation of reactive radicals. Furthermore, O_3/UV process is one of the successful AOPs for degradation of various organic pollutants in water. In recent decades, investigation of photocatalytic ozonation process ability in degradation of organic pollutants has been made in several works for instance, photocatalytic ozonation of oxalic acid by g-C_3N_4/graphene composites by Yin et al., [8], phenazopyridine by TiO_2 nanoparticles thin film by Fathinia et al., [9], urban wastewater and surface water using immobilized TiO_2 by Moreira et al., [10] and amoxicillin and diclofenac using TiO_2 by Moreira et al., [11].

The scope of this study was to immobilize ZnO nanoparticles on the surface of montmorillonite (MMT) and evaluate the application of ozone assisted photocatalytic degradation to overcome the ZnO photocatalysis limitations to use for photocatalytic degradation of the MET as organic pollutant.

2. Materials and methods

2.1. Materials and reagents

Montmorillonite K10 was purchased from Sigma-Aldrich Co., USA. This solid consists of SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O and K_2O with wt. % of 66.9, 13.8, 2.75, 1.58, 0.29, 0.15 and 1.65, respectively. Cation exchange capacity (CEC) of the MMT was 120 meq/100 g. Metronidazole ($C_6H_9N_3O_3$) was purchased (Sigma-Aldrich, St. Louis, MO, USA) and dissolved in distilled water. Table 1 shows the structure and properties of MET in this study. All other utilized reagents were of analytical grade (Sigma-Aldrich, St. Louis, MO, USA) and were used as received without further purification. Distilled water was used throughout the experiments.

2.2. Preparation of ZnO/MMT nanocomposite

The ZnO/MMT nanocomposite was prepared using the following method including: Step one—development of MMT suspension by dispersion of 1 g of MMT in 100 mL distilled water. Step two—dropwise addition of cetyltrimethylammonium bromide (CTAB) with the concentration of 1 CEC to the MMT suspension. Step three—dissolving 1 g of zinc chloride in 20 mL of distilled water and adjustment of solution pH to 12.5 using sodium hydroxide solution. Step four—mixing the prepared suspensions in steps two and three for 6 h Step five—separation of suspended ZnO/MMT particles from the aqueous solution by centrifugal separator. Step six—washing with distilled water and centrifuging to remove any non-adhesive impurities from ZnO/MMT particles. Step seven—drying ZnO/MMT particles at 90 °C for 3 h to remove moisture. ZnO nanoparticles were synthesized using the methods described in steps three to five of ZnO/MMT preparation method.

2.3. ZnO/MMT nanocomposite characterization

The ZnO nanoparticles, MMT particles and ZnO/MMT nanocomposite were characterized using powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FT−IR) and N_2 adsorption/desorption apparatuses. XRD was done by the PANalytical X'Pert PRO apparatus (Germany) with monochromatic CuKα X-radiation (45 kV, 40 mA, 0.15406 nm). The surface morphology of the material was studied by SEM model Mira3 FEG-SEM (Tescan, Czech) and HR-TEM model JEOL JEM-2100F (Japan) operated at 200 kV. FT-IR spectra were recorded by Tensor 27, Bruker spectrometer (Germany). Textural properties of the ZnO and ZnO/MMT samples were determined from N_2 adsorption/desorption isotherms at 77 K on a Gemini 2385 nitrogen adsorption apparatus (Micromeritics Instruments, USA) and their pore structure analyzed using Brunauer–Emmett–Teller (BET), and Barrett–Joyner–Halenda (BJH) equations. The generated reaction intermediates during the photocatalytic ozonation process at optimum conditions were identified using a gas chromatograph (6890, Agilent Technologies, CA) coupled with a mass spectrometer (5973, Agilent Technologies, Canada).

2.4. Metronidazole removal experiment

All experiments were conducted in a batch cylindrical quartz tube with total capacity of 900 mL. In a typical procedure, the degradation reactions were initiated by continuously UV-A illumination (nominal power of 8 W) and ozone bubbling into the quartz tube contains ZnO/MMT nanocomposite and MET solution with desired concentrations and pH. All the experiments were carried out at room temperature. To determine the variation of MET concentration during the photocatalytic ozonation process at pre-selected time intervals, samples were withdrawn from the tube and analyzed spectrophotometrically at 317 nm using a UV spectrophotometer (Varian Cary 100 UV–vis Spectrophotometer, Australia).

The removal efficiency (%) for each sample was equal to $(C_0 - C_t)/C_0$ where C_0 and C_t (mg/L) are the initial and the final concentrations of MET in the solution, respectively. In the case of photocatalytic degradation experiments, the similar process to photocatalytic ozonation was used except ozone bubbling into the quartz tube. Dissolved ozone concentration for different processes was determined by the procedure proposed by Bader and Hoigne [12].

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