



# Sonocatalytic removal of naproxen by synthesized zinc oxide nanoparticles on montmorillonite



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## ABSTRACT

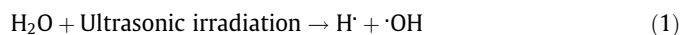
ZnO/MMT nanocomposite as sonocatalyst was prepared by immobilizing synthesized ZnO on the montmorillonite surface. The characteristics of as-prepared nanocomposite were studied by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM) and X-ray diffraction (XRD) techniques. The synthesized samples were used as a catalyst for sonocatalytic degradation of naproxen. ZnO/MMT catalyst in the presence of ultrasound irradiation was more effective compared to pure ZnO nanoparticles and MMT particles in the sonocatalysis of naproxen. The effect of different operational parameters on the sonocatalytic degradation of naproxen including initial drug concentration, sonocatalyst dosage, solution pH, ultrasonic power and the presence of organic and inorganic scavengers were evaluated. It was found that the presence of the scavengers suppressed the sonocatalytic degradation efficiency. The reusability of the nanocomposite was examined in several consecutive runs, and the degradation efficiency decreased only 2% after 5 repeated runs. The main intermediates of naproxen degradation were determined by gas chromatography–mass spectrometry (GC–Mass).

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## 1. Introduction

Disposal of large amount of wastewater from various sources that contain potentially toxic organic compounds is a major problem, because they have extremely harmful effects on human body, living organisms and ecological systems [1,2]. The conventional degradation methods are ineffective for degradation and mineralization of organic compounds since these effluents are resistant to destruction by conventional methods [3]. In this regard, advanced oxidation processes (AOPs) are considered as an alternative innovative method with in situ reactive radicals production [4]. Ultrasound (US) process, ozonation, Fenton and photocatalysis with semiconductors are such AOP's that are based on the production of highly reactive hydroxyl radicals with high oxidation potential for the degradation of organic pollutants [5,6]. Since 1990, ultrasound process has been recognized as an attractive advanced technology for the degradation of organic contaminants in wastewater [4,7]. The main advantages of the ultrasonic process are easy to operate and high degradation efficiency without creating any secondary pollutants [8]. Ultrasound irradiation causes the

production of developed acoustic cavitation (the formation, growth, and collapsing of bubbles) consisting of hot spots with high local temperatures (5000 K) and pressures (1000 atm) for short periods of time. Volatile and hydrophobic compounds oxidized within the gaseous cavitation bubbles region while non-volatile and hydrophilic compounds exposed to degradation with the produced ·OH and other reactive radicals according to the following reactions [9–11]:



Despite many advantages of sonochemical process, complete mineralization of the target compounds via sonolysis alone requires large amounts of energy and high reaction time [12,13]. To overcome these problems, ultrasonic irradiation can be improved by adding a suitable semiconductor as sonocatalyst to accelerate the reaction [14,15]. The presence of heterogeneous catalysts provides additional nucleation sites that enhance the number of cavitation bubbles [16,17]. Zinc oxide (ZnO) has attracted

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considerable interest due to its unique physical, chemical and optical characteristics such as high UV absorption potential, wide band gap (3.37 eV) and low cost [18,19]. Various methods have been reported to increase the catalytic activity of ZnO such as semiconductor coupling, metal doping, non-metal doping and immobilization of ZnO on the materials surface with large surface area [3].

In this paper, ZnO nanoparticles, as a sonocatalyst, have been synthesized and immobilized on the surface of montmorillonite K10 (MMT) for the degradation of a drug. To the best of our knowledge, there is no detailed report on the sonocatalytic performance of ZnO/MMT nanocomposite for the removal of naproxen. The effect of different key factors on the sonocatalytic degradation of naproxen, such as initial concentration of naproxen, ZnO/MMT dosage, pH of the solution, the presence of organic and inorganic anions and the power of ultrasonic generator have been studied. GC–MS analysis was also used to identify the intermediates produced during sonocatalysis of naproxen.

## 2. Materials and methods

### 2.1. Materials

Naproxen ( $C_{14}H_{14}O_3$ , 98%) was purchased from Sigma–Aldrich, (USA) and dissolved in distilled water. Characteristics and chemical structure of naproxen are shown in Table 1.  $ZnCl_2$ , HCl and NaOH were purchased from Merck, Germany. Cetyltrimethylammonium bromide (CTAB) and montmorillonite K10 (MMT) were purchased from Sigma–Aldrich Co. (USA). All other chemicals were of analytical grade.

### 2.2. Catalyst synthesis and characterization

ZnO/MMT nanocomposite was prepared through synthesis of ZnO nanoparticles on the surface of MMT. In order to reach a homogenous suspension of MMT, 1 g of MMT was dissolved in 100 mL distilled water and stirred for 24 h. Then the desired amount of CTAB was added to the MMT solution with stirring. Then, 1 g of  $ZnCl_2$  was added to 20 mL distilled water. 1 M NaOH solution was added drop wise to the above solution until the pH reached to 12.5. The prepared zinc chloride was added to CTAB/MMT suspension and the mixture was stirred for 6 h. Finally, the obtained precipitate was washed with distilled water and ethanol and dried at 90 °C for 3 h.

Scanning electron microscope (SEM) model (MIRA3 FEG-SEM Tescan, Czech) and high-resolution transmission electron microscope (HR-TEM) model JEM 2100F, JEOL (Japan) operated at 100 k were used to investigate the surface morphology of the MMT particles and ZnO/MMT composite. Crystal structures of pure MMT, ZnO particles and ZnO/MMT composite were determined using X-ray powder diffraction (XRD) measurements by P analytical X'Pert PRO diffractometer (Germany). The Brunauer–Emmett–Teller (BET) equation was used to measure the total specific surface areas ( $S_{BET}$ ). An Agilent 6890 gas chromatograph with a 30 m to 0.25 mm HP-5MS capillary column coupled with an Agilent 5973

mass spectrometer (Canada) was used to identify produced intermediates during sonocatalysis of naproxen.

### 2.3. Sonocatalytic degradation experiments

The sonocatalytic degradation of naproxen was carried out in an ultrasonic apparatus (WUC-D10H, 40 kHz, 665 W, Korea) under air atmosphere. In a typical approach, 100 mL of naproxen solution with known initial concentration containing desired amount of catalyst was sonicated with a frequency of 60 kHz and output power of 650 W at natural pH. At desired time intervals, a required volume of sample was taken out and the remaining naproxen concentration was determined using Varian Cary 100 UV–Vis spectrophotometer (Australia) at a maximum wavelength of 230 nm. UV–Vis spectral changes of naproxen in the presence of ZnO/MMT nanocomposite as a function time under ultrasonic irradiation were studied and the results are presented in Fig. 1. The maximum peak observed at the wavelength of 230 nm decreased gradually as the time increased, and it almost disappeared after the irradiation time of 120 min, revealing the sonocatalytic degradation of naproxen on the surface of the ZnO/MMT nanocomposite.

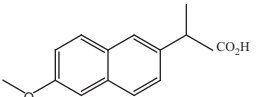
## 3. Results and discussion

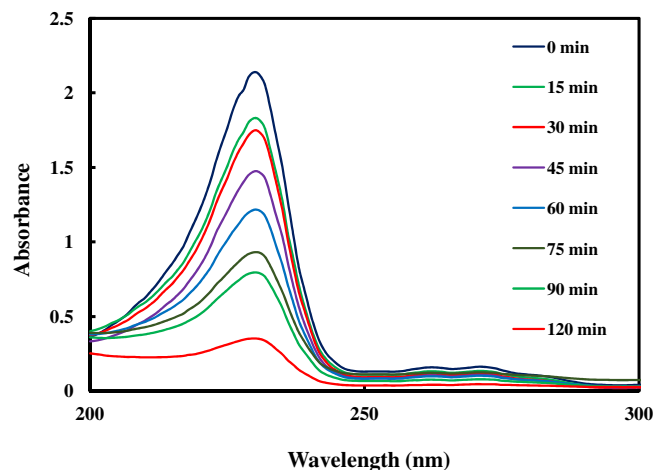
### 3.1. Characterization of ZnO/MMT nanocomposite

Fig. 2 shows the SEM images of MMT and synthesized ZnO/MMT nanoparticles. When the SEM images of the MMT (Fig. 2(a)) and the ZnO/MMT (Fig. 2(b)) samples compared with each other, it is clearly seen that the ZnO particles immobilized on the porous surface of MMT. Fig. 3 shows the HR-TEM images of synthesized ZnO nanoparticles on MMT. Fig. 3((a) and (b)) shows the HR-TEM images of bare MMT with a porous surface. Fig. 3((c) and (d)) shows the HR-TEM images of ZnO/MMT nanocomposite. Plate-like ZnO particles are obvious in HR-TEM images indicating the proper synthesis of nanosized ZnO on porous surface of MMT. These images show the shape and particle size distribution of ZnO–MMT sample indicating that the ZnO–MMT particles are within the nanoscale ( $\leq 100$  nm).

The XRD pattern of the synthesized ZnO/MMT nanocomposite (Fig. 4) exhibited dominant peaks at  $2\theta$  value of 31.71°, 34.41°, 36.21°, 47.51°, 56.61°, 63.0°, 66.08°, 68.0°, 68.28°, 71.64°, and 75.96° which corresponded to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) planes of

**Table 1**  
Characteristics of naproxen.

Chemical structure	Molecular formula	$\lambda_{max}$ (nm)	$M_w$ (g/mol)
	$C_{14}H_{14}O_3$	230	230.259



**Fig. 1.** The changes in the UV–vis spectrum of 10 mg/L of naproxen during different treatment time (experimental conditions: [Catalyst] = 0.5 g/L, pH = 4.5 and US Power = 650 W/L).

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