



Sonocatalytic removal of naproxen by synthesized zinc oxide nanoparticles on montmorillonite



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ABSTRACT

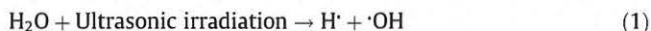
ZnO/MMT nanocomposite as sonocatalyst was prepared by immobilizing synthesized ZnO on the montmorillonite surface. The characteristics of as-prepared nanocomposite were studied by scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM) and X-ray diffraction (XRD) 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 AOPs 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 $\cdot\text{OH}$ 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.

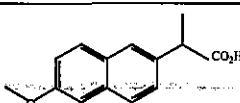
3. Results and discussion

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 (≤ 100 nm).

The XRD pattern of the synthesized ZnO/MMT nanocomposite (Fig. 4) exhibited dominant peaks at 2θ 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	λ_{max} (nm)	M_w (g/mol)
	$C_{14}H_{14}O_3$	230	230.259

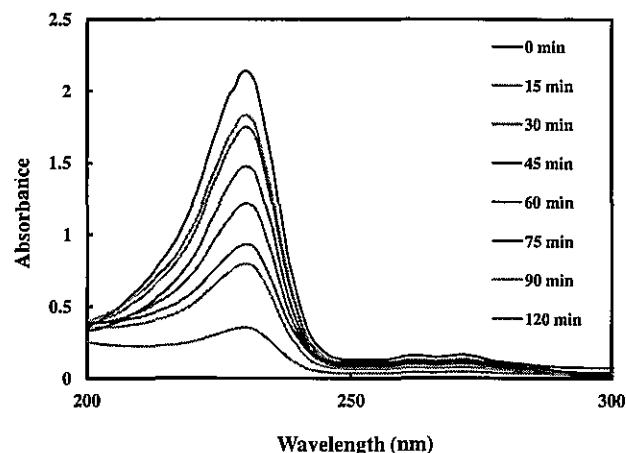


Fig. 1. The changes in the UV-vis spectrum of 10 mg/L of naproxen during different treatment time (experimental conditions: [Catalyst] = 0.5 g/L, pH = 4.5 and US Power = 650 W/L).

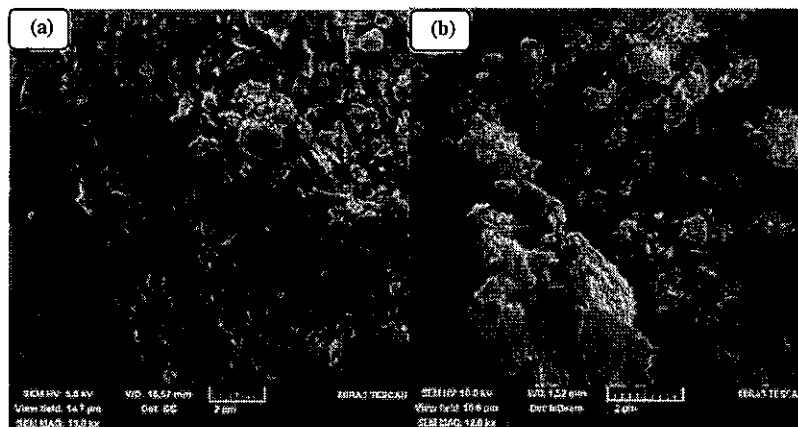


Fig. 2. SEM images of (a) MMT and (b) ZnO/MMT nanocomposite.

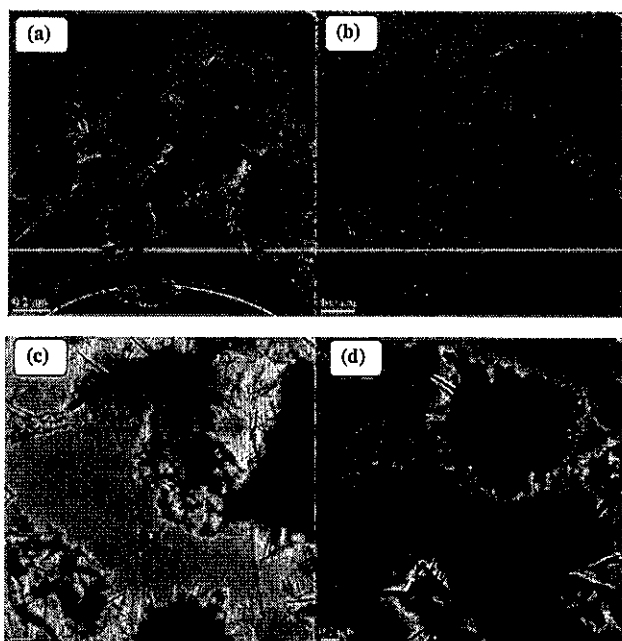


Fig. 3. HR-TEM images of (a and b) MMT and (c and d) ZnO/MMT nanocomposite.

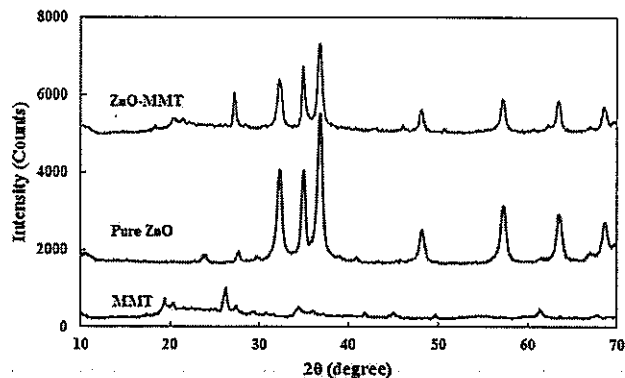


Fig. 4. The XRD patterns of MMT, Pure ZnO and ZnO-MMT nanocomposite.

ZnO, respectively (JCPDS Card 36-1451) [20]. The surface areas were calculated by the BET method. Immobilization of the ZnO nanoparticles on the MMT surface caused an increase in the specific surface area of ZnO nanoparticles from 38.22 to 70.54 m²/g.

3.2. Effect of operational parameters on sonocatalytic process

3.2.1. Effect of ZnO/MMT dosage

To investigate the effect of ZnO/MMT dosage, sonocatalytic degradation experiments were carried out with different ZnO/MMT dosage from 0.25 g/L to 1.25 g/L. The results are presented in Fig. 5. The naproxen degradation efficiency increased with increasing ZnO/MMT dosage. Increasing sonocatalyst dosage leads to an increase in the active sites of catalyst, resulting in improved production of hydroxyl radicals which are responsible for sonocatalytic degradation of naproxen [4,20].

3.2.2. Effect of initial concentration of naproxen

In order to determine the effect of initial concentration of naproxen on the sonocatalytic degradation efficiency, experiments were carried out by varying the concentration of naproxen from 5 mg/L to 20 mg/L. The values of ZnO/MMT dosage, initial pH and power of ultrasonic generator were constant at 0.5 g/L, 4.50 and 650 W. As displayed in Fig. 6, the removal efficiency of naproxen decreased with increasing the initial concentration of naproxen.

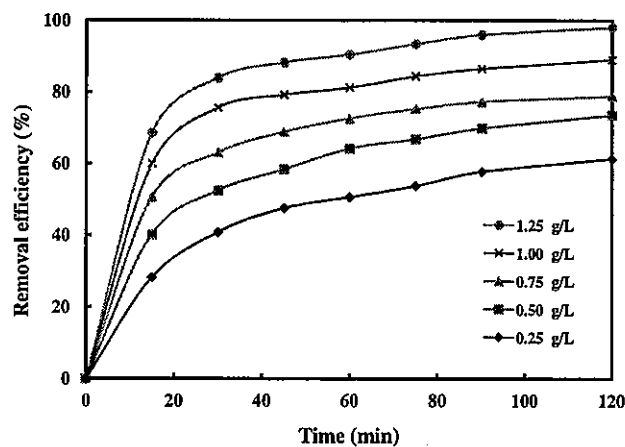


Fig. 5. Effect of catalyst dosage on the sonocatalytic degradation of naproxen in the presence of ZnO/MMT nanocomposite (experimental conditions: [NAP]₀ = 10 mg/L, pH = 4.5 and US power = 650 W/L).

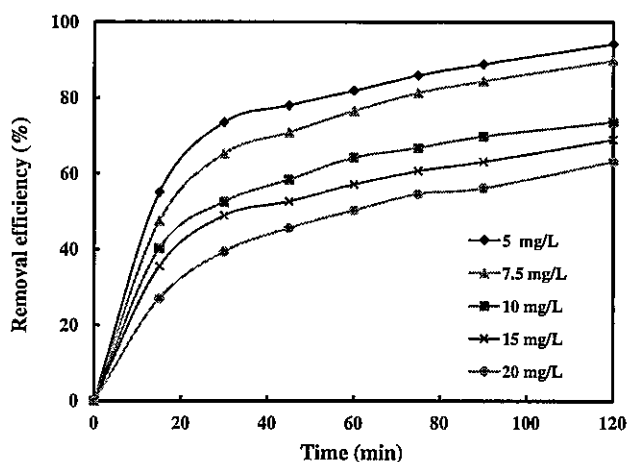


Fig. 6. Effect of initial naproxen concentration on the sonocatalytic degradation efficiency of naproxen in the presence of ZnO/MMT nanocomposite (experimental conditions: [Catalyst] = 0.5 g/L, pH = 4.5 and US power = 650 W/L).

The number of naproxen molecules that adsorbed on the surface of the ZnO/MMT nanocomposite, increased with increasing the initial concentration of naproxen. Therefore, high number of hydroxyl radicals is required for the degradation of pollutant molecules. However the production of hydroxyl radicals remains constant for a given irradiation time, ultrasonic power and catalyst dosage [21,22]. The results indicated that sonocatalytic degradation process is favored at low concentrations of naproxen.

The Langmuir–Hinshelwood (L–H) model is often used to evaluate the kinetic behavior of the sonocatalytic degradation reactions at the heterogeneous catalytic surface. Langmuir–Hinshelwood kinetic expression is given by Eqs. (5) and (6) [22]:

$$r = -\frac{d[C]}{dt} = k_c \frac{k_{ads}[C]}{1 + k_{ads}[C]} = k_{obs}[C] \quad (5)$$

$$\frac{1}{k_{obs}} = \frac{1}{k_c k_{ads}} + \frac{[C]_0}{k_c} \quad (6)$$

where C_0 is the initial concentration of naproxen (mg/L), k_c is the reaction rate constant (mg/L min), k_{ads} is the adsorption equilibrium constant (L/mg) and k_{obs} is the pseudo-first-order rate constant (min^{-1}). When initial concentration is plotted versus $1/k_{obs}$, the reaction rate constant and the adsorption equilibrium constant are found to be 40.511 mg/L min and 210.18 L/mg, respectively. The high regression coefficient (0.959) supported the fitting of sonocatalytic degradation of naproxen by Langmuir–Hinshelwood kinetic model.

3.2.3. Effect of pH

pH of the solution plays a key role in the catalytic degradation of pollutants since it determines the surface charge of the catalyst and pollutant. Therefore, the effect of pH value in the range of 4.5–11 on the sonocatalysis of naproxen was investigated and the obtained results are presented in Fig. 7. Acidic pH favored the sonocatalytic degradation of naproxen. The zero point charge (pH_{pzc}) of ZnO/MMT is 8.4 [23]. Above and below of the zero point charge, the catalyst surface is negatively and positively charged, respectively [4]. Accordingly, the ZnO/MMT surface is protonated below the pH of 8.4, and above this pH, the catalyst's surface is predominantly negatively charged due to the adsorption of OH^- ions. At high pH values ($\text{pH} > \text{pH}_{pzc}$), OH^- ions that are adsorbed on the catalyst's surface restrain the formation of hydroxyl radicals, which are responsible for the degradation process, consequently the

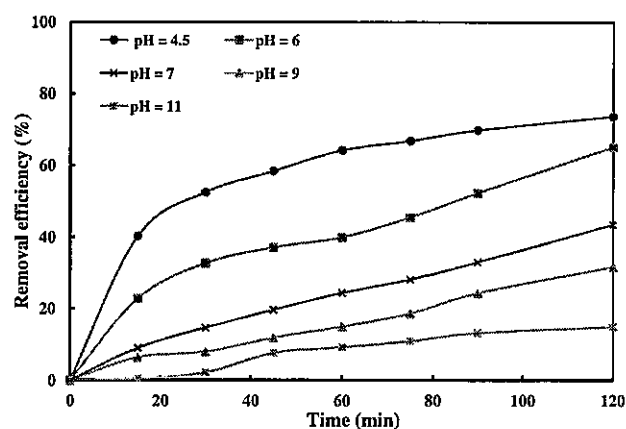


Fig. 7. Effect of pH on the sonocatalytic degradation of naproxen in the presence of ZnO/MMT nanocomposite (experimental conditions: [Catalyst] = 0.5 g/L, [NAP]₀ = 10 mg/L and US power = 650 W/L).

degradation efficiency decreases [3,16]. Under acidic conditions ($\text{pH} < \text{pH}_{pzc}$), naproxen molecules as an anionic contaminant with negative charge, can be adsorbed on the surface of positively charged ZnO/MMT nanocomposite. Thus, the degradation efficiency logically enhances.

3.2.4. Effect of radical scavengers

Real wastewater usually contains organic and inorganic species, which can affect the activity of catalysts. To investigate the effect of the organic and inorganic species on the sonocatalytic degradation process, the experiments were carried out using chloride, sulfate, carbonate, fluoride and iodide as inorganic scavengers and chloroform, $\text{Na}_2\text{-EDTA}$, t-butanol and benzoquinone as organic scavengers (Figs. 8 and 9). In this set of experiments, the initial concentration of naproxen, the sonocatalyst dosage and the concentration of ionic species were constant at 10 mg/L, 0.5 g/L and 10 mg/L, respectively. As shown in Figs. 8 and 9, degradation efficiency of naproxen decreased in the presence of all used radical scavengers. According to the results obtained from the experiments, the degradation efficiency decreased from 73.60% to 69.10%, 63.30%, 58.89%, 48.94% and 35.16% in the presence of

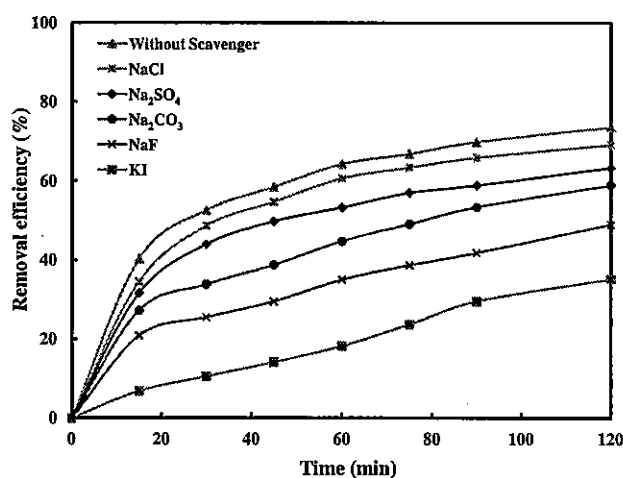


Fig. 8. Effect of inorganic scavengers on the sonocatalytic degradation of naproxen in the presence of ZnO/MMT nanocomposite (experimental conditions: [Catalyst] = 0.5 g/L, [NAP]₀ = 10 mg/L, pH = 4.5, [Scavenger]₀ = 10 mg/L and US power = 650 W/L).

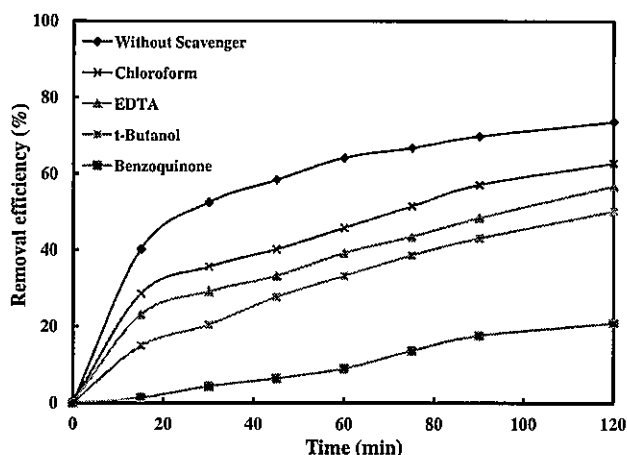


Fig. 9. Effect of different organic ions on the sonocatalytic degradation of naproxen in the presence of ZnO/MMT nanocomposite (experimental conditions: [Catalyst] = 0.5 g/L, [NAP]₀ = 10 mg/L, pH = 4.5, [Scavenger]₀ = 10 mg/L and US power = 650 W/L).

chloride, sulfate, carbonate, fluoride and iodide, respectively at the reaction time of 120 min. Chloride anion has the scavenging effect according to the following reactions [20,24]:



The deactivation of hydroxyl radicals by sulfate anions can be explained by the following reaction [25]:



Likewise, carbonate ions demonstrated a negative effect on the sonocatalytic degradation efficiency of naproxen. The CO_3^{2-} ions in aqueous solutions react with hydroxyl radicals to form less active CO_3^- , which decreases the degradation efficiency of naproxen. The probable reaction exhibiting the scavenging effect of sodium carbonate is given in Eq. (11) [4,26,27].



A considerable decrease in the removal efficiency of naproxen was observed with the addition of iodide ions. I^- ions mainly trapped h^+ and OH^\cdot affecting the sonocatalytic degradation of naproxen [27]. NaF addition exhibited a substantial suppression on the naproxen degradation, due to its scavenging effect on the generated holes. The difference between the scavenging effects of fluoride and iodide may be attributed to the different electron affinities of the two ions. Another reason for scavenging effect of fluoride ions may be its stronger adsorption ability on the surface of the sonocatalyst compared to pollutant molecules. Therefore, the surface of the sonocatalyst would be dominated with fluoride ions rather than pollutant molecules in the presence of fluoride ions, resulting in the decreased removal efficiency [28].

The effect of organic radical scavengers on the sonocatalytic degradation of naproxen was also investigated (Fig. 9). Sonocatalytic degradation efficiency of naproxen decreased from 73.60% to 62.77%, 56.81%, 50.20% and 20.89% in the presence of chloroform, $\text{Na}_2\text{-EDTA}$, t-butanol and benzoquinone, respectively. The observed reduction in the degradation efficiency with the addition of chloroform may be attributed to the attack ability of the chloroform molecules on the hydroxyl radicals which leading to decrease

in the hydroxyl radicals generation and subsequently in the degradation efficiency [29,30].

The presence of t-butanol and $\text{Na}_2\text{-EDTA}$ in aqueous solution inhibited the naproxen degradation by scavenging the generated holes (h^+) as illustrated in Eq. (12) [31]:



Among the organic scavengers, p-benzoquinone, which is known as radical scavenger, has led to the greatest reduction in degradation efficiency. Based on these results, it can be concluded that free radical attack is the dominant controlling mechanism of the sonocatalytic degradation of naproxen [32].

3.2.5. Effect of ultrasonic power

Ultrasonic power is an important operational parameter because of its effect on cavitation activity. Fig. 10 displays the effect of ultrasonic power on the sonocatalytic degradation efficiency of naproxen. The values of catalyst dosage, initial concentration of naproxen and pH were constant at 0.5 g/L, 10 mg/L and 4.5, respectively. By increasing the ultrasound power from 350 W/L to 650 W/L, the degradation efficiency is increased from 35.62% to 73.60%, respectively. Increasing degradation efficiency with increasing power of ultrasonic generator is due to the increased production of hydroxyl radicals. Also, the mechanical effects of ultrasound can enhance the mass transfer diffusion. This result indicated that the high ultrasonic power is favored the sonocatalytic degradation of naproxen.

3.2.6. Comparison of different processes in the degradation of naproxen

A comparative study for the degradation of naproxen was carried out and the results are presented in Fig. 11((a) and (b)). The values of initial naproxen concentration, catalyst dosage and pH were constant at 10 mg/L, 0.5 g/L and 4.5. As clearly seen in Fig. 11(a), catalytic degradation efficiency in the presence of ZnO/MMT catalyst is higher than that of ZnO and MMT under similar experimental conditions. As can be also seen in Fig. 11, the degradation efficiency of naproxen in the presence of US/ZnO/MMT and US/ZnO is higher than that of ZnO/MMT and ZnO indicating the effective role of used catalysts for the active radical production in the presence of ultrasound irradiation [17,33,34]. As known, heterogeneous catalysts lead to the formation of more cavitation bubbles consequently increasing the generation of hydroxyl radicals via the pyrolysis of H_2O molecules [28,35].

The improved ability of the ZnO/MMT nanocomposite in the sonocatalytic degradation of naproxen compared with that of

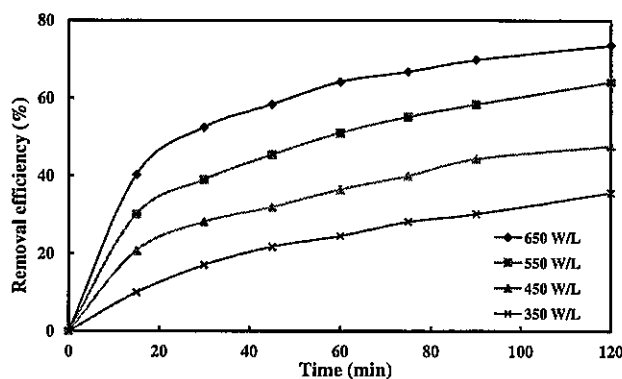


Fig. 10. Effect of ultrasonic power on the sonocatalytic degradation of naproxen in the presence of ZnO/MMT nanocomposite (experimental conditions: [Catalyst] = 0.5 g/L, [NAP]₀ = 10 mg/L and pH = 4.5).

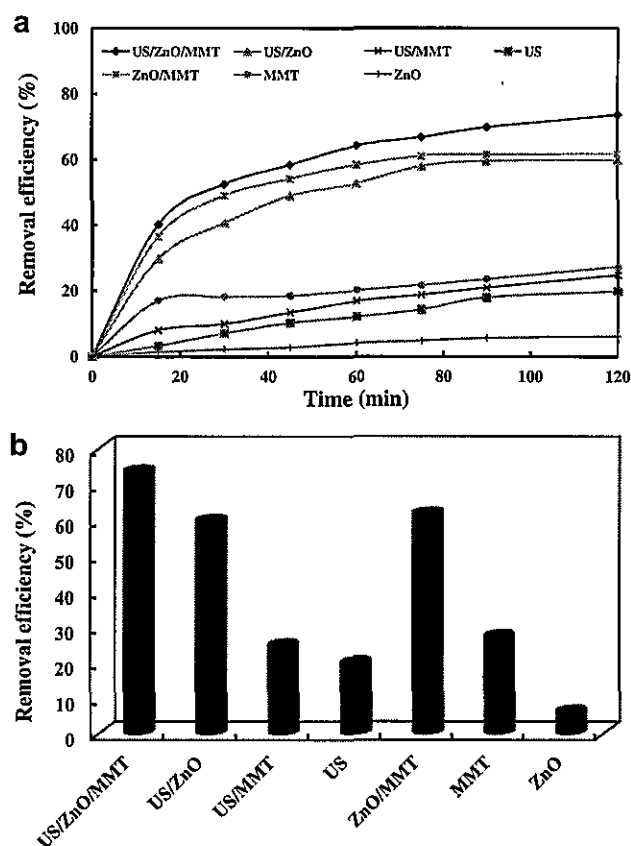


Fig. 11. Comparison of different processes in the removal efficiency of naproxen (a) at different time, (b) at 120 min decolorization (experimental conditions: [Catalyst] = 0.5 g/L, [NAP]₀ = 10 mg/L, pH = 4.5 and US power = 650 W/L).

ZnO can be attributed to the increase in the available surface area of ZnO/MMT, resulting in considerable enhance in the adsorption capability of the catalyst for the production of more hydroxyl radical as a stronger oxidizing agent [13,36]. Removal efficiency is insignificant for both sonolysis and adsorption process onto ZnO surface. This results may be attributed to the low surface area of ZnO nanoparticles [31]. Only 19.9% degradation efficiency was obtained after 120 min using sonolysis alone. The low generation rate of $\cdot\text{OH}$ radicals during the direct sonolysis process limits its efficiency compared to sonocatalytic process [37]. The main reason for the increased sonocatalytic degradation efficiency is due to the increase in the cavitation effect resulting in increased generation of hydroxyl radicals. On the other hand, the mechanical effects of ultrasound can enhance the mass transfer diffusion [38]. Dai et al. [39] reported similar results for sonocatalytic degradation of Rhodamine B catalyzed by $\beta\text{-Bi}_2\text{O}_3$ particles under ultrasonic irradiation in aqueous solution.

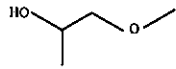

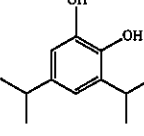

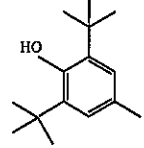
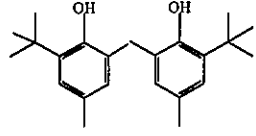
3.2.7. Naproxen degradation by-products

GC–Mass analysis was used to identify the naproxen sonocatalysis intermediates. Accordingly, six compounds were successfully recognized by comparing with commercial standards when the match factor was above 90%. The retention time and molecular weight of produced intermediates after 60 min of degradation process is shown in Table 2.

3.2.8. Reusability of the sonocatalyst

Catalyst reusability is a very important parameter from an economical point of view. To examine the reusability of the ZnO/MMT

Table 2
Identified by-products during degradation of naproxen by sonocatalytic process after 60 min.

No.	Structure	t_r (min)	M_w (g/mol)	Compound
1		3.039	90.121	1-Methoxy-2-Propanol
2		8.67	107.10	Trimethyl [5-methyl-2-(1-methylethyl) phenoxy]
3		34.765	222.32	1,2-Benzenediol, 3,5-bis(1,1-dimethylethyl)-
4		3.627	226.45	Hexadecane
5		18.020	252.22	2,6-Bis (1,1-dimethylethyl)-4-methyl phenol
6		30.215	340.49	Phenol, 2,2'-methylenebis [6-(1,1-dimethylethyl)-4-methyl

nanocomposite, the sonocatalytic degradation experiments were carried out with catalyst dosage of 0.5 g/L, initial naproxen concentration of 10 mg/L and the reaction time of 120 min. In each run, the ZnO/MMT nanocomposite was recycled after washing and drying. The results are presented in Fig. 12. As can be seen, the degradation efficiency reduced from 73.2% to 71.6% after five repeated runs. Hence, the sonocatalyst has good reusability up to five runs.

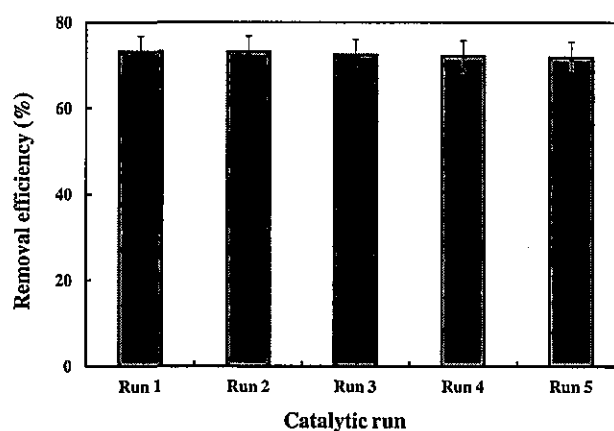


Fig. 12. Reusability of the ZnO/MMT nanocomposite in sonocatalysis of naproxen (experimental conditions: [Catalyst] = 0.5 g/L, [NAP]₀ = 10 mg/L, pH = 4.5 and US power = 650 W/L).

4. Conclusion

In this study, ZnO/MMT nanocomposite was synthesized and used as catalyst in sonocatalytic degradation of naproxen. SEM and HR-TEM images of MMT and ZnO/MMT indicated the immobilization of ZnO on the porous surface of MMT. The observed increase in degradation efficiency in the presence of ZnO/MMT compared to sonolysis alone indicated that the addition of catalyst led to more hydroxyl radical generation due to its nucleation effect for cavitation bubbles. Addition of radical scavengers reduced the sonocatalytic degradation efficiency indicating that the free radicals are dominant controlling mechanism in the sonocatalytic process. Based on the obtained results from reusability test studies, it is seen that ZnO/MMT nanocomposite is a suitable catalyst for the removal of organic contaminants from wastewater.

Acknowledgments

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