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Photocatalytic removal of two antibiotic compounds from aqueous solutions using ZnO nanoparticles

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ABSTRACT

Zinc oxide (ZnO) nanoparticles were synthesized, characterized, and used for photocatalytic removal of amoxicilline and sulfamethoxazole from contaminated water. Microwave-assisted gel combustion synthesis method was optimized for type and amount of complexing agent and calcination temperature, in order to obtain the best photocatalytic activity. Characterization of ZnO nanoparticles according to their scanning electron microscopy and transmission electron microscopy images and X-ray diffraction pattern showed homogenous spherical nanoparticles with an average crystalline size of 25.82 nm. Effects of several operational factors such as pH of antibiotic solution, initial concentration of antibiotic, ZnO nanoparticles loading amount, and presence of NaCl salt or buffered solution were investigated. Results showed complete removal of antibiotic compounds in six hours using ZnO nanoparticles/UV-C irradiation. Mineralization of organic content were 62.8 and 20.8% for amoxicilline and sulfamethoxazole, respectively. Photocatalytic removal of both antibiotics followed the Langmuir–Hinshelwood model in the range of concentration of 5–20 mg L^{-1}. ZnO nanoparticles were used for three subsequent runs without significant decrease in their photocatalytic activity.

Keywords: Amoxicilline; Photocatalytic degradation; Sulfamethoxazole; Contaminated water; Zinc oxide

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1. Introduction

Antibiotics are widely used in both human and veterinary medicine for treating and preventing infectious diseases and promoting the growth of livestock. As a result of extensive use and incomplete metabolism, a large amount of these compounds enter sewage effluents every day [1]. Several studies have reported the occurrence of antibiotics in natural water samples and their potential risk for aquatic organisms and people consuming antibiotic-contaminated water due to promotion of growth of resistant bacteria [2–4]. In most countries, wastewater treatment plants (WWTPs) are established to prevent the entrance of harmful contaminants into the aquatic environment

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via municipal and industrial wastewater. However, treatment technologies used in these plants are not usually capable of removing micro-level pollutants like antibiotics and concerns about their presence have encouraged the development of more efficient treatment methods [5].

Photocatalytic degradation possesses several advantages over other methods in the area of wastewater treatment. Some of these advantages include complete mineralization of the pollutant molecule, low cost, and minimum facility requirements [6]. This technology is based on the photoactivation of a semiconductor material by artificial or sun light, which eventually leads to the formation of strong oxidants such as hydroxyl radical and superoxide radical anions [7,8]. Among several semiconductor materials, ZnO is reported as an efficient and cost-beneficial photocatalyst that can be used in large scale municipal, hospital, and industrial WWTPs [9–11]. It has been shown that ZnO photocatalytic activity increases significantly when using nano-sized semiconductor crystallites instead of bulk materials because of extending the available surface area for photocatalytic reactions [12,13].

Amoxicillin (AMX) and sulfamethoxazole (SMX) are two frequently used antibiotic compounds in human and veterinary medicine. AMX is a semi-synthetic β-lactam antibiotic. More than 86% of this compound excretes from the body unmetabolized and it has been detected in many water samples like treated effluents and surface water at $\mu g\,L^{-1}$ level and at higher $mg\,L^{-1}$ level in antibiotic manufacturing effluents [14,15]. SMX, a sulfonamide-type synthetic antibiotic, is refractory to biodegradation, hydrolysis, and most conventional treatments used in WWTPs [16]. As a result, this compound has been among the most frequently detected pharmaceuticals in the environment. It has been found in treated effluents at $\mu g\,L^{-1}$ and even in drinking water at lower $ng\,L^{-1}$ levels [17].

In this present study, ZnO nanoparticles were synthesized using microwave-assisted gel combustion method. The method was optimized for type and amount of complexing agent and calcination temperature to obtain homogenous, nano-sized zinc oxide with high photocatalytic activity. Characterization of the synthesized zinc oxide was performed according to its scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images and X-ray diffraction (XRD) pattern. ZnO nanoparticles were used for photocatalytic degradation of AMX and SMX. Effect of several operational factors including pH of the solution, photocatalyst loading amount, initial antibiotic concentration, presence of salt, and buffered solution were investigated for both antibiotics. Since one of the most important advantages of photocatalytic degradation is removal of organic matter and not just decomposition of the pollutant to other substances, mineralization of the organic content was also monitored.

2. Experimental

2.1. Materials and reagents

Sulfamethoxazole and amoxicilline trihydrate were purchased from Virchow Laboratories Limited (Hyderabad, India) and Aurobindo Pharma Limited (Andhra Pradesh, India), respectively. Analytical grade zinc nitrate tetrahydrate, ammonium hydroxide 25%, citric acid, glycin, urea, hydrochloric acid 37%, ortho-phosphoric acid 85%, sodium hydroxide, and disodium hydrogen phosphate were purchased from Merck (Darmstadt, Germany).

2.2. Preparation of ZnO nanoparticles

Microwave-assisted gel combustion method used in our previous work [18], was modified and used for synthesizing zinc oxide nanoparticles. Method modification was performed in order to obtain smaller particle size, extended surface area, and higher photocatalytic activity. Three different complexing agents, urea, glycin, and citric acid were employed for synthesizing ZnO nanoparticles at neutral pH value. Effects of complexing agent/Zn^{2+} ions ratio and calcination temperature on morphology and photocatalytic activity of ZnO nanoparticles were also investigated.

2.3. Characterization of ZnO nanoparticles

ZnO nanoparticles were characterized according to their SEM (KYKY-EM3200, Beijing, China) and TEM (Philips CM30, the Netherlands) images. XRD pattern obtained from a D8-advance diffractometer, cooperation product of Bruker AXS and Siemens) was used for determining the identity, phase of ZnO nanoparticles. XRD pattern was analyzed using X'Pert HighScore software (Philips, Netherlands) and PDF2-2003 database (International Center for Diffracion Data, PA, USA) for possible pattern matches and crystallographic parameters.

2.4. Photocatalytic experiments

Sulfamethoxazole and amoxicilline $500\,\mu g\,mL^{-1}$ stock solutions were prepared using deionized water obtained from a Milli-Q® system (Millipore, Milford, MA, USA). Working solutions were prepared by further dilution of stock solutions with water and adjusting their pH by 1 N HCl or NaOH.

In order to investigate the efficiency of photocatalytic removal in buffered solutions, AMX- and SMX-working solutions were prepared by diluting their stock solutions with 0.2 M phosphate buffer solution.

Photocatalytic experiments were conducted inside a UV cabinet made from medium-density fiberboard with 120 cm length, 50 cm width, and 40 cm height. Magnet stirrers were placed in the cabinet and a 30-W UV-C lamp (OSRAM®, Munich, Germany) was installed above them. All experiments were performed on 200 mL of antibiotic solution poured in Pyrex containers with 10 cm inner diameter and 7 cm height. Solutions were stirred magnetically using 5 cm magnets at 300 rpm. After 30 min of stirring in dark in order to reach the equilibrium point of antibiotic adsorption/desorption on the surface of ZnO nanoparticles, UV-C lamp was turned on. Antibiotic solutions were irradiated directly from a 15 cm distance. Effect of solution pH on photocatalytic degradation was investigated by adjusting the initial pH of antibiotic solutions to 4, 7, and 10 using 1 N HCl or 1 N NaOH. Photolytic degradation experiments were also performed in these initial pH values. Effect of initial antibiotic concentration in the range of 5–20 $\mu g\ mL^{-1}$, ZnO nanoparticles loading amount in the range of 0.25–2 $g\ L^{-1}$, presence of NaCl salt in two concentration levels, and phosphate buffer ions on photocatalytic degradation process were also investigated.

Samples were collected every 1 h and analyzed for antibiotic concentration after removing the photocatalyst nanoparticles by centrifuging at 3,000 rpm for 20 min, (Hettich EBA 21, Massachusetts, USA). Chemical analyses were performed using a UV–Vis spectrophotometer (PerkinElmer, Lambda 15, Massachusetts, USA). Samples were also analyzed using an automatic total organic carbon analyzer (TOC-V, Shimadzu, Japan) for their organic carbon content.

3. Results and discussion

3.1. ZnO nanoparticles

Table 1 shows type and amount of complexing agent materials and calcination temperatures, used for synthesizing ZnO nanoparticles. The synthesized materials were compared for their photocatalytic activity based on the photocatalytic removal of SMX in one hour.

Table 1 shows that ZnO nanoparticles synthesized using citric acid at three fold of Zn^{2+} ions concentration (ZnO 9) have the highest photocatalytic activity. This can be due to better complexing activity of citric acid compared with urea and glycin. Citric acid has three carboxyl groups in its structure that in pH values above 6.8, like what we used in this study, form strong complexes with Zn^{2+} ions and provide a good dispersity to obtain homogenous nanoparticles in subsequent steps [19].

ZnO 10 synthesis procedure was the same as ZnO 9 except for calcinating at lower temperature. SEM images of ZnO 9 and ZnO 10 showed that higher calcination temperature has caused the growth of rod structures with lower surface area and photocatalytic activity in ZnO 9 (Fig. 1).

According to these observations, ZnO 10 was chosen for further photocatalytic experiments. Fig. 2 shows TEM image and XRD pattern of ZnO 10. Phase and purity of the nanoparticles were established by interpretation of the XRD pattern. All the diffraction peaks can be indexed as the hexagonal phase of standard ZnO (zinc white, P63MC) and presence of well-defined sharp peaks indicates the formation of a single phase of zinc oxide nanoparticles. Using the Scherer equation (Eq. (1)), the average size of crystallites was calculated as 25.82 nm. Comparing the intensity of crystalline peaks to that of all peaks in the XRD pattern revealed a degree of crystallinity of 77%.

$$D = \frac{0.89\lambda}{\beta \cos \theta} \tag{1}$$

where D is the average size of crystallites in nm; λ is the wavelength of X-ray radiation; β is the full width of the peak at half maximum; and θ is the diffraction angle.

3.2. Effect of initial pH of antibiotic solution

The predominant role of pH in photocatalytic degradation can be explained by both stability of antibiotic solution under UV irradiation and interaction of antibiotic molecules with photocatalyst nanoparticles whose surface charge vary in aqueous solutions with different pH values. Since adsorption of pollutants on the surface of photocatalyst materials is the first step of photocatalytic reactions, these interactions are important for efficient photocatalytic degradation. Surface charge of mineral substances is usually defined by their point of zero charge (pH_{pzc}),

Table 1
ZnO nanoparticles synthesis conditions and photocatalytic activities

ZnO nanoparticles	Complexing agent type	Complexing agent/Zn^{2+} ratio	Calcination temperature (℃)	Photocatalytic activity against SMX (%)[a]
ZnO (1)	Urea	1/1	800	32
ZnO (2)	Urea	2/1	800	34.6
ZnO (3)	Urea	3/1	800	34.7
ZnO (4)	Glycin	1/1	800	32.9
ZnO (5)	Glycin	2/1	800	36.4
ZnO (6)	Glycin	3/1	800	41
ZnO (7)	Citric acid	1/1	800	49
ZnO (8)	Citric acid	2/1	800	48.3
ZnO (9)	Citric acid	3/1	800	54.6
ZnO (10)	Citric acid	3/1	500	60.2

[a] Operational conditions: photodegradation experiments were performed on 200 mL of 10 mg L^{-1} antibiotic solutions (pH 7), containing 0.25 g L^{-1} ZnO nanoparticles.

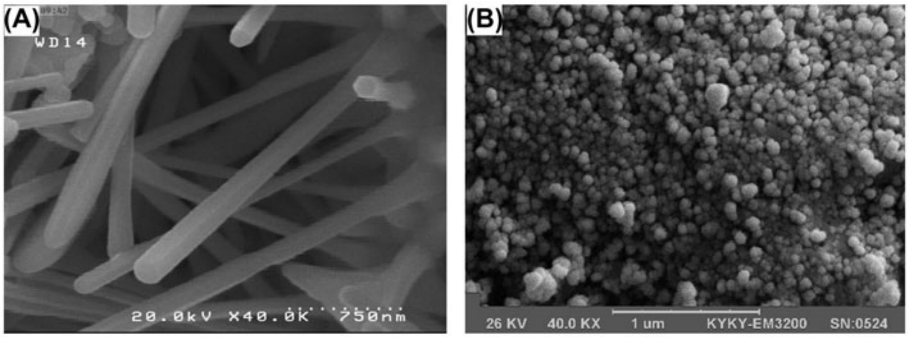

Fig. 1. SEM images of ZnO nanoparticles. (A) ZnO 9, calcined at 800℃ and (B) ZnO 10, calcined at 500℃.

the pH at which the surface has a net neutral charge. At pH values below the pH_{pzc}, H^+ ions reside on surface rather than the low pH solution, resulting in positively charged surface, alternatively, when pH_{pzc} is exceeded, H^+ ions enter high pH solution, resulting in negatively charged surface. ZnO has been reported to have the pH_{pzc} of 9, which means positive surface charge at pH 4 and 7 and negative surface charge at pH 10 [20].

Fig. 3 shows degradation profiles of antibiotic compounds in three investigated pH values. Photolytic degradation profile in the pH value in which the most degradation has occurred is also shown for each antibiotic. Fig. 3(A) indicates better photocatalytic degradation of AMX at pH 10. The extra amine group on the side chain of AMX increases its stability against hydrolysis compared with conventional penicillins in acidic environment of stomach [21]. Although this property enables its oral administration, AMX is still among the most susceptible antibiotics to hydrolysis, especially in basic solutions. From the photodegradation profiles, it can be concluded that basic hydrolysis of AMX performs as an assistant factor, probably by degrading AMX to simpler structures for further photocatalytic degradation.

Fig. 3(B) shows that SMX degradation decreases with the increase in pH from 4 to 7 and then to 10. Although sulfonamides are highly stable towards hydrolysis, they decompose readily in aqueous solutions under the influence of UV light. Sulfamethoxazole photodegradation has been found to be strongly dependent on the state of ionization, and it is more stable in anion form at pH values above its $pK_a = 5.6$ [22–24]. Lowest degradation observed at pH 10 is also the result of electrostatic repulsion between SMX anions and negatively surface charged ZnO nanoparticles.

Based on above findings, pH values 4 and 10 were chosen for further photocatalytic experiments on SMX and AMX, respectively.

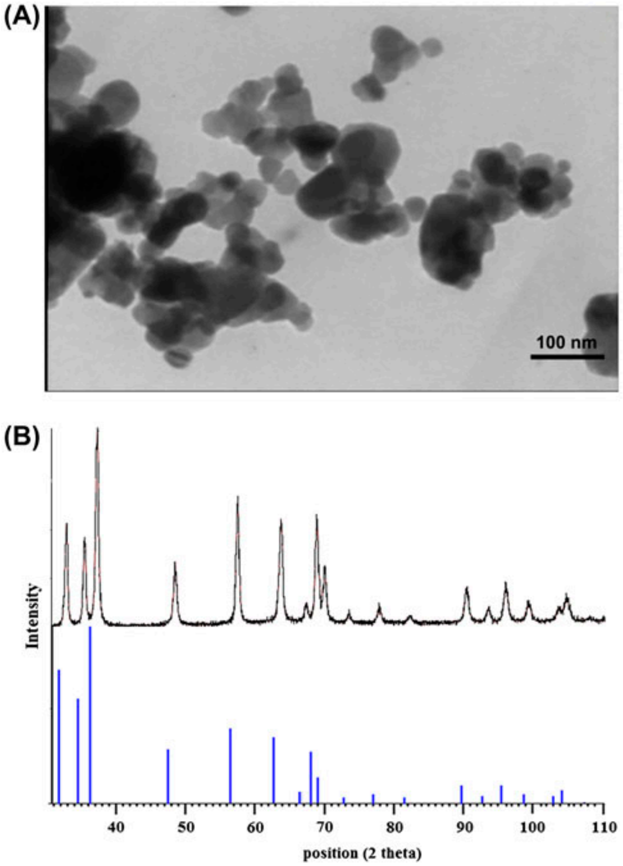

Fig. 2. (A) TEM image of ZnO 10 and (B) XRD patterns of ZnO 10 and standard zinc oxide (P63MC).

3.3. *Effect of initial antibiotic concentration and kinetic analysis*

Effect of varying initial concentrations of antibiotics on photocatalytic degradation was investigated, using a range of concentrations between 5 and 20 mg L^{-1} (Fig. 4).

Initial concentration of pollutant has a fundamental effect on the degradation rate of heterogeneous photocatalytic reactions. Photocatalytic degradation of AMX and SMX follow pseudo-first-order kinetics according to Eq. (2).

$$r = -\frac{dC}{dt} = k_{obs}C \tag{2}$$

In this equation, k_{obs} represents the apparent pseudo-first-order kinetics constant (mg L^{-1} min^{-1}), C (mg L^{-1}) is the concentration at each time (t), and C_0 (mg L^{-1}) is the initial concentration of pollutant. This equation can be transformed to Eq. (3), after integration.

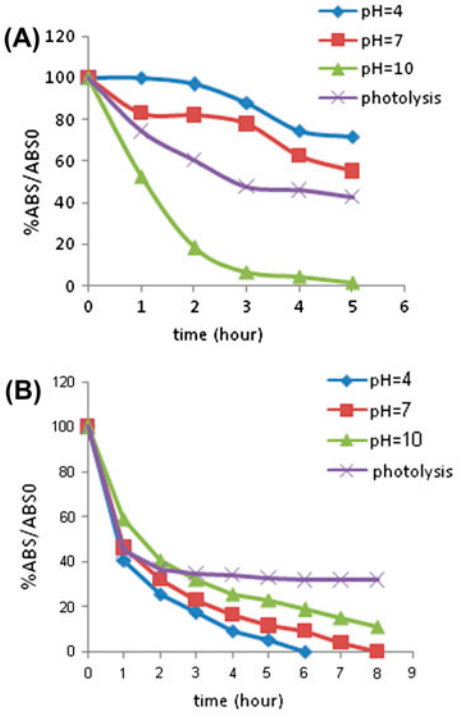

Fig. 3. Photocatalytic degradation of (A) AMX and (B) SMX in different pH values. Operational condition: photodegradation experiments were performed on 200 mL of 10 mg L^{-1} antibiotic solutions adjusted to the desired pH with 1 N HCl or 1 N NaOH, containing 0.25 g L^{-1} ZnO nanoparticles.

$$-\ln\frac{C}{C_0} = k_{obs}t \tag{3}$$

As can be seen in Fig. 5, plots of $-\ln(C/C_0)$ vs. time for different initial concentrations of both antibiotics yield linear curves that provide the values of k_{obs} after regression analysis (Table 2). From data presented in Table 2, it is deduced that lower initial concentrations of both antibiotics are in better agreement with pseudo-first-order kinetics and have higher rate constants. It means that at lower concentrations, a larger portion of the available antibiotic concentration is degraded every one hour, although total amount of degradation per hour increases with initial concentration. Degradation profiles and rate constants indicate faster degradation of AMX compared with SMX. AMX is also degraded more efficiently at higher initial concentrations. These observations can be explained by inherent instability of AMX chemical structure, especially in pH value that experiments were performed in. On the other hand, SMX is known for its refractory

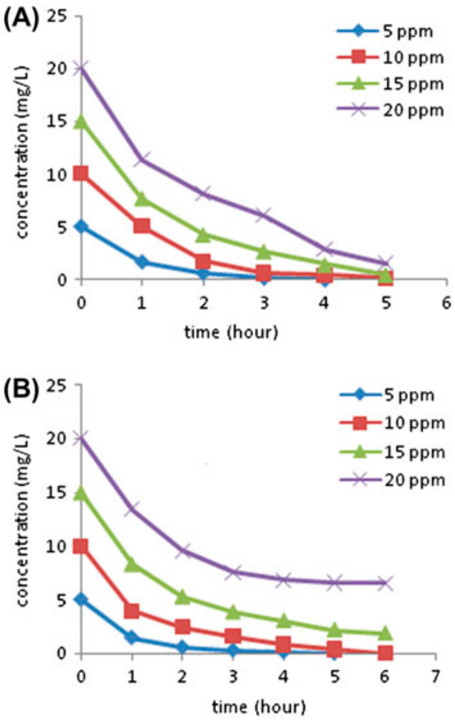

Fig. 4. Photocatalytic degradation of varying initial concentrations of (A) AMX and (B) SMX. Operational condition: same as Fig. 3, antibiotic solutions were adjusted to pH 10 for AMX and pH 4 for SMX.

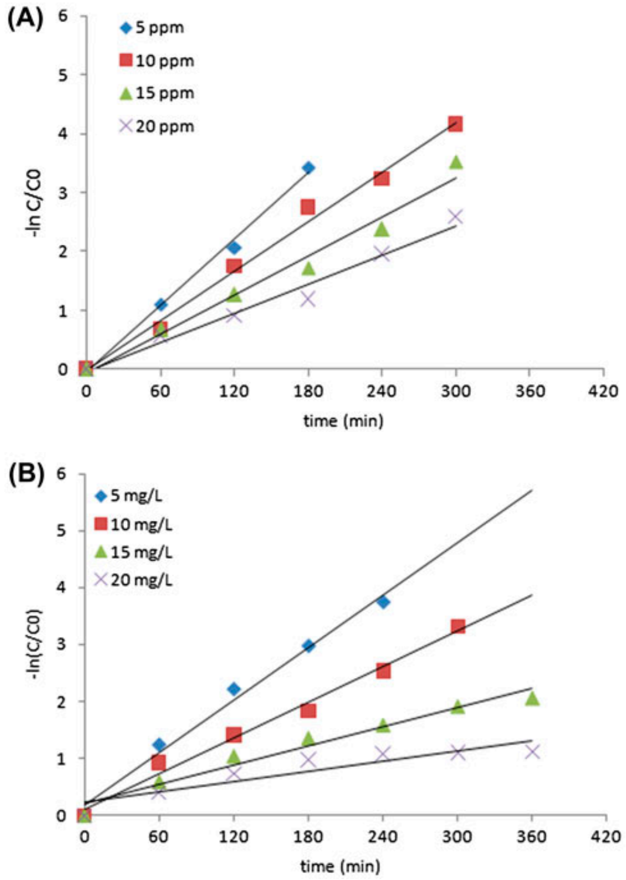

Fig. 5. Plots of $-\ln(C/C_0)$ vs. time for different concentrations of (A) AMX and (B) SMX.

structure which resists against different treatment methods.

Another useful rate expression for heterogeneous photocatalytic reactions is Langmuir–Hinshelwood (L–H) model which determines the surface reaction and adsorption constants using the relationship between initial degradation rate and initial concentration of the pollutant (Eq. (4)) [25]. These constants provide good vision of what happens during the surface reaction. Photocatalytic reactions proceed on the surface of semiconductor materials and it will not be surprising that their rate is proportional to the surface coverage of the photocatalyst by pollutant molecules [26]. As mentioned above, equilibrium of adsorption/desorption of antibiotic molecules on the surface of ZnO nanoparticles was achieved in almost 30 min. This was recognized through stirring 10 mg L^{-1} of antibiotic solutions containing 0.25 g L^{-1} ZnO nanoparticles in dark. Samples were taken every 5 min and analyzed

Table 2
Pseudo-first-order kinetics apparent constant values and corresponding regression coefficients for different initial concentrations of AMX and SMX

	AMX		SMX	
Initial concentration, C_0 (μg/mL)	k_{obs}	R^2	k_{obs}	R^2
5	0.018	0.995	0.015	0.987
10	0.014	0.991	0.010	0.987
15	0.011	0.978	0.006	0.963
20	0.008	0.975	0.005	0.842

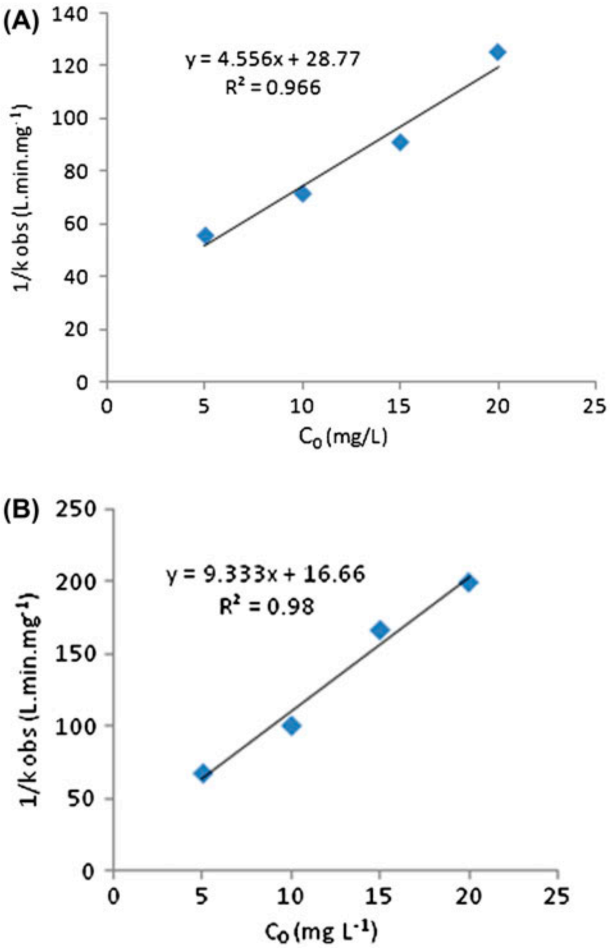

Fig. 6. Linear variation of $1/k_{\mathrm{obs}}$ values vs. their corresponding initial concentrations for (A) AMX and (B) SMX.

for the amount of antibiotic molecules adsorbed on the surface of ZnO nanoparticles. This amount reached 1.6 and 7.3% of antibiotic concentration for AMX and SMX, respectively. Antibiotic concentration in this point was considered as initial antibiotic concentration (C_0) and then irradiation started for photocatalytic degradation.

$$r_0 = -\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{k_{\mathrm{c}} \cdot \mathrm{KLH} \cdot C_0}{1 + \mathrm{KLH} \cdot C_0} = k_{\mathrm{obs}} \cdot C_0 \tag{4}$$

Eq. (4) can be written as below (Eq. (5));

$$\frac{1}{k_{\mathrm{obs}}} = \frac{1}{k_{\mathrm{c}} \cdot \mathrm{KLH}} + \frac{C_0}{k_{\mathrm{c}}} \tag{5}$$

In these equations, k_{c} and K_{LH} represent the rate constant of surface reaction (mg L^{-1} min^{-1}) and L–H adsorption equilibrium constant (L mg^{-1}), respectively. Obtaining linear curves via plotting $1/k_{\mathrm{obs}}$ values vs. their corresponding initial concentrations, confirmed that photocatalytic degradation of AMX and SMX obey the L–H model (Fig. 6). According to Eq. (4), k_{c} and K_{LH} were calculated as 0.22 mg L^{-1} min^{-1} and 0.16 L mg^{-1} for AMX and 0.11 mg L^{-1} min^{-1} and 0.56 L mg^{-1} for SMX, respectively. According to these data, AMX molecules get adsorbed and degraded at a relatively similar pace, but in the case of SMX, adsorption takes place more rapidly and degradation reaction seems to be the rate-limiting step in whole photocatalytic degradation process.

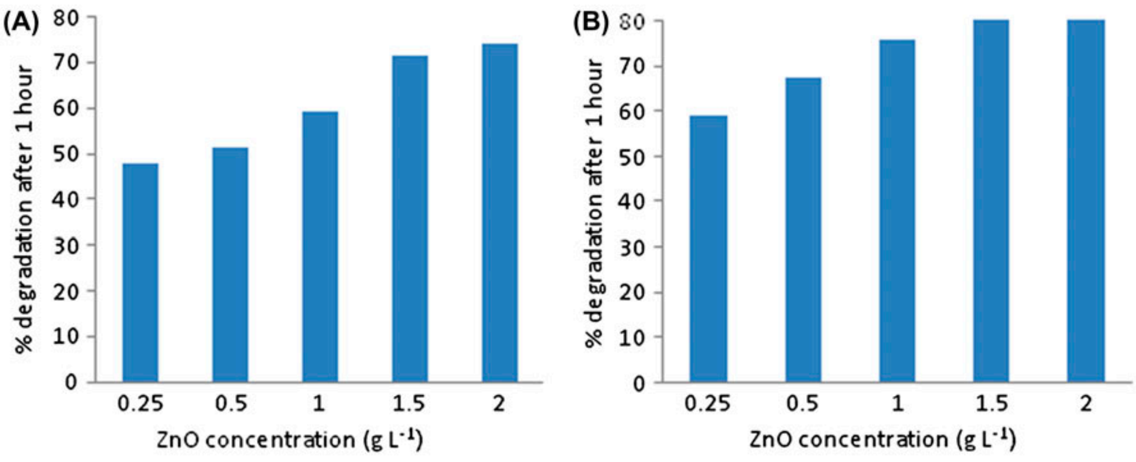

Fig. 7. Efficiency of different concentrations of ZnO nanoparticles for degrading (A) AMX and (B) SMX. Operational condition: same as Fig. 3, antibiotic solutions were adjusted to pH 10 for AMX and pH 4 for SMX. Percent of antibiotic degradation using each photocatalyst concentration was investigated after 1 h.

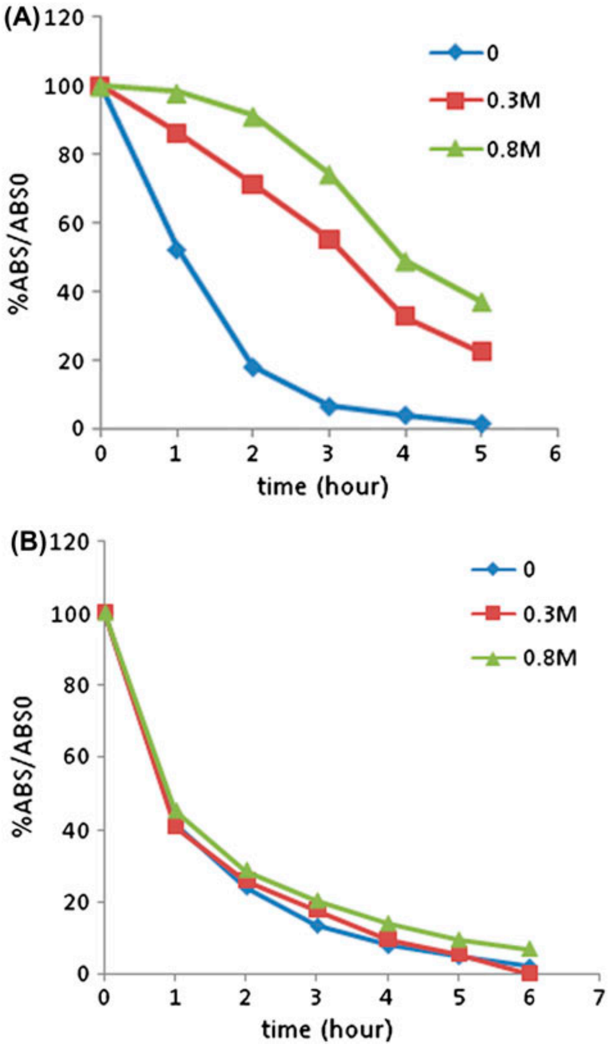

Fig. 8. Effect of presence of NaCl on photocatalytic degradation of (A) AMX and (B) SMX. Operational condition: same as Fig. 3, antibiotic solutions in water or 0.3 M or 0.8 M NaCl solution were adjusted to pH 10 for AMX and pH 4 for SMX.

3.4. Effect of ZnO concentration

Photocatalytic degradation of AMX and SMX were performed using different concentrations of ZnO nanoparticles. Fig. 7 shows that photocatalytic activity improves by increasing the photocatalyst concentration from 0.25 to 1.5 g L^{-1}, while further increase to 2 g L^{-1} made just a slight increase in antibiotic degradation. Increasing the photocatalyst concentration at first phase provides more active sites on the surface of ZnO nanoparticles for antibiotic molecules to be adsorbed and degraded. This phenomenon continues up to ZnO concentration of 1.5 g L^{-1}, based on the operational conditions of this study like reactor geometry, wavelength, and intensity of light source that affect the illumination of photocatalyst nanoparticles. At higher photocatalyst concentrations, screening effect of excess nanoparticles decreases the penetration of UV light and avoids further improvement in photocatalytic activity [26,27]. According to these observations, the best ZnO concentration for obtaining the highest antibiotic degradation using the experimental setup of this study is 1.5 g L^{-1}.

3.5. Effect of presence of NaCl salt

This test was performed in order to investigate the photocatalytic degradation of antibiotic compounds in solutions containing mineral ions and salts such as NaCl. Presence of mineral ions affects photocatalytic degradation of organic pollutants in different ways. After being adsorbed on the surface of photocatalyst materials, they can hinder photocatalytic degradation by interfering with electron transport and free radical production or conversely improve it through trapping valence band electrons and inhibiting their recombination with holes.

Fig. 8 compares AMX and SMX degradation profiles in water and 0.3 or 0.8 M NaCl solutions. These profiles show that while photocatalytic degradation of AMX significantly decreases in the presence of NaCl, SMX degradation is not affected. It seems that physicochemical properties of pollutant molecule play the main role in determining the effect of mineral ions on photocatalytic reactions.

3.6. Effect of buffered antibiotic solution

Photocatalytic degradation of antibiotic compounds was performed in 0.2 M phosphate buffer solution in order to investigate the effect of buffered solution on maintaining the initial pH and also possible interactions of phosphate ions with photocatalytic activity [28]. As mentioned above, pH of antibiotic solution is a key factor due to its effect on both adsorption of antibiotic molecules on the surface of photocatalyst particles and also their susceptibility to degradation. Although antibiotic solutions are adjusted to the pH value in which the highest degradation occurs, degradation of the main compound to a variety of degradation products results in the fluctuation of pH during the photocatalytic experiment. As Fig. 9 shows, pH of buffered solutions of antibiotics was maintained constant during the experiments. However, photocatalytic degradation decreased significantly which can be the result of adsorption of phosphate ions on the surface of ZnO nanoparticles and inhibiting their

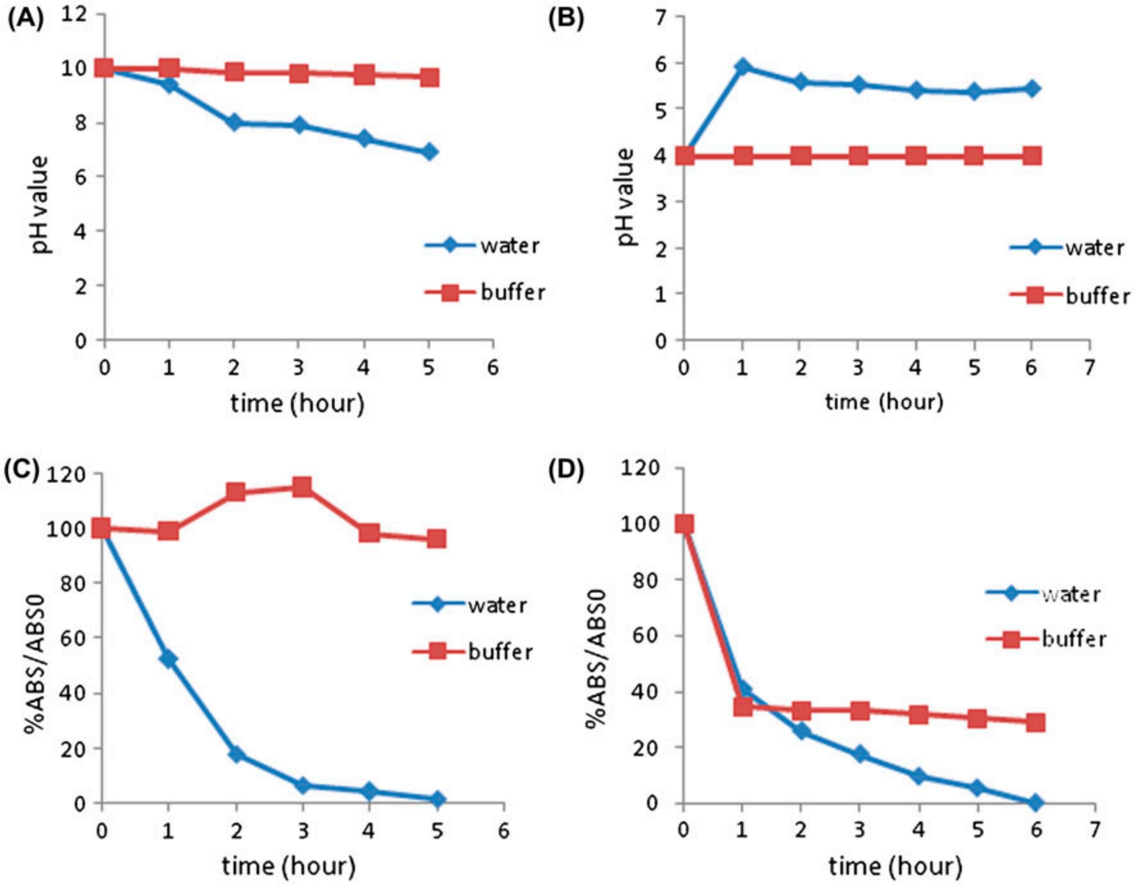

Fig. 9. Effect of buffered solutions of antibiotics on photocatalytic degradation. (A) pH profile of AMX solution, (B) pH profile of SMX solution, (C) degradation profile of AMX, and (D) degradation profile of SMX. Operational condition: same as Fig. 3, antibiotic solutions in water or 0.2 M phosphate buffer were adjusted to pH 10 for AMX and pH 4 for SMX.

active sites for pollutant molecules to be adsorbed and degraded.

3.7. Mineralization of antibiotic solutions

Concentration of total organic carbon (TOC) was used as an index for ability of ZnO nanoparticles in mineralization of antibiotic solutions [29]. After six hours of photocatalytic degradation, which leads to complete removal of main compounds, TOC removal was 62.8 and 20.8% for AMX and SMX, respectively. Extending the reaction time to 12 and then 24 h did not change the amount of TOC concentration. Although mineralization did not continue until complete disappearance of organic matter, partial mineralization is likely to be sufficient for removing the antimicrobial properties of both antibiotics and their adverse effects on the environment and human health. However, further studies are needed to confirm this suggestion [30].

3.8. Reusability of ZnO nanoparticles

Reusability is an important feature of heterogeneous photocatalyst materials for their practical application [31]. In order to investigate the efficiency of ZnO nanoparticles in second and third cycle of use, they were removed after being used for the first time. Two subsequent photodegradation experiments were then performed using these photocatalysts after being washed with water, dried and weighed, each time. Results shown in Fig. 10 indicate the stability of ZnO nanoparticles for at least three photodegradation cycles, although degradation efficiency has decreased about ten percent after each cycle.

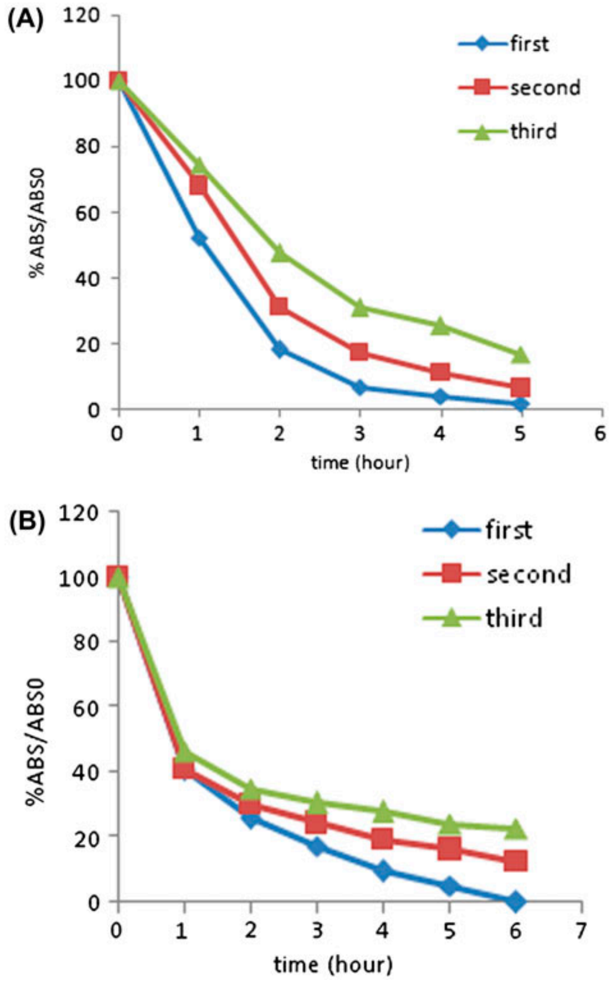

Fig. 10. Photocatalytic degradation of (A) AMX and (B) SMX using recycled ZnO nanoparticles. Operational condition: same as Fig. 3, antibiotic solutions were adjusted to pH 10 for AMX and pH 4 for SMX.

4. Conclusion

ZnO/UV-C was an efficient photocatalytic system for removal and mineralization of AMX and SMX from aqueous solutions. Microwave-assisted gel combustion method using citric acid as complexing agent at three fold of Zn^{2+} ions concentration and low calcination temperature produced the most active photocatalyst material with average crystallite size of 25.82 nm. Photocatalytic degradation was significantly dependent on operational and environmental factors such as pH of antibiotic solution, photocatalyst loading amount, initial antibiotic concentration, and presence of different ions.

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