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Photocatalytic degradation of some β-lactam antibiotics in aqueous suspension of ZnS nanoparticles

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ABSTRACT

The photodegradation of β-lactam antibiotics such as amoxicillin (AMO), ampicillin (AMP), penicillin G (PEG), penicillin V (PEV), and cloxacillin (CLX) is studied in the presence of ZnS nanoparticles as photocatalyst. The ZnS nanoparticles are prepared by controlled precipitation method and characterized by transmission electron microscopy image. The optimized conditions for degradation of β-lactam antibiotics are pH 4.5 and 0.5 mg L^{-1} of catalyst. The degradation rate of β-lactam antibiotics is in order of: CLX > PEG > PEV > AMP > AMO, that is mutual agreement with order of β-lactam Antibiotics instability. The photodegradation rate of CLX, PEG, PEV, AMP, and AMO are obtained 5.51×10^{-2}, 3.23×10^{-2}, 2.85×10^{-2}, 1.70×10^{-2} and 1.45×10^{-2} min^{-1}, respectively, at initial concentration of 50 mg L^{-1}. The oxidation of antibiotics molecules is confirmed with decreasing of chemical oxygen demand (COD) values of β-lactam solutions. The proposed method is used for degradation of high amounts of β-lactam antibiotics (1,000 mg L^{-1}) in real samples.

Keywords: β-lactam; Antibiotic; Degradation; ZnS; Photocatalyst

1. Introduction

Among all the pharmaceutical compounds that cause contamination of the environment, antibiotics occupy an important place due to their high consumption rate in both veterinary and human medicine [1]. A problem that may be created by the presence of antibiotics in low concentration in the environment is the development of antibiotic resistant bacteria [2–4]. The incidence of antibiotic resistant bacteria has increased and many people believe the increase is due to the use of antibiotics [5]. Antibiotics act as persistent and bioaccumulative contaminants and by their nature, they are biologically active compounds, developed to have an effect on organisms [5]. Therefore, they have the potential to negatively affect either aquatic or terrestrial ecosystems, even in low concentrations. Thus, the large amounts of antibiotics in the range of mg L^{-1} in wastewater of pharmaceutical industrials can affect seriously on the environmental conserve [6,7]. Besides that, antibiotics can also produce antibacterial resistance among micro-organisms and be responsible for several allergenic responses [6,7]. β-Lactam antibiotics such as amoxicillin AMO), ampicillin (AMP), penicillin G (PEG), penicillin V (PEV), and cloxacillin (CLX) show antimicrobial properties from the presence of a β-lactam ring. They are widely used in human and

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veterinary medicine. With respect to environmental subsistence effects of β-lactam antibiotics, the development of purification methods of wastewater even in high concentrations of pollutants is a drastic effort [7]. The proposed method to purification must be inexpensive, effective, and safe.

The concern regarding water contamination and consequent man exposure to it has stimulated the development of methods capable of removing pharmaceutical residues efficiently. Based on this need, the advanced oxidation processes (AOP) have been investigated, due to their potential as alternatives or as a complement to conventional wastewater treatment, since the hydroxyl radicals generated from these processes are highly reactive and efficient in oxidizing a great variety of organic contaminants [8–10].

The use of semiconductors such as TiO_2, ZnS, ZnO, CdS, Fe_2O_3, and so on in photodegradation process as photocatalyst is one serious technique for increasing the rate of destruction [11,12]. The high photocatalytic activity, resistance to photocorrosion, low cost, nontoxicity, and favorable band gap energy are the advantages of a worthy suitable photocatalyst. Thus, synthesis of different photocatalysts with various compositions and study of organic pollutants destruction can be an attractive field of researches [13]. Photocatalytic reaction is initiated when a photoexcited electron is promoted from the filled valence band of semiconductor to the empty conduction band as the absorbed photon energy, h, equals or exceeds the band gap of the semiconductor. Thus in concert, electron and hole pair (e^-–h^+) are generated in conduction band and valence band, respectively [12,13].

In the light of the literature studies, this study was designed to provide a systematic approach for photocatalytic degradation of AMO, AMP, PEV, PEG, and CLX in real samples. The pH of samples and the dosage of photocatalyst nanoparticles are optimized while degradation efficiency of antibiotic compounds was the objective functions to be optimized.

2. Experimental

2.1. Chemicals and standards

All of materials were purchased from highest purity. All solutions were prepared with double distilled water.

Antibiotics of AMO ($C_{16}H_{19}N_3O_5S, \geq 900$ μg per mg, Ref. A8523), AMP ($C_{16}H_{18}N_3NaO_4S$, D-(−)-α-aminobenzylpenicillin sodium salt, Ref. A0166), PEV ($C_{16}H_{17}N_2O_5SK$, phenoxymethylpenicillinic acid potassium salt, Ref. P4807), PEG ($C_{16}H_{17}KN_2O_4S$, benzylpenicillin potassium salt, Ref. P7794), and CLX ($C_{19}H_{17}ClN_3O_5SNa{\cdot}H_2O$, Ref. C9393) were obtained from Sigma–Aldrich.

The aqueous stock solutions of 1,000 mg L^{-1} of antibiotic compounds were prepared and from these calibration standards with concentrations between 50 and 1,000 mg L^{-1} were prepared in distilled water. Acetonitrile HPLC grade and o-phosphoric acid 85% p.a., all from Merck, were utilized.

The $Zn(CH_3COO)_2{\cdot}2H_2O$ and $Na_2S{\cdot}9H_2O$ as precursors were used to prepare the ZnS nanoparticles. 2-Mercaptoethanol ($HOCH_2CH_2SH$) was used as capping agent in synthesis process of nanoparticles. Hydrochloric acid and sodium hydroxide were used to adjust of pH of samples.

For preparation of ZnS nanoparticles, 50 ml of 0.1 mol L^{-1} Na_2S solution in a decanter vessel was added drop by drop into 50 ml of 0.1 mol L^{-1} zinc acetate and 0.5 mol L^{-1} 2-mercaptoethanol solutions while the mixture was stirred vigorously at room temperature. The ZnS nanoparticles were separated, washed with deionized water and ethanol several times, and dried in an oven at 80°C for 4 h [14–18].

2.2. Photodegradation of antibiotics and analysis of samples

The photodegradation of antibiotic compounds catalyzed by ZnS nanoparticles was performed in a cylindrical glass reactor at 25°C. The degradation was carried out using a 500 W halogen lamp as the visible light source with UV cut-off filter (Toshiba UV-D35, >350 nm) [19]. Slurry solutions containing ZnS (0.1–1.0 g L^{-1}) and antibiotic (50–1,000 mg L^{-1}) was magnetically stirred and irradiated under simulated visible light. Each degradation experiment is repeated three times to study the reliability of the data. The concentration of antibiotic compounds was analyzed by a high-performance liquid chromatograph (Alliance 2,690, UV-detection at wavelengths of 230–254 nm) using a C18 column. The mobile phase was mixture of acetonitrile: KH_2PO_4 solution (0.02 M) with V/V% of 4:96 at pH 5.0 ± 0.1 which was fed to HPLC with a flow rate of 0.5 mL min^{-1} running in isocratic conditions. Antibiotic compounds solutions (0–1,000 mg L^{-1}) with injection volume of 0.1 ml were used as calibration standards.

The Millipore membrane filters and centrifugation of samples were used to remove the particles before analysis of samples. The peak area of antibiotic compounds was used to calculate the residual concentration of β-lactam antibiotics and degradation efficiency was estimated by Eq. (1).

$$\%\text{Degradation} = 100\,[1 - (C_t/C_0)] \quad (1)$$

where C_o and C_t are antibiotic concentration at initial and time t, respectively.

The pH of the antibiotic solutions was adjusted by using HCl or NaOH 1 mol L^{-1} at range of pH 2.5–12.0 (final condition) by a pH meter (Metrohm 661) with a pH electrode (Metrohm Company). Chemical oxygen demand (COD) was determined by a standard dichromate method [20].

3. Results and discussion

3.1. Photodegradation of antibiotic compounds catalyzed by ZnS nanoparticles

The synthesis of ZnS nanoparticles is confirmed by transmission electron microscopy (TEM) image (Fig. 1). Also, Fig. 2 shows the X-ray diffraction pattern of nanosized ZnS. The XRD peaks correspond to the Bragg angles for the (1 1 1), (2 2 0), and (3 1 1) planes of cubic ZnS.

The effect of ZnS nanoparticles as photocatalyst in photodegradation of antibiotic compounds is shown in Fig. 3. The data are the average of three times replications. The pH of sample is 4.5 and the dosage of ZnS is 0.1 g/L. As seen, an increasing of three to five times in degradation efficiency is observed at presence of ZnS nanoparticles. Metal sulfides are considered attractive candidates for photocatalytic reactions [21,22]. The valence band of metal sulfides normally consists of 3p orbitals of S, which result in a more negative valence band and narrower band gap (3.54 eV at 300 K for ZnS) as compared to metal oxides [21].

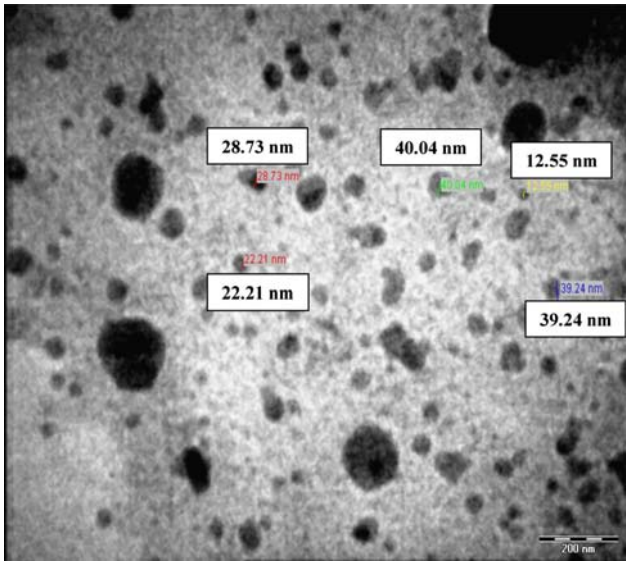

Fig. 1. TEM image of ZnS nanoparticles.

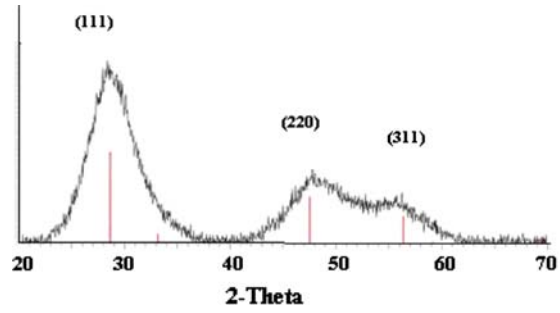

Fig. 2. X-ray diffraction pattern of nanosized ZnS.

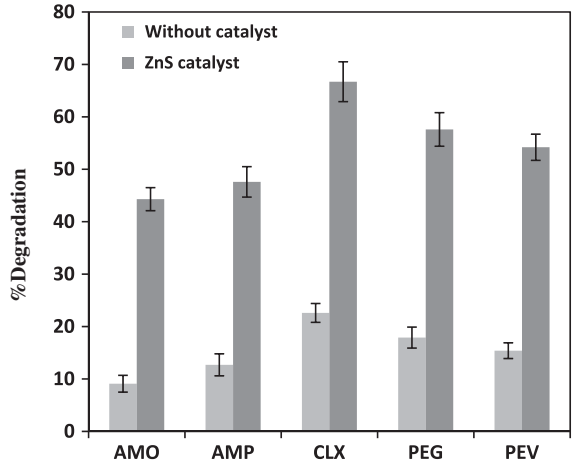

Fig. 3. The photocatalytic effect of nanosized ZnS (0.1 g/L) on the degradation of β-lactam antibiotics (500 mg L^{-1}); pH 4.5 and time of 60 min.

Zinc sulfide shows a remarkable chemical stability against oxidation and hydrolysis. Seriously, the chemical stability is retained with decreasing of particles size to just a few nanometers [22–25]. Thus, nanosized ZnS are interesting entities for catalytic activities such as photocatalytic degradation of pollutants and hydrogen production from splitting of water. ZnS nanomaterials show good photocatalytic activity due to rapid generation of electron–hole pairs by photoexcitation and highly negative reduction potentials of excited electrons [26–30]. The band gap of nanosized ZnS is less than 3.54 eV and therefore, the nanoparticles show approximately an absorption peak in wavelength of $\geq$ 350 nm.

AMO, AMP, CLX, PEV, and PEG are semi-synthetic penicillin obtaining their antimicrobial properties from the presence of a β-lactam ring. These antibiotic compounds show maximum absorbance at wavelengths of less than 300 nm, and they can absorb light below 300 nm. Therefore, β-lactam compounds can be degraded by irradiation with wavelengths higher than 300 nm. Also, degradation of antibiotics is

presumptive from antibiotic hydrolysis at the absence of any photocatalyst. The hydrolysis reaction would proceed through the attack of the nucleophile H_2O to the β-lactam ring followed by ring opening [2]. As a result, the increasing of degradation of antibiotic compounds in aqueous suspension of ZnS nanoparticles is mainly due to the active species of hydroxyl radicals, holes, superoxide ions, and hydroperoxyl radicals that are produced during the photocatalytic process.

The effect of isopropanol as a scavenger is studied to estimate the oxidation mechanism of β-lactam compounds. The degradation yield of amoxicillin is decreased from 44.3% to 33.9% at presence of 6% V/V iso-PrOH. Isopropanol as a good scavenger is more easily oxidized by $OH^{\bullet}$ radicals with rate constant of reaction 1.9×10^9 M^{-1} s^{-1}. The reduction of degradation yield indicates that the $OH^{\bullet}$ radicals play a considerable role in the photodegradation process [14,15].

Despite of the low amounts of antibiotic compounds in natural waters (in range of ng L^{-1} to mg L^{-1}), degradation of high amounts of these compounds (1,000 mg L^{-1}) show ability of proposed method for treatment of polluted waters.

3.2. Optimization of degradation process

The pH of wastewater influences the characteristics of organic pollutants, particularly the charge of species, solubility in water, and hydrophobicity [11]. The antibiotic compounds with carboxylic group and other functional groups show a wide variation in charge and thus the physicochemical properties. The pH of point of zero charge (pHpzc) of zinc sulfide is 7.0–7.5 [16]. Therefore, the surface charge of ZnS nanoparticles is negative at pH > pHpzc and positive at pH < pHpzc. These characteristics affect significantly on the adsorption–desorption properties of pollutant molecules on the surface of zinc sulfide.

The effect of antibiotics solution pH on the degradation yields at time of 60 min is shown in Fig. 4. The minimum degradation is seen at pH 2.5 that is consequent from electrostatics repulsion between antibiotic molecules and surface of catalyst. However, the degradation increase with increasing of samples pH. The more degradation at basic pH is due to the hydrolysis of antibiotics. So that, a 100% degradation is obtained at pH = 12.0. But, prevailing degradation is due to the active species of photocatalytic reactions at natural pH of the antibiotics solutions (pH of 4–5). Also, the degradation rate of antibiotic

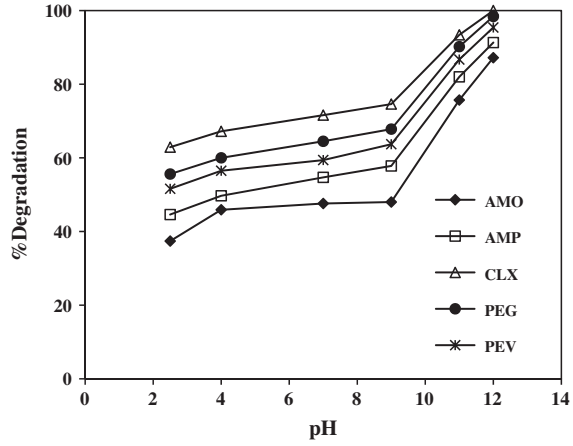

Fig. 4. The pH effect on the degradation of β-lactam antibiotics (500 mg L^{-1}) catalyzed by ZnS (0.1 g L^{-1}) nanoparticles at time of 60 min.

compounds did not show any considerable change at pH range of 4–9. Therefore, the degradation reactions are followed at pH of 4.5 that is pH of prepared solutions of antibiotic compounds. The blank samples of antibiotic solutions at pH 4.5 showed a degradation < 5% that is due to hydrolysis of antibiotics.

The rate of photocatalytic reaction is strongly dependent on dosage of the catalyst. Usually, the rate of heterogeneous photocatalytic process increase with catalyst loading [31]. However, in photodegradation reactions, the catalyst concentration must be optimized, in order to avoid excess catalyst and ensure total absorption of efficient photons [32]. Fig. 5 shows the degradation efficiency of antibiotic

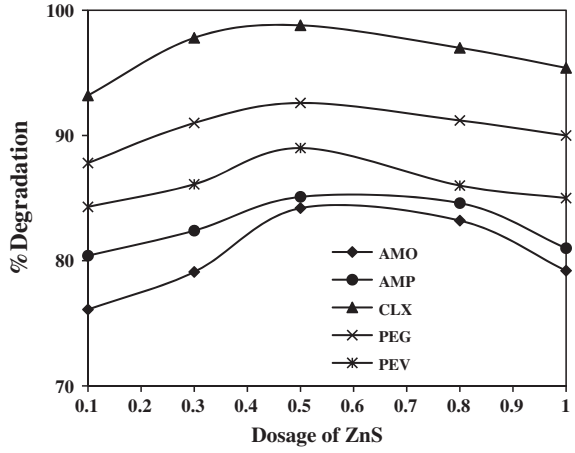

Fig. 5. The effect of ZnS dosage on the photodegradation of β-lactam antibiotics (500 mg L^{-1}); pH 4.5 and time of 120 min.

compounds at different amounts of nanosized ZnS in amplitude of 0.1–1.0 g L^{-1}. The results indicate the increasing of degradation with increasing the amount of catalyst from 0.1 to 0.5 g L^{-1} and then diminish with loading of photocatalyst above of 0.5 g L^{-1}. The increasing of the degradation rate may be due to the enhancement in the availability of active sites and thus the increasing of the number of antibiotic molecules adsorbed on the surface of catalyst as well as the increasing the density of particles in the area of illumination. At higher catalyst loading of 0.5 g L^{-1}, the degradation of antibiotic molecules decreases because the activated molecules are deactivated by agglomeration. The radiation penetration is also decreased and the radiation scattering increase at higher amounts of photocatalyst [33].

3.3. Rate of antibiotics degradation

Organic molecules with adherent effectively to the surface of the catalyst will be more ready to direct degradation [34]. Thus, it is expected that the photocatalytic degradation of antibiotic compounds is dependent on the molecular structure and initial concentration (C_o). Usually, the kinetics data of the photocatalytic reactions are fit to specific models of Langmuir–Hinshelwood (L–H) mechanism [35].

$$R = -dC/dt = k\mathrm{KC}/(1 + \mathrm{KC}) \quad (2)$$

where K is the Langmuir–Hinshelwood adsorption equilibrium constant (L mg^{-1}) and k is the rate constant of surface reaction (mg $L^{-1}min^{-1}$). At low concentrations of substrate (the concentrations of below 1,000 mg L^{-1}) and when the product $\mathrm{KC} << 1$, Eq. (2) collapses to an expression similar to that applicable for first-order kinetics.

$$-dC/dt = k\mathrm{KC} = k_{app}C \quad (3)$$

In Eqs. (2) and (3), C is the (time dependent) antibiotic concentration and k_{app} (min^{-1}) in Eq. (3) is a pseudo-first-order rate constant.

The pseudo-first-order rate constant of antibiotics degradation reactions at range of 50–1,000 mg L^{-1} is calculated with measurement of antibiotic concentration at various times. The calculated rate constants and uncertainty of data are given in Table 1. The R^2 values of fitted curves are between 0.9872 and 0.9941. As seen, the degradation rate of antibiotics decreases with increasing initial concentration. Apparently, the adsorption of antibiotic molecules on the catalyst surface and the absorption of photons by antibiotic molecules are increased at higher concentrations. Therefore, the reduction of number of photons for generation of electrons–holes and the active sites at the catalyst surface are due to decreasing of degradation efficiencies [12,13].

Also, the photodegradation rate catalyzed by ZnS nanoparticles is in order of: CLX > PEG > PEV > AMP > AMO. The significant properties of penicillin molecule, including its antibacterial activity and chemical activity could possibly be described due to the reaction of the β-lactam ring with the thiazolidine ring. The strain extended the reaction of the five-membered thiazolidine ring with the four-membered β-lactam ring leading to nonplanarity of the molecule that is make it to a large angle and torsional rotation [36]. These parameters are due to any kind of nucleophilic attack in particular at presence of acid, base or even neutral molecules of water. Thus, the hydrolysis of the penicillin β-lactam bond has more pronounced susceptibility at these conditions. As a result, the greater instability of penicillin molecule is mainly responsible for degradation rate. Therefore, the order of photodegradation rate of antibiotic molecules is

Table 1
The pseudo-first-order rate constant, k_{app} (min^{-1}), and standard deviation ($n = 3$) of antibiotic photodegradation catalyzed by ZnS nanoparticles at various initial concentrations

Antibiotic	Concentration, mg L^{-1}				
	50	250	500	750	1,000
Amoxicillin	$1.45 \pm 0.10 \times 10^{-2}$	$1.14 \pm 0.14 \times 10^{-2}$	$1.06 \pm 0.07 \times 10^{-2}$	$0.94 \pm 0.07 \times 10^{-2}$	$0.73 \pm 0.10 \times 10^{-2}$
Ampicillin	$1.70 \pm 0.12 \times 10^{-2}$	$1.42 \pm 0.09 \times 10^{-2}$	$1.18 \pm 0.06 \times 10^{-2}$	$1.00 \pm 0.06 \times 10^{-2}$	$0.83 \pm 0.09 \times 10^{-2}$
Penicillin V	$2.85 \pm 0.15 \times 10^{-2}$	$1.85 \pm 0.07 \times 10^{-2}$	$1.46 \pm 0.10 \times 10^{-2}$	$1.12 \pm 0.08 \times 10^{-2}$	$0.97 \pm 0.11 \times 10^{-2}$
Penicillin G	$3.23 \pm 0.08 \times 10^{-2}$	$2.64 \pm 0.10 \times 10^{-2}$	$1.81 \pm 0.12 \times 10^{-2}$	$1.50 \pm 0.11 \times 10^{-2}$	$1.22 \pm 0.06 \times 10^{-2}$
Cloxacillin	$5.51 \pm 0.09 \times 10^{-2}$	$3.43 \pm 0.08 \times 10^{-2}$	$2.46 \pm 0.11 \times 10^{-2}$	$1.99 \pm 0.09 \times 10^{-2}$	$1.33 \pm 0.08 \times 10^{-2}$

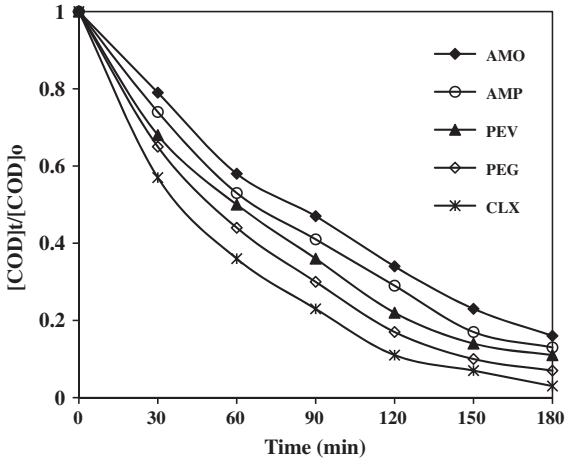

Fig. 6. The ratio of [COD]t/[COD]o vs. time for β-lactam antibiotics (1,000 mg L^{-1}); pH 4.5.

supported with the order of instability of penicillin molecules.

3.4. The COD measurements of antibiotics solutions

Chemical oxygen demand (COD) values have been related to the total concentration of organic materials in the solution and the decrease of COD is used to reflect the degree of the oxidation degree during the photocatalytic experiment. The ratio of $[COD]_t/[COD]_o$ for a concentration 1,000 mg L^{-1} of antibiotics is shown in Fig. 6. $[COD]_o$ and $[COD]_t$ are the chemical oxygen demand values before and after degradation at time t, respectively. As seen, the complete nearly oxidation of *antibiotics* molecules will occur within 180 min [37,38].

3.5. The leaching and reusability of ZnS nanoparticles

The leaching of zinc from ZnS nanoparticles is studied with measurement of zinc ion concentration by atomic absorption spectroscopy with a sample containing 50 mg L^{-1} amoxicillin and 0.5 mg L^{-1} of ZnS after 120 min. The result shows a leaching < 2% for zinc in solid ZnS. Thus, ZnS nanoparticles as photocatalyst are stable in degradation process at pH 4.5.

To check the reusability of the photocatalyst, we have carried out the degradation of amoxicillin under optimized and similar conditions for three cycles. The ZnS nanoparticles is separated, washed with water and ethanol, and dried at 80°C for 120 min. For three photocatalytic cycles, the reusability of photocatalyst is obtained with the pseudo-first-order rate constants (k_{app}) 1.44×10^{-2}, 1.37×10^{-2} and 1.22×10^{-2} min^{-1}.

4. Conclusion

The β-lactam compounds of AMO, AMP, PEV, PEG, and CLX can be degraded under visible irradiation and at presence of ZnS nanoparticles as photocatalyst. The rate of degradation depends on the pH of samples, dosage of catalyst, initial concentration, and structural of β-lactam compounds. The degradation rate increases with decreasing of stability of antibiotic molecules. The degradation yield of 82–100% is obtained for β-lactam compounds (50 mg L^{-1}) in duration time of 120 min at pH of 4.5 and 0.5 mg L^{-1} of ZnS nanoparticles.

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