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Survey on the removal of ciprofloxacin from aqueous solutions by nano-sono-catalytic process

Artur Marek Banach[a], Abdolraufeh Mollazehi[b], Shahin Ahmadi[b,*]

[a]*Department of Biochemistry and Environmental Chemistry, Institute of Biotechnology, The John Paul II Catholic University of Lublin, Konstantynów 1I Str., 20-708 Lublin, Poland, Tel. +4881 454 54 42; email: abanach@kul.pl*
[b]*Department of Environmental Health, Zabol University of Medical Sciences, Zabol, Iran, Tel. +989184957156; emails: sh.ahmadi398@gmail.com (S. Ahmadi), molazehi125@gmail.com (A. Mollazehi)*

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ABSTRACT

The pollution of water with pharmaceutical compounds can cause problems in the ecosystems. Antibiotics have special importance due to their induction of bacterial resistance. The aim of this study was the investigation the performance of sono-catalytic degradation process of ciprofloxacin (CIP), one of the antibiotics. The effects of pH, contact time, dosage and initial CIP concentration on the degradation of CIP were examined. The analysis of obtained data revealed that among factors tested, the catalyst dose had the greatest impact on the removal efficiency of CIP—under the dose of 0.25 g of catalyst CIP removal efficiency amounted to 70.48%. The results of this study allowed us to conclude that the sono-catalytic degradation process in the presence of ZnO nanoparticles strongly affects the CIP removal from aqueous environments.

Keywords: Antibiotic; Removal; Nano-sono-catalytic; Aqueous environments; ZnO nanoparticles

1. Introduction

Antibiotics present in the environment act as a factor that could potentially affect microbial communities [1]. The antibiotics enter into the waters along with the sewage originating from pharmaceutical industries, veterinary clinics, hospitals, and agriculture [1,2]. Ciprofloxacin (CIP) classified in fluoroquinolone class has been widely prescribed for the treatment of intra-abdominal infections, the certain type of infectious diarrhea, respiratory tract infections, and urinary tract infection [2,3]. The accumulation of fluoroquinolone in ecosystems resulted in increased resistance of bacteria against antibiotic treatment and chromosomal mutation [3,4].

Several treatment methods have been proposed for the removal of CIP from contaminated waters, including photo decomposition [5], electrolysis [6], adsorption [1,3], oxidation [2,6], biodegradation [2], and other processes, involving advanced technologies to destroy the CIP structure [6,7]. Ultrasonic irradiation of aquatic environment can result in the increase and destruction of gas bubbles (cavitation) thus producing high transient temperature and pressure, what eventually leads to the formation of free radicals ($OH^\bullet$ and $OOH^\bullet$) via thermal breakup of water and oxygen. These radicals penetrate into water and oxidize dissolved organic compounds [7]. The amount of heat generated by the ultrasound (US) causes the formation of water molecules and the production of free radicals ($O^\bullet$, $H^\bullet$, and $OH^\bullet$), or some oxidants such as hydrogen peroxide, which can react with organic compounds [8]. The mechanism proposed for the production of OH by ultrasonic (US) is given by the following Eqs. (1) and (2):

$$H_2O + \;))) \rightarrow OH^\bullet + H^\bullet \tag{1}$$

$$OH^\bullet + O_2 \rightarrow HO_{2^-} \tag{2}$$

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* Corresponding author.

$$H_2O_2 + \bar{e} \rightarrow OH^- + OH^\bullet \quad (3)$$

$$OH^\bullet + \text{Antibiotic} \rightarrow \text{Degradation Products} \quad (4)$$

Ultrasonic along with catalyst could oxidize the antibiotics and change them to less toxic or harmless by-products for microorganisms [10]. The presence of silica particles, active carbon, active alumina, copper, and zinc oxides (ZnO), for example, increase the cavitation effect and the decomposition rate of organic molecules [11]. Nanoparticles (NPs) of metal oxides include F_2O_3, ZnO, and TiO_2. They provided unique optical, catalytic, semiconductor, and piezoelectric properties that are developed technologically [8,10]. In order to disintegrate and remove the pollutants that have low biodegradability, the application of sonochemical process with the presence of catalysts compared with other advanced oxidation process (AOP) is proposed as new approach in sewage treatment. This process, which provided high catalytic capacity, could be applied as an effective method [12].

This study aimed on investigating the efficiency of sono-catalytic process using ZnO NPs and persulfate in AOP to disintegrate and remove the CIP from aqueous solutions.

2. Material and methods

2.1. Materials

CIP (molecular mass 385.8 mol·wt, purity higher than 99.6% and molecular formula $C_{17}H_{18}FN_3O_3HClH_2O$) and zinc oxide NPs (ZnO NPs) (purity of 99%, specific surface area 90 m^2/g, particle size 20 nm) were supplied by Sigma-Aldrich, USA. All reagents (sodium persulfate [$Na_2S_2O_{8,}$ 99%], sodium hydroxide [NaOH, 98%], sulfuric acid [$H_2SO_{4,}$ 99.99%]) were of analytical grade and purchased from Merck (Germany). All the solutions were prepared with chemicals of at least analytical grade using deionized water. The stock solutions of CIP were prepared daily and stored in amber colored glass bottles. To determine the exact diameter of the NP, scanning electron microscopy (SEM) (HITACHI Model S-3000 H) provided some information about the morphology of nanocatalytic surface.

2.2. Ultrasonic procedure

The rector of determining surface included a digital ultrasonic (model = Elma CD, Germany, 4820, volume = 3.7 L, frequency = 60 kHz, input energy per unit = 2.5 W/cm^2) appliance that made of Plexiglas with a piezoelectric transducer having a diameter of 5 cm fixed at the bottom of the vessel including100 mL samples in the bath with US waves. It is schematically shown in Fig. 1.

2.3. Batch experiments

The effect of different parameters such as pH (3, 5, 7, and 9), contact time (10, 20, 40, 60, 80, and 120 min), pollutant concentration (25, 50, 100, and 150 mg/L), and ZnO NPs concentration (0.1, 0.15, 0.2, and 0.25 g/L) was studied in nano-sono-catalytic process. The pH of the water sample was adjusted by adding HCl or NaOH (0.1 or 0.01 N) solutions in each bottle. The final pH of the water sample was measured using an MIT 65 pH meter. The pH of the water sample was adjusted by adding HCl or NaOH (0.1 or 0.01 N) solutions in each bottle. The prepared CIP solution was poured into the Erlenmeyer flask and ZnO NPs were added. The Erlenmeyer flask with its contents was placed inside the ultrasonic apparatus under US waves (60 kHz) according to the set different times were refined. The initial and final CIP concentrations in the solutions were analyzed by a UV–visible recording spectrophotometer (Shimadzu model: CE-1021-United Kingdom) at a wavelength of maximum absorbance (λ_{max}) 275 nm [4]. The removal R (%) of the studied parameters from CIP was calculated based on the following formula [13,14]:

$$\%R = \frac{(C_0 - C_f)}{C_0} 100 \quad (5)$$

where C_0 and C_e are the initial and equilibrium-liquid phase concentrations of CIP (mg/L), respectively.

3. Results and discussion

3.1. SEM analysis on ZnO NPs

SEM has been a primary instrumentation for characterizing the surface morphology. SEM image is shown in Fig. 2. The SEM image shows that the ZnO NPs consist of lamellar-like structures.

3.2. Changes in UV-Vis spectrum

Fig. 3 shows the CIP UV-Vis spectrum for different reaction times. It is clear that the highest peak of CIP first

Fig. 1. The schematic illustration of sonochemical process.

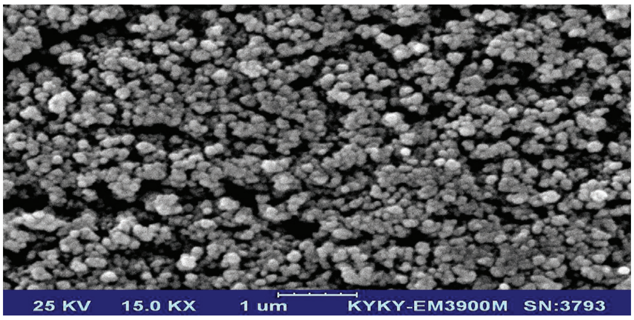

Fig. 2. SEM image of the ZnO NPs.

sample was observed at 275 nm, and it declined gradually by passing the time which indicated the decomposition and removing the CIP. After the reaction was begun, a sudden increase was observed in UV spectrum, which indicated the formation of mandatory products with aromatic rings that were resistant to degradation.

3.3. *Effects of pH on nano-sono-catalytic process*

Fig. 4 shows that by pH increase, deleting efficiency of antibiotics also undergoes an increase. pH_{zpc} of ZnO NPs equals 7.5 and pK_a CIP is 5.7, which are because there are some electrostatic forces at nano-particle level of zinc oxide and antibiotics in a way that at high pH of 7.5, ZnO NPs level has negative load and antibiotics have too. Therefore, the repulsive forces between them have no intention to reveal any reaction, which consequently leads to low efficiency. At pH lower than 7.5 of ZnO NPs level, a positive load; hence, due to electrostatic forces the deleting efficiency increases [15]. The implemented studies by Guo and Li [16] also show that H^+ ions play an influential part in producing $OH^\bullet$ and $H^\bullet$ radicals.

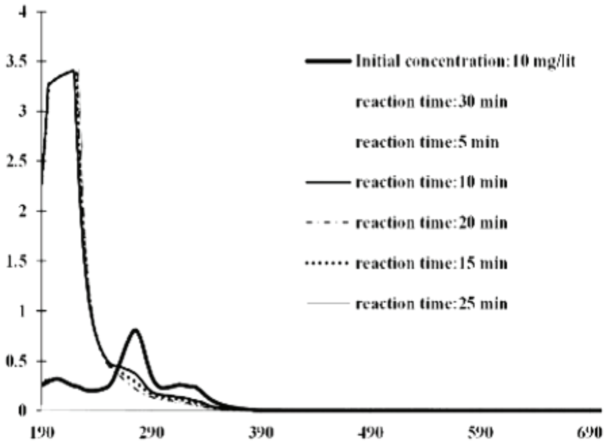

Fig. 3. Changes in UV-Vis spectrum of CIP.

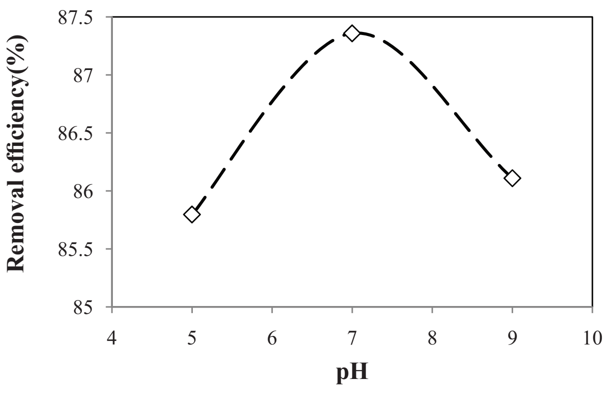

Fig. 4. Effect of pH on removal efficiency of CIP (time: 60 min, ZnO NPs: 0.15 g/L, initial concentration: 100 mg/L, frequency: 60 kHz).

3.4. *Effects of ZnO NPs and CIP concentration*

The effect of concentration of ZnO NPs on the removal of CIP was studied by varying the catalyst concentrations from 0.1 to 0.25 g/L (Fig. 5). In general, ultrasonic was considered as the energy source to activate NP. NPs provided huge surface and high energy and they tended to accumulate [17]. Although ultrasonic distributes the NPs, its strength is not enough to distribute them in high concentration. So, the efficiency of a removal is fixed by adding the NPs [18]. The obtained results were in accordance with those in the studies on varying concentration of TiO_2 NPs on the disintegration of organic pollutants in different process of AOPs [19].

3.5. *Effects of Time and CIP concentration*

To study the reaction time and primary concentration of CIP on its removal efficiency, the different concentrations of CIP (25, 50,100, and 150 mg/L) in different retention times (10, 20, 40, 60, 80, and 120 min) were compared with

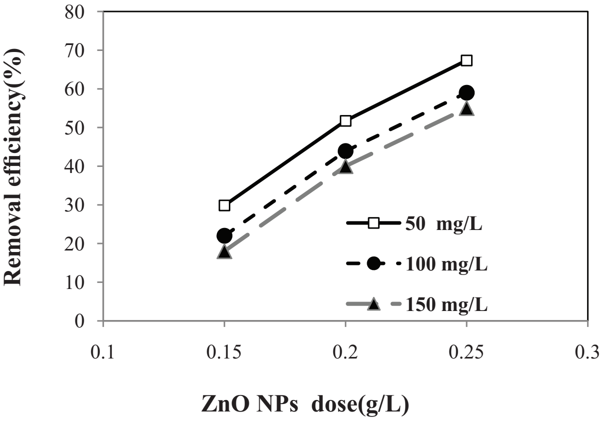

Fig. 5. Effect of ZnO NPs dosage on removal efficiency of CIP (time: 60 min, pH: 7, initial concentration: 100 mg/L, frequency: 60 kHz).

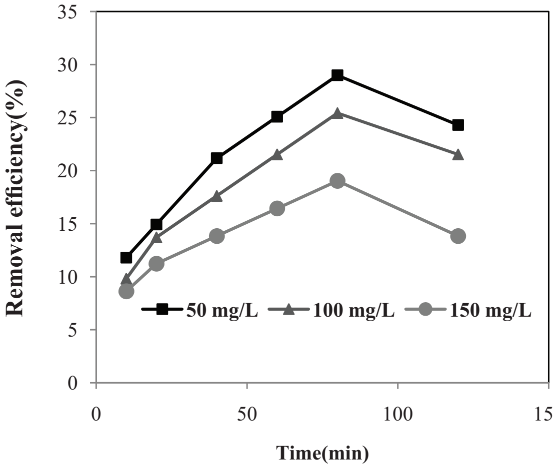

Fig. 6. Effect contact time on removal efficiency of CIP (ZnO NPs: 0.25g/L, pH: 7, frequency: 60 kHz).

ZnO NPs optimal concentration. The results are shown in Fig. 6. The rate of removal increased in the time period of 60–80 min, and then it was fixed and decreased by reducing the CIP primary concentration. The efficiency of CIP decomposition was increased with the decrease of the CIP primary concentration in the same conditions of NPs concentration and free hydroxyl radical density. Therefore, CIP radical reaction with hydroxyl radicals at low concentration would be increased, and it resulted in an increase of CIP decomposition by free radical [20].

3.6. Kinetic of nano-sono-catalytic

To investigate the kinetic of CIP disintegration using nano-sono-catalytic, pseudo-first-order kinetics, and Langmuir-Hinshelwood (L-H) of different organic compounds, especially antibiotics, were studied [20]. The test was applied in optimum conditions to study the disintegration synthetic (contact time 80 min, pH = 7, and concentration of NPs = 0.25 g/L). The reduction of CIP concentration was observed as a function of irradiation time and data were fitted to a pseudo-first order rate model according to following equation [21,22]:

$$\ln\left(\frac{c}{c_0}\right) = -k't \tag{6}$$

The slope of the plot of $\ln\left(\frac{c}{c_0}\right)$ vs. time gives the value of rate constant k', min^{-1}, so the reaction follows a pseudo-first order scheme. Here, c_0 denotes the initial concentration, mg/L, and c is the concentration value at time t, mg/L.

The applied equation for L-H model is as follows [23]:

$$\frac{1}{K_{\text{obs}}} = \frac{1}{K_C K_{LH}} + \frac{[CIP]_0}{K_C} \tag{7}$$

In this relation, the preliminary intensity of $[\text{CIP}]_0$ initial antibiotics CIP (mg/L), K_{LH} is the fixed balanced absorption of L-H model and k_c is the fixed reaction speed level(mg/L min). By drawing $1/K_{\text{obs}}$ against $[\text{CIP}]_0$, a direct line obtained through which the fixed balanced of L-H model and reaction–speed level could be determined. The results show that $\left(\frac{c}{c_0}\right)$ against t means a good relation. The amount of fixing coefficient for regression line is 0.9987; hence, antibiotic-deleting reaction of pseudo-first-order model follows it (Table 2 and Figs. 7 and 8).

4. Conclusion

In this study, the high efficiency of CIP removal was in pH = 7. It was found that the efficacy of nano-sono-catalytic process in the removal of this pollutant was negligible and at the best conditions only 70.48%. The results of this study showed that the nano-sono-catalytic process using zinc oxide NPs (ZnO NPs) is very effective and can be used for removal of CIP antibiotics from aqueous solutions.

Table 1
Pseudo-first order kinetic for the CIP degradation process

	Pseudo first order	
C_0 (mg/L)	K (min^{-1})	R^2
50	3.1×10^{-3}	0.9909
100	2.6×10^{-3}	0.98356
150	1.9×10^{-3}	0.9987

Table 2
Langmuir-Hinshelwood model for the CIP degradation process

k_c	K_{LH}	R^2
0.53	0.0086	0.9313

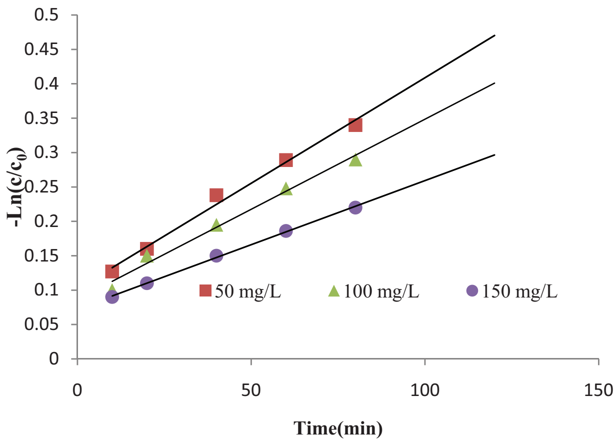

Fig. 7. Pseudo-first order plot for degradation of CIP by nano-sono-catalytic process.

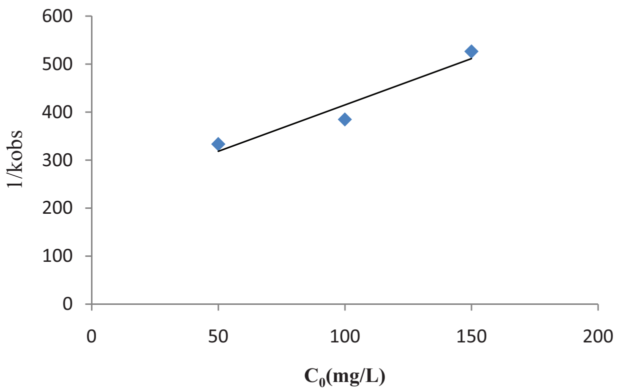

Fig. 8. Langmuir-Hinshelwood plot for degradation of CIP by nano-sono-catalytic process.

References

[1] S. Ahmadi, A. Banach, F.K. Mostafapour, D. Balarak, Study survey of cupric oxide nanoparticles in removal efficiency of ciprofloxacin antibiotic from aqueous solution: adsorption isotherm study, Desal. Wat. Treat., 89 (2017) 297–303.
[2] S. Ahmadi, F.K. Mostafapour, Survey of efficiency of dissolved air flotation in removal Penicillin G potassium from aqueous solutions, Br. J. Pharm. Res., 15 (2017) 1–11.

[3] S.A.C. Carabineiro, T. Thavorn-Amornsri, M.F.R .Pereira, P. Serp, J.L. Figueiredo, Comparison between activated carbon, carbon xerogel and carbon nanotubes for the adsorption of the antibiotic ciprofloxacin, Catal. Today, 186 (2012) 29–34.

[4] N. Khoshnamvand, Sh. Ahmadi, F. Mostafapour, Kinetic and isotherm studies ciprofloxacin an adsorption using magnesium oxide nanopartices, J. Appl. Pharm. Sci., 7 (2017) 079–083.

[5] V. Homen, L. Santos, Degradation and removal methods of antibiotics from aqueous matrices—a review, J. Environ. Manage., 92 (2011) 2304–2347.

[6] Y. Han, X. Quan, S. Chen, H. Zhao, C. Cui, Y. Zhao, Electrochemically enhanced adsorption of aniline on activated carbon fibers, Sep. Purif. Technol., 50 (2006) 365–372.

[7] K. Kümmerer, Antibiotics in the aquatic environment – a review – part I, Chemosphere, 75 (2009) 417–434.

[8] I. Michael, L. Rizzo, C.S. McArdell, C.M. Manaia, C. Merlin, T. Schwartz, Urban wastewater treatment plants as hotspots for the release of antibiotics in the environment: a review, Water Res., 47 (2013) 957–995.

[9] H. Ghodbane, O. Hamdaoui, Degradation ofAcid Blue 25 in aqueous media using1700kHz ultrasonic irradiation: ultrasound/Fe(II) and ultrasound/H_2O_2 combinations, Ultrason. Sonochem., 16 (2009) 593–598.

[10] S. Rahdar, C.A. Igwegbe, A. Rahdar, S. Ahmadi, Efficiency of sono-nano-catalytic process of magnesium oxide nanoparticle in the removal of Penicillin G from aqueous solution, Desal. Wat. Treat., 106 (2018) 330–335.

[11] N.K. Nga, P.T.T. Hong, T.D. Lam, T.Q. Huy, A facile synthesis of nanostructured magnesium oxide particles for enhanced adsorption performance in reactive blue 19 removal, J. Colloid Interface Sci., 398 (2013) 210–216.

[12] S. Ghodke, S. Sonawane, R. Gaikawad, K. Mohite, TiO_2/Nanoclay nanocomposite for phenol degradation in sonophotocatalytic reactor, Can. J. Chem. Eng., 90 (2012) 1153–1159.

[13] G.Z. Kyzas, J. Fu, N.K. Lazaridis, D.N. Bikiaris, K.A. Matis, New approaches on the removal of pharmaceuticals from wastewaters with adsorbent materials, J. Mol. Liq., 209 (2015) 87–93.

[14] S. Ahmadi, F. Kord Mostafapour, E.Bazrafshan, Removal of aniline and from aqueous solutions by coagulation/flocculation–flotation, Chem. Sci. Int. J., 18 (2017) 1–10.

[15] L. Yin, J. Niu, Z. Shen, J. Chen. Mechanism of reductive decomposition of pentachlorophenol by Ti-doped β-Bi_2O_3 under visible light irradiation, Environ. Sci. Technol., 44 (2010) 5581–5586.

[16] Z.M. Guo, G. Li, Degradation of phenol by nanomaterial TiO in wastewater, Chem. Eng. J., 119 (2006) 55–59.

[17] M. Klavarioti, D. Mantzavinos, D. Kassinos, Removal of residual pharmaceuticals from aqueoussystems by advanced oxidation processes, Environ. Int., 35 (2009) 402–417.

[18] L. Sanchez-Prado, R. Barro, C. Garcia-Jares, M. Llompart, M. Lores, C. Petrakis, N. Kalogerakis, D. Mantzavinos, E. Psillakis, Sonochemical degradation of triclosan in water and wastewater, Ultrason. Sonochem., 15 (2008) 689–694.

[19] M. Salehi, H. Hashemipour, M. Mirzaee, Experimental study of influencing factors and kinetics in catalytic removal of methylene blue with TiO_2 nanopowder, Am. J. Environ. Eng., 2 (2012) 1–7.

[20] L. Hou, H. Zhang, X. Xue, Ultrasound enhanced heterogeneous activation of peroxydisulfate by magnetite catalyst for the degradation of tetracycline in water, Sep. Purif. Technol., 84 (2012) 147–152.

[21] S. Esplugas, J. Gimenez, S. Contreras, E. Pascual, M. Rodriguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res., 36 (2002) 1034–1042.

[22] D.W. Lee, S.K. Ihm, K.H. Lee, Mesostructure control using a titania-coated silica nanosphere framework with extremely high thermal stability, Chem. Mater., 17 (2005) 4461–4467.

[23] S. Khezrianjoo, H.D. Revanasiddappa, Langmuir-Hinshelwood kinetic expression for the photocatalytic degradation of Metanil Yellow aqueous solutions by ZnO catalyst, Chem. Sci. J., 2012 (2012) 1–8.