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Original Article

Evaluation of Sono-photocatalytic Removal of Ciprofloxacin Antibiotic Using Magnesium Oxide Nanoparticles from Aqueous Solutions

Ferdos Kord Mostafapour[1], Mohammadreza Radmehr[2], Shaziya Haseeb Siddiqui[3], Davoud Balarak[1,*]

[1]Department of Environmental Health Engineering, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, IRAN.
[2]Student Research Committee, Zahedan University of Medical Sciences, Zahedan, IRAN.
[3]Department of Chemistry, Sam Higginbottom University of Agriculture Technology and Sciences (SHUATS), Allahabad, Uttar Pradesh, INDIA.

ABSTRACT

Objectives: The entry of antibiotics into surface and groundwater will cause problems in the environment. This study aimed to investigate the removal efficiency of ciprofloxacin (CFX) from aqueous solutions using the sonophotocatalytic process of Magnesium Oxide Nanoparticles (MgO). **Materials and Methods:** This study is an experimental-laboratory study performed in a reactor with a discontinuous system. In this study, the effect of parameters such as solution pH, MgO dose, reaction time in two processes, photocatalyst and sonocatalyst, initial concentration of antibiotic and the power of UV lamps in the photocatalytic reactor at ultrasonic frequencies of 35 and 130 kHz on the reduction of CFX in aqueous solution was investigated. **Results:** The results showed that the process of photosonocatalysis with MgO can effectively lead to the removal of the antibiotic CFX. In the process of using a photosonocatalyst with a pH of 7 and ultrasonic waves with a frequency of 35 kHz and an optimal time of 30 min, 0.3 g/L of MgO, CFX concentration of 150 mg/l, UV lamp with a power of 30 watts and the optimal irradiation time of 60 min was obtained as the optimal variables in the removal of CFX antibiotic. **Conclusion:** The results showed that the photosonocatalytic process with the help of MgO is an effective and efficient method to remove the CFX antibiotic from aqueous solutions.

Keywords: Ciprofloxacin, Magnesium Oxide Nanoparticles, Photocatalyst, Sonocatalyst.

Correspondence
Davoud Balarak
Department of Environmental Health Engineering, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, IRAN.
Email id: dbalarak2@gmail.com
ORCID ID: 0000-0003-3679-9726

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INTRODUCTION

Antibiotics are administered to prevent (prophylaxis) or treat infections.[1] Antibiotics are generally categorized into six groups namely fluoroquinolones (FQs), macrolides, tetracyclines, aminoglycosides, cephalosporins, and penicillins.[2] FQs are broad-spectrum class of bactericidal antibiotics, which are used to prevent or treat infections without affecting the host cells.[3] As per the mode of action, FQs inhibit the synthesis of essential enzymes involved in DNA replication.[4] FQs can only be partially metabolized within human and animal bodies, and are frequently found in urban discharges and at wastewater treatment plants.[5] FQs are recognized among other emerging environmental contaminants with great public health concern due to the ecotoxicological effects and potential to increase microbial resistance.[6] Among several FQs, CFX is the most often used fluoroquinolone antibiotic.[4,5] CFX has been found in agricultural soils (119.8 μg kg^{-1}),[7] freshwater (6.5 mg L^{-1}),[8] manure (45.59 mg kg^{-1}),[9] and urban sewage sludge (426 mg kg^{-1}).[10] According to Mathew and Unnikrishnan (2012), CFX concentrations in effluents of wastewater treatment plants of pharmaceutical companies in India have reached up to 31 mg/L^{-1}.[10] Regardless of the reality that these chemicals can be found in low doses makes them difficult to investigate, their persistence in drinking water for an extended length of time may have considerable negative impacts on human and environmental health.[9] Regardless of the fact that these materials are present in low amounts, it is hard to evaluate them, their presence in drinking water for an extended length of time may have considerable negative impacts on human health and the environment.[10]

CFX can being easily found in wastewater, surface water and groundwater.[11] This fact represents a huge concern about the potential adverse effects that it may cause to the environment and public health.[12] Given this scenario, it is necessary to develop methodologies for CFX removal from aquatic systems, since the conventional processes usually used in water and wastewater treatment plants are insufficient to completely remove emerging contaminants.[13] Thus alternative strategies

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have to be employed, such as the membrane separation process,[14] adsorption,[15] electrocoagulation[16] and photocatalysis.[17] Among the various advanced oxidation processes, the use of ultrasonic and photocatalytic processes as wastewater treatment has become more widely used. The most important advantage of these processes is the lack of material transfer and performance in all environmental conditions. In addition, the low cost of commercial catalysts, non-toxicity, availability, and the establishment of a stable photochemical process are other advantages.[18]

In photocatalytic decomposition, contaminants are decomposed under UV radiation and in the presence of metal oxide particles such as TiO_2 and ZnO, etc. The mechanism of this process is ultraviolet radiation to the semiconductor material, followed by electron excitation from the capacitance band to the conduction band. Electron excitation causes the production of hydroxyl radicals in aqueous media, which is effective in decomposing antibiotics.[19]

Semiconductor phenocatalysts of metal oxide nanoparticles as catalysts in recent years due to the lack of environmental problems have attracted the attention of many scientists and also nanoparticles have a high surface area. MgO, due to its destructive absorption properties, is a promising material as an adsorbent and due to its nanoscale and high specific surface area, it can be an ideal adsorbent for degradation of toxic chemical agents. The particle has advantages such as non-toxicity, high thermal stability, environmental friendliness and low cost.[20-22] The aim of this study was to investigate the combined efficiency of the photosonocatalytic process using CFX as an advanced oxidation process to decompose and remove the antibiotic CFX from the aqueous medium.

MATERIALS AND METHODS

Required chemicals include CFX antibiotic with 98% purity from Sigma Aldrich, MgO with average size of 20 nm and density of 3.58 g/cm^3 by Sigma Aldrich, HCL and NaOH from Merck were used. All solutions used in this process are prepared by adding a certain antibiotic concentration to distilled water. Also used devices and instruments include DR 5000 UV-vis spectrophotometer, UV radiation reactor, SONIC 3MX ultrasonic bath, 8, 15 and 30 watt UV lamp, AZ 86505 digital pH meter, digital scale KERNAEJ laboratory, 42 Whatman paper filter.

CFX removal experiments

This experimental-laboratory study was performed in a batch reactor on different concentrations of a synthetic solution containing the CFX antibiotic. All prototypes of CFX antibiotic solution in this study were prepared synthetically. In this study, due to the nature of the CFX, which has different properties at different pHs, the effect of the pH variable in the acidic, neutral and alkaline ranges (3, 5, 7, 9 and 11) was investigated. Also, the effect of important variables of ultrasonic radiation frequency (35 and 130 kHz), concentration of MgO nanoparticles (0.1, 0.3, 0.5, 0.7, 0.9, 1 mg / l), CFX concentration (10, 25, 50, 100, 150, 200 mg/L), UV radiation time and ultrasonic waves (15, 30, 45, 60, 75, 90, 120 min) and UV radiation power (8, 15, 30 W) on the removal of CFX.

In this study, UV radiation reactors and ultrasonic bath reactors have been used in series. The prepared synthetic solution is placed in a 250 cc Erlenmeyer flask inside a UV reactor. The reactor is made of a chamber with a wall covered with glossy aluminum sheets to reflect UV and increase radiation efficiency. In order to uniform the solution of the samples during irradiation, we have installed the reactor beam on the KS500 shaker device. The distance of UV lamp from the samples is 15 cm. The effluent of the UV reactor is transferred to the ultrasonic bath to continue the process. All experiments were performed at laboratory temperature (23°C). The concentration of CFX output of each reactor was measured by spectrophotometry using a spectrophotometer model DR 5000 UV-Vis made in USA at a wavelength of 276 nm.

RESULTS

Examination of the results of Figure 1. shows that increasing the pH from 3 to 7 leads to enhancing the CFX removal efficiency from 55.2 to 78.6%. However, as shown in the Figure, with increasing the pH from 7 to 11, the removal efficiency is declined with a steeper slope. Based on the Figure, optimal pH was obtained to be equal to 7 with a CFX removal efficiency of 78.6%.

The results of the effect of nanoparticle dose showed that by increasing the amount of MgO nanoparticles from 0.1 to 0.3 g/L (Figure 2), we see an increase in CFX removal efficiency from 58 to 80%. Nonetheless, as shown in the Figure, by increasing the nanoparticle dose from 0.3 to 1 mg/L, antibiotic removal efficiency had a declining trend. The study of the Figure shows that the optimal amount of MgO with a CFX removal efficiency of 80.4% is 0.3 g/L.

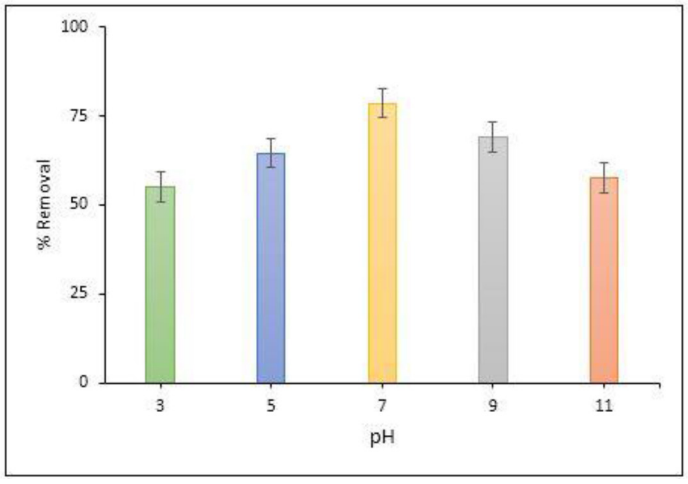

Figure 1: Effect of pH on CFX removal efficiency (C_0 = 50 mg/L, UV=15 W, time=90 min, Dose=0.3 g/L, frequency= 35 KH).

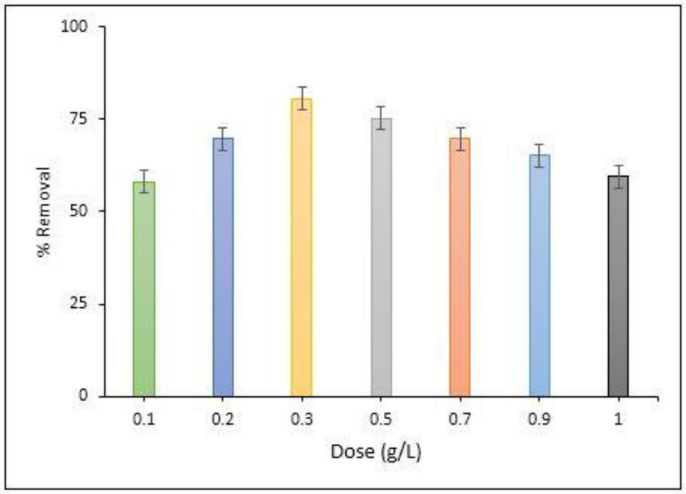

Figure 2: Effect of dose on CFX removal efficiency (C_0 = 50 mg/L, UV=15 W, time=90 min, pH=7, frequency= 35 KH).

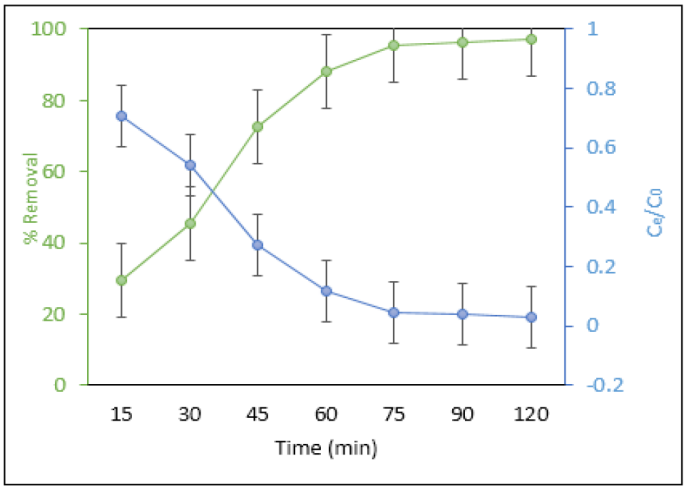

Figure 4: Effect of time on CFX removal efficiency (dose = 0.3 g/L, UV=15 W, C_0 = 150 mg/L, pH=7, frequency= 35 KH).

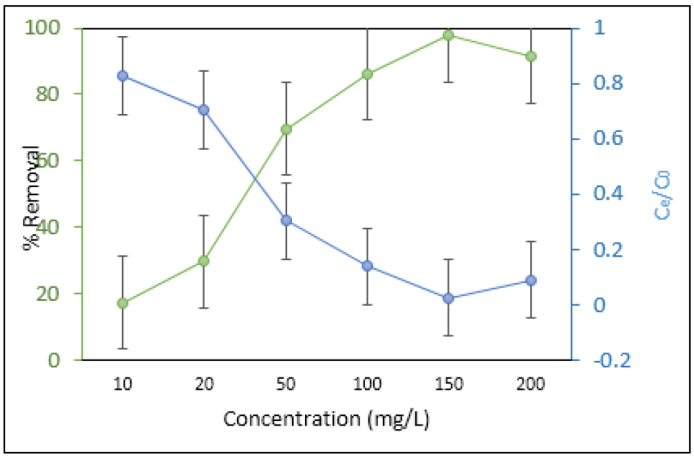

Figure 3: Effect of concentration on CFX removal efficiency (dose = 0.3 g/L, UV=15 W, time=90 min, pH=7, frequency= 35 KH).

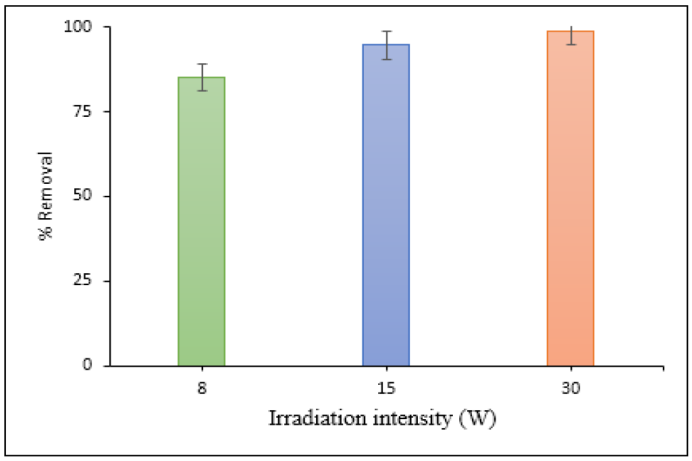

Figure 5: Effect of irradiation intensity on CFX removal efficiency (dose = 0.3 g/L, C_0 = 150 mg/L, pH=7, frequency= 35 KH).

The general results showed that by increasing the concentration of CFX from 10 to 150 mg/L, the removal efficiency increases significantly (Figure 3), and by increasing the concentration to values more than the identified optimal amount, the antibiotic removal decreases. At this stage, the effect of the photocatalytic process on the CFX removal was far greater than the sonocatalytic process.

The results of this study in Figure 4 showed that with increasing the time of UV irradiation, the CFX removal efficiency develops significantly.

With increasing irradiation intensity in Figure 5, the removal efficiency enhances significantly. The highest efficiency was detected during the use of a lamp with an intensity of 30 watts, and the lowest efficiency was observed when a lamp with an intensity of 8 watts was employed.

DISCUSSION

The effect of pH change on the CFX molecule has shown that at pH values less than 6.1, the surface charge of the CFX becomes cationic and positive due to the protonation of amine groups. At pH values above 7.8, the CFX molecule is converted to the anionic form due to the loss of protons from the carboxylic group in the antibiotic structure. In the pH range of 6.1 to 7.8, the loss of protons of the carboxyl group leads to the production of negatively charged carboxylates, however, the amine group is protonated and the charge remains positive. Therefore, in this pH range, most of the CFX molecule in an aqueous solution is uncharged, in other words, it has a positive end and a negative end.[23,24]

The CFX is affected by pH in the environment, which molecular form of the CFX is also different according to the pH. In acidic pH values less than 5.5, CFX is in the protonated form, and therefore the predominant form is cations. In relatively neutral

pH values between 5.5 and 7.7, hydrogen is separated from the carboxyl group, and the zwitterionic form (bipolar ion) becomes the predominant form. In solutions with a pH greater than 7.7, hydrogen is separated from the amine group and thus loses the proton, and the anionic form of CFX becomes predominant.[25,26]

This decrease in efficiency with increasing the dose of nanoparticles can be due to the attraction role of nanoparticles in amounts greater than the optimal concentration that MgO nanoparticles in the process prevent the production of hydroxyl radicals and cause the production of hydroxyl radicals.[27,28]

As depicted by the results, the combination of two photocatalytic and ultrasonic processes, known as the sonophotocatalytic process, exhibited greater efficiency compared to the single-use of photo-catalytic and ultrasonic processes for removal of the desired pollutant.[29] In the sonophotocatalytic process, due to the simultaneous application of ultrasonic waves with the photocatalytic process, the production of hydroxyl radicals has increased, which is led to develop the removal efficiency.[30]

Increasing the concentration of the contaminant enhances the removal efficiency, which can be due to the unsaturation of the catalyst at low concentrations. With increasing concentration, the active sites of the catalyst will be filled by the contaminant.[31,32]

The reason for this increase in removal rate with increasing irradiation time can be due to creating more cavities and corrosion on the surface of MgO nanoparticles during the process and thus an increase in the adsorption surface area and an increase in the effect of catalytic properties in increasing removal efficiency.[33]

Irradiation intensity determines the amount of light absorbed by a semiconductor catalyst at a given wavelength. The rate at which photocatalysis begins to form in a photochemical reaction is strongly dependent on light.[32,33]

As the intensity of UV radiation increases, more electrons are excited; this increase in electron excitation is due to the increase in the intensity of irradiation emitted to the surface of the nanoparticles. An increase in the number of excited electrons improves the production of active hydroxyl radicals, which the rate of photocatalytic oxidation develops by increasing the produced active hydroxyl radicals.[31]

CONCLUSION

In this study, the CFX was degraded using MgO nanoparticles by the sonophotocatalytic method. The parameters affecting the degradation of the studied antibiotic were including the initial concentration of CFX, MgO dosage, contact time, radiation intensity, and pH. As shown by the results, the photocatalytic process had the best efficiency at a pH of 7. The irradiation intensity of 30 watts, the frequency of 35 kHz, and the MgO dosage of 0.3 g/L were the optimal conditions for other studied parameters. Finally, it can be said that MgO nanoparticles in combination with the sonophotocatalytic process can effectively remove CFX from aqueous solutions. However, the photocatalytic process, like that of the sonocatalytic process, performed well in removing the antibiotic.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

ABBREVIATIONS

MgO: Magnesium Oxide Nanoparticles; **CFX:** Ciprofloxacin.

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