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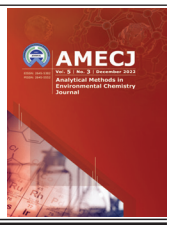

Catalytic ozonation process using ZnO/Fe_2O_3 nanocomposite for efficient removal of captopril from aqueous solution

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ABSTRACT

The presence of pharmaceutical compounds in aqueous media, even in low concentrations, has caused adverse effects on human, animal, and environmental health. Captopril is a widely used pharmaceutical compound detected in the environment at different concentrations. Because of the concern and problems caused by the presence of captopril in water and the aquatic ecosystem, it appears necessary to remove it from the environment. The current study investigated captopril removal by a catalytic ozonation process using ZnO/Fe_2O_3 nanocomposite as a low-cost catalyst. The effects of variables such as ZnO/Fe_2O_3 nanocomposite dosage (0.5-2.5 g L^{-1}), solution pH (3-11), initial captopril concentration (10-70 mg L^{-1}), and ozone dosage (0.2-1.5 mg min^{-1}) on captopril removal were investigated. The removal captopril of 99.4% was obtained in the optimum condition, including ZnO/Fe_2O_3 nanocomposite dosage of 2.0 g L^{-1}, solution pH of 5.0, initial captopril concentration of 40 mg L^{-1}, and ozone dosage of 0.5 mg min^{-1}. The ZnO/Fe_2O_3 nanocomposite as a catalyst was a critical component in the catalytic ozonation process. According to the obtained results, the catalytic ozonation process in the presence of ZnO/Fe_2O_3 nanocomposite has high efficiency in removing captopril from water sources.

1. Introduction

Recently, the attention of many researchers working in the field of water and wastewater treatment has focused on the removal of pharmaceutical compounds as a new group of emerging pollutants [1]. After humans and animals consume pharmaceutical compounds, part of them in their unmetabolized and metabolized form is excreted from the body and enters the environment [2]. Captopril is a commonly used pharmaceutical compound prescribed to reduce high blood pressure, treat heart failure, protect the heart and blood vessels against damage and heart attack, and protect the kidneys in diabetic patients [3, 4]. Captopril is a potent, competitive inhibitor of the angiotensin-converting enzyme, the enzyme responsible for converting angiotensin I to angiotensin II. Angiotensin II is a potent mediator that causes the narrowing of blood vessels and retention of sodium and water in the body [5].

Captopril has been detected in various environments such as water and soil). The captopril concentration in the environment causes dizziness,

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cough, hyperkalemia, impotence, nocturnal enuresis, nausea, vomiting, diarrhea, insomnia, Stevens-Johnson syndrome, gynecomastia, thrombocytopenia, and angioedema. Considering the problems caused by the presence of captopril in the environment, removing captopril from the aquatic environment is essential [3, 4]. Although conventional processes in water and wastewater treatment can remove a part of pharmaceutical compounds during the treatment process, conventional treatment processes cannot thoroughly remove these compounds, so we finally need advanced oxidation processes to treat these pollutants [6].

Ozonation technique is one of the advanced oxidation processes in water and wastewater treatment. Ozonation is used in water and wastewater treatment for several purposes such as disinfection, removal and control of taste, odor, and color, oxidation of iron and manganese and other mineral contaminants, algae control, improving the coagulation process, and oxidation of persistent organic contaminants [7, 8].

As a strong oxidant, Ozone molecules break down recalcitrant and hazardous organic compounds into smaller molecules [9, 10]. The ozonation reaction is accomplished through two pathways (direct and indirect). In the direct method, the ozone molecule appears as an electron acceptor and thus oxidizes the organic pollutants. Nevertheless, in the indirect method, the ozone molecule is converted into a radical (˙OH) during chain reactions, which has a higher oxidation potential than ozone. The indirect method decomposes pollutants with incredible speed and power [11, 12]. Ozone presents a high reactivity mainly attributed to its electronic configuration. It is a selective molecule that attacks electron-rich functional groups like double bonds, amines, and activated aromatic rings [13, 14]. In recent years, heterogeneous catalytic ozonation has received much attention in water treatment due to its high oxidation potential. In the current work, the effect of main operational variables, including solution pH, catalyst dosage (ZnO/Fe_2O_3 nanocomposite), initial captopril concentration, and reaction time was evaluated during the catalytic ozonation for removal of captopril from aqueous solution.

2. Material and methods

2.1. Chemical

Captopril ($C_9H_{15}NO_3S$, CAS N: 62571-86-2) was purchased from Darou Pakhsh Pharmaceutical Company. Sodium chloride (NaCl, CAS Number: 7647-14-5; Molecular Weight: 58.44), sodium hydroxide (NaOH, CAS 1310-73-2. Molecular Weight 40.00), hydrochloric acid (HCl, reagent, 37%; CAS Number: 7647-01-0; EC Number: 231-595-7), sodium thiosulfate ($Na_2S_2O_3$, $_{CAS}$ Number: 7772-98-7; Molecular Weight: 158.11), ferric chloride ($FeCl_3$, $_{CAS}$ 7705-08-0, EC Number 231-729-4), zinc oxide (ZnO, CAS 1314-13-2, Molecular Weight 81.39), acetonitrile anhydrous (CAS Number: 75-05-8, Molecular Weight: 41.05) , trifluoroacetic (TFA, CAS 76-05-1, Molecular Weight 114.02), and potassium iodide (KI, CAS 7681-11-0, Molecular Weight 166.00), were obtained from Sigma, Germany. All chemicals were of analytical reagent grade.

2.2. Instrumental

The determination of captopril concentration was analyzed using high-performance liquid chromatography (HPLC) system (HPLC 862 Bar, Knauer Smartline, Germany). This system consisted of a photodiode array (PDA) detector, set at 282 nm, and a C_{18} column (RP-C_{18}, 5 µm 4.6 ×150 mm) kept at 30˚C, with an injection flow rate of 1.2 mL min^{-1}. The mobile phase solution was applied using 15% acetonitrile and 85% trifluoroacetic/water acid (2% v/v) [16]. Digital PH meter (meterohom 827 pH lab, Switzerland) was used.

2.3. Preparation of the ZnO/Fe_2O_3 nanocomposite

In a theoretical procedure, 19.4 mg $FeCl_3$ and 200 mg ZnO particles were added to 50 mL of deionized water, and the mixture was dispersed at 100 °C for 12.0 h (Fig.1). After cooling to 20 °C, the nanoparticles were separated using centrifugation

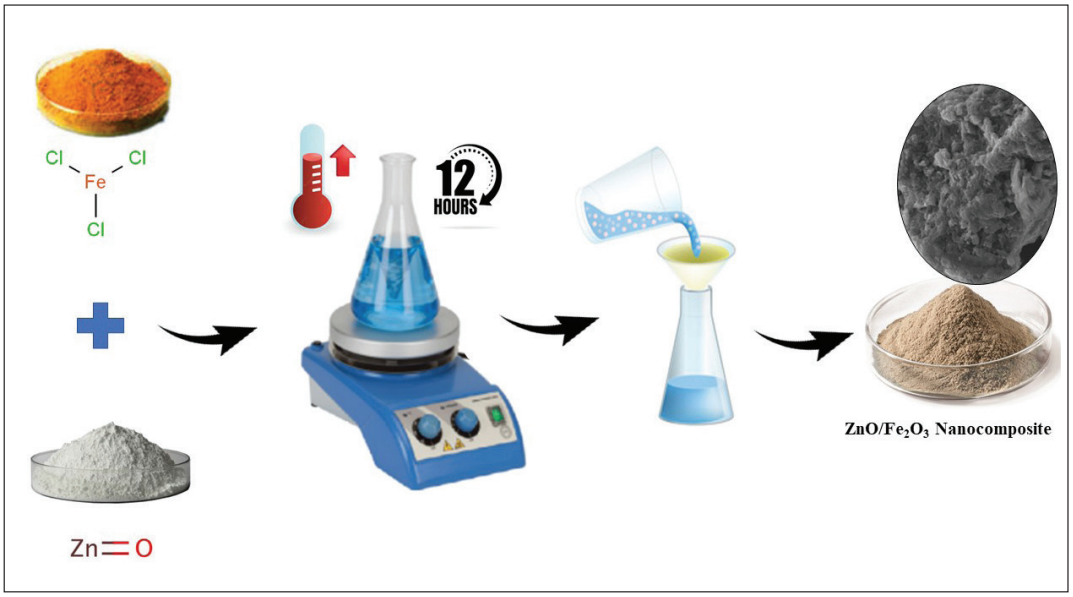

Fig.1. Procedure for Preparation of the ZnO/Fe_2O_3 nanocomposite

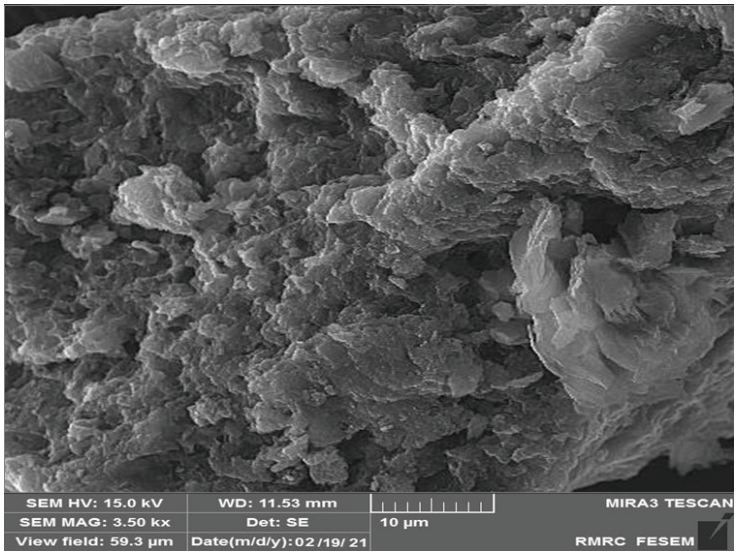

Fig.2. SEM images of the ZnO/Fe_2O_3 nanocomposite

and washed several times with ethanol and deionized water. The ZnO/Fe_2O_3 nanocomposite was dried at 100°C for 3.0 h and then was used as the catalyst in the ozonation process for the degradation of captopril [15]. FE-SEM of nanoparticles of ZnO/Fe_2O_3 nanocomposite showed in Figure 2.

2.4. Catalytic ozonation experiments

The catalytic ozonation of captopril was performed in a 500 mL Pyrex reactor with 8.0 cm diameter and 12 cm high and equipped with a magnetic stirrer at room temperature. Ozone was generated from the air using an ozone generator (ARDA, Model MOG+10) with an input rate of 5 g h^{-1}. The reactor included an input/output port for the ozone gas stream. Ozone was introduced through a porous fritted diffuser that can produce reasonably fine bubbles. The excess ozone at the outlet was adsorbed by a sequential 2% potassium iodide solution. The solution pH was adjusted using NaOH or HCl in the catalytic ozonation process. After performing the reaction in each experimental run, 5 mL of sample was

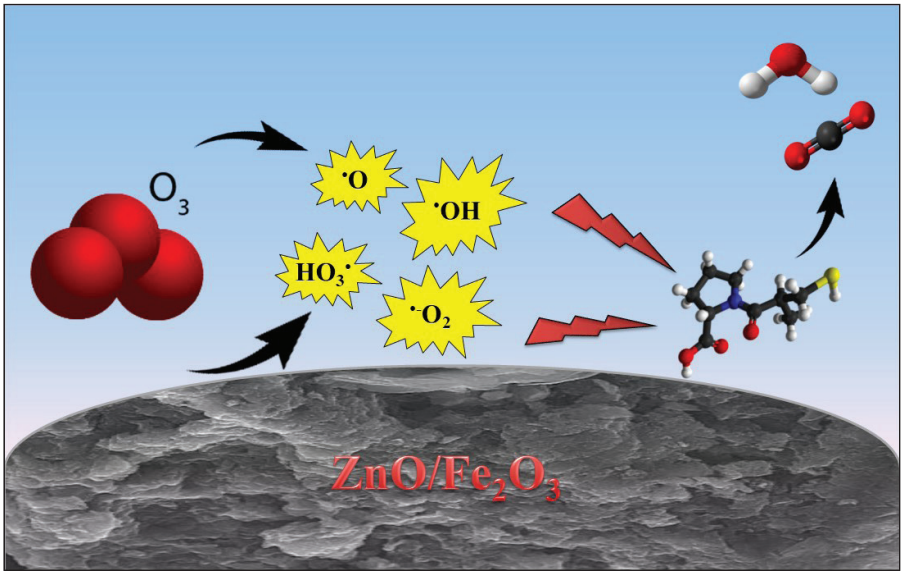

Fig.3. Mechanism of removal of captopril based on the catalytic ozonation and the ZnO/Fe_2O_3 nanocomposite

taken and filtered by PTFE filters to analyze for degradation efficiency of captopril using the catalytic ozonation process. Mechanism of removal of captopril based on the ZnO/Fe_2O_3 nanocomposite by the catalytic ozonation which was presented in Figure 3.

3. Results and discussion

3.1. Effect of solution pH

The effect of solution pH is one of the critical parameters in the catalytic ozonation process for removing contaminants. Therefore, in the present study, the effect of solution pH was investigated in the range of 3.0 to 11.0 for removal of captopril from aqueous solution, in the constant condition, including initial captopril concentration of 30 mg L^{-1}, ZnO/Fe_2O_3 nanocomposite dosage of 1.0 g L^{-1}, and ozone dosage of 0.5 mg min^{-1}. The obtained results are shown in Figure 4. According to the achieved results, it was found that the removal

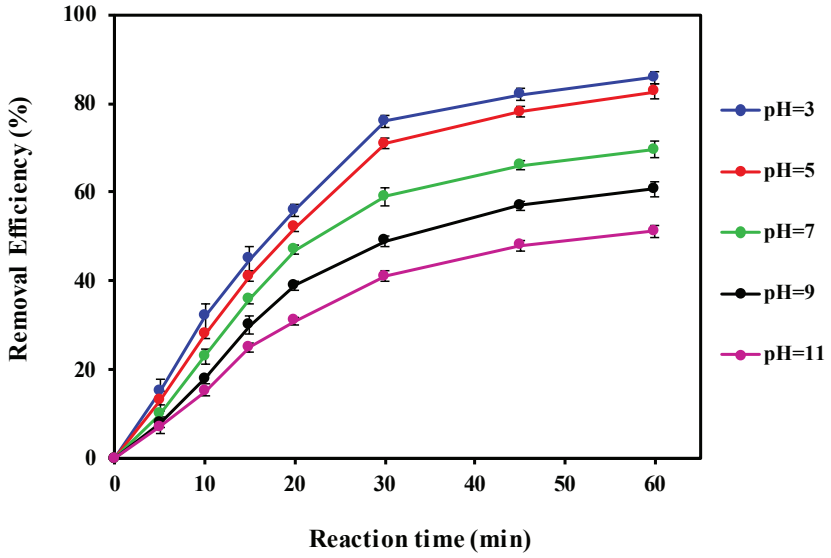

Fig. 4. Effect of solution pH and reaction time for removal captopril using catalytic ozonation. Experimental conditions: initial captopril concentration of 30 mg L^{-1}, ZnO/Fe_2O_3 nanocomposite dosage of 1.0 g L^{-1}, ozone dosage of 0.5 mg min^{-1}.

efficiency of captopril decreased with the increase of pH solution. As the pH value increased from 3 to 11, the removal efficiency of captopril decreased from 85.8% to 51.2% after 60 min. The removal efficiency in the acid conditions is better than in alkali conditions because high pH in the solution leads to the creation of more free radical scavengers derived from the mineralization of organic material, resulting in a decrease in the concentration of •OH. Generally, ozone oxidation pathways include direct oxidation by ozone molecules and radical oxidation by •OH. Direct oxidation is more selective and dominates under acidic conditions. While radical oxidation is less selective and predominates under primary conditions [17, 18]. Since the removal efficiency at a solution pH of 5 (82.6%) is very close to the removal efficiency at a solution pH of 3 (85.8%), due to the destructive effects of acidic conditions, a pH of 5 was chosen as the optimal solution pH in the catalytic ozonation process for removal of captopril.

3.2. Effect of ZnO/Fe_2O_3 nanocomposite dosage

The effect of catalyst dosage (ZnO/Fe_2O_3 nanocomposite) on captopril removal in the catalytic ozonation process was investigated in the range of 0.50–2.5 g L^{-1}. In the constant condition, including solution pH of 5, initial captopril concentration of 30 mg L^{-1}, and ozone dosage of 0.5 mg min^{-1}. According to the obtained results, the captopril removal efficiency increased with increasing ZnO/Fe_2O_3 nanocomposite dosage. As seen in Figure 5, the removal efficiency of captopril increased to 72.3%, 82.6%, 88.6%, 95.6%, and 98.2% when the catalyst dosage (ZnO/Fe_2O_3 nanocomposite) was increased to 0.50, 1.0, 1.5, 2.0, and 2.5 g L^{-1}, respectively. Nevertheless, the captopril removal efficiency at the catalyst (ZnO/Fe_2O_3 nanocomposite) dosage of 2.0 g L^{-1} is very close to 2.5 g L^{-1} (less than 3%). Therefore, a catalyst dosage of 2.0 g L^{-1} was chosen as the optimum catalyst dosage. The obtained results illustrate that ZnO/Fe_2O_3 nanocomposites show high performance on catalytic oxidation removal of captopril. During catalytic ozonation, catalysts can promote the ozonation process and generate active free radicals. Consequently, enhancing the degradation and mineralization of organic contaminants [10, 14].

3.3. Effect of the initial captopril concentration

The effect of the initial concentration of captopril on the removal efficiency using the catalytic ozonation process was investigated in the range from 10 to 70 mg L^{-1}. In the stable condition, including solution pH of 5, ZnO/Fe_2O_3 nanocomposite dosage of 2.0 g L^{-1}, and ozone dosage of 0.5 mg min^{-1}. The results are displayed in Figure 6. The removal efficiency of

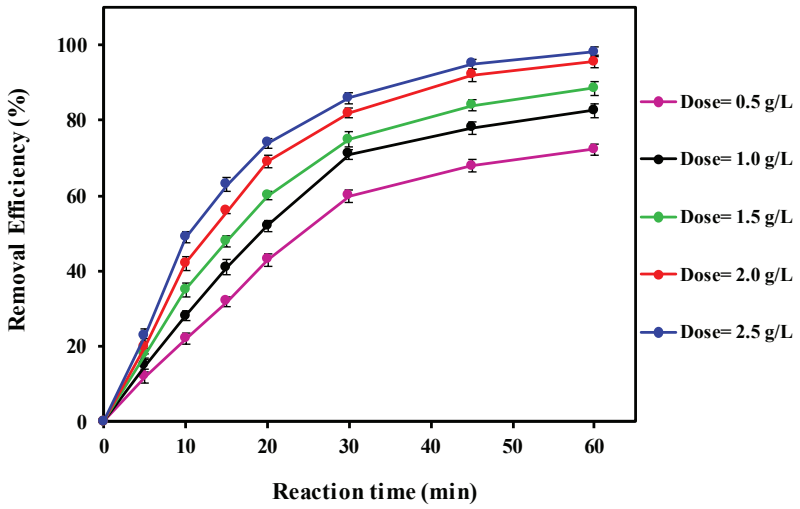

Fig. 5. Effect of ZnO/Fe_2O_3 nanocomposite dosage and reaction time for removal captopril using catalytic ozonation. Experimental conditions: initial captopril concentration of 30 mg L^{-1}, solution pH of 5.0, ozone dosage of 0.5 mg min^{-1}.

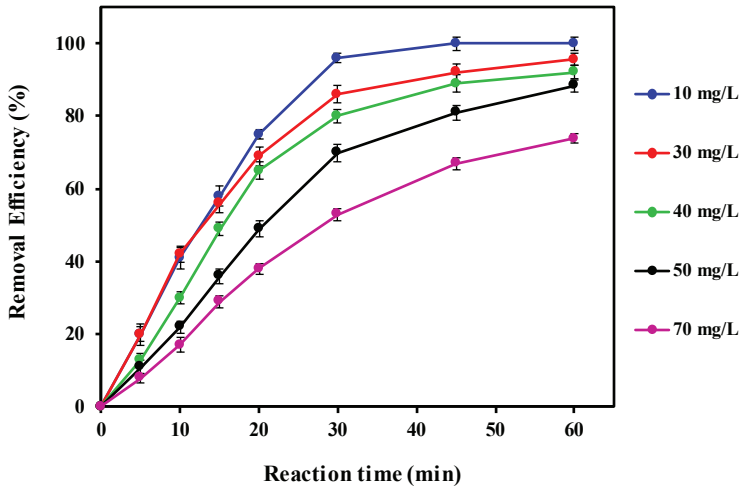

Fig. 6. Effect of initial captopril concentration and reaction time for removal captopril using catalytic ozonation. Experimental conditions: solution pH of 5.0, ZnO/Fe_2O_3 nanocomposite dosage of 1.0 g L^{-1}, ozone dosage of 0.5 mg min^{-1}.

captopril indeed decreased with the increase of the initial concentration. After 60 min of reaction time, when the initial concentration of captopril increased to 10, 30, 40, 50, and 70 mg L^{-1} removal efficiency reached 100.0%, 95.6%, 92.1%, 88.4%, and 73.9%, respectively. This phenomenon can be due to, at constant conditions, the ozone concentration in the reactor being constant, so the amount of ·OH in the reactor would be constant under the same conditions. The high concentration of captopril would consume more ·OH, so the removal efficiency is reduced with the increase of the initial concentration of contaminants [19, 20]. Due to the captopril removal efficiency at a concentration of 40 mg L^{-1} being a good performance (above 90%), a captopril concentration of 40 mg L^{-1} was selected as the optimum concentration.

3.4. Effect of ozone dosage

Figure 7 shows the removal efficiency of captopril under different ozone dosages. Various levels of ozone dosage were set by adjusting the inlet gas

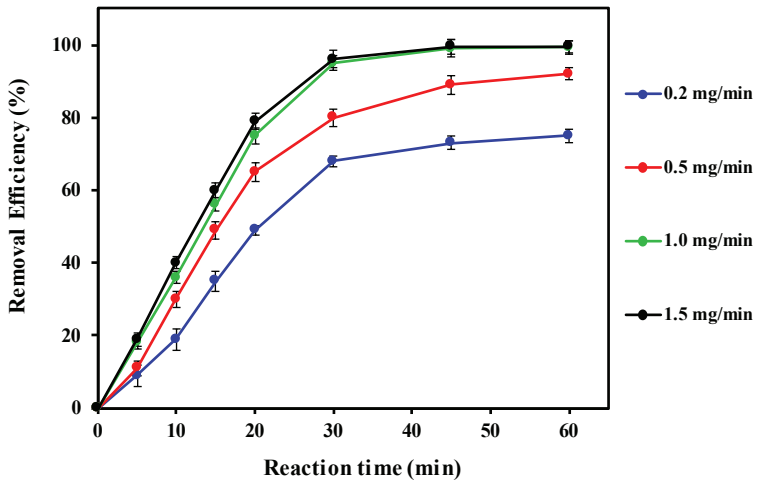

Fig. 7. Effect of ozone dosage and reaction time for removal captopril using catalytic ozonation. Experimental conditions: solution pH of 5.0, ZnO/Fe_2O_3 nanocomposite dosage of 2.0 g L^{-1}, initial captopril concentration of 40 mg L^{-1}.

concentration. The ozone dosage effect in the range of 0.2 to 1.5 mg min^{-1} was investigated in constant conditions, including solution pH of 5, ZnO/Fe_2O_3 nanocomposite dosage of 1.0 g L^{-1}, and initial captopril concentration of 40 mg L^{-1}. The experimental results are presented in Figure 4. According the results, the captopril removal efficiency increased to 75.0%, 92.1%, 99.4%, and 99.6% when the ozone dosage was increased to 0.2, 0.5, 1.0, and 1.5 mg min^{-1}, respectively. More than 99.4% of captopril is removed within 45 minutes when the ozone dosage is 1.0 mg min^{-1}.

Further increase of ozone dosage (≥1.0 mg min^{-1}) had no significant effect on the captopril removal efficiency. This result is probably because the ozone dosage of 1.0 mg min^{-1} reached the maximum ozone utilization of the ZnO/Fe_2O_3 nanocomposite. Thus, the optimum ozone dosage was selected as 1.0 mg min^{-1} [21, 22]. He *et al.* removed the metoprolol and ibuprofen using catalytic ozonation; their results showed that in optimal conditions, the catalyst dosage was 0.1 g L^{-1} [21].

Bai et al. removed the sulfamethazine using a catalytic ozonation process ($Ce_{0.1}Fe_{0.9}OOH$ as a catalyst), their results indicated that under optimal conditions including pH of 7.0, catalyst dosage of 0.2 g L^{-1}, ozone dosage of 15 mg min^{-1}, and sulfamethazine concentration of 20 mg L^{-1}, TOC removal efficiency was obtained of 44% at during 120 min [23]. In addition, Qi et al. removed the phenacetin using catalytic ozonation with $CuFe_2O_4$ and its precursor; their results showed that in optimal conditions (pH of 7.72, catalyst dosage of 2.0 g L^{-1}; ozone dosage of 0.36 mg min^{-1}, and phenacetin concentration of 0.2 mM), the TOC removal efficiency was obtained of 90% at during 180 min [24]. Moreover, Zhao *et al*. removed the phenol using catalytic ozonation with $NiFe_2O_4$ as a catalyst; their results showed that in optimal conditions (pH of 6.5, catalyst dosage of 1.0 g L^{-1}; ozone dosage of 0.75 mg min^{-1}, and phenol concentration of 300 mg L^{-1}), the phenol removal efficiency was obtained of 38.9% at during 60 min [25].

4. Conclusion

This current study aims to evaluate the removal efficiency of captopril using ZnO/Fe_2O_3 nanocomposite as a low-cost catalyst by a catalytic ozonation process. The maximum captopril removal efficiency was 99.4% under optimal conditions. During catalytic ozonation, catalysts can promote the ozonation process and generate active free radicals. It enhanced the degradation and mineralization of organic contaminants. Solution pH and initial captopril concentration had an inverse effect, and the catalyst and ozone dosage directly affected the removal efficiency of captopril. The catalytic ozonation process is an eco-friendly advanced oxidation process successfully applied to remove captopril from polluted water.

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Conflict of interest: The authors declare that they have no conflict of interest regarding the publication of the current paper.

Ethical approval: The Ethics Committee of Kerman University of Medical Sciences approved the study (IR.KMU.REC.1401.099).

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