



Ciprofloxacin removal from aqueous solutions by ozonation with calcium peroxide

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ABSTRACT

Ciprofloxacin (CIP) belongs to the fluoroquinolones group and is widely applied in therapeutics. The presence of fluorine in CIP increases its stability in the environment. Advanced oxidation processes are among the most effective methods used to remove hazardous and resistant pollutants in the environment. This study aimed to determine the efficiency of the ozonation process with calcium peroxide for the removal of CIP from aqueous solutions. The removal efficiency of CIP and chemical oxygen demand under optimal conditions, that is, pH = 3, CIP concentration = 5 mg/L, concentration of CaO₂ = 0.025 mg/L, temperature = 25°C, ozonation rate = 1 g/min and contact time = 50 min, was obtained 95.6% and 80.1% as well as 85.4% and 73.6%, in synthetic and simulated wastewater samples (municipal wastewater + CIP), respectively. Thermodynamic studies have shown that CIP decomposition with ozonation and CaO₂ is an endothermic process. The kinetics of CIP decomposition followed the pseudo-first-order equation. The use of the ozonation process with calcium peroxide is an efficient method for CIP removal.

Keywords: Ciprofloxacin; Calcium peroxide; Advanced oxidation; Catalytic ozonation

1. Introduction

Antibiotics are rarely metabolized in the body after they are used, and approximately 30% to 90% of them remain active after removal [1,2]. There is substantial evidence that antibiotics are found in various water sources at different concentrations. These compounds have been identified in-ground, surface, waste and even drinking water. Pharmaceutical compounds are transmitted to aquatic environments through various sources such as pharmaceutical industries, hospital wastewater and human and animal wastes

[3,4]. The presence of antibiotics in the environment (including water and soil), even at low concentrations, leads to the development of antibiotic-resistant pathogens that potentially threaten the function of the ecosystem and endanger human health. Antibiotic-resistant bacteria are increasing and many researchers believe that this increase is due to the unusual use of antibiotics [5,6].

Ciprofloxacin (CIP) belongs to the fluoroquinolones group and is widely applied in therapeutics [7]. The presence of fluorine in CIP increases its stability in the environment and for this reason, it is considered an environmental pollutant [8].

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CIP is an antibiotic commonly used to treat bacterial infections [9]. The concentration of CIP is estimated as 1 µg/L in waste and surface waters, >150 µg/L in hospital effluents and 30 mg/L in pharmaceutical factories [10]. The presence of CIP is harmful, even at low concentrations, and can lead to widespread antibiotic resistance. The effect of these materials on non-target pathogens changes the structure of aquatic algae, interferes with photosynthesis and results in the development of apparent abnormalities in plants [9–11].

Different methods have been proposed for the removal of CIP antibiotics from aqueous solutions. Use of ultraviolet (UV) photolysis [12], adsorption, [13], UV/H₂O₂ and O₃/H₂O₂ [14], zinc hydroxide nanoparticles on activated carbon [15], nanostructured composites by ultrasonic wave [16], nanowire adsorbents [17], natural walnut carbons [18], use of photocatalyst processes [19–27] and magnetic nano biocomposites [28] are among the common methods for CIP removal.

Advanced oxidation processes (AOPs) are the most effective technology used for the decomposition and removal of hazardous, resistant and non-biodegradable organic pollutants in aqueous solutions [29]. AOPs not only phase-transfer pollutants but also destroy them, which is an advantage [30]. These processes can convert organic compounds into water and carbon dioxide [31]. AOPs, with highly reactive hydroxyl radical (*OH) as the main oxidative species, have received considerable attention as an alternative technique to transform and decontaminate soluble human antibiotics and other toxic organic compounds [5,32]. In some cases, oxidation via *OH radical is slow and the application of reducing radicals, such as hydrated electron (e_{aq}⁻) or a hydrogen atom (*H), may be useful [33]. Simultaneous generation of both reducing and oxidizing radical species leads to the destruction of a wide range of pollutants [34].

Over the past few years, hybrid processes such as ozone and hydrogen peroxide (H₂O₂) [35], ozone and UV radiation [36], the ozonation process combined with the Fenton process and the catalytic ozonation process have been used [37]. Calcium peroxide (CaO₂) is an effective source of H₂O₂ production [38] and can be dissolved in water slowly to release oxygen molecules. Moreover, CaO₂ is decomposed in water and converted to H₂O₂ and calcium oxide [39]. The advantages of CaO₂ include compatibility with the environment, easy transportation, low cost compared to other substances, long-term effect and high-impact [40]. Roma et al. [41] using the UV/H₂O₂ method, Yue et al. [42] using multi-wall carbon nanotubes, Sinha et al. [43] using the modified advanced oxidation method and Gharaghani and Malakootian [24] using fixed ZnO nanoparticles on a glass plate succeeded in removing CIP. Moreover, Honarmandrad et al. [44] used O₃/CaO₂ for the removal of metronidazole and Malakootian and Honarmandrad [45] used the ozonation process with CaO₂ for the removal of reactive blue 19 dye. This study aimed to remove CIP from aqueous solutions by ozonation with CaO₂. Integrative methods such as ozonation with CaO₂ have high efficiency for the removal of resistant pollutants in a short time. Accordingly, in this research, the ozonation process with CaO₂ was used for CIP removal and parameters such as pH, contact time, CIP concentration, CaO₂ concentration, and temperature were optimized; moreover, optimum conditions were considered on a simulated wastewater sample.

2. Materials and methods

A stock solution with a CIP concentration of 1,000 mg/L was prepared with dilution in deionized water daily. The amount of ozone in 1 g/min was determined. The gas output from the ozone generator was passed from two containers containing a solution of 2% potassium iodide for 10 min. After 10 min of ozonation, a solution of 200 mL potassium iodide was removed and thereafter 10 mL of 2 N sulfuric acid were added to the solution. Furthermore, the solution was titrated using 0.005 N sodium thiosulfate until the yellow color of iodine disappeared. Afterward, 1–2 drops of starch were added and the titration was continued until the disappearance of the blue color. In the end, the consumption volume of sodium thiosulfate was recorded. The produced ozone was determined from Eq. (1). Concentrations of 5, 10, 20, 30, and 40 mg/L were removed from the stock solution of CIP. Afterward, the CIP concentrations were blended with concentrations of 0.025, 0.05, 0.075, and 0.1 mg/L of CaO₂, pH of 3, 5, 7, 9 and 11 and temperature of 25°C, 35°C, and 45°C, and the solution was stirred with a shaker. Subsequently, the solution was ozonized with contact times of 10, 30, 40 and 50 min and then centrifuged. Thereafter, a spectrophotometer was used to obtain the CIP removal efficiency in the synthetic sample. The kinetics of reactions and thermodynamics were obtained for the synthetic sample.

To set the exact temperature, the chamber temperature was continuously controlled by a sensor, which was placed inside the chamber. The sensor acted quickly when the temperature was changed. The electronic thermostat quickly turned the heater on if the chamber temperature was below the desired temperature and it turned the heater off otherwise. A sensor was connected to the thermostat, which kept the temperature at 25°C, 35°C, and 45°C.

The simulated wastewater sample was prepared from sewage generated from the Kerman wastewater treatment plant, and all the tests were performed using this sample. The CIP degradation efficiency in the simulated wastewater was measured with an HPLC device (KNAUER-D14163, Germany) using a column with the properties of C8; 259 mm × 4.6 mm × 5 mm, a UV detector at the wavelength of 272 nm with a hybrid mobile phase HCl 10 µM (micromolar), and acetonitrile with a 80 to 20 compound ratio and an input flow rate of 1 mL/min. The experiment was repeated in triplicates, and the results were reported as mean. Data analysis was carried out by using descriptive statistics. Finally, the CIP removal efficiency was calculated from Eq. (2) [46]:

$$\text{Ozone concentration (mg/L)} = \frac{(A + B) \times N \times 24}{T(\text{min})} \quad (1)$$

A: consumption of sodium thiosulfate for the first container (mL); B: consumption of sodium thiosulfate for the second container (mL); T: ozonation time (min); N: normality of sodium thiosulfate.

$$\text{Removal efficiency (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

C_i : CIP initial concentration (mg/L); C_f : CIP residue concentration (mg/L).

In this study, the ozone generator ARDA (model (MOG-5 G/H), an air compressor (model FL25), a pH meter (Model EDT-R357), a flow meter, a centrifuge (model-150), and a spectrophotometer (Shimadzu/UV 1800, Japan) were used.

CIP with a purity of 99% was purchased from (Temad, Tehran, Iran). CaO_2 with a purity of 98%, sulfuric acid, and sodium hydroxide were purchased from (Merck, United States).

3. Results and discussion

3.1. Effect of pH on CIP removal efficiency

The results of the experiments on the effect of pH on the removal efficiency of CIP from aqueous solutions are shown in Fig. 1.

According to Fig. 1 it was observed that 50 min after the process at CIP concentration = 5 mg/L, CaO_2 concentration = 0.025 mg/L, temperature = 25°C and pH = 3, the maximum CIP removal efficiency in the synthetic sample was 95.6%. The removal efficiency decreased with increasing pH such that the removal efficiency at pH = 11 was 43.7% in the synthetic sample.

In AOPs, changes in pH by the production of various radicals affect the amount of oxidation [47]. CaO_2 is stable and highly soluble at low pH. It also reacts with hydrogen ions to produce H_2O_2 at low pH. Therefore, the main purpose of using CaO_2 is to produce H_2O_2 . In acidic pH, the H_2O_2 production efficiency and the CaO_2 dissolution rate increase [48]; thus, the removal efficiency increases with decreasing pH.

In an acidic condition, CaO_2 reacted with H^+ and produced H_2O_2 according to Eqs. (3)–(5):

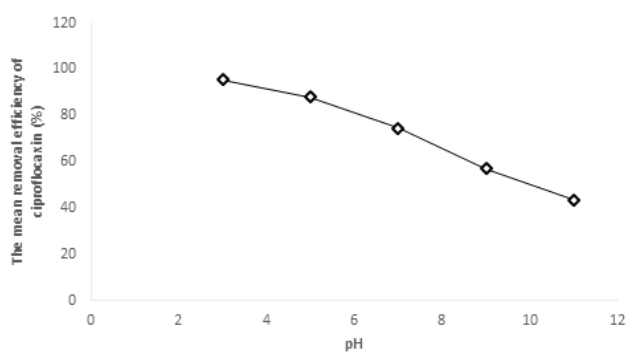
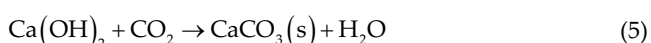
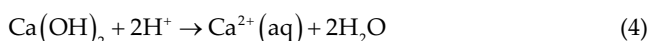
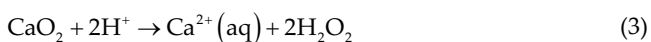


Fig. 1. Effect of pH on the removal efficiency of CIP from aqueous solutions by the ozonation process with CaO_2 (CIP concentration = 5 mg/L, CaO_2 concentration = 0.025 mg/L, temperature = 25°C, ozonation rate = 1 g/min and contact time = 50 min).

These results are consistent with those reported by Qian et al. [49] in China, who reported the removal of toluene by CaO_2 , Northup et al. [39] in the USA, who showed the modification of the Fenton method by CaO_2 , Roma et al. in England [41], who studied CIP removal by the UV/ H_2O_2 method, Khan et al. [50] in South Korea, who studied tetracycline degradation by ozonation in the aqueous phase, Sayed et al. [51] in Pakistan, who used an AOP for CIP degradation in water, and Honarmandrad et al. [44], who used O_3/CaO_2 for the removal of metronidazole.

3.2. Effect of calcium peroxide (CaO_2) concentration on CIP removal efficiency

The results of the experiments on the effect of the CaO_2 concentration on the removal efficiency of CIP from aqueous solutions are shown in Fig. 2.

Fig. 2 shows that the removal efficiency of CIP with the 0.025 mg/L CaO_2 concentration in the synthetic sample was 95.6%. The CIP removal efficiency increased by decreasing the CaO_2 concentration. When the amount of CaO_2 was 0 and 0.025 mg/L, the CIP removal efficiency in the synthetic sample was obtained 43.4% and 95.6%, respectively.

Moreover, the removal efficiency decreased by increasing the CaO_2 concentration.

Ozone can decompose to oxygen and radicals such as hydroxyl radical OH^\bullet and superoxide ($\text{O}_2^{\bullet-}$) [52]. Produced radicals are highly strong oxidants, which react with various substances. The mechanism of ozone decomposition with H_2O_2 is shown in Eq. (3), which caused to produce hydroxyl radicals. Moreover, Eqs. (6)–(8) are simultaneously involved in the aquatic solution, which caused to reduce the process efficiency by increasing hydroxyl radicals in the solution [53]:

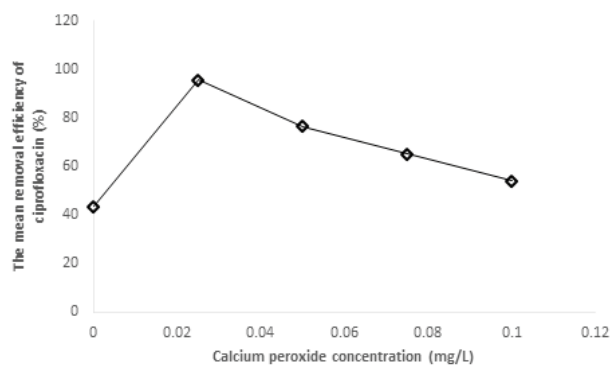


Fig. 2. Effect of the CaO_2 concentration on the removal efficiency of CIP from aqueous solutions by the ozonation process with CaO_2 (CIP concentration = 5 mg/L, pH = 3, temperature = 25°C, ozonation rate = 1 g/min and contact time = 50 min).

The high percentage of oxidants in the environment reduces radicals and converts some part of oxidant radicals to intermediate substances and other compounds [54].

These results are consistent with those reported by Honarmandrad et al. [44] in Iran, who used the ozonation process with CaO_2 for the removal of metronidazole antibiotics from aqueous solutions, Zhang et al. [55] in China, who attempted to degrade trichloroethylene in aqueous solutions using CaO_2 activated by ferrous ions, Rahmani et al. [53] in Iran, who used a combined AOP, that is, electrooxidation–ozonation, for CIP removal from aqueous solutions, and Malakootian and Honarmandrad [45] in Iran, who used O_3/CaO_2 for the removal of reactive blue 19 dye.

3.3. Effect of CIP initial concentration on CIP removal efficiency

The results of the experiments on the effect of CIP concentration on the removal efficiency of CIP from aqueous solutions are shown in Fig. 3.

According to Fig. 3, it was observed that the removal efficiency decreased when the initial CIP concentration increased. Accordingly, the maximum CIP removal efficiency with the CIP concentration of 5 mg/L was obtained 95.6% in the synthetic sample. Moreover, the minimum CIP removal efficiency with the CIP concentration of 40 mg/L was obtained 65.2% in the synthetic sample.

Also, the removal efficiency decreased when the initial CIP concentration increased. These results are consistent with those reported by Olyaie et al. [54] in Iran for the removal of arsenic contamination from aqueous solutions using CaO_2 nanoparticles, Bahrami et al. [56] in Iran for the removal of metronidazole from aqueous solutions using the ozonation process, Orge et al. [57] in Portugal for the photocatalytic-assisted ozone degradation of metolachlor aqueous solutions using ozone and Souza and F  ris [58] in Brazil for the degradation caffeine using O_3 and O_3/UV . By increasing the concentration of pollutants, oxidizing substances such as ozone molecules and hydroxyl radicals decreased. When the concentration of pollutants was low, the removal efficiency increased and pollutant decomposition became complete, leading to lower production of intermediate materials [53].

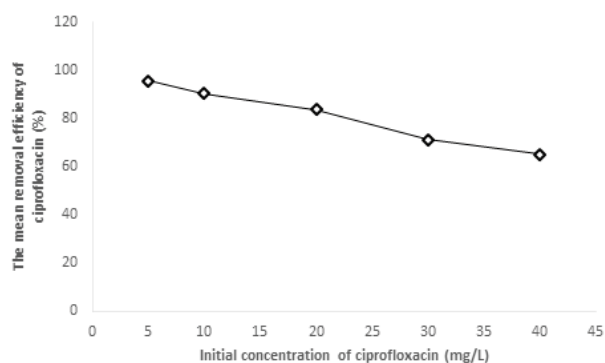


Fig. 3. Effect of the CIP initial concentration on the removal efficiency of CIP from aqueous solutions by the ozonation process with CaO_2 (CaCO_3 concentration = 0.025 mg/L, pH = 3, temperature = 25°C, ozonation rate = 1 g/min and contact time = 50 min).

3.4. Effect of contact time on CIP removal efficiency

The results of the experiments on the effect of contact time on the removal efficiency of CIP from aqueous solutions are shown in Fig. 4.

Fig. 4 shows that as contact time increased, the removal efficiency increased. Accordingly, the maximum CIP removal efficiency at 50 min contact time was obtained 95.6% in the synthetic sample whereas the minimum CIP removal efficiency at 10 min contact time was obtained 66.9% in the sample.

Moreover, the removal efficiency increased by increasing contact time. These results are consistent with those reported by Bahrami et al. [56] in Iran for metronidazole removal from aqueous solutions using the ozonation process, Malakootian et al. [59] in Iran for antibiotic tetracycline removal by modified zeolite with cationic surfactant, Jung et al. [60] in South Korea for amoxicillin removal by UV and $\text{UV}/\text{H}_2\text{O}_2$ processes, Gharaghani and Malakootian [24] in Iran for CIP degradation using ZnO nanoparticles immobilized on a glass plate and Kermani et al. [61] in Iran for metronidazole degradation by the catalytic ozonation process in the presence of MgO nanoparticles. Moreover, by increasing contact time, the production of radical hydroxyl and ozone molecules also increased, leading to increased removal efficiency.

3.5. Effects of ozonation alone and in combination with calcium peroxide (CaO_2) on CIP removal efficiency

The effects of ozonation alone and ozonation with CaO_2 on CIP removal are shown in Fig. 5. The maximum removal rates by ozonation and ozonation with CaO_2 were 43.5%, and 95.6%, respectively. The removal efficiency was observed to be greater using ozonation with CaO_2 than using the other two methods. According to Eqs. (3) and (6)–(8), CaO_2 produced H_2O_2 and reacted with ozone to produce radical OH^* , and radical OH^* had a great effect on dye removal [53].

3.6. Determination of CIP degradation kinetics

To determine the kinetics of CIP decomposition, the kinetics of the reactions were investigated. To this end, the

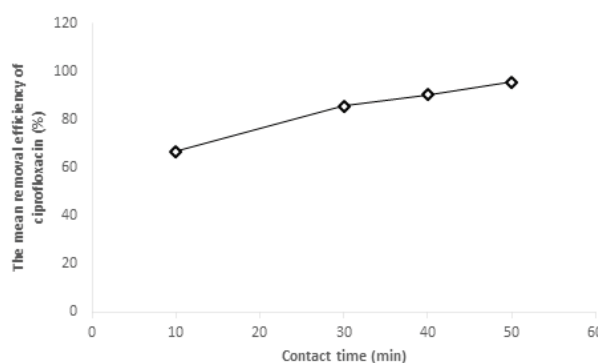


Fig. 4. Effect of contact time on the removal efficiency of CIP from aqueous solutions by the ozonation process with CaO_2 (CIP concentration = 5 mg/L, CaCO_3 concentration = 0.025 mg/L and pH = 3, temperature = 25°C and ozonation rate = 1 g/min).

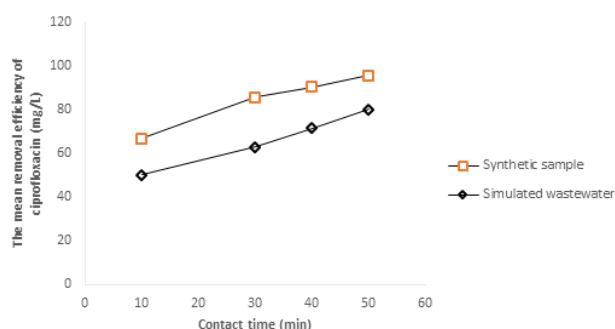


Fig. 5. Effects of ozonation alone and in combination with CaO_2 on the removal efficiency of CIP (CIP concentration = 5 mg/L, pH = 3, temperature = 25°C, ozonation rate = 1 g/min and contact time = 50 min).

pseudo-first-order and pseudo-second-order kinetics were considered for CIP decomposition. Generally, the pseudo-first-order kinetic is used for the degradation of most drugs or antibiotics [24,62]. According to the results, the kinetics of the decomposition followed the pseudo-first-order equation. The results obtained from the kinetic study are presented in Table 1.

The results showed that the pseudo-first-order kinetic data model followed the correlation coefficients $R^2 = 0.999$.

These results are consistent with those reported by Rosal et al. [62] for the removal of pharmaceutical products using an AOP, Gharaghani and Malakootian [24] for CIP removal using ZnO nanoparticles immobilized on a glass plate and Trapido et al. [63] in Finland for the degradation of chlorophenols using ozone, ozone/UV and UV/ H_2O_2 . The pseudo-first-order kinetics are consistent with the results of the mentioned researches.

3.7. Determination of CIP degradation thermodynamics

The constant thermodynamic equilibrium (K°) for temperature variations can be used to calculate thermodynamic functions, such as enthalpy changes and standard entropy (ΔH° and ΔS°), as well as standard energy-based on Gibbs changes (ΔG°).

$$\Delta G = -RT \ln \quad (9)$$

$$K^\circ = \frac{q_e}{C_e} \quad (10)$$

Table 1
Results of the pseudo-first-order kinetics at different CIP concentrations

C_0	R^2	k_{obs}	Equations
5	0.999	0.0404	$y = 0.0404x - 0.0239$
10	0.9875	0.0334	$y = 0.0334x - 0.1049$
20	0.9884	0.0241	$y = 0.0241x - 0.0697$
30	0.9843	0.0161	$y = 0.0161x - 0.046$
40	0.9742	0.0113	$y = 0.0113x - 0.0454$

$$\ln K^\circ = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R} \quad (11)$$

In Eq. (11), R , T and K° are the total gas concentration (8.314 J/K mol), the absolute temperature (K) and the distribution coefficient, respectively. Moreover, ΔH and ΔS can be calculated from the slope and intercept of the linear plot of K vs. $1/T$. Using Eq. (10) and the $\ln K^\circ$ changes to $1/T$, we can obtain the value of enthalpy changes and the standard entropy from the gradient and width of the origin of the drawn line, respectively [64]. The thermodynamic variables are shown in Table 2.

According to the results, the enthalpy was positive while the standard entropy was negative. Moreover, changes in Gibbs energy increased by increasing temperature.

The positive value of ΔH° and the negative value of ΔS° , respectively, indicated the thermo stability in the process of CIP decomposition by the ozonation process with CaO_2 . Evaluation of free energy changes in the Gibbs standard showed that the CIP decomposition was obtained at 25°C. This temperature was the optimum temperature and by increasing temperature, the degradation conditions became unfavorable and the spontaneous reaction was reduced. Thermodynamic studies have shown that CIP decomposition with ozonation and CaO_2 is an endothermic process. These results are in line with those reported by Gharaghani and Malakootian [24] for CIP removal using an AOP, showing that CIP decomposition was reduced by increasing temperature [24].

3.6. CIP removal from a simulated wastewater sample

The maximum CIP removal efficiency by the ozonation process with CaO_2 was obtained 95.6% in the synthetic sample under optimal conditions of 50 min contact time, pH = 3, 5 mg/L CIP concentration, 0.025 mg/L CaO_2 concentration, and 1 m/min ozonation rate. Moreover, the CIP removal efficiency and the chemical oxygen demand (COD) reduction in the simulated wastewater sample (the Kerman wastewater treatment plant sewage + CIP antibiotics) was 80.1% and 73%, respectively, under the optimal conditions. Additionally, there was a decrease in the removal efficiency in the simulated wastewater solution, which was caused by interferences, such as cations and anions present in the wastewater. Table 3 shows the results of the quality assessment of the Kerman wastewater treatment plant sewage after adding 5 mg/L CIP.

Furthermore, the maximum CIP removal efficiency and the COD reduction by the ozonation process with CaO_2

Table 2
Adsorption kinetics equilibrium parameter values

Temperature (k°)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol)
298	16.37	7.1	-16.733
308	14.67		
318	13.8		

Table 3
Characterization of municipal wastewater

Parameter	Amount
COD	481 mg/L
BOD	269 mg/L
EC	3.60 $\mu\text{S}/\text{m}$
TDS	1972 mg/L
pH	7.56
Turbidity	225 NTU

were 80.1% and 73%, respectively, at the Kerman wastewater treatment plant sewage under optimal conditions of 50 min contact time, pH = 3, 5 mg/L CIP concentration, 0.025 mg/L CaO_2 concentration and 1 g/min ozonation rate. The decrease in the CIP removal efficiency in the simulated wastewater sample was caused by interferences, including cations and anions present in the wastewater, turbidity and total dissolved solids.

4. Conclusions

The maximum CIP removal efficiency by this process was 95.6 and 80.1 in the synthetic and simulated wastewater samples, respectively, under optimal conditions of 50 min contact time, pH = 3, 5 mg/L CIP concentration, 25°C temperature, 1 g/min ozonation rate and 0.025 mg/L CaO_2 concentration. Moreover, the COD removal efficiency was obtained 85.4% and 73.6% in the synthetic and simulated wastewater samples, respectively, under the optimal conditions. Also, the kinetics of decomposition followed the pseudo-first-order equation. Thermodynamic studies have shown that CIP decomposition with ozonation and CaO_2 is an endothermic process.

Despite having high electricity consumption as its limitation, the ozonation process with CaO_2 is regarded as an effective method due to its relatively high efficiency in CIP removal, strong oxidation, and decomposition of resistant organic compounds and thus can be used for CIP removal from the wastewater of pharmaceutical industries.

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