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Investigating the use of ozonation process with calcium peroxide for the removal of metronidazole antibiotic from aqueous solutions

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ABSTRACT

Advanced oxidation processes are one of the most efficient and effective methods for decomposing dangerous organic contaminants which are resistant and non-biodegradable in the aquatic solution. The aim of this study is to determine the efficiency of ozonation process with calcium peroxide for the removal of the metronidazole from aqueous solutions. This research is an experimental. A synthetic sample was prepared with a concentration of 5–40 mg L^{-1} of the metronidazole. The removal efficiency of metronidazole and chemical oxygen demand (COD) by ozonation and calcium peroxide in different conditions such as pH, calcium peroxide concentrations, contact time, concentration of the metronidazole and 1 g of ozone per minute was examined. The optimal conditions for synthetic samples were obtained. Metronidazole and COD removal under optimal conditions with real samples were also tested. The maximum removal of metronidazole and COD with a concentration of 5 mg L^{-1} metronidazole, pH = 3, 0.025 mg L^{-1} of calcium peroxide, contact time of 40 min, were obtained in synthetic samples as 90.1% and 86.6%; and in real samples as 79.5% and 71%, respectively. Due to the relatively high removal efficiency of ozonation with calcium peroxide for the removal of metronidazole as a resistant combination to decomposition, this method is an effective method for the removal of contaminants.

Keywords: Metronidazole; Calcium peroxide; Catalytic ozonation; Advanced oxidation; Aqueous solutions

1. Introduction

Antibiotics are rarely metabolized completely in the body after use. Approximately 30%–90% of them remain active after disposal [1,2]. There is much evidence that most of these compounds in water are present in amounts of nanograms to micrograms per liter. These compounds in groundwater, surface water, wastewater and drinking water have been observed. Medicinal compounds are transmitted via various sources such as pharmacy, hospital waste and disposal of human and animal wastes into the aquatic environment [3,4]. The existence of antibiotics such as water and soil in the environment even in low concentration has led to the development of antibiotic-resistant pathogens which potentially threaten the ecosystem and human health. Antibiotic-resistant bacteria are on the increase, and many researchers believe that this increase is as a result of indiscriminate use of antibiotics [5,6].

Metronidazole (2-methyl-5-nitroimidazole-1-ethanol) ($C_6H_9N_3O_3$) is one of the nitroimidazole antibiotics category. It is one of the most widely utilized antibiotics in the world with antibacterial and antiinflammatory properties and it has been used to treat infectious diseases caused by anaerobic bacteria and protozoa such as amoebiasis, *Giardia lamblia* and *Trichomonas vaginalis* [7]. In addition, metronidazole is utilized as a food additive in poultry and fish in order to remove parasites [8]. Metronidazole has an annular structure and has different effects on humans, which can be attributed to its

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carcinogenic and mutagenic potential because this antibiotic can induce DNA damage in lymphocytes [9].

According to the International Agency for Research on Cancer (IARC), the mutagenic and genotoxic nature of metronidazole antibiotic on human cells and carcinogenic nature for animals has been proven [7]. One to ten (1 to 10) ng mL^{-1} of metronidazole antibiotic concentration has been found in surface water and sewage [10]. Due to the low degradability and high solubility in water (9.5 g dm^{-3}), this antibiotic cannot be eliminated from aquatic solution by conventional treatment, and its accumulation in the aquatic environment will cause side effects on human health and the environment [8]. Metronidazole is an inhibitor of cytochrome P450 system and after entering the wastewater, the chemical oxygen demand of wastewater is increased.

Several ways for eliminating the metronidazole antibiotic in aquatic environments have been suggested. The use of gamma ray [11], adsorption, optical dispersion, coagulation and centrifuges [12], chemical oxidation of iron salts, Fenton processes, photocatalyst of TiO_2, photolysis UV, UV/H_2O_2 and O_3/H_2O_2 [13] has been indicated. Malakootian et al. [14–18] conducted researches on removal of pharmaceutical compounds from aqueous solutions.

Advanced oxidation processes (AOPs) are based on physicochemical processes that produce in situ powerful transitory species, principally hydroxyl radicals ($HO^{\bullet}$), by using chemical and/or other forms of energy, and have a high efficiency for organic matter oxidation; in fact, under proper conditions the species to be removed are converted completely to CO_2, H_2O and innocuous mineral salts [19]. The principal mechanism of AOPs function is the generation of highly reactive free radicals. Consequently, combination of two or more AOPs expectedly enhances free radical generation, which eventually leads to higher oxidation rates [20]. AOPs due to the simplicity, low cost and high efficiency is one of the most common technology for the removal of pollutants especially decomposition and removal of dangerous organic contaminants, which are resistant and non-biodegradable in the aquatic environment [21]. This process can convert organic compounds into water and carbon dioxide [22]. So far, different types of AOPs for water and wastewater treatment have been expanded and examined, in addition to the original use of ozone as an oxidant [23]. Ozone is a powerful oxidizing agent (E_0 = 2.08 V), when compared with other agents, such as H_2O_2 (E_0 = 1.78 V), and can react with several classes of compounds through direct or indirect reactions [19]. In many cases, the use of ozonation alone for the removal of resistant organic compounds has a low efficiency and produces toxic and dangerous intermediate materials.

In recent years, combination processes such as ozone and hydrogen peroxide as Proxan [24], ozone and ultraviolet light [25] and ozonation in combination with Fenton process and catalytic ozonation process have been used [26]. Calcium peroxide is an effective source for the production of hydrogen peroxide [27]. The unique features of calcium peroxide include dissolving slowly in water and releasing oxygen molecules [28]. In addition, calcium peroxide decomposes in water and is converted to hydrogen peroxide and calcium oxide. Among the advantages of calcium peroxide, environmentally compatible, easy handling, low cost compared with other substances, long-term and high-impact can be noted [29].

The aim of this study is to determine the efficiency of ozonation process with calcium peroxide for the removal of the antibiotic metronidazole from aquatic environments.

2. Materials and methods

The research is empirical that was accomplish in the first half of 2016 at Environmental Health Engineering Research Center in Kerman University of Medical Science. The stock solutions with a concentration of 1,000 mg L^{-1} of metronidazole were prepared on a daily basis. Thereafter, spectrophotometer was employed for scanning the antibiotic. The maximum absorption at a wavelength of 319 nm was obtained. The amount of ozone of 1 mg/min was determined. The gas output from ozone generator was passed for 10 min from two containers containing 2% solution of potassium iodide. Both containers contained 250 mL of potassium iodide solution. After 10 min of ozonation, 200 mL of potassium iodide solution was taken. Thereafter, 10 mL of 2 N sulfuric acid was added. In the following, the solution was titrated by using 0.005 N sodium thiosulfate until the disappearance of the yellow color of iodine. Thereafter, one to two drops of starch was added and the titration was continued until the disappearance of the blue color. At the end, the volume of consumption of sodium thiosulfate was recorded. The ozone produced was determined from Eq. (1):

$$\text{Ozone concentration}\left(\text{mg.L}^{-1}\right)=\frac{\left(A+B\right)\times N\times 24}{T(\text{min})} \tag{1}$$

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

The calibration curves for pH of 3, 5, 7, 9 and 11 were drawn. Concentrations of 5, 10, 20, 30 and 40 mg L^{-1} of stock solution were taken. Thereafter, they were mixed with concentrations of 0.025, 0.05, 0.075 and 0.1 mg L^{-1} of calcium peroxide and were stirred by a shaker. Then, the solution was ozonized at a time of 5–50 min. Then, the solution was centrifuged. In the next step, the amount of absorption of the sample was measured by a spectrophotometer. The real sample was prepared from effluent of primary sediment tank of Kerman wastewater treatment plant using the activated sludge method. The result of determination of quality of sewer of wastewater treatment plant in Kerman is shown in Table 1.

Then, the metronidazole antibiotic with the concentrations of 5–40 mg L^{-1} was added manually to the sewer. All of the tests were performed on the real sample. All of the experiments were carried out in the laboratory temperature (22°C ± 1°C). The experiment was repeated three times and the results were reported as mean. Data analysis was carried out by using descriptive statistics and SPSS software version 18. At the end, the metronidazole removal efficiency was calculated from Eq. (2) [30]:

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

Table 1
Quality of turbidity, COD, BOD, TDS, EC, pH of wastewater treatment plant in Kerman

Parameters	Amount
COD	481 mg L^{-1}
BOD	269 mg L^{-1}
pH	7.56
TDS	1,972 mg L^{-1}
EC	360 µs/m
Turbidity	225 NTU

Note: COD — chemical oxygen demand; BOD — biochemical oxygen demand; TDS — total dissolved solids; and EC — electrical conductivity.

where C_i is the initial concentration of antibiotic (mg L^{-1}) and C_f is the residue concentration of antibiotic (mg L^{-1}).

Metronidazole antibiotic as micro with a purity of 99% was purchased from Pars Darou Pharmaceutical Company (Tehran, IRAN) and other substances, such as calcium peroxide with a purity of 98%, sulfuric acid and sodium hydroxide were purchased from Merck (Darmstadt, Germany). In this study, the ozone generator devices called ARDA (model MOG-5 G/H), air compressor (model FL25), pH meter (model EDT-R357), flow meter, L centrifuge (model 150) and spectrophotometry (model Schimadzu/UV–visible 1800) were used.

3. Results and discussion

Changes in UV–visible light spectrum and determination of metronidazole antibiotic, which is the highest point in metronidazole antibiotic prototype was observed at a wavelength of 319 nm.

3.1. Effect of contact time

Results of the effect of contact time on the removal of metronidazole antibiotic are shown in Fig. 1.

With increasing contact time, the removal efficiency is increased. Hence, at time of 5 min, the removal efficiencies in synthetic and real samples were obtained as 53% and 40.5%, respectively. At contact time of 50 min, maximum efficiencies in synthetic and real samples were obtained as 94.3% and 82%, respectively. Since there is no significant difference in relation to the removal of the metronidazole antibiotic between contact time of 40–50 min, contact time of 40 min was determined as the optimum exposure time. High contact time means high volume reactor and higher construction costs. The optimal time was determined as 40 min. The results demonstrated that by increasing contact time from 5 to 50 min, removal of metronidazole was increased. By increasing contact time, the removal efficiency was increased; this is because the production of hydroxyl radicals is more than ozone molecules. Contact time as the time required to achieve the desired targets in a refining process, is one of the important variables in designing and leading a process of oxidation. High contact time means high volume reactor and higher construction costs which is very important. Bahrami et al. in 2014 in Iran using ozonation process demonstrated that by increasing contact time from 15 to 35 min, metronidazole removal efficiency was increased from 45% to 100% [31]. Zhang et al. in 2012 in Korea investigated the removal of amoxicillin antibiotic by direct photolysis processes UV and UV/H_2O_2 and concluded that by increasing the contact time to 80 min, removal efficiency reached 99% [32]. Kermani et al. in 2013 in Iran using catalytic ozonation in the presence of magnesium oxide nanoparticles, concluded that by increasing contact time from 15 to 20 min, removal efficiency was increased from 92% to 99% [33]. Orge et al. [34] in Portugal using photocatalytic-assisted ozone degradation of metolachlor aqueous solution concluded that using ozone alone by increasing contact time from 10 to 30 min, the concentration of metolachlor decreased from 0.2 to 0 mg L^{-1} which is in line with the results of this study.

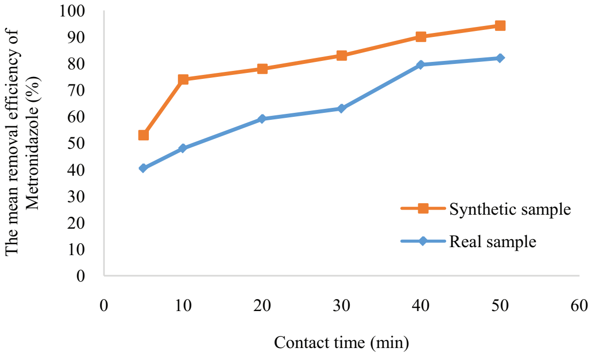

Fig. 1. The effect of contact time on the efficiency of ozonation process with calcium peroxide for the removal of metronidazole antibiotic.

3.2. Effect of pH

The results of the effect of pH on the removal of the metronidazole antibiotic are shown in Fig. 2.

40 min after the ozonation process with calcium peroxide at pH = 3, maximum removal efficiencies were obtained as 90.1% for synthetic samples and 79.5% for real samples. With increase in pH, the efficiency of the process is reduced. At pH 11 and 40 min after the process, the removal efficiencies in synthetic and real samples were 63% and 38%, respectively. An optimum pH of 3 was determined for the removal of the

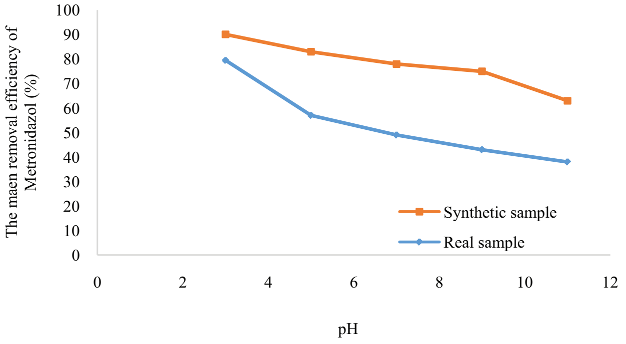

Fig. 2. Effect of pH on the efficiency of the ozonation process with calcium peroxide on the removal of metronidazole.

metronidazole antibiotic. The removal efficiency is reduced with increasing pH. In AOPs, the change in pH via the production of different radicals is effective on oxidation rate [35]. pH plays an important role in the reaction of calcium peroxide with pollution. Calcium peroxide at low pH has high stability and higher solubility. At low pH, this material reacts with hydrogen ions to produce hydrogen peroxide. The main reason of using calcium peroxide is to obtain hydrogen peroxide. In acidity pH, the dissolution rate of hydrogen peroxide and calcium peroxide increases [36]. Moreover, with the release of calcium carbonate, the pH is increased and it creates appropriate conditions for discharging wastewater into the environment [37]. Calcium peroxide reaction in an acid solution is carried out according to Eqs. (3)–(5):

$$CaO_2 + 2H^+ \rightarrow Ca^{2+}(aq) + 2H_2O_2 \tag{3}$$

$$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+}(aq) + 2H_2O \tag{4}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3(s) + H_2O \tag{5}$$

Qian et al. [38] in China used calcium peroxide for the removal of toluene and showed that removal efficiency is increased when pH is reduced to 6. Northup et al. [28] in America using calcium peroxide in reform Fenton showed that reducing pH from 12 to 6 increases the concentration of hydrogen peroxide. Staehelin and Hoigne [39] in Spain using decay of ozone demonstrated that reducing the pH to <6 increase the concentration of H_2O_2 and removal efficiency. Roma et al. [40] in England investigated the decomposition and removal of ciprofloxacin using UV/H_2O_2 in three pH (3, 7 and 10) in aqueous solutions and concluded that the process of acidic pH 3 has been very successful. Khan et al. [41] in South Korea using ozonation process for the removal of tetracycline demonstrated that reducing pH from 7 to 2.2 increases the removal efficiency, such that at pH = 2.2, the tetracycline antibiotic was completely removed. The results of the use of organic substances and calcium peroxide are in line with the results of all the research.

3.3. Effect of calcium peroxide

Results of the effect of concentration of calcium peroxide on the removal of metronidazole antibiotic are shown in Fig. 3.

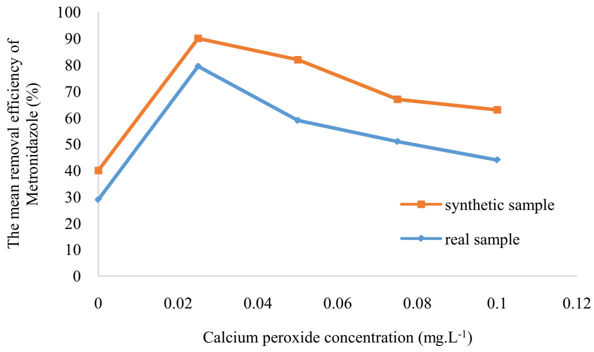

Fig. 3. The effect of calcium peroxide on efficiency of ozonation process with calcium peroxide.

A concentration of 0.025 mg L^{-1} of calcium peroxide removed 90.1% of the metronidazole antibiotic in synthetic samples and 79.5% in real samples. With reduction in calcium peroxide concentration, the removal efficiency was reduced. When the amount of calcium peroxide was 0 mg L^{-1}, the metronidazole removal efficiencies of at least 40% in synthetic sample and 29% in real sample were obtained. Calcium peroxide concentration was determined as 0.025 mg L^{-1}. With increase in calcium peroxide, metronidazole removal efficiency was reduced. The presence of radicals is limited in solution and acts as radical capture and causes the oxidizing of radicals to intermediate materials [42]. In AOPs, the type and amount of oxidizing agent are the important factors. The presence of too oxidizer acts as a radical scavengers and makes part of oxidizing radicals, converted to intermediates and other compounds. The mechanism of ozone decomposition with hydrogen peroxide was done according to Eq. (3) that cause to the production of hydroxyl radicals. Simultaneously, the following Eqs. (6)–(8) is also involved in the aquatic solution that cause reduces the efficiency of the process when increasing the presence of hydroxyl radicals in the solution [31]:

$$OH^{\bullet} + H_2O_2 \rightarrow H_2O + HO^{\bullet}_2 \tag{6}$$

$$OH^{\bullet} + HO_2 \rightarrow H_2O + O_2 \tag{7}$$

$$HO^{\bullet}_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{8}$$

Rahmani et al. in 2015 in Iran with research on ciprofloxacin antibiotic removal by ozonation process demonstrated that with increase in calcium peroxide from 0.025 to 0.1 mg L^{-1}, ciprofloxacin removal efficiency was reduced from 90% to 68% [37]. Zhang et al. [32] in China demonstrated that by increasing the amount of calcium peroxide from 8.4 to 8.8 mg L^{-1}, trichloroethylene removal efficiency was reduced, which is in line with the results of this study.

3.4. Effect of the metronidazole concentration

The results of the initial concentration of the metronidazole antibiotic are shown in Fig. 4.

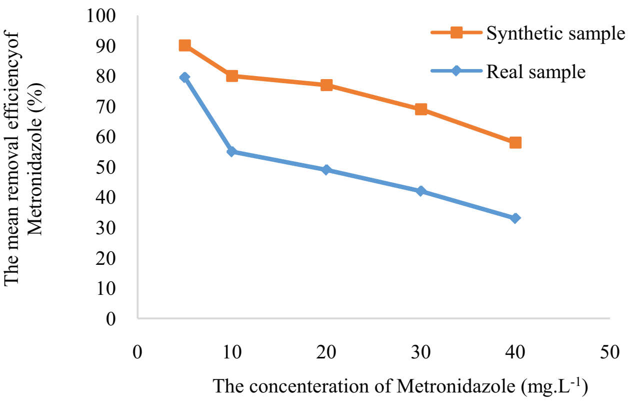

Fig. 4. The effect of initial concentration of the metronidazole antibiotic on the efficiency of ozonation process with calcium peroxide.

The removal efficiency decreases with increasing concentration of metronidazole. Hence, at a concentration of 5 mg L^{-1}, metronidazole maximum removal efficiencies of synthetic and real samples were obtained as 94.3% and 79.5%, respectively, and at a concentration of 40 mg L^{-1}, in synthetic and real samples, the removal efficiencies were obtained as 63% and 41%, respectively. The optimum concentration of metronidazole was determined as 5 mg L^{-1}. With increase in concentration of metronidazole, removal efficiency was reduced, such that with increase in the concentration from 5 to 40 mg L^{-1}, the removal efficiency was reduced from 90% to 63%. With increase in the concentrations of pollutants, consumption of oxidizing substances such as ozone molecule and hydroxyl radicals increases. Whenever the concentration is lower, the contaminant removal efficiency is higher, decomposition of pollutants and production of intermediate is reduced [31]. Olyaie et al. in 2012 in Iran with research on arsenic removal from aquatic solutions using calcium peroxide demonstrated that by increasing concentrations of arsenic from 0.2 to 2 mg L^{-1}, the removal efficiency is reduced from 91.88% to 88.78% [42]. Bahrami et al. [31] in Iran with a research on the removal of metronidazole with ozonation process demonstrated that by increasing the concentration of metronidazole from 10 to 40 mg L^{-1}, removal efficiency was reduced from 51% to 12% after 5 min contact time, which is in line with the results of this study.

The removal efficiencies of metronidazole and COD in synthetic samples were obtained as 90.1% and 86.6%, respectively, and 79.5% and 71% in real samples, respectively. The removal efficiencies of metronidazole and COD in real samples were 10.6% and 15.6%, respectively, which was less than that of the synthetic samples. The reason for this reduced efficiency is due to the existence of organic substances such as proteins, carbohydrates, fats, solvents and phenol in urban wastewater that caused the consumption of oxidizing substances such as ozone and hydroxyl radical molecules before other substances such as pharmaceuticals, organic materials and antibiotics [43,44]

In optimal conditions, the removal efficiency of 5 mg L^{-1} of metronidazole in real samples (sewer + metronidazole antibiotic) was obtained as 79.5%, and in comparison with synthetic samples, these conditions were less efficient. In addition, the amount of COD removal in synthetic and real samples was obtained as 86.6% and 71%, respectively.

4. Conclusion

Due to the relatively high efficiency of ozonation method with calcium peroxide for the removal of metronidazole in addition to advantages such as strong oxidization, decomposition of refractory organic compounds, indivisible and high removal efficiency of metronidazole in real samples when compared with synthetic samples with difference <10.6%, this method is advisable for the removal of metronidazole from aqueous solutions.

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