Catalytic ozonation for removal of antibiotic oxy-tetracycline using zinc oxide nanoparticles

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Abstract

The traditional wastewater treatment plants are mostly not designed to deal with polar micropollutants such as pharmaceuticals. Therefore, antibiotics must be completely removed before their emission to ecosystems. Catalytic ozonation is used to increase the efficiency of sole ozonation further. In the present study, semi-batch experiments were conducted to investigate the efficiency of sole ozonation and catalytic ozonation in the degradation of oxy-tetracycline (OTC) as an environmental hazards contaminant in an aqueous solutions. Zinc oxide nanoparticles (ZnO) were used as a catalytic agent with ozone (ZnO/O₃). The influence of operational parameters such as pH (3–11), initial oxy-tetracycline concentration (10–100) mg/l, temperature (15–35)°C, ozone generation rate (0.138–1.38)mg/s and catalyst dosage (25–200) mg/l on the ZnO/O₃ process was investigated. Ozone dosage was found to have the noticeable effect on the degradation process; however, the ZnO dosage was found to be less effective. The optimum condition was 1.38 mg/s at pH=7, and after 35 min, a 94% of OTC removal was achieved. The results demonstrated that catalytic ozonation was a very effective method for degradation and mineralization of OTC in aqueous solution.

Keywords Oxy-tetracycline · Catalytic ozonation · ZnO nanoparticles · Removal efficiency

Abbreviations

OTC	Oxy-tetracycline
AOPs	Advanced oxidation processes
SOP	Sole ozonation processes
COP	Catalytic ozonation processes
O ₃	Ozone

Introduction

Various pollutants are emerging in our environment, these pollutants that can cause an environmental problem inside water system (Alwared and Jaber 2020). In the recent years, environmental pollution with pharmaceutical antibiotics has attracted more attention due to their effect on the environmental and human health (Mohammed et al. 2020). Antibiotics are a large group of medicines used to treat

infectious diseases in humans and animals caused by various types of bacteria. According to reports, about 15% of the world's total manufactured drugs are antibiotics (Nasseh et al. 2019). Pharmaceutical antibiotics are biologically active compounds that are often soluble in water, but not easily biodegradable in natural circumstances. About 70% of consumed antibiotics cannot be metabolized, including hospital effluents, treatment plant wastewater, and livestock excretion from feces and urine (Mohammed et al. 2020). The low antibiotic concentration in the aqueous environment (1–100 ppb), its presence in human drink water may cause diarrhea, headaches, nausea, tremors, vomiting, etc. (Mohammed et al. 2019b). Because of their reduced elimination by conventional wastewater treatment processes, various antibiotics have been released into the aqueous site by a sewage treatment plants (STP). Actually, many antibiotics, for example, sulfonamides, and oxy-tetracycline have been discovered downstream of STP release sites, in sea and river in various countries (Tran et al. 2018). Antibiotic resistance bacteria has been appear as a result of the existence of little concentration of antibiotic and their alteration products in the aquatic environment that create the right condition and movement and efficiency of removal of these concentrations in treatment plants has been incomplete (Boxall et al. 2003;

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Li et al. 2008). Oxy-tetracycline (OTC) is the most widely used in agricultural activities for antibiotic application to enhance survival rate of embryo; meanwhile, it normally decays very slowly in nature due to its complex chemical structure. As a result, there are many research teams have tried to develop efficient technique to remove OTC (Kimera et al. 2015; Kerdnawee et al. 2017). Advanced oxidation processes (AOPs) have been excessive possible to eliminate various pollutants. AOPs have the advantage of rapid oxidation of pollutants to harmless end products (Alward et al. 2014). AOPs such as Fenton, photocatalytic oxidation and ozonation were used to remove antibiotics (Trovó et al. 2009; Hou et al. 2013a; Hou et al. 2013b; Salman et al. 2020). Catalytic Ozonation, one of the most important processes of AOPs, currently used for removing organic compounds in a minimum process time and enormous removal rate (Amutha et al. 2014; Bai et al. 2016). AOPs include in situ generation of very reactive oxygen species (ROS) by small selectivity, for example, superoxide anion radicals (O_2^-), H_2O_2 , O_3 and hydroxyl radicals (OH), with wide-ranging degradation to CO_2 , H_2O and inorganic ions or acids (Dalrymple et al. 2007; Kanakaraju et al. 2018). Combining ozonation with catalysis have been used to enhance the removal of antibiotics and their products (Nawrock and Kasprzyk-Hordern 2010; Kråkström et al. 2020). Catalysts used in combination with ozonation can be either homogenous or heterogeneous. The advantage of heterogeneous catalyst is the easy separation of the catalyst from the liquid and the possibility to reuse the catalyst (Gharbani and Mehrizad 2014). Among the catalysts, metal oxides, such as zinc oxide (ZnO) nanoparticles, have a high potential for application in water and wastewater treatment due to their high surface area and low cost of production (Nasseh et al. 2019). In addition, ZnO has a number of antimicrobial, adsorptive, and toxicant favorable degradation properties (Cuerda-Correa et al. 2019).

The aim of this work is to investigate the removal rate of OTC via sole (SOP) and catalytic ozonation process (COP) by using ZnO nanoparticle, through various operating variables, including catalyst dose, temperature, ozone generation rate, and initial OTC concentration.

Mechanism of ozonation

Ozonation might be a promising process for antibiotics degradation that is providing advantages such as its ability to degrade organic and inorganic pollutants, with no chemical sludge remaining after the process, and have less danger for the reason that no stock of any chemical (like hydrogen peroxide) is critical and remaining ozone can be decomposed easily to oxygen in water (Gharbani and Mehrizad 2014). Two ways that takes place in the mechanism of oxidation by ozone: Direct reaction with liquefied ozone (O_3), its

great oxidation potential ($E^\circ = 2.08$ V) or indirect oxidation through the formation of radicals (OH). The extension of both mechanisms throughout the degradation of a compound depends on factors such as the nature of the contaminant, the dose of ozone, or the pH of the medium. Normally, under acidic conditions ($pH < 4$), direct ozonation prevails

However, on the other hand, the indirect way at $pH > 9$ is the utmost important one. Normally, degradation rates in ozonation processes rise as pH does, free radicals as in reaction (2) from the decomposition of ozone in the base medium. Oxidative indirectly reaction with ozone is like these:

At base surroundings, the reaction can be taken into account:

A reduction in the oxidation capacity in this reaction results in a fast hydroperoxyl radicals generation ($E^\circ = 1.65$ V) as a result, the OH radicals ($E^\circ = 2.80$ V); detriment and that led to eliminate oxidation capacity (Cuerda-Correa et al. 2019).

Catalytic ozonation

catalytic ozonation process can be used to enhance the degradation efficiency of organic pollutants, including homogeneous and heterogeneous catalytic ozonation. In homogeneous catalytic ozonation process, liquid catalysts, especially transition metal ions are used, such as Co^{+2} , Cd^{+2} , Ag^{+1} , Cr^{+3} , Zn^{+2} , Fe^{+2} , Mn^{+2} in reaction solution. These catalysts can excite ozone to generate hydroxyl radicals (OH) and improve degradation efficiency. In heterogeneous catalytic ozonation process, solid catalysts such as metal oxide, activated carbon, porous materials, and their composite materials are

added into reaction solution (Kasprzyk-Hordern et al. 2003; Wang and Zhuan 2019).

Materials and methods

Chemicals

Powder oxy-tetracycline (OTC), Molecular formula ($C_{22}H_{24}N_2O_9$), Molecular weight (460.4 g/mol), water solubility > 100 mg/ml (21 °C), was achieved from general company for drugs industry (Samarra, Iraq), zinc oxide (ZnO) with particle size (30 nm). The pH value of solutions has been controller through the experiments by addition of 0.1 M NaOH or HCL. Stock solution of OTC was arranged by dissolving a suitable amount of OTC powder antibiotic in 1 L of distilled water. Due to the unpredictability in the laboratory environments, the preparation of stock solutions at the experimental work time. The structure and properties of OTC are shown in Fig. 1. (Li et al. 2008).

Figure 2 shows the schematic diagram of the semi-batch reactor for ozonation experiments. The setup contains 1 L glass stirrer reactor, an oxygen source with high-purity (> 98% by volume), an ozone generator (Shanghai ENALY M&E; model: OZX05K), and a gas distribution system (i.e., diffuser) to generate micro bubbles. 1 L/min of O_2 flow rate of was supplied to the ozone generator which was used to convert oxygen gas to ozone gas by the corona-discharge technique. To mix the water continuously, magnetic stirrer was used. The samples were collected at specified period time, centrifuged at 2000 rpm for 10 min to separate catalyst from taken sample and then measure OTC concentrations.

Analytical method

pH was measured by the use of a pH meter (ISOLAB.). The temperature controlled by magnetic stirrer. The initial and remaining OTC concentrations have been determine in accordance with the standardization records that were gotten via UV/VIS spectrophotometers (Model: Cary-100 conc., Varian, USA)., with a peak wavelengths at 274 nm according to the absorbance analysis.

Fig. 1 Structure of oxy-tetracycline (Li et al. 2008)

Fig. 2 Graphic diagram of the experimental set-up: (1) Oxygen source (2) Flow meter (3) Ozone generator (4) Magnetic stirrer (5) Diffuser (6) Ozone bubble (7) Catalyst particles

Results and discussion

Characterization of ZnO

TEM image (Transmission Electron Microscopy) (Fig. 3) showed that the ZnO nanoparticles have an irregular shape, but most of them are roughly spherical with an average size of < 100 nm. Thus, these particles are within the nano-size range. Also, the agglomeration of these nanoparticles is low, as their dispersion appears to be in a mono-dispersed manner (Mohammed et al. 2019a).

Effect of pH

The pH value is considered as one of the important factors affecting the behavior and fate of antibiotics in an environment. This parameter can effect on the route of degrading of organic pollutants by two ways. The first is the transportation of ozone from gas phase into liquid phase (direct effect).

Fig. 3 TEM image of ZnO nanoparticles

The second is degradation of ozone into various radicals (indirect effect) (Nasseh et al. 2019). In general, the rate of ozone decomposition increases with increasing solution pH since the hydroxyl ions catalyst the decay of ozone to form radicals serving as reactive species (Li et al. 2008). In this study, the pH range was taken as (3, 5, 7, 9, 11) to examine the effect of the media on the removal rate, the highest removal efficiency was observed at pH of 7 (84%) at time 35 min, similar to these results were also reported by Li et al. (2008) as shown in Fig. 4.

From Fig. 4, it can be seen that the degradation efficiency after 10 min increased not more than 6%. At pH (3, 5, 7, 9, 11), the removal efficiency was (80, 82, 84, 83, 81)%, respectively, after 35 min for OTC concentration of 50 mg/l and ozonation rate = 1.38 mg/s. In the current study, pH 7 has been found the best possible condition for the treatment of OTC. For OTC, its removal efficiency was showed slight dependence on pH. Similar results were as well reported in the literature, for instance, the Ozonation of Methylene orange dye (Nashmi et al. 2019) and the Ozonation of CN^- ions was studied by Rice (1997) it was pointed out that pH had slight effect on cyanide Ozonation to cyanate. In accordance with the mechanism predicted by Staehelin and Hogine (1985), OH^- ions act in response with dissolved ozone to generate O_2^- free radicals, and H^+ ions promote O_2^- free radicals to convert into HO_3 free radicals, which are in turn decomposed to OH free radicals (Sotelo et al. 1989). Both H^+ and OH^- ions are needed for the production of OH free radicals. Additionally, the existence of acid/base-active phenolic hydroxyl and amine groups in OTC (an amphoteric antibiotic) determines that OTC may exist in different ionic species at different solution pHs. The OTC molecule has three acid dissociation constants depending on the pH ($\text{pK}_a = 3.57, 7.5, \text{ and } 9.44$) and existed as cationic

Fig. 4 The effect of pH with time on the removal efficiency of OTC (OTC conc. = 50 mg/l, ozone generation rate = 1.38 mg/s, reaction time = 35 min, at room temp.)

form in strong acid solutions at $\text{pH} < 3.57$, zwitterion at $3.57 < \text{pH} < 7.5$ and anionic form at $\text{pH} > 7.5$ (Harja and Ciobanu 2017). Li et al. (2008) reported the by-products can be more oxidized to smaller molecules such as carbon dioxide and water.

Figure 5 shows the alteration of pH value during ozonation process. As it can be seen, the initial pH of 7, 9, and 11 decreases gradually most probably as a result of carboxylic acid accumulation in the process water. Under acidic conditions, the ozonation does not measurably affect the solution pH. Similar to these results were also reported by Li et al. (2008).

Effect of catalyst dosage

Catalysts can provide active sites for catalytic or adsorptive reactions among ozone, liquid, and organic compounds; therefore, the usage of catalysts in aqueous solution is an essential factor. Generally, surface areas and the reactive sites can be increased by increasing the catalyst dose, (Huang et al. 2015). Meanwhile, a higher apparent reaction rate constant for catalytic ozonation would be obtained. However, considering the constant concentration of pollutants, excessive amount of catalyst would decrease the concentration of pollutants and ozone per unit area, which could decrease the catalytic efficiency (Nie et al. 2012). Therefore, it was necessary to optimize the catalyst dosage based on the experimental results. The efficiency of the catalytic ozonation process depends to a great extent on the catalyst and its surface properties as well as the pH of the solution that influences the properties of the surface active sites and ozone decomposition reactions in aqueous solutions (Kasprzyk-Hordern et al. 2003).

The catalytic ozonation performance of the ZnO was evaluated within 50 mg/l OTC initial concentration (Fig. 6). In the sole ozonation process, the degradation efficiency of OTC could only reach 81% within 10 min. The addition of ZnO caused as important development

Fig. 5 Change of pH with time of OTC (OTC conc. = 50 mg/l, ozone generation rate = 1.38 mg/s, at room temp.)

Fig. 6 The effect of ZnO dosage with time on the removal efficiency of OTC (OTC conc.=50 mg/l, pH=7, ozone generation rate=1.38 mg/s, at room temp.)

Fig. 7 The effect of pH on ZnO with time on the removal efficiency of OTC (OTC conc.=50 mg/l, ZnO=100 mg/l, ozone generation rate=1.38 mg/s, at room temp.)

for the degradation of OTC. The efficiency of removal of OTC in the COP reached 91% within 10 min and reached 94% in 35 min at 100 mg/l ZnO. The adsorptive removal would be neglected as the OTC adsorption onto nano-ZnO was just about 6.5% after 60 min. The experiment of absorption carried by add 200 ml of the OTC solution (conc. = 50 mg/L) in the flask at pH (3, 5, 7, 9, 11), ZnO dosage (100 mg/L) and shaking for 60 min (figure not shown). It is signifying that the degradation of OTC was mainly caused by oxidation.

The dose of ZnO (100 mg/l) was testing in different pH (3, 7, and 9), and finding the pH 7 is the best to degradation of OTC as shown in Fig. 7

Figure 8 shows a combination between the degradation of OTC using different processes (oxidation by Oxygen, ozonation, catalytic ozonation, and adsorption OTC on ZnO).

Fig. 8 Combination of removal efficiency for different processes for OTC (OTC concentration=50 mg/l, ozone generation rate=1.38 mg/s, at room temp.)

Fig. 9 Effect Of Ozonation Rate On OTC Removal Efficiency (pH=7, OTC conc.=50 mg/l, at room temp)

Effect of ozone generation rate

Ozone generation rate will be changed from 0.138 mg/s to 1.38 mg/s at pH=7 and constant OTC concentration (50 mg/L) to investigate its effect on the degradation rate of OTC. Figure 9 shows that degradation efficiency was enhanced with increasing the initial ozone concentration. Because an increase in the influent ozone gas concentration results in an increase in aqueous ozone concentration which either directly reacts with the OTC or decomposes to produce $HO\cdot$ which in turn reacts with the pollutant (Li et al. 2009). From Fig. 9, it was obviously shown when the generation rate of ozone increased from 0.138 mg/sec to 1.38 mg/sec, the removal efficiency for OTC increases from 81 to 83% through 35 min, while the degradation efficiency increased from 88 to 94% with increasing ozone generation rate from 0.138 mg/s to 1.38 mg/s in the presence of 100 mg/l ZnO nanoparticle. This indicates that

even with a little ozone concentration, the removal rate is high, this is an economical feature for treating antibiotics via ozonation process. The mass transfer rate and the volumetric mass transfer coefficient of ozone increases with increase in ozone concentration. More ozone can be absorbed and react with OTC molecules, finally improving the decomposition of OTC (Wang and Zhuan 2019). From Fig. 9, it can be seen that in SOP at 0.138 mg/s, the removal efficiency reached 78% after 10 min and 81% after 35 min, and at in COP, the removal efficiency reached 82.5% after 10 min and 88% after 35 min. While, at 1.38 mg/s in SOP, the removal efficiency reached 81% after 10 min and 84% after 35 min, and at in COP, the removal efficiency reached 91% after 10 min and 94% after 35 min for pH = 7, and OTC concentration of 50 mg/l, ZnO = 100 mg/l. It is noted that the increased in removal efficiency from 10 to 35 min not more than 5%.

Effect of temperature

Reaction temperature is an important parameter for almost all chemical reactions. Ozonation and catalytic ozonation are no exclusion as well. On the other hand, there are two different effects of increasing reaction temperature in SOP and COP, the first that increases reaction temperature can cause a quicker reaction rate between oxidizing agent and pollutants (Lan et al. 2013; Yan et al. 2013). On the other hand, the solubility of ozone in water is opposite to the temperature (Huang et al. 2011). In this work, temperature was taken as (15, 25, 35)°C to investigate effect it's on the removal rate of OTC, the highest removal efficiency was observed at 15 °C as shown in Fig. 10. The above abnormal phenomena are caused by the balance of both the solubility of ozone and reaction rate of ozonation. On the other side, the solubility of ozone decreases in aqueous phase as the temperature rises (Giri et al. 2008), this led to decrease in

Fig. 10 The effect of temperature with time on the degradation efficiency of OTC (OTC conc.=50 mg/l, pH=7, ozone generation rate = 1.38 mg/s, ZnO = 100 mg/l)

HO in the solution that oxidized OTC molecules. The same phenomenon is observed in a previous examination on using natural brucite to improve the ozonation of phenol (He et al. 2008), removal of tetracycline and ofloxacin by using nano-Mg(OH₂) (Lü et al. 2015). From Fig. 10, it can be seen that in SOP at 15 °C, the removal efficiency reached 81% after 10 min and 84% after 35 min, and at 35 °C, the removal efficiency reached 67% after 10 min and 74% after 35 min for pH = 7, ozonation rate = 1.38 mg/s, and OTC concentration of 50 mg/l. While, in COP at 15 °C, the removal efficiency reached 91% after 10 min and 94% after 35 min, and at 35 °C, the removal efficiency reached 79% after 10 min and 86% after 35 min for pH = 7, ZnO = 100 mg/l, ozonation rate = 1.38 mg/s, and OTC concentration of 50 mg/l.

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Influence of initial OTC concentration

In the water environment (typically in nano—or micrograms per liter), antibiotics concentrations was commonly hard to carry out experiments with low concentrations in the laboratory and justly concentrations of high amounts of antibiotics are used for the purpose of experiments. Different concentrations were taken (10, 25, 50, 75, 100) mg/L, at pH = 7

Fig. 11 Effect of the initial concentration OTC on the removal efficiency (pH = 7, ozone generation rate = 1.38 mg/s, at room temp)

Fig. 12 Testing first-order kinetic for OTC

and the ozone generation rate is 1.38 mg/s. Increasing in the OTC primary concentration results in reduction in the pollutant removal rate (Fig. 11). After 5 min and with the initial concentration of 10 mg/L, the degradation efficiency of OTC gotten 95%. Although for 50, 100 mg/L were only 72%, 51%, respectively, showing that more OTC is oxidized by ozone at lower initial concentration. This can be unstated by considering that the reaction follows first order kinetics (Fig. 12). Increasing OTC initial concentration causes increase in the concentration of degradation intermediates, as a result, extra ozone consumption for the more removal and oxidation of by-products (Lü et al. 2015; Li et al. 2009; Sun et al. 2019).

Kinetics study

In the present study, the kinetics of OTC degradation was studied for both SOP and COP, and the theoretical and experimental data are depicted in Figs. 12 and 13. The applicability and validation of the first- and second-order

Fig. 13 Testing second-order kinetic for OTC

Table 1 The results of experimental kinetic data of degradation in SOP and COP reaction with the first-order equation

Type of process	Equation, where $Y = \ln(C/Co)$, and $x = t$	k_a (1/min)	R^2
O ₃ only	$Y = -0.0784x - 0.2034$	0.078	0.9269
O ₃ /ZnO	$Y = -0.1083x - 0.2541$	0.108	0.9436

Table 2 The results of experimental kinetic data of degradation in SOP and COP reaction with the second-order equation

Type of process	Equation, where $Y = \ln(C/Co)$, and $x = t$	k_a (1/min)	R^2
O ₃ only	$Y = 0.0038x + 0.0262$	0.0038	0.8343
O ₃ /ZnO	$Y = 0.0099x + 0.0541$	0.0099	0.8592

model and Eq. (9) were judged according to the values of determination of coefficient (R^2). However, the kinetic reaction rate parameter (k_a) for first-order model is determined from the slope of the best fit line of the plot of $\ln(C/Co)$ versus reaction time (t), to second-order model is determined from the slope of the best fit line of the plot of $(1/C)$ (Nasseh et al. 2019). The results of these parameters are listed in Table 1 and Table 2. It can be seen that the first-order model fitted well the kinetic data (Fig. 12) as high well R^2 values were obtained (> 0.9). (In addition, in catalytic ozonation process the k_a values significantly increased. Furthermore, the k_a values determined were high, a high degradation of OTC (1).

$$\ln\left(\frac{C_t}{C_o}\right) = -k_a t \quad (9)$$

where k_a (min^{-1}) is the rate constant for pseudo-first-order reaction, and $t(\text{min})$ represents the specific reaction time.

Conclusion

The obtained results indicate that the catalytic ozonation by ZnO nanoparticles could be an efficient treatment to degrade oxy-tetracycline in comparison with sole ozonation process. The degradation efficiency of OTC in catalytic ozonation (ZnO/O_3) process was found to have the noticeable effect on the efficiency of removal and decrees of reaction time by 93% and 15 min, respectively. The effect of pH was investigated, and it was found that the OTC removal rate was showed slight dependence on pH. The effect of temperature on the catalytic ozonation of OTC was investigated, and it was found that the OTC removal rate increased with decrease in temperature. Also, the effect of increasing initial concentration of OTC was investigated, and it was found that with the increase in the initial concentration of antibiotic in the aqueous solution, the degradation efficiency of these antibiotics by ozone molecules decreases.

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Compliance with ethical standard

Conflict of interest All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version. This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue. The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript. On behalf of all authors, the corresponding author states that there is no conflict of interest.

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