Oxalic acid degradation from aqueous solution using ozonation process in the presence of magnesium oxide nanoparticles catalyst stabilized on activated carbon

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ABSTRACT

Aims: In this work, activated carbon, magnesium oxide (MgO), and MgO stabilized on activated carbon derived from sweet corn were applied as catalysts for oxalic acid degradation from aqueous.

Materials and Methods: Sweet corn pile was used for the production of activated carbon, and magnesium nitrate applied for the production of MgO. Ozone concentration determined using iodometry method, and oxalic acid concentration was determined by a spectrophotometer at 210 nm. Moreover, the effect of MgO, activated carbon and oxalic acid concentration, pH, contact time, and oxalic acid mineralization were investigated.

Results: The results showed that ozonation in the presence of activated carbon or MgO and/or MgO stabilized on activated carbon, increased the decomposition rate of oxalic acid. Removal efficiency of oxalic acid with increasing catalysts dose of 0.05–1 g, pH of 3–11, and time of 1–30 min have increased from 72% to 85%, 72% to 85%, and 92% to 95% respectively. Furthermore with increasing of oxalic acid from 40 to 100 mg/L, the removal efficiency decreased from 96% to 88%.

Conclusion: According to this study, catalytic ozonation processes have shorter time and more removal efficiently than the single ozonation process. Moreover, the results showed that oxalic acid was mineralized significantly and interfering factors have negligible effect on the catalytic ozonation process than the single ozonation.

Key words: Catalytic ozonation, corn activated carbon, magnesium oxide nanoparticles, oxalic acid

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INTRODUCTION

The purpose of water and wastewater treatment is the removal and degradation of undesirable contaminants to

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provide safe drinking water, prevent water pollution, and protect the environment.[1] In nature, for safe drinking water supply, it is necessary to remove some complex organic compounds that may be present. Some of these compounds such as humic and tannic acids with long ring chains are not completely removed through conventional water treatment processes. On the other hand, the use of chlorine to disinfect water sometimes lead to the production of some dangerous by-products.[1]

In addition, ozone disinfection generates stronger organic acids with shorter chains interfering with the water disinfection process and supports the growth of micro-organisms in distribution network.[1] Furthermore, in industrial wastewater treatment, especially the chemical oxidation of cyclic organic compounds, such as chlorobenzenes and phenol derivatives result in the production of organic acids such as formic, oxalic, and acetic acids. In the case of water chlorination, these organic acids may result in disinfection by-products generation such as trihalomethanes.[2]

Actually, one of the drawbacks with regard to the ozone oxidation of organic compounds is the production of oxalic acid.[3] Oxalic acid ($C_2O_4H_2$) as a by-product of complex organic compounds. This by-product has a more stable structure than other organic acids and is incredibly resistant to chemical degradation.[3]

In industries, oxalic acid is applied for textile printing and dyeing, whitening and bleaching, polishing, wood painting, and cleaning.[4] Oxalic acid is extremely irritant for eyes and skin. It is also stimulant and highly toxic to the respiratory tract. In addition, acute exposure to oxalic acid irritates the stomach, reduces blood calcium level, and also affects the nervous system and kidney.[4] Oxalic acid is one of the strongest organic acids with acidity value (pKa) of 1.3 and 4.3.[5] This colorless and odorless substance has a molecular weight of 126.07 g/mol, melting point of 101.5°C, and vapor pressure of <0.001.[6]

Unfortunately, complex organic compounds may be found in water and wastewater through conventional treatment methods, such as ozonation. Accordingly, the production of oxalic acid as a by-product is inevitable.[1,7]

Therefore, the by-products should be removed using new or modified existing methods. Some conventional methods used to eliminate decomposition of organic compounds in water include adsorption,[8] advanced oxidation processes,[9-11] ozonation,[12,13] and biodegradation.[14] Biotechnology is a suitable method for the removal of oxalic acid, but it is not common in conventional water treatment processes.[12] The high oxidation potential of ozone is considered to remove natural organic compounds and trihalomethanes precursors in water purification technology.[1,7,13,15-17]

According to earlier studies, ozone has low efficiency for the removal of some natural organic compounds.[16,17] Presently, to improve the efficiency of ozonation process, employment of catalysts is considered.[18] Catalysts increase ozone oxidation potential and reduce the amount of required ozone, this method is known as catalytic ozonation process (COP).[19] The process is conducted in two ways: (1) Heterogeneous and (2) homogeneous.

In comparison to the homogenous type, heterogeneous catalytic ozonation is more efficient because it has higher degradation efficiency, easy operation, and leaves no residual in treated wastewater.[20] The properties of convenient catalysts used in heterogeneous ozonation are high activity, passive resistance, and long-term stability at high temperatures, mechanical stability, resistance to abrasion, nonselective reactions, and physical and chemical stability under various operating conditions.[21] Catalysts are usually metal oxides, metal compounds, and metals or metal oxides coated on various media. Common metal oxides include Al_2O_3, TiO_2, ZnO, FeOOH, and MnO_2.[18,22-25]

Catalyst efficiency will be greatly increased, if a synthesized nanocatalyst is applied due to increase in their surface area and functional groups.[22] The presence of catalyst nanoparticles in the ozonation process produces hydroxyl radicals as a strong secondary oxidant agent.[21] Since ozonation alone is not able to remove oxalic acid due to low constant rate of ozone (kO_3 <4 × 10^{-2}/M/s), even at long periods, therefore to increase the efficiency, metal oxide nanoparticles are used as catalyst.[13,18] The oxidation potential of hydroxyl radical is 2.8 eV, whereas ozone is 2.06 eV, as such the hydroxyl radicals oxidize organic compounds much better than ozone.[21,26,27] The separation of nanoparticles from effluent, particularly in large scale projects, is very difficult and expensive.[21] To overcome this problem, researchers stabilize nanoparticles on different granules.[21] In several cases, magnesium oxide (MgO) is used as a catalyst in the process of ozonation.[19,28] MgO is a heterogeneous catalyst with high catalytic potential that enables it to remove organic compounds.[1] Its specific surface area ranges from 307 to 397 m^2/g.[18] In addition, it is hard, nontoxic, and has very low solubility in water.[13,29,30] In previous works, MgO nanoparticles efficiently degraded catechol and phenol in integration with ozonation process.[13,18] Furthermore, it has been revealed that oxalic acid removal increased significantly in the presence of nanoparticles.[13,24]

Granular activated carbon (GAC) was produced from sweet corn wastes and used as a catalyst and a support for MgO nanoparticles.[15,16] In this study, with regard to cost, availability, and ease of production, magnesium compounds were used for the production of MgO nanoparticles. A fluidized bed reactor was used for contact between ozone in the gas phase, oxalic acid solution in the liquid phase,
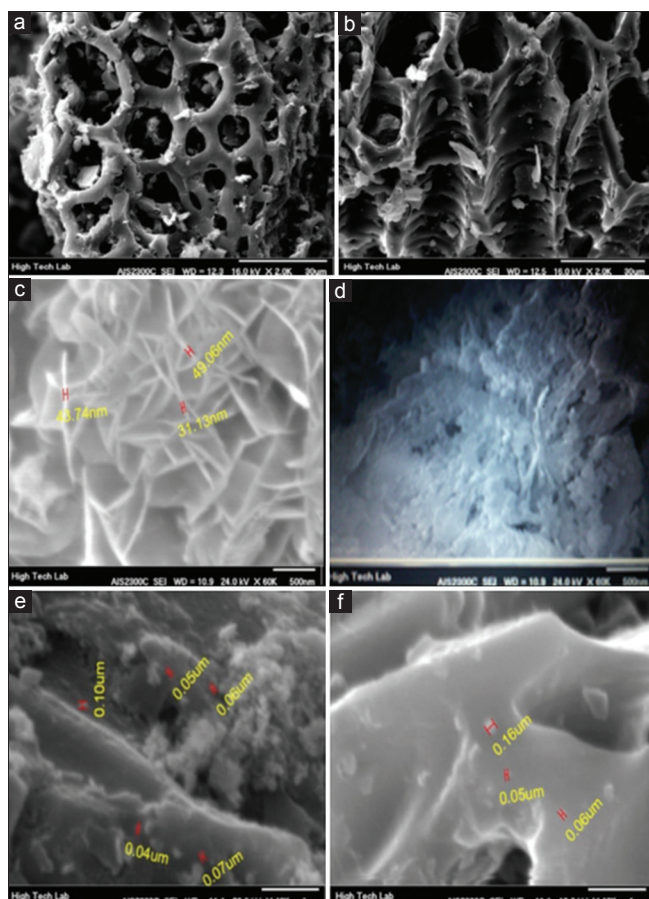
Figure 1: Scanning electron microscopy micrographs of (a) granular activated carbon before of process; (b) granular activated carbon after of process; (c) magnesium oxide after of process; (d) magnesium oxide before of process; (e) granular activated carbon/magnesium oxide before of process; (f) granular activated carbon/magnesium oxide after of process

Figure 2: Energy dispersive analysis of X-rays analysis of (a) granular activated carbon; (b) magnesium oxide; (c) magnesium oxide/granular activated carbon composite

and Mg nanoparticles coated on activated carbon in the solid phase.

The simplicity, low cost of operation, and flexibility were the benefits of the applied reactor.[15,16] Previous studies have proven the synergistic effects of ozonation in the presence of stabilized nanoparticles on removal of pollutants.[31] The main objective of this research was to study the ozone oxidation process in the presence of MgO nanoparticles coated on activated carbon produced from sweet corn for the removal of oxalic acid from aqueous solutions. The innovations of this study therefore include the following: (1) Activated carbon production of sweet corn wastes and coating of MgO. (2) Determination of oxalic acid mineralization using a fluidized bed reactor and the catalytic ozonation process. (3) Comparison of oxalic acid removal using only ozonation with catalytic ozonation processes.

In addition, the influence of various parameters such as ozone contact time, catalyst dose, pH, and interfering factors on hydroxyl radicals production were studied.
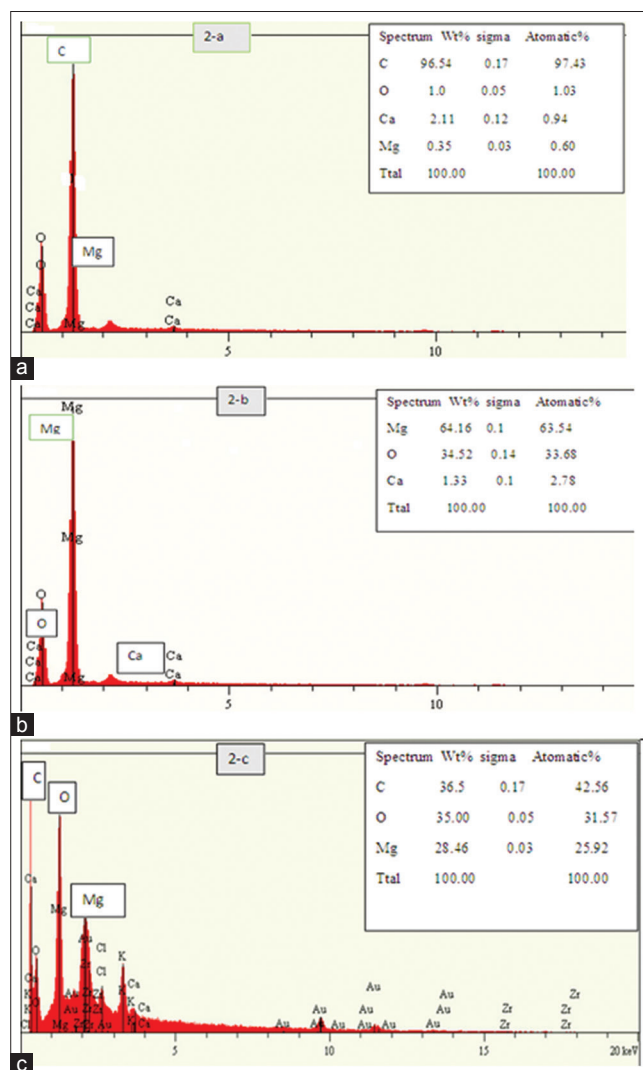
MATERIALS AND METHODS

Activated carbon was prepared from sweet corn (Zea mays saccharata) waste. The preparation and production of activated carbon was as follows: The corn grains were first removed from corn kernels, the wastes were then washed using distilled water severally and consequently washed with 0.01 N sulfuric acid and dried in an oven at 105°C for 24 h. After that, the dried material was grinded and placed in a closed reactor and put in furnace at 600°C for 1 h, then, carbon materials were put into the 1 N sulfuric acid for 24 h. After washing with distilled water severally, put in the oven at 104°C for 24 h. Finally, screening and grading were performed using standard American Society for Testing and Materials miscellaneous sieves (mesh 40–80). The sol-gel method was used to produce the MgO/GAC composite.

In this method, 26.27 g magnesium nitrate (MgO (NO_3) $6H_2O$) (99%) was solved in 500 ml distilled water, and then
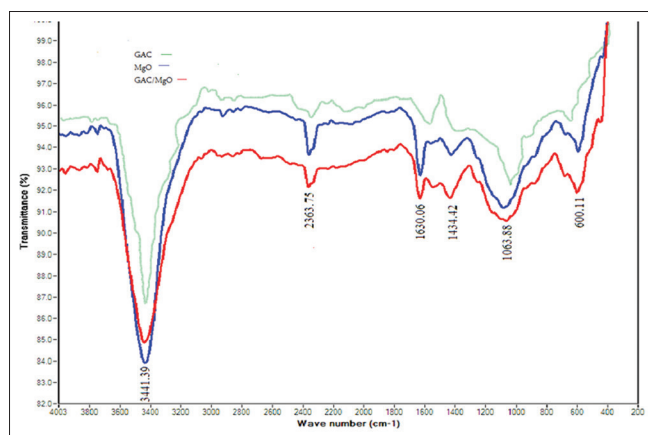
Figure 3: Fourier transform infrared spectra of granular activated carbon; magnesium oxide and magnesium oxide/granular activated carbon composite

Figure 4: The effect of solution pH on oxalic acid degradation for single ozonation process, catalytic ozonation process with granular activated carbon, catalytic ozonation process with magnesium oxide and catalytic ozonation process with magnesium oxide/granular activated carbon (Oxalic acid: 100 mg/L, catalyst: 10 g/L, O_3: 1.68 mg/min and contact time: 30 min)

4 ml of caustic soda (1 N) was added under constant stirring for 5 min to form a homogeneous Mg (OH)$_2$ suspension. After that, 50 g of the prepared GAC (16–20 mesh) was added and stirred vigorously for about 1 h. The supernatant was drawn after being allowed to settle for 1 h, and the remaining sediment dried in air at 100°C for 3 h. Calcinations were performed in air at 500°C for 2 h, so as to convert Mg (OH)$_2$ to MgO nanocrystals.[32]

The morphological, chemical composition, surface functional groups of sweet corn, MgO nanoparticles, and GAC/MgO composite were analyzed using energy dispersive analysis of X-rays (EDAX), scanning electron microscopy (SEM), and Fourier transform infrared (FTIR). The pH$_{zpc}$ of the absorbent was determined using the method described by Mandal *et al*.[11]

This study was experimental in bench mode, and all chemical materials used were of analytical grade. A fluidized bed reactor was set up for catalytic ozonation processes. It consisted of a 200 ml cylindrical Pyrex container, a quartz diffuser at the bottom of the reactor, ozone generation and supply system, and off-gas ozone demolition system connected to a concentrated KI solution.

The iodometry method was used to determine the amount of ozone.[33] The pH of solution was measured using a pH meter (BP3001). The oxalic acid concentration in solution before and after the processes was determined using a spectrophotometer (UV/VIS-2100, USA) at a wavelength of 210 nm. In addition, the mineralization of oxalic acid was determined using chemical oxygen demand (COD) according to standard methods.[34]

All experiments were carried out in triplicate and the results are given as means and relative standard deviations of <5%.

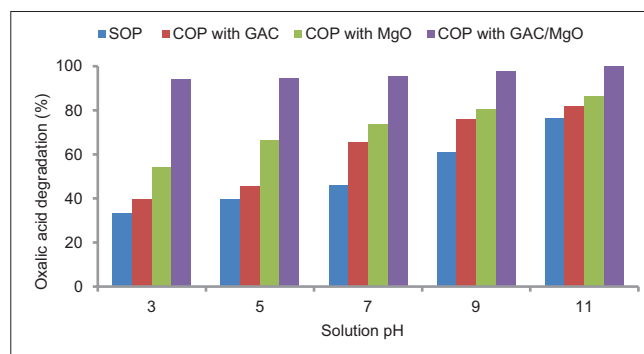The degree of oxalic acid degradation and mineralization was calculated from Equations 1 and 2.

$$\text{Degradation \%} = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

$$\text{Mineralization \%} = \frac{COD_o - COD_t}{COD_o} \times 100 \qquad (2)$$

Equations 1 and 2 should be provided.

Where C_o and C_t are oxalic acid concentrations before and after the reaction and COD_o and COD_t are COD concentrations before and after the degradation.

In this study, the effect of various effective variables such as catalyst dosages (0.05–1 g), confounding factors, pH (3–11), contact time (0–30), and oxalic acid concentration (40–100 mg/L) were investigated. Furthermore, oxalic acid decomposition kinetics in single ozonation processes (SOPs) and catalytic ozonation processes were studied.

RESULTS

The study showed that activated carbon made from sweet corn coupe, MgO nanoparticles, and MgO nanoparticles coated on activated carbon as a catalyst, improved oxalic acid removal by ozonation process. The results showed that by increasing the catalyst dosage, pH and time, the rate of oxalic acid degradation increased. The reaction rate of oxalic acid degradation is the first order reaction in the catalytic ozonation process. Furthermore, the results showed that the catalytic ozonation process in the presence of activated carbon, MgO nanoparticles, and MgO nanoparticles coated on activated carbon had better performance as compared with the ozonation process. Since the raw material used in this study can be found abundantly and inexpensively, it can be used to enhance the efficiency of ozonation process in
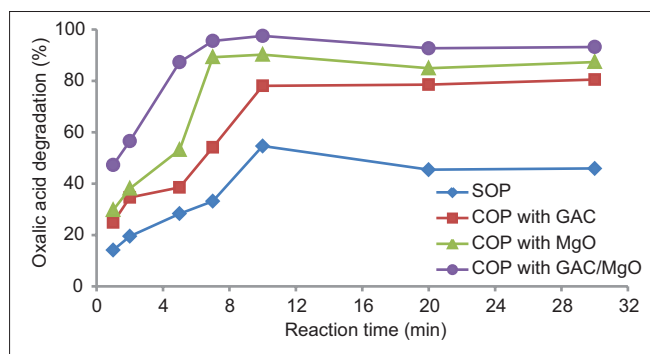
Figure 5: The effect of time on oxalic acid degradation for single ozonation process and catalytic ozonation process with granular activated carbon, catalytic ozonation process with magnesium oxide and catalytic ozonation process with magnesium oxide/granular activated carbon (Oxalic acid: 100 mg/L, O_3: 1.68 mg/min and pH: 7)

Figure 6: The effect of oxalic acid on degradation process for single ozonation process (O_3: 1.68 mg/min and pH: 7)

water and wastewater treatment for the removal of various pollutants, especially oxalic acid.

Figure 1a and b shows the SEM images of activated carbons produced from sweet corn heap. As it can be seen, before adsorption (1a) activated carbon has more pores than used activated carbon (1b). In Figure 1c and d shows MgO nanoparticles before and after adsorption process, respectively. Figure 1e and f show that MgO nanoparticles fixed on activated carbon gained from sweet corn heap, before and after the adsorption process, respectively. Figure 1e shows that the amount of activated carbon after fixing MgO nanoparticles has drastically changed. The difference between the two figures represents the decrease in pores and also the level and number of fixed nanocatalysts.

Figure 2 shows the EDAX metal analysis of GAC, MgO and the MgO/GAC combination. As Figure 2a shows, GAC is mostly made up of carbon and a small amount of oxygen and magnesium (Mg = 0.35, O = 1 and C = 96.54). In Figure 2b, MgO is made up of magnesium and oxygen without any carbon (O = 34.52 and Mg = 64.16). From Figure 2c, GAC/MgO is made up of carbon, magnesium, and oxygen (O = 28.46, Mg = 35 and C = 36.54). It is completely clear in this figure that MgO nanocrystals are fixed on activated carbon.

Figure 3 presents FTIR spectrum analysis of functional groups of the catalyst. From the figure in wavelength of FTIR related to activated carbon produced by sweet corn heap, nanoparticles of MgO and nanoparticles of MgO fixed on the activated carbon of sweet corn heap are represented. with comparing the FTIR spectrums of GAC, MgO, and GAC/MgO nanoparticles, it is obvious that the percentage of infrared release of utilized catalysts are as follows: GAC < MgO < MgO/GAC.

The effect of pH
In this study, the effect of pH solution for the degradation of oxalic acid were investigated using SOP and COP (compound
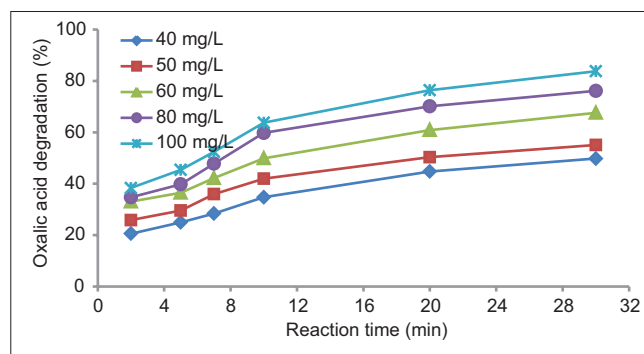
ozonation process) in different catalyst values. Figure 4 shows the effect of initial pH on the process for degrading 100 mg/L oxalic acid with ozonation rate of 1.68 mg/min for 2–30 min in SOP and COP processes and in the presence of GAC, MgO, and GAC/MgO catalysts. The highest efficiencies of oxalic acid degradation in COP process were for GAC, MgO, and GAC/MgO, respectively. Accordingly, SOP had the least removal efficiency. The results also revealed that pH has no considerable effect on COP process in the presence of MgO/GAC; whereas it had the highest effect on SOP process.

The effect adsorption process by the catalysts
In this study, the effect of adsorption process on oxalic acid reduction was investigated in the absence of ozone and with the identical time and conditions of ozonation at pH of 7 with 1 g activated carbon per 100 ml of oxalic acid solution. The results showed that at pH = 7 and 30 min, activated carbon and activated carbon covered by MgO nanoparticles eliminated 5% and 9% of oxalic acid, respectively.

The effect of reaction time
The effect of reaction time in 2–30 min intervals was examined on the decomposition of oxalic acid at pH = 7 [Figure 5]. In SOP process, oxalic acid decomposition had a stable procedure during the reaction; whereas in COP process, the increasing process of oxalic acid elimination for the first 7 min was high, but gradually decreased during the time. Oxalic acid elimination efficiency in COP and SOP processes with GAC, MgO, and GAC/MgO catalysts, in pH = 7, were 98.1%, 89.7%, 83.5%, and 50.6%, respectively, after 30 min of reaction.

The effect of oxalic acid concentration
The effect of oxalic acid density on elimination efficiency of COP and SOP processes was investigated in five different densities: 40, 50, 60, 80, 100 mg/L; the related results are represented in Figures 6-9. As the figures show, the efficiency of oxalic acid degradation in SOP process with the densities of 40, 50, 60, 80, and 100 was

46.54%, 52.14%, 63.5%, 73.2%, and 77.54%, respectively, after 30 min of ozonation. The efficiency of oxalic acid degradation in the presence of GAC for densities of 40, 50, 60, 80, and 100 after 30 min was, respectively, 58.76%, 80.95%, 81.3%, 82.61%, and 90.94%; whereas, the oxalic acid degradation efficiency in the presence of GAC/MgO catalyst in 40, 50, 60, 80, and 100 mg/L densities were 92.66%, 93.66%, 94.66%, 96.7%, and 99.84%, respectively, after 30 min.

The effect of granular activated carbon, magnesium oxide, and granular activated carbon/magnesium oxide

The effect of amount and the kind of different catalysts on the elimination of oxalic acid procedure is represented in Figure 10. As the amount of GAC increases from 0.025 to 1 g/L, the efficiency increases from 46.18% to 68.5%. As the amount of MgO increases from 0.025 to 1 g/L, the efficiency increases from 78.4% to 94.43%. Furthermore, as the amount of GAC/MgO increases from 0.025 to 1 g/L, the efficiency of elimination increases from 89.91% to 99.88%. Finally, as the amount of GAC/MgO catalyst increases to 0.75 g/L, the efficiency of elimination increased; after that in higher amounts of the catalyst, the percentage stayed rather stable.

Kinetic of oxalic acid degradation

Table 1 shows the kinetic of oxalic acid degradation in COP and SOP processes in pH = 7 and the optimized amount of the variables. Oxalic acid degradation rate in these processes follows the pseudo first order kinetic with the following formula:

C_o and C_t are the density of oxalic acid in time zero and "*t*" of reaction.[31,35] A comparison of rate quotient in different processes shows that the rate of COP several times more than SOP process in oxalic acid elimination.

Oxalic acid mineralization

The investigation of oxalic acid mineralization in COP and SOP processes and determining the effect of GAC, MgO, and GAC/MgO catalysts using the efficiency of COD elimination in optimal conditions (the amount of catalyst is 1 g/L, ozone is 1.68 mg/L, and pH = 7) within the time limit of 2–30 min was performed, and the results are represented in Figure 11. As the reaction time increases, COD elimination efficiency in both COP and SOP processes increased, and after 30 min in GAC, MgO, and GAC/MgO processes, they were 93.2%, 66.65%, 50.21%, and 30.21%, respectively. The efficiency of COD elimination in COP was constantly higher than SOP.

Oxalic acid degradation mechanism

The production of radicals, especially hydroxyl radical is among the most important priorities of advanced oxidation process. To distinguish radical scavengers in COP processes, tert-butanol was used, and its results are shown in Figure 12. The results show that oxalic acid elimination in ozone catalyzer process using activated carbon, MgO nanoparticles, and carbon coated with MgO nanoparticles decreased from 84% to 56% and from 83% to 79% and also from 98% to 65%, respectively. In ozonation procedure, the elimination process decreased from 68% to only 48%. The results showed that radical scavengers in ozonation of covered carbon, has had more effect on oxalic acid degradation efficiency decrease.

DISCUSSION

The most outstanding features of a catalyst are its surface features and chemical make-up (compound), which have an important role in changing ozone to activated radicals. Surface features are different in each activated carbon

Table 1: Kinetic information for degradation of oxalic acid in COP and SOP

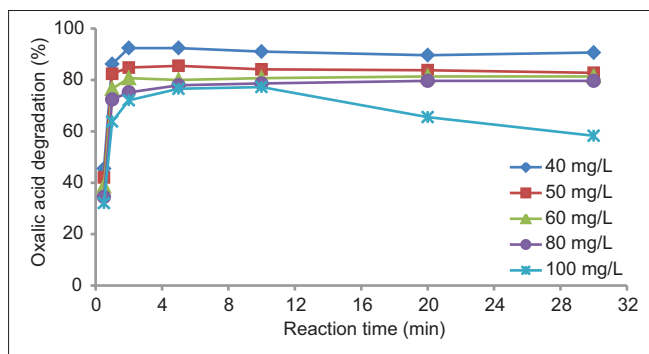| Process	The pseudo first order kinetic of process		
	$K_{app}/K_{app-SOP}$	K_{app}	R^2
SOP	1	0.0026	0.95
COP-GAC	9.6	0.025	0.98
COP-MgO	5.8	0.015	0.98
COP-GAC/MgO	23.2	0.076	0.97

Figure 7: The effect of oxalic acid on degradation process for catalytic ozonation process with granular activated carbon (O_3: 1.68 mg/min and pH: 7)
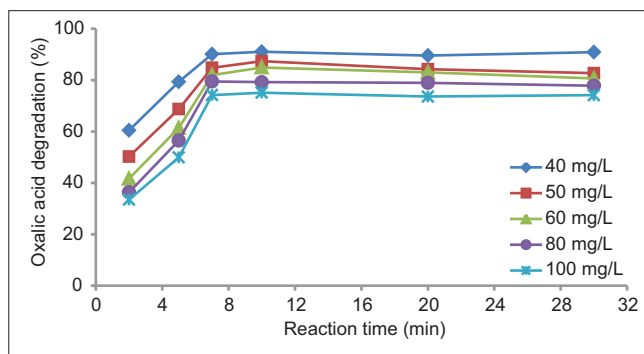
Figure 8: The effect of oxalic acid on degradation process for catalytic ozonation process with magnesium oxide (O_3: 1.68 mg/min and pH: 7)
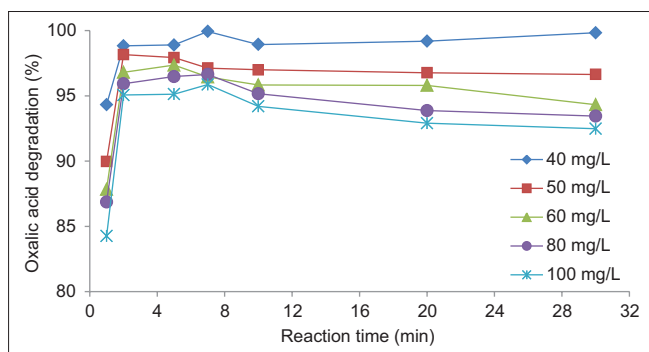
Figure 9: The effect of oxalic acid on degradation process for catalytic ozonation process with magnesium oxide/granular activated carbon (O_3: 1.68 mg/min and pH: 7)
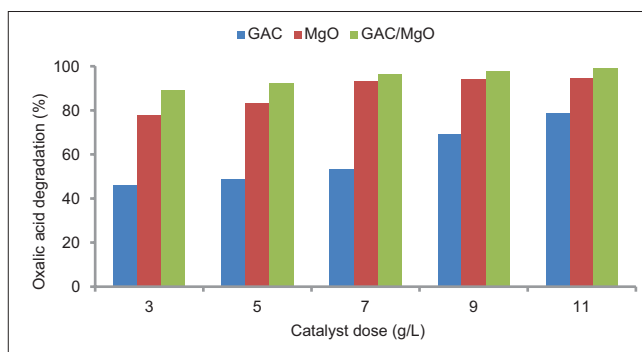

Figure 10: Compare the amount and type of catalyst for oxalic acid degradation in catalytic ozonation process (Oxalic acid: 100 mg/L, O_3: 1.68 mg/min, pH: 7 and contact time: 20 min)
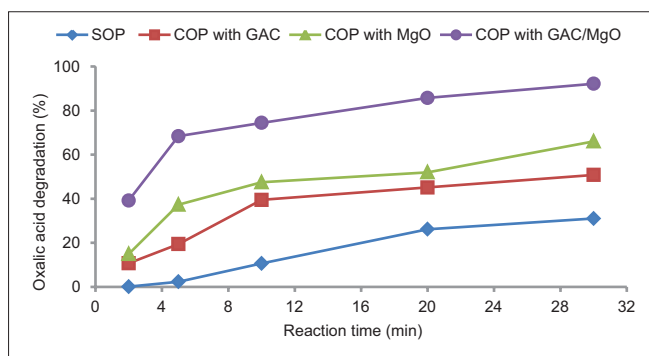

Figure 11: The effect of reaction time (2–30 min) on oxalic acid mineralization for single ozonation process, catalytic ozonation process with granular activated carbon, catalytic ozonation process with magnesium oxide and catalytic ozonation process with magnesium oxide/granular activated carbon (Oxalic acid: 100 mg/L, catalyst: 1 g/L, O_3: 1.68 mg/min and solution pH: 7)
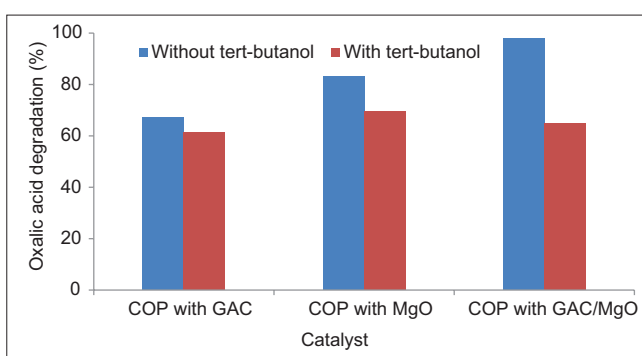

Figure 12: The effect of tert-butanol on degradation and mineralization of oxalic acid in single ozonation process and catalytic ozonation process with granular activated carbon, catalytic ozonation process with magnesium oxide and catalytic ozonation process with magnesium oxide/granular activated carbon (Oxalic acid: 100 mg/L, catalyst: 1 g/L, O_3: 1.68 mg/min, solution pH: 7 and contact time: 20 min)

depending on its molecular structure, production and activation method.[36,37] To distinguish the functional groups on the surface of GAC, MgO, and GAC/MgO catalysts, FTIR technique was utilized. Functional groups are one of the most effective factors in the surface adsorption mechanism of organic pollutants of water on the catalyst surface. The functional groups at GAC and GAC/MgO surfaces include O-H, C = O, O-H, C = C, C-O, C-O-C, and C-H. The known functional groups in these catalysts are in line with similar studies results.[38] As a result of covering activated carbon with MgO, the intensity of the peaks related to functional groups of activated carbon has decreased, which represents the MgO fixation on the catalyst.

pH is also one of the effective factors in catalyst ozonation process by influencing oxalic acid structure and the catalyst's superficial load, and also by forming and functioning of functional groups. Ozone reacts with organic materials directly or indirectly (especially hydroxyl radicals).[14,24] In ozonation process, as the pH increases, the role of indirect mechanism increases in organic material decomposition in water. In indirect mechanism of ozone, high oxidation

potential hydroxyl radicals are produced that can increase the ability of the process in organic material decomposition.[14,24] In this study, in both processes, as pH increased, elimination efficiency increased, too. In SOP process, the highest elimination efficiency was in initial pH of 9, then in pHs of 7, 5, and 3, since the amount of hydroxyl radical production decreased. The study of pH effect on oxalic acid degradation in COP and SOP processes showed that oxalic acid degradation in COP is affected less by pH. This is related to MgO ability as an alkaline compound with the acidity of pKa = 10.3 and pH_{zpc} = 12.4 in water pH increase in COP process. These results have been verified in previous studies, too.[14,30,39,40] In Fernández-Jiménez and Palomo study, as the pH increased, the adsorption amount of oxalic acid on TiO_2 increased, and the adsorbed oxalic acid was as hydrogenoxalate. The highest elimination efficiency was for pH = 10. The rate of reaction in pH = 3 and pH = 10 was 5.759×10^{-8}/M/s and 14.19×10^{-8}/M/s, respectively.[39,41]

In this study, the effect of reaction time in 1–30 min was studied on oxalic acid degradation in SOP and COP processes

in pH = 7. As the time increased in SOP process, elimination efficiency had a stable additive procedure. This procedure in pH = 11 was a little more than pH = 7 and pH = 9. Since in alkaline pH, in addition to ozone, some hydroxyl radical is produced that increases the efficiency. Whereas in COP process, increase in efficiency of oxalic acid elimination was higher in first 7 min, and decreased as time passed. In heterogenic catalyst activities, the surface adsorption features of metal oxides are important; in a way that the surface adsorption is mostly one of heterogenic catalyst ozonation processes. Normally, there are three mechanisms for heterogenic catalyst ozonation.[32,42]

- Chemical adsorption of ozone in the catalyst surface that forms activated types and reacts with nonabsorbable organic molecules
- Chemical adsorption of organic molecules (ionic and nonionic) on catalyst surface and their reaction with gas ozone and ozone dissolved in liquid
- Simultaneous adsorption of ozone and organic molecule on the catalyst and their reaction as a result.

Therefore, regarding the abovementioned issues, ozone and oxalic acids are absorbed on the catalyst surface in the first 7 min. This has been observed in previous studies as well.[27,32]

After surface adsorption phase (the first 7 min of reaction) up to 20 min, the oxalic acid degradation efficiency still continued with a lower increased rate than the previous phase. This is due to the degradation of ozone and radical production in COP process. In COP process, the increase in ozone dissolution in water and the beginning of ozone degradation reactions are two important factors in metal catalyst effect mechanisms. In metal oxide catalyst mechanisms of ozonation process, it is generally assumed that ozone and the organic molecules are both absorbed to the catalyst surface simultaneously, and as a result of adsorption, ozone produces $O^\bullet$ radicals, or $HO^\bullet$ radicals. To produce hydroxyl radicals, $O_2^{\bullet-}$ gives one electron to another ozone molecule, which results in ozone anion production; ozone anion acts as the chain reaction catalyst leading to the production of hydroxyl radicals.[27] Therefore, after surface adsorption phase (the first 7 min of the reaction up to 20 min), the chain reactions of radical production increase drastically due to ozone adsorption and oxalic acid on catalysts surface; as a result, degradation procedure of oxalic acid increases. After 20 min, the additive procedure of oxalic acid elimination efficiency continued less severely because the oxalic acid density decreased in the reactor.

The surface reaction of activated carbon with ozone in heterogeneous conditions is as follows:

$$OH^- + S \leftrightarrow OH–S$$

Where, "S" stands for activated carbon surface and in fact, activated carbon is the initiator, and S is the promoter of reaction, leading to chain reactions of radical formation.[27] The results showed that the catalyst GAC/MgO have a

considerable synergistic effect with ozone; so that in 30 min and in identical conditions, it has a higher efficiency in comparison to other catalysts.

The degradation rate of oxalic acid in SOP and COP processes at pH = 7 in its different densities was conforming to pseudo first order kinetic [Table 1]. The constant of oxalic acid degradation reaction rate in higher densities was more than lower densities, because the contact between oxalic acid, the catalyst, and hydroxyl radical accessibility increased. Oxalic acid elimination rate in COP and, especially COP/MgO processes were several times higher than SOP process due to more adsorption, more accessibility, and production of oxidizer radicals. In Moussavi *et al.* study, catechol degradation was investigated with this process, and their results corresponded to the present study, except for the fact that catechol had higher oxidation capability than oxalic acid, and therefore the rate of reaction was higher.[32]

In this study, the effect of initial density of oxalic acid was investigated on its elimination efficiency in COP and SOP processes. The results showed that as the pollutant dose increases in catalyst constant amounts, the elimination efficiency decreases. A comparison of the findings shows that COP process has had a far better performance than ozonation process alone in higher densities. Furthermore, if COP process is utilized to degrade oxalic acid, especially in less densities such as 40 mg/L, the reaction needed time will be much less, and as a result the volume of the reactor and the related expenses will be much less.

The increase in catalyst dose increases the surface area and activated sites of ozone adsorption. This increase in adsorption increases the surface reactions and radical production in catalyzer ozonation process.[31,41] As the catalyst dose increases from 0.025 to 1 g/L, oxalic acid degradation efficiency increases. In the first phase, as the catalyst dose increases due to surface adsorption, oxalic acid elimination efficiency increases as well with a high rate, and as the catalyst was added the rate of elimination efficiency was reduced relatively. The acceleration of degradation rate in COP in comparison to SOP can be attributed to the beginning of chain reaction and hydroxyl radical production. In the next phase of COP process, as the catalyst dose increased from 0.025 to 1 g/L, the additive procedure of oxalic acid degradation was lower. This increase in degradation efficiency can be attributed to an increase in the amount of catalyst in the reactor, and as a result, an increase in chain reactions and hydroxyl production. The weight ratio of reactor's pollutant to catalyst is an important parameter in chemical processes, especially COP process. This ratio is normally calculated by experimental methods, since the chemical reactions in these processes are complicated. Therefore, lower efficiency in degradation procedure in this phase in comparison to other phases can be attributed to low density of oxalic acid ratio to the catalyst dose.[32,41]

To investigate the mineralization amount of oxalic acid in COP and SOP processes and also to determine the GAC, MgO, and GAC/MgO catalysts affect the COD elimination efficiency in optimal amount of variables and in the reaction time of 1–30 min was studied. As the reaction time increased COD elimination efficiency in both COP and SOP processes increased. COD elimination efficiency in COP process was constantly higher than SOP process. This is due to hydroxyl radical production. Hydroxyl radicals have a nonselective oxidation capability higher than ozone molecules. The reaction rate constant of oxalic acid was higher with hydroxyl radicals, and oxalic acid changed to minerals in COP process.[21,27] The comparison of efficiencies between COP and SOP processes show that the highest amount of synergistic effect of GAC/MgO catalyst with ozone in COD elimination was gained in 10 min of reaction. Thus, carbon covered by MgO nanoparticles showed a higher mineralization capability because it produces more oxidizer radicals. The mineralization capability of ozone alone was the least. Other studies confirmed these findings.[32,43]

One of the problems related to advanced oxidation process is the existence of interfering factors. These interferers or radical consumers, including sulfate, carbonate, chloride, and nitrate, exist in natural water and decrease the efficiency of advanced oxidation processes.[28,32,43,44] The reaction rate constant of tert-butanol reaction with hydroxyl radicals ($K_{\bullet OH} = 6 \times 10^8$/M/s) is much higher than ozone molecules ($kO_3 = 3 \times 10^3$/M/s).[21,27] In this study, radical scavenger of tert-butanol was utilized to distinguish hydroxyl radical production in COP process. This combination is widely used in advanced oxidation processes as radical scavenger for determining hydroxyl radical role. Tert-butanol is highly soluble in water and has a low adsorption rate in catalyst and quickly reacts with free hydroxyl radicals.[13,45] In comparison, COP process efficiency in the absence and presence of radical scavenger showed that much of oxalic acid degradation in ozone catalyst process is related to the produced radicals, and the amount of produced radicals in ozonation process is less than catalyst ozonation processes. These findings accord to other studies that have been the basis of production and oxidation processes by hydroxyl radicals.[32,46]

CONCLUSION

According to the findings of this study, the SOP process has low efficiency for oxalic acid degradation in aquatic solution. Adding the catalyst to SOP process increased degradation efficiency of oxalic acid. The COP process has high efficiency for oxalic acid degradation in aquatic solution, because the presence of catalyst nanoparticles in the ozonation process produces hydroxyl radicals as a strong secondary oxidant agent. As such the hydroxyl radicals oxidize organic compounds much better than ozone. Therefore, using COP processes for removing resistant pollutants in water and, especially in industrial sewages is much more efficient.

Conflicts of interest

There are no conflicts of interest.

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