

A comparison of single and catalytic ozonation for decolorization of malachite green

Rahimeh Parvarideh, Ali Ahmad Aghapour, Seyed Javad Jafari, Sima Karimzadeh, Hassan Khorsandi*

Department of Environmental Health Engineering, School of Health, Urmia Medical Sciences University, Urmia, Iran. emails: hassankhorsandi@yahoo.com (H. Khorsandi), parvaride.rahime@gmail.com (R. Parvarideh), aaaghapour@gmail.com (A.A. Aghapour), sjavadj@gmail.com (S.J. Jafari), sima.karimzade@yahoo.com (S. Karimzadeh)

Received 19 August 2018; Accepted 19 February 2019

ABSTRACT

Considering harmful environmental and health effects of malachite green (MG), its removal from dye wastewater is necessary. Accordingly, the aim of this interventional–experimental study is to compare single and alumina-catalytic ozonation processes (COPs) for decolorization of MG in a lab-scale reactor for the first time. The full decolorization of 50 mg L⁻¹ MG was carried out in single ozonation process (SOP) after 30 min but after 15 min in the case of COP. For 3,000 mg L⁻¹ MG, the decolorization efficiency increased from 95.38% to 99.53% after 30 min in optimal conditions by converting the process from SOP to COP. However, the chemical oxygen demand removal increased from 60% to 82.35%, but the total organic carbon (TOC) removal rose from 62.39% to 69.76%. The reaction rate coefficients of COP at the initial MG concentrations of 50 and 3,000 mg L⁻¹ are about 3.6 and 14 times, respectively, more than the reaction rate coefficients of SOP.

Keywords: Alumina; Catalytic ozonation; Malachite green; Wastewater

1. Introduction

Every year, 26,000 dye types are produced at around 700 × 10⁶ kg worldwide. Some about 10,000 dye types are used in different industries including textile, paper, rubber, plastics, cosmetics, food and fish farming [1–3]. Every year, an estimated 280 × 10⁶ kg of colored materials from different classes with high chemical stability and low biodegradation directly enter the sewage worldwide [4]. Apart from their esthetic effects, dye effluents, because of their interference with the penetration of light into the depths of the rivers, disturb the ecological balance and cause eutrophication. Moreover, the existence of aromatic rings, metal ions and halides, especially chlorides in the structure of colors brings about an increase in their toxicity, carcinogenicity, mutagenicity and teratogenicity in living organisms [5]. Malachite

green (MG), C₂₃H₂₅ClN₂, is a cationic triphenylmethane dye with high stability in acidic environments [6,7]. Its chemical structure is illustrated in Fig. 1.

Apart from its extensive use in material dyeing including that of wool, silk, hemp, leather, paper and nylon, MG is also used as an antifungal, antibacterial and antiparasitic in aquaculture industry. MG, due to the existence of nitrogen in its structure, is highly toxic and any contact with it by inhalation or ingestion can cause serious harm to respiratory system, carcinogenicity, mutagenicity, chromosomal fractures, growth disorders and reduced fertility in humans [5,9,10].

The median lethal dose (LD₅₀) for MG by inhalation is 275 mg kg⁻¹ and by dermal exposure is 2,000 mg kg⁻¹ [7]. The US Food and Drug Administration considers MG as a chemical indicator for carcinogenic testing [10]. The discharge of wastewater containing MG into aquatic ecosystems causes serious harm to the aquatic animals' liver, kidney, gill, intestine and gonads [11].

* Corresponding author.

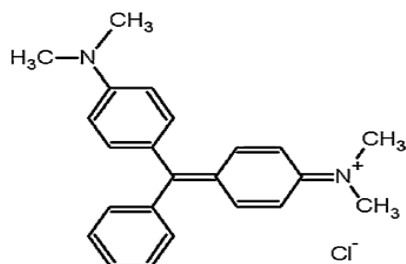


Fig. 1. Chemical structure of Malachite Green [8].

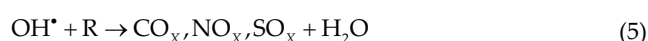
Due to the adverse effects of MG, its use has been banned in the European Union. However, due to its low costs, availability, high effectiveness and a lack of a good alternative, MG is still used in many countries [10].

Considering its harmful environmental and health effects, the removal of MG from dye wastewater is necessary. Based on literature, in order to remove MG, different methods including photocatalytic degradation [12–14], coagulation and flocculation [15], ozonation [16], Fenton [17], sonochemical [18], adsorption [19,20] and biodegradation [11,21] were studied.

Single ozonation process (SOP) is one of the advanced oxidation methods that, due to the high oxidation power ($E_0 = 2.07$ V), can attack various refractory organic compounds with the speed of $0.01\text{--}10^4$ mol L⁻¹ s⁻¹ [22].

In many cases, ozone cannot completely oxidize resistant and non-degradable organic compounds and, owing to incomplete oxidation, results in production and accumulation of toxic and dangerous by-products. In order to increase the power of ozone mineralization by converting it into more active forms such as hydroxyl radicals in aqueous solutions, catalytic ozonation process (COP) has become popular over the past few years. This process has been successfully used to remove dyes, various volatile organic compounds such as aromatic compounds, alkyls, chlorides, *n*-containing compounds and *S*-containing compounds [23–25].

Reactions (1)–(5) show the mechanism of oxidation of pollutants by catalytic ozonation [23].



He et al. [26] investigated heterogeneous catalytic ozonation of paper-making wastewater with $\alpha\text{-Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ as a catalyst for increased total organic carbon (TOC) and color removals. They indicated that TOC removal rates reached 51% using $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$, 37% in the presence of $\gamma\text{-Al}_2\text{O}_3$ and only 26% with ozonation alone after 60 min of treatment.

Kusvuran et al. [16] studied the efficiency of SOP in removing MG at pHs of 10, 7 and 3. The maximum

decolorization efficiency of SOP was 99.1% for decomposition of 1.82 mM MG in 20 min. This is while the efficiency of TOC removal was about 10% after 20 min and 47.4% after 100 min. They identified the intermediate products of MG ozonation according to Fig. 2.

Dong et al. [27] showed that although COP using mineral brucite in decomposition of Red X-3B increase from 47% to 98% compared with the SOP, the chemical oxygen demand (COD) removal increased from 9% to 32.5%.

Beltran et al. [28] showed that the removal of oxalic acid with the process of COP using $\text{TiO}_2/\text{Al}_2\text{O}_3$ was 80% in 3 h, while in absence of catalyst, the removal rate decreased to 2%.

γ -alumina is the most common catalyst and catalyst support due to its low cost, very stable surface OH groups, good thermal stability, high specific surface area, surface acidity and specific sites for anchoring cationic, anionic and metallic species. Therefore, we used it as the catalyst in COP in order to remove MG [29].

Considering the advantages and potential of COP and due to its absence in the studies on the removal of MG, the aim of the present study is to compare single (SOP) and alumina-catalytic (COP) ozonation processes for decolorization of MG for the first time.

2. Methods

In this interventional-experimental study, the efficiency of SOP and COP processes was studied using activated γ -alumina in the removal of MG from aqueous solutions. To analyze the specified goals, the effect of different parameters, including contact time (2, 5, 7, 10, 15, 20, 25, 30 and 60 min), pH (3, 5, 7, 8.5 and 10), initial concentration of MG (50, 100, 200, 300, 500, 1,000, 2,000 and 3,000 mg L⁻¹), concentration of soluble ozone (3.4–4.4 mg min⁻¹) and catalyst amount (1, 2 and 5 g L⁻¹) were all studied. In order to analyze the specific goals of this study, a pyrex cylindrical reactor with a useful volume of 1 L was designed and constructed. The reactor has two holes above it, one for ozone entry and the other for exhaust gas discharge that a diffuser was installed at the end of the inlet pipe for a better spread of ozone in solution. An oxygen concentrator with a capacity of 5 L min⁻¹ and an ozone generator were used to provide the required ozone (Fig. 3). 1-N solutions of sodium hydroxide and sulfuric acid were used to adjust the pH.

The absorbance of standard solutions of MG was measured by using DR 5000 spectrophotometer (Hach,

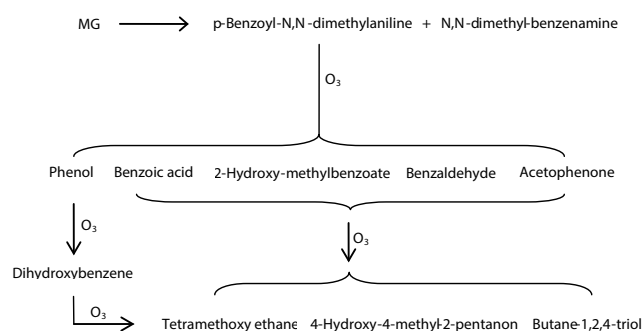


Fig. 2. Proposed degradation pathway of MG by SOP [16].

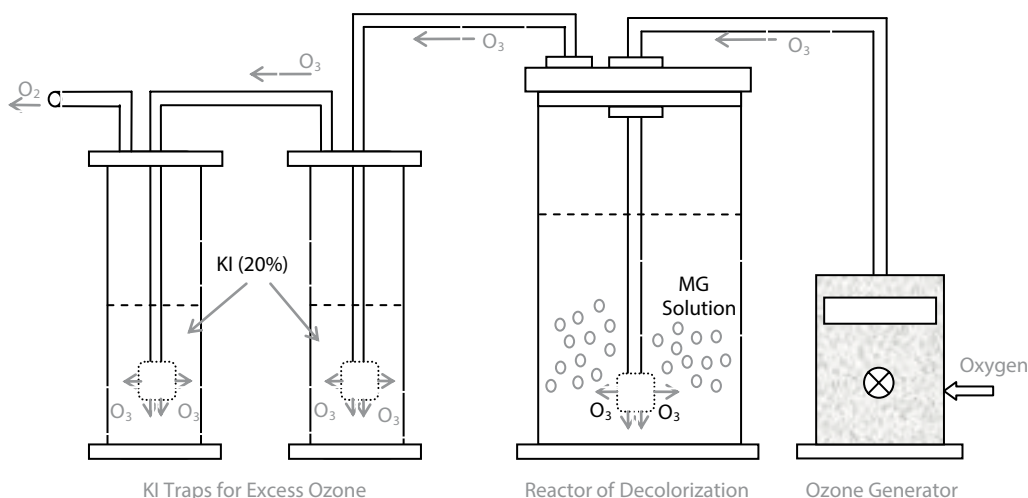


Fig. 3. Reactor in use.

Germany) at the maximum absorbance frequency of MG ($\lambda_{\max} = 618 \text{ nm}$). The calibration curve is constructed by plotting absorbance values against concentration of standard solutions. The straight line graph passing through origin has been obtained.

Then, the absorbance of the MG solution before and after SOP and COP was obtained at 618 nm. Finally, concentration of MG was determined using the calibration curve.

Factors affecting the process of the study including contact time, pH, ozone concentration, catalyst dose and initial concentration of MG were all analyzed in separate stages. In examining the effect of each variable on the performance of the process, other parameters affecting the reaction were considered constant.

During the process, the ozone gas flow continuously entered the reactor through the bottom and, after its contact with the solution, exited the top of the reactor. The surplus ozone was neutralized in two gas washing bottles containing 20% potassium iodide. The ozone mass flow rate produced by an ozone generator was determined by KI based on the Standard Method for the Examination of Water and Wastewater [30]. The COD test was carried out by closed reflux method with thermal digestion based on colorimetry of reduced chromium ion and according to Standard Methods for the Examination of Water and Wastewater [30]. To determine the mineralization rate of MG, TOC concentration was measured by the Shimadzu TOC analyzer (Japan).

A nano $\gamma\text{-Al}_2\text{O}_3$ catalyst (Merck, Germany) was used in the COP process. Its specifications were presented in Table 1.

All consumables including MG, potassium iodide, sodium thiosulfate, starch, sulfuric acid and potassium hydroxide were prepared from Merck Co.

3. Results and discussion

3.1. Effect of pH on the decolorization

The effect of pH changes on decolorization of MG from aqueous solutions by SOP and COP is shown in Fig. 4, according to which decolorization of MG by SOP in alkaline conditions is more efficient than in acidic and neutral

Table 1
Aluminum oxide nanoparticles (Al_2O_3) features

Characteristic	Value/description
Purity	99+%
APS	20 nm
SSA	>138 $\text{m}^2 \text{g}^{-1}$
Morphology	nearly spherical
Color	White
Specific heat capacity	880 $\text{J kg}^{-1}\text{K}^{-1}$
Density	3,890 kg m^{-3}

conditions. According to Fig. 4(a), although, in acidic and neutral conditions, an increase in ozone dose from 3.4 to 4.4 mg min^{-1} has a remarkable effect on the efficiency of SOP in decolorization of MG, there was no significant difference in decolorization at various concentrations of ozone in alkaline conditions. According to Fig. 4(b), there was no remarkable difference in decolorization of MG by COP in alkaline, acidic and neutral conditions.

Accordingly, a pH of 8.5 and an ozone dose of 3.4 mg min^{-1} were chosen as optimum conditions for comparing decolorization of MG by SOP and COP processes.

Decolorization of MG in acidic conditions is carried out by the direct attack of ozone, but in alkaline conditions, it is conducted by the indirect attack of different radicals including hydroxyl radical, resulting from ozone decomposition [16,31,32]. In alkaline conditions, ozone depletion begins with one of the following reactions [31]:



Peroxide (HO_2^-) and superoxide ($\text{O}_2^{\cdot-}$) anions react with ozone and form the ozonide ion (O_3^-):

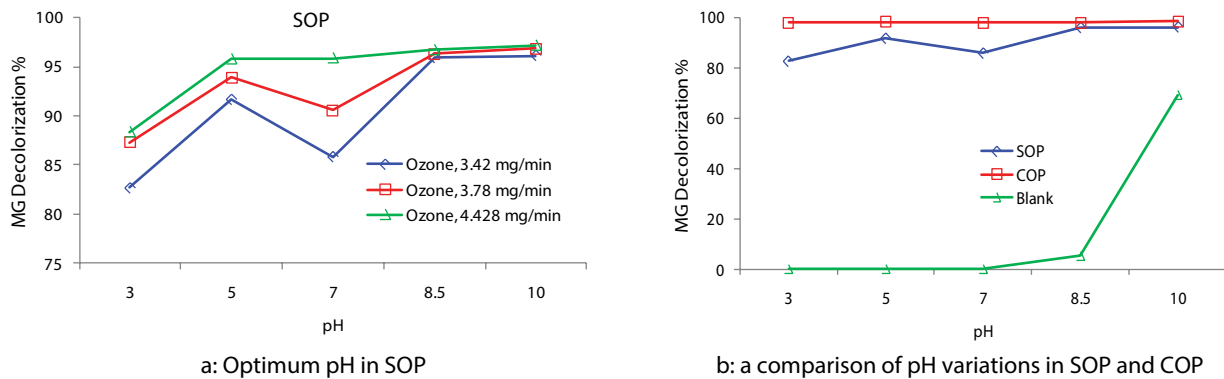
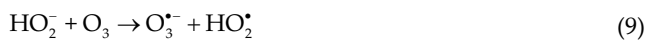


Fig. 4. Effect of pH on decolorization of MG using SOP and COP. (a) optimum pH in SOP and (b) a comparison of pH variations in SOP and COP ($MG_0 = 300 \text{ mg L}^{-1}$; $t = 5 \text{ min}$; ozone dose = 3.4 mg min^{-1} ; adsorbent dose = 1 g L^{-1}).



In order to produce hydroxyl radical, the ozonide is decomposed by one of the following methods:



Finally, hydroxyl radical may react with more ozone and lead to the production of more superoxide anions, which ultimately ends in the production of hydroxyl radical.

Hydroxide in alkaline conditions, as a primary factor in ozone depletion, plays a major role in production of hydroxyl radical. Due to its higher oxidation potential ($E_0 = 2.8 \text{ V}$), hydroxyl radical is more active than ozone molecule ($E_0 = 2.08 \text{ V}$) [16,32] and, with higher oxidation rate, leads to an increase in the decolorization efficiency of SOP in alkaline conditions. Moreover, in alkaline conditions, hydroxylation of colored conjugated cation results in the formation of a non-ionic and non-resonant carbinol, which in turn leads to color reduction [33,34].

The ionization constant of MG at equilibrium conditions is 6.9 ($pK_a^{MG} = 6.9$). Accordingly, its ionization ratio at pHs of 4, 6.9, 7.4, and 10.1 equals 100%, 50%, 25%, and 0% [32].

Thus, by increasing the pH from 3 to 5, the formation of non-ionic carbinol will begin to increase, and the decolorization efficiency is facilitated by direct oxidation of ozone. In neutral conditions, direct oxidation of MG by ozone is not very important and its oxidation is controlled by reaction with hydroxyl radical [33]. Hence, because of the limited concentration of hydroxyl radical, the efficiency of SOP in oxidation of MG is reduced in neutral conditions in comparison

with alkaline and acidic conditions. Therefore, in this study, at an initial MG concentration of 300 mg L^{-1} and an ozone dose of 3.4 mg min^{-1} , by increasing pH from 3 to 8.5, the efficiency of SOP in decolorization of MG increased from 82.66% to 95.88%.

In spite of increasing the possibility of hydroxyl radical production, the constant efficiency of decolorization in a specific ozone dose in the pH range of 8.5–10 is attributed to non-selective oxidation and increasing the likelihood of radicals participation in degradation of intermediate products.

The fact that there is no significant difference in the decolorization efficiency of SOP for different ozone flows at a certain alkaline pH might be due to the constant hydroxide concentration as a factor in ozone depletion for production of hydroxyl radicals. This is while at a certain acidic pH, by increasing ozone dose, direct selective attacks on MG also increase and a significant difference is found in decolorization of ozonation process.

In conditions of $pH < (pH_{zpc}^{\gamma Al_2O_3} = 9.15)$, a positively charged alumina does not have a significant effect on the adsorption of the cationic form of MG, but absorption and deposition of positive charges on alumina are provided through the van der Waals force [34] and thus the conditions for increasing the MG oxidation are provided. On the other hand, alumina, by increasing the pH of the reaction environment, provides the conditions for converting the cationic form of MG into nonionic carbinol, thereby increasing the COP efficiency without affecting the initial pH, as compared with the SOP. The outcomes are consistent with the results of the studies by Das et al. [34] and Kusvuran et al. [16].

3.2. Effect of catalyst dose on the decolorization

The effect of different concentrations of gamma alumina catalyst (γAl_2O_3) was analyzed to improve the efficiency of ozonation in decolorization of MG. According to the results, the efficiency of COP at γ -alumina concentrations of 1, 2 and 5 g L^{-1} in decolorization of 300 mg L^{-1} of MG was 97.96%, 97.9% and 97.7%, respectively. Therefore, the selective catalyst concentration was determined to be 1 g L^{-1} . Although the difference in the efficiency of SOP and COP in decolorization of 300 mg L^{-1} of MG at optimum catalyst dosage and pH, and at reaction time of 5 min was only about 2%, the difference

in their COD removal was about 33%. The results were consistent with the findings of Moussavi and Mahmoudi [35] for the removal of azo dye Reactive Red 198 using the COP.

3.3. Effect of the initial MG concentration and reaction time on the decolorization

The effect of the initial MG concentration and reaction time on decolorization of SOP and COP is shown in Fig. 5. As it is observed, with increasing initial MG concentration from 50 mg L⁻¹ to 3,000 mg L⁻¹, the efficiency of MG decolorization at different times is reduced in both processes. By increasing the initial MG concentration, the consumption of oxidizing agents such as ozone or free radicals, including hydroxyl radicals, increases. This is while the dose of ozone injected and, consequently, the amount of hydroxyl radicals produced are constant. As a result, color decomposition at high concentrations is slowed down and reduces the efficiency of decolorization [35]. The results are consistent with the findings of Kusvuran et al. [16] for the decolorization of MG by SOP and those of Song et al. [36] about the decolorization of Reactive Black 5 by the process of ozonation-coagulation.

According to the results, full MG decolorization at a concentration of 50 mg L⁻¹ was achieved in the SOP after 30 min, but it was after 15 min in the COP. By increasing the initial MG concentration to 500 mg L⁻¹ and after upgrading the SOP to the COP, the efficiency of decolorization increased from 97.86% to 98.37% at 15 min and from 99.56% to 99.6% at 30 min. Hence, as a result of this process upgrade, the remaining MG concentration decreased from 10.7 to 8.14 mg L⁻¹ after 15 min and from 2.2 to 1.89 mg L⁻¹ after 30 min. With the continued increase in the initial MG concentration to 3,000 mg L⁻¹ and by converting the SOP to the COP, the decolorization efficiency increased from 84.23% to 93.22% at the reaction time of 15 min and from 95.38% to 99.53% at 30 min. Thus, by upgrading the SOP to the COP, the MG concentration decreased from 473 to 203.15 mg L⁻¹ after 15 min and from 138.4 to 13.97 mg L⁻¹ after 30 min.

According to Fig. 5, with increasing reaction time, the efficiency of MG decolorization increased in SOP and COP. By increasing reaction time, the possibility of decomposition and degradation of ozone-producing hydroxyl radicals was increased, and by increasing the oxidizing species, the possibility of contact and degradation of pollutants was further enhanced [37]. The results of the study are consistent with

the study by Zhou et al. [38] about the decolorization of MG by the ultrasonic-assisted ozonation process.

3.4. Adsorption of MG on $\gamma\text{Al}_2\text{O}_3$

The adsorption efficiency of 300 mg L⁻¹ MG on 2 g L⁻¹ gamma alumina at pH of 8.5 was determined to be 42.18% after 5 min and 72% after 60 min. By increasing the initial MG concentration to 3,000 mg L⁻¹, adsorption efficiency increased to 53.5% after 5 min and 73.3% after 60 min. Based on presented results, however, $\gamma\text{Al}_2\text{O}_3$ does not have enough efficiency for MG removal, it can enhance the efficiency of ozonation for MG decolorization.

3.5. Removal of COD and TOC resulting from MG

In order to analyze MG oxidation in SOP and COP, COD changes were studied under optimum conditions at initial MG concentrations of 300 mg L⁻¹ (COD_{eq} = 600 mg L⁻¹) and 3,000 mg L⁻¹ (COD_{eq} = 7,000 mg L⁻¹). As shown in Fig. 6, by upgrading the SOP to the COP, COD removal with an initial concentration of 600 mg L⁻¹ (MG_{eq} = 300 mg L⁻¹) increased from 23% to 55.66% after 5 min and from 65% to 66.67% after 30 min. Accordingly, as a result of this upgrade, after 30 min the remaining COD concentration decreased from 210 to 140 mg L⁻¹. By increasing the initial COD concentration to 7,000 mg L⁻¹ (MG_{eq} = 3,000 mg L⁻¹) and by upgrading SOP to COP, COD removal increased from 25% to 57.55% after 5 min and from 60% to 82.35% after 30 min. Hence, as a result of this upgrade, the remaining COD concentration decreased from 2,750 to 1,235 mg L⁻¹ after 30 min.

The low efficiency of the SOP and COP in COD removal compared with MG decolorization confirms the low efficiency of these processes in the full oxidation of MG and the intermediate products. Catalysts, including alumina, with a high surface area and active sites such as hydroxyl groups, increase ozone adsorption and degrade it, resulting in an increase in the production of active radicals, especially hydroxyl radicals, in the COP [34]. Typically, there are three mechanisms for heterogeneous COP: first is the chemical adsorption of ozone on the catalyst surface, which results in the formation of reactive species and reacts with non-absorbing organic molecules; the second is the chemical adsorption of organic molecules on the catalyst surface and their oxidation by ozone; and the third is the chemical absorption of ozone and organic molecules on the

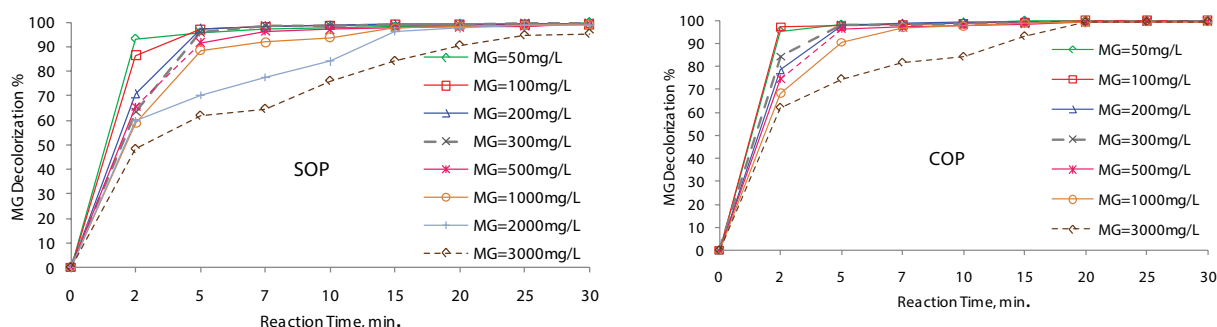


Fig. 5. Effect of the initial MG concentration and reaction time on decolorization (pH = 8.5; ozone dose = 3.4 mg min⁻¹).

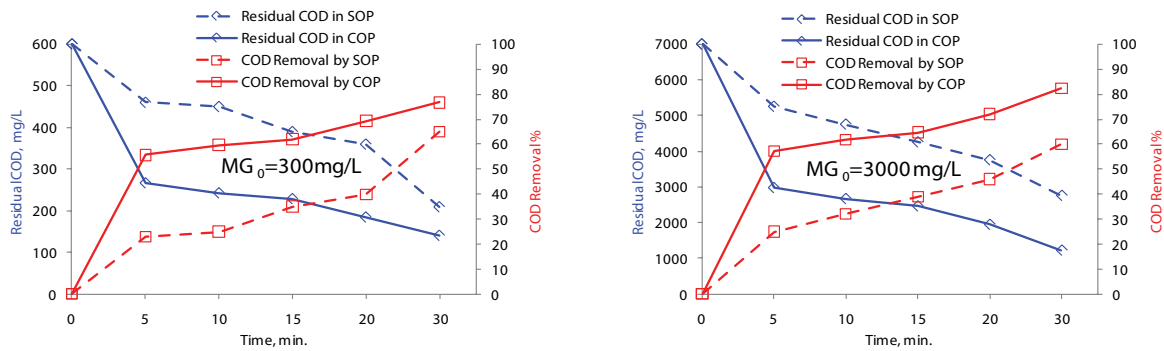


Fig. 6. Removal of COD resulting from MG by SOP and COP ($MG_0 = 300$ and $3,000 \text{ mg L}^{-1}$; $\text{pH} = 8.5$; ozone dose = 3.4 mg min^{-1} ; nano-alumina dose = 1 g L^{-1}).

catalyst surface and their reaction with each other [28,39,40]. The presence of catalysts improves not only the oxidation capacity but also the ability of ozone to convert side products into CO_2 [40]. Accordingly, the van der Waals adsorption reactions, direct and indirect oxidation are all involved in the COP using alumina for MG removal. Therefore, the efficiency of the COP in MG oxidation and intermediate products is higher than SOP.

Dong et al. [27] increased the removal of COD from 9% to 32.5% by studying the removal of Brilliant red X-3B dye using catalytic ozonation with the mineral brucite.

In order to analyze MG mineralization in SOP and COP, TOC resulting from MG were studied under optimum conditions with initial concentrations of 300 mg L^{-1} ($\text{TOC}_{\text{eq}} = 195 \text{ mg L}^{-1}$) and $3,000 \text{ mg L}^{-1}$ ($\text{TOC}_{\text{eq}} = 2,090 \text{ mg L}^{-1}$). As shown in Fig. 7, by upgrading the SOP to COP, the removal of TOC at an initial concentration of 195 mg L^{-1} ($MG_{\text{eq}} = 300 \text{ mg L}^{-1}$) increased from 10.77% to 37.43% after 5 min and from 18.97% to 44.61% after 30 min. Accordingly, as a result of this upgrade, after 30 min the remaining COD concentration decreased from 158 to 108 mg L^{-1} . By increasing the initial TOC concentration to $2,090 \text{ mg L}^{-1}$ ($MG_{\text{eq}} = 3,000 \text{ mg L}^{-1}$) and by converting the SOP to COP, the TOC removal increased from 53.52% to 76.6% after 5 min and from 62.39% to 76.69% after 30 min. Hence, as a result of this upgrade, the remaining TOC concentration decreased from 786 to 632 mg L^{-1} after 30 min.

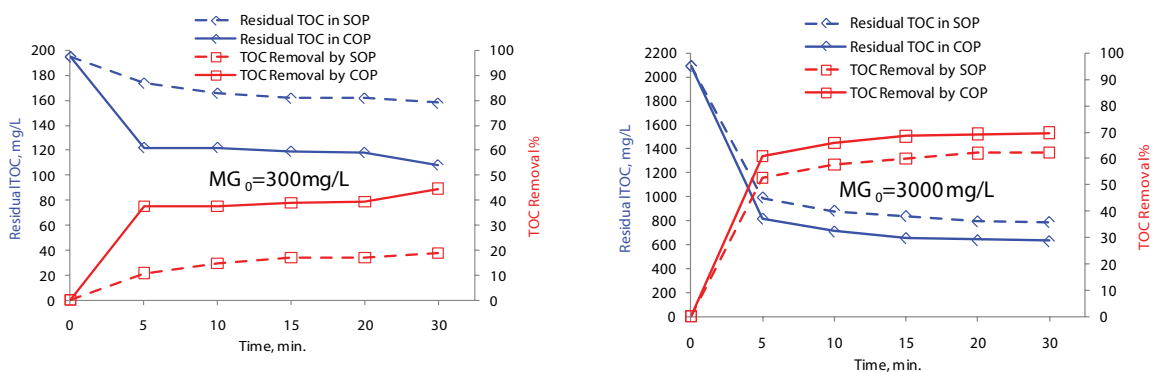


Fig. 7. Removal of TOC resulting from MG by SOP and COP ($MG_0 = 300$ and $3,000 \text{ mg L}^{-1}$; $\text{pH} = 8.5$; ozone dose = 3.4 mg min^{-1} ; nano-alumina dose = 1 g L^{-1}).

The low efficiency of SOP and COP for TOC removal in comparison with COD confirms the low capability of these processes in mineralization of intermediate products at different stages of MG oxidation.

3.6. Decolorization kinetics of MG in SOP and COP

Considering the presence of MG, ozone and hydroxyl radicals reagents in SOP and COP, and nonlinearity of changes in MG concentration over the reaction time as shown in Fig. 5, pseudo-first-order and pseudo-second-order decolorization kinetics were analyzed for MG removal by SOP and COP. According to Fig. 8, inverse MG concentration changes are more correlated with the reaction time in both processes. Therefore, the kinetics of MG decolorization in SOP and COP follow a pseudo-second-order reaction.

According to Fig. 8 and Table 2, by increasing the initial MG concentrations from 50 to $3,000 \text{ mg L}^{-1}$, the rate constant of $1/MG$ vs. reaction time has decreased from 0.0506 to 0.0002 min^{-1} in SOP and from 0.1827 to 0.008 min^{-1} in COP. Thus, with increasing concentrations, the reaction rate of decolorization has also increased. Accordingly, the reaction rate coefficients of COP at the initial MG concentrations of 50 and $3,000 \text{ mg L}^{-1}$ are about 3.6 and 14 times, respectively, more than the reaction rate coefficients of SOP. Similarly, the MG decolorization time in the COP is reduced in comparison with the SOP.

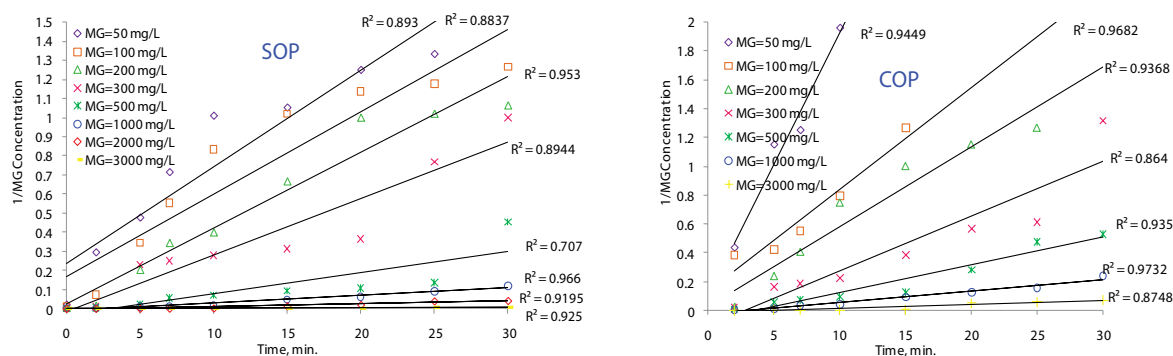


Fig. 8. Inverse of the concentration of MG vs. reaction time in SOP and COP.

Table 2

Kinetic parameters of MG decolorization by SOP and COP

MG ₀ (mg L ⁻¹)	Pseudo-second-order				Pseudo-first-order			
	K _{app} min ⁻¹		R ²		K _{app} min ⁻¹		R ²	
	SOP	COP	SOP	COP	SOP	COP	SOP	COP
50	0.0506	0.1827	0.893	0.9682	-0.099	-0.0615	0.5638	0.2229
100	0.0433	0.071	0.8837	0.9449	-0.1189	-0.0902	0.5798	0.4023
200	0.0397	0.0544	0.953	0.9368	-0.1488	-0.145	0.6579	0.5984
300	0.0296	0.038	0.8944	0.864	-0.1488	-0.1505	0.6365	0.7204
500	0.0111	0.0194	0.707	0.935	-0.1422	-0.1575	0.7969	0.7956
1,000	0.004	0.008	0.966	0.9732	-0.1471	-0.1619	0.8803	0.822
2,000	0.0016	–	0.9195	–	-0.1521	–	0.9519	–
3,000	0.0002	0.0028	0.925	0.8748	-0.0986	-0.1856	0.9736	0.9462

4. Conclusions

- $\gamma\text{Al}_2\text{O}_3$ along with ozonation can enhance the efficiency of MG decolorization by adsorption through the van der Waals force.
- The low efficiency of the SOP and COP in COD removal compared with MG decolorization confirms the low efficiency of these processes in the oxidation of MG and intermediate products.
- The low efficiency of SOP and COP in TOC removal in comparison with COD confirms the low capability of these processes in the mineralization of intermediate products at different stages of MG oxidation.
- The kinetics of MG decolorization in SOP and COP follows pseudo-second-order reactions. Accordingly, the reaction rate coefficients of COP at the initial MG concentrations of 50 and 3,000 mg L⁻¹ are about 3.6 and 14 times, respectively, more than the reaction rate coefficients of SOP.

Acknowledgement

The authors would like to thank the Deputy of Research and Technology of Urmia Medical Sciences University, which funded the study.

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