

## ORIGINAL RESEARCH PAPER

# Optimization of the catalytic ozonation process using copper oxide nanoparticles for the removal of benzene from aqueous solutions

L. Mohammadi<sup>1</sup>, E. Bazrafshan<sup>1,\*</sup>, M. Noroozifar<sup>2</sup>, A.R. Ansari Moghaddama<sup>1</sup>,  
A.R. Khazaei Feizabad<sup>3</sup>, A.H. Mahvi<sup>4</sup>

<sup>1</sup>Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran

<sup>2</sup>Analytical Research Laboratory, Department of Chemistry, University of Sistan and Baluchestan, Zahedan, Iran

<sup>3</sup>English Department, Zahedan University of Medical Sciences, Zahedan, Iran

<sup>4</sup>Department of Environmental Health, Graduate School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

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**ABSTRACT:** The current study aimed to examine the overall feasibility of the use of copper oxide nanoparticles as a catalyst in ozonation process for the removal of benzene from aqueous solutions under experimental conditions. This experimental study was conducted on a laboratory scale reactor in a semi-batch mode. The effect of critical operating parameters such factors as pH, concentration of benzene, reaction time and nano-catalyst dose on the removal of benzene was investigated. The samples included with benzene concentrations (10-200 mg/L), pH (3-13), catalyst dose (0.1-0.5 mg), and ozonation time (5-50 min). Findings indicated that the removal of benzene depended on various utilization parameters. The highest efficiency was achieved at reaction time of 50 min, pH of 12, initial benzene concentration of 10 mg/L and catalyst dose of 0.5 g. Among the studied factors, the maximum and the minimum contributions were made by the dose of nanoparticles (83%) and the reaction time (~73%). The software predicted that use of 0.13 g of the catalyst at pH of 12 and ozonation time of 5 min would lead to a removal efficiency of 68.4%. The catalytic ozonation process was able to remove benzene, and addition of copper oxide nanoparticles as a catalyst together with the ozonation process increased the benzene removal efficiency. The values of  $R^2 = 0.9972$ , adjusted  $R^2 = 0.9946$ , and predicted  $R^2 = 0.9893$  indicated that the model was acceptably predicted by the software and fitted the data obtained in the experiments.

**KEYWORDS:** *Aqueous solution; Benzene; Catalytic ozonation; Copper oxide nanoparticles (CuO-NPs); Nano-catalyst.*

## INTRODUCTION

Water is not a commercial good but it is an important part of natural heritage that must be protected. Wastewater is produced in various industries and processes including pharmaceutical, textile, acrylic fiber, pesticide and other industries which contaminate

water resources by discharging numerous non-degradable compounds into them (Choi *et al.*, 2010; Bazrafshan *et al.*, 2012a; Bazrafshan *et al.*, 2012b; Bazrafshan *et al.*, 2012c; Kakavandi *et al.*, 2014; Zazouli *et al.*, 2014). It is sometimes impossible to decompose these compounds using the natural biological treatment processes (Mahamuni *et al.*, 2006). Benzene is widely used in industries as a solvent for organic compounds, for cleaning equipment and

\*Corresponding Author Email: [ed\\_bazrafshan@yahoo.com](mailto:ed_bazrafshan@yahoo.com)  
Tel.: +98 915 341 1120 Fax: +98 54 3329 5811

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in subsequent processes, and enters groundwater through leakage of fuel products from the storage tanks, pipes, and sites which are unsuitable for waste burial. The Environmental Protection Agency (EPA) of the United States considers benzene a primary pollutant, classifies it as one of the carcinogens of the A group that has definite carcinogenic effects, and sets a maximum permissible level of 5 µg/l for benzene in drinking water because of its adverse impact on human health (Bina *et al.*, 2012). The compounds containing benzene are mainly found in the wastewater produced at chemical industries and in refineries and have a high potential for contaminating surface and groundwater. They are also considered as the compounds that pose high risks to the environment due to their effects on human health (De Mello *et al.*, 2010). Therefore, removal of these compounds from water resources, especially from surface and groundwater resources, is mandatory. A variety of models yet have been used to remove pollutants, especially petroleum compounds, from water resources including. Some of these models are aeration, adsorption processes with the help of activated carbon and natural and artificial adsorbents, oxidation with the help of some oxidants, and biological methods (Khamparia *et al.*, 2017a; Moussavi *et al.*, 2011; Khamparia *et al.*, 2016a; Khamparia *et al.*, 2016b; Khamparia *et al.*, 2016c; Gupta *et al.*, 2015; Jaspal *et al.*, 2012; Malviya *et al.*, 2012; Mittal *et al.*, 2009). Reasons such as high set up and utilization costs, the need for a skilled workforce for setting up and utilization, inability of microorganisms in adapting to remove these compounds, presence of electron acceptors, and production of toxic secondary compounds have constrained the use of these methods (Mahvi *et al.*, 2009; Moussavi *et al.*, 2011). However, utilization of advanced oxidation methods with various options such as ozonation, use of hydrogen peroxide, UV rays, and some semi-conductors, including titanium dioxide, to increase efficiency and facilitate the process of removing these compounds have been recognized as suitable substitutes for the above-mentioned methods (Stepnowski *et al.*, 2002). The most important reason for using the advanced oxidation method is the production of free hydroxyl radicals (OH<sup>•</sup>) that can react with a wide spectrum of organic pollutants and can convert them into harmless products (Sánchez-Polo *et al.*, 2005). So far, ozonation has been used as an effective process for the removal of many

resistant pollutants (Kurniawan *et al.*, 2006). Due to its oxidative power and strong disinfectant properties, it has been widely considered in water and wastewater technology as an oxidant for the removal of natural organic pollutants that are hard to decompose. In many cases, use of ozone alone has a relatively low efficiency in removing resistant and non-degradable organic compounds. Moreover, ozone by itself cannot completely oxidize organic compounds and leads to their mineralization (Kruithof *et al.*, 2007). In this way, use of ozone can increase the production of toxic and hazardous intermediate compounds. Therefore, catalytic ozonation has become popular in recent years. In catalytic ozonation processes (COPs), a solid material is added as a catalyst to the process of ozonation, which increases the rate of oxidation and degradation of pollutants by increasing ozone decomposition and through producing more active free radicals (Rosenfeldt *et al.*, 2006). Ozone is a strong oxidant that can directly enter into reaction with pollutants in water and/or may be converted into free hydroxyl radicals which are stronger oxidants and, in turn, can degrade the pollutants. Catalytic ozonation is one of the advanced oxidation processes (Umar *et al.*, 2013), and can take place in a homogeneous or a heterogeneous process. In the homogeneous process, ion transporters such as iron, manganese, nickel, and silver with two positive charges are used in a uniform solution. The heterogeneous catalytic ozonation process takes place by utilizing metallic oxides such as bivalent and trivalent iron oxides, and oxides of cobalt, lead, silver, and of other metals on beds of titanium dioxide, silicon dioxide, manganese dioxide, and magnesium oxide (Ramachandran *et al.*, 2013). In the catalytic ozonation process, the adsorption process and/or chemical reactions take place on the catalyst surface and induce the production of hydroxyl radicals from ozone molecules. Hydroxyl radicals have stronger oxidizing power compared to ozone molecules and, eventually, lead to the removal of pollutants (Umar *et al.*, 2013). The heterogeneous catalytic ozonation process has been recognized as a suitable method for wastewater treatment because it is a low-cost process, has a potential to recover the catalyst, and does not cause secondary pollution (Zeng *et al.*, 2009). Metals or reinforced metallic oxides (Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, Cu/TiO<sub>2</sub>, etc.) and some porous materials (granular activated carbon, zeolite, etc.) are among the main catalysts proposed

and used in this method (Sui *et al.*, 2012; Khamparia *et al.*, 2017b; Farzadkia *et al.*, 2015). Nano-sized alkaline earth metal oxides, including nano-sized copper oxide, are promising materials to be used as catalysts due to their strong adsorptive properties, high levels of reactivity (Moussavi *et al.*, 2009a), ease of production from minerals that are abundantly found (Moussavi *et al.*, 2009b), large surface areas of nanoparticles, and presence of greater numbers of active sites for suitable chemical reactions (Absalan *et al.*, 2011). Among these metallic oxides, use of copper oxide nanoparticles (CuO-NPs) as catalysts has attracted the attention of many researchers since 1990 due to their large effective area and the greater effect of their quantum-sized particles compared to copper masses. CuO-NPs have been used very effectively to remove many compounds including mercury, arsenic, phenols, and enrofloxacin (Fakhri *et al.*, 2015; Fink *et al.*, 2012; Ji *et al.*, 2011; Martinson and Reddy, 2009). It has been observed that use of CuO-NPs together with ozonation can accelerate the removal of humic acid and reduce COD in aqueous solutions (Turkay *et al.*, 2014). Recently, statistical models of optimizing various processes have been used in many fields. Among the statistical models used in environmental health engineering, response surface methods are employed for evaluating the effects of independent variables on response performance and for predicting the best degree of response. The response surface method (RSM) is a set of statistical methods used to develop, improve, and optimize the processes. Reduction in the number of experiments and investigation of the effects of interactions between variables are among the advantages of RSM (Wu *et al.*, 2012; Khamparia *et al.*, 2017a). This research aimed to study the removal of benzene from aqueous environments through catalytic ozonation by CuO-NPs. This study was carried out in water and wastewater laboratory of Zahedan University of Medical Sciences in Iran in 2015.

## MATERIALS AND METHODS

This analytical study was conducted to determine the performance of catalytic ozonation by using copper oxide nanoparticles to remove benzene from synthetic solutions. The samples were synthetically prepared in the laboratory by using benzene, methanol, and distilled water. The chemicals with high purity, required for the preparation of the aqueous solution, were purchased from Merck Company, Germany.

The contact reactor employed in this study (Fig. 1) was cylindrical with a volume of 1000 milliliter, and was used under closed conditions in the COP process using various doses of CuO-NPs with different times of ozonation at various pH values to treat the water samples contaminated with benzene. The reactor was used at room temperature, and 500 cc of the synthetic sample with various concentrations of benzene was used at each stage. Before performing the experiments, H<sub>2</sub>SO<sub>4</sub> and NaOH 1M were used to modify and adjust the pH values of the samples. Based on the designed model and the results from previous studies, 0.1- 0.5 mg of the nanoparticles was used. The flow rate of ozone gas was set at 0.2 g/h using an ozone generator manufactured by Pasargad Ozone Makers Company (DONALI). The CuO-NPs were purchased from Sigma-Aldrich Company in powder form with the size of less than 50 nm and with an exposed surface (based on BET analysis) of 120 m<sup>2</sup>/g. At the end of reaction in the reactor, the amount of remaining benzene in the samples was measured by injecting 1µl of each extracted sample into an Agilent 7890A model GC (made in Palo Alto, CA, USA) using the FID method with an HP-5 capillary GC column with the length of 30 m and thickness of 0.25 µm. At the time of injection, the incubator was at 40°C and the GC operated at 500 rpm for 10 min at injection temperature of 120°C. The initial temperature of the furnace was kept at 40°C for 2 min and then was gradually raised to 80°C (at the rate of 20°/min) and was kept at this temperature for 1 min. The injector and detector temperatures were set at 250 and 300°C, respectively. The flow rate of nitrogen gas was adjusted at 3 ml/min. The amount of the pollutant removed from the synthetic samples in the catalytic ozonation process was determined using Eq. 1.

$$\text{Removal efficiency (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

Where, C<sub>i</sub> and C<sub>e</sub> are initial and effluent concentration of benzene (mg/L) respectively.

For statistical computations, all the mentioned independent variables were denoted as X<sub>1</sub>, X<sub>2</sub>, X<sub>3</sub>, and X<sub>4</sub>, respectively. Based on the preliminary experiments, the ranges and levels used in the experiments are selected and listed in Table 1. The principal effects and interactions between the selected factors were determined. The experimental design matrix in a central composite design (CCD) is presented in Table 2. Using RSM, the most commonly used second-

order polynomial equation was developed to fit the experimental data and determine the relevant model terms as presented by Eq. 2.

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=j}^{k-1} \sum_{i=j+1}^k \beta_{ij} X_i X_j \quad (2)$$

Where, Y represents the predicted response (benzene degradation by the catalytic ozonation);  $\beta_0$  and  $\beta_i$  are constant coefficient and linear coefficient respectively,  $\beta_{ii}$  and  $\beta_{ij}$  are quadratic coefficients and the interaction coefficients respectively, and  $X_i$  and  $X_j$  are coded values of the independent process factors which refer to the factors i and j, respectively.

## RESULTS AND DISCUSSION

Considering the recorded initial amount of benzene in the samples and calculation of the amount of benzene remaining in the samples, the efficiency of benzene degradation at each stage in single ozonation process (SOP), in adsorption by CuO-NPs, and in catalytic ozonation processes (COP) was calculated. Results are presented in Table 2. The analysis of variance of regression parameters of the RSM quadratic model for benzene degradation by catalytic ozonation processes (COP) is presented in Table 3. As shown in Table 3, the regression was strongly significant at an F-value of 42.92 for benzene reduction ( $P < 0.001$ ). The statistical significance of the second-order equation revealed that the regression

Table 1: Experimental range and level of the independent variables

Independent variables	Coded symbol	Coded levels and actual factor levels		
		-1	0	+1
pH	$X_1$	3	7.5	12
CuO-NPs dose (mg/L)	$X_2$	0.1	0.3	0.5
Time of ozonation (min)	$X_3$	5	27.5	50
Concentration of benzene (mg/L)	$X_4$	10	105	200

Table 2: Design of the experiment and its results

Run order	$X_4$	$X_3$	$X_2$	$X_1$	COP efficiency (%)		Ads. efficiency (%)		SOP efficiency (%)	
1	3	0.5	5	10	68.02	67.25	20.57	20.58	22.57	22.4
2	3	0.1	50	200	54.66	53.65	13.96	13.95	22.74	22.9
3	7.5	0.16	27.5	105	62.35	62.35	15.05	15.27	26.07	26.19
4	12	0.5	50	200	65.24	64.40	19.45	19.46	25.56	25.73
5	12	0.5	5	200	57.61	56.70	14.53	14.46	19.79	19.605
6	7.5	0.3	27.5	105	65.33	65.10	17.31	17.27	26.31	26.20
7	12	0.5	5	10	70.99	70.25	20.59	20.59	25.39	25.22
8	7.5	0.3	27.5	171.5	59.56	59.72	15.51	15.95	23.57	23.77
9	3	0.5	50	200	62.27	61.40	19.43	19.45	22.74	22.90
10	7.5	0.3	43.25	105	68.56	67.35	19.19	18.77	28.07	26.16
11	7.5	0.3	27.5	105	65.33	65.09	17.31	17.20	26.31	26.18
12	3	0.1	5	200	47.03	45.95	9.04	8.95	16.97	16.78
13	12	0.1	5	10	63.37	62.50	15.12	15.09	25.40	25.22
14	3	0.1	50	10	68.03	67.20	20.02	20.08	28.34	28.52
15	7.5	0.3	27.5	105	65.33	65.10	17.31	17.27	26.31	26.18
16	3	0.1	5	10	60.41	59.50	15.10	15.08	22.57	22.40
17	12	0.1	50	200	57.62	56.65	13.97	13.96	25.56	25.73
18	7.5	0.3	27.5	105	65.33	65.08	17.31	17.26	26.31	26.19
19	7.5	0.44	27.5	105	67.68	66.10	18.88	18.77	26.07	26.18
20	10.65	0.3	27.5	105	67.38	66.40	17.18	17.28	27.48	27.59
21	7.5	0.3	27.5	105	65.33	65.11	17.31	17.28	26.31	26.18
22	7.5	0.3	27.5	105	65.33	65.09	17.31	17.27	26.31	26.20
23	7.5	0.3	27.5	38.5	68.92	67.17	19.75	19.41	27.49	27.50
24	12	0.1	5	200	50.00	48.95	9.06	8.96	19.79	19.60
25	3	0.5	50	10	75.65	74.95	25.49	25.58	28.34	28.52
26	3	0.5	5	200	54.64	53.7	14.51	14.45	16.97	16.78
27	7.5	0.3	11.75	105	63.22	62.85	15.75	16.27	24.03	26.16
28	12	0.5	50	10	78.61	77.95	25.50	25.59	31.17	31.35
29	4.35	0.3	27.5	105	65.31	64.70	17.17	17.17	25.50	25.61
30	12	0.1	50	10	71.00	70.20	20.03	20.09	31.17	31.35

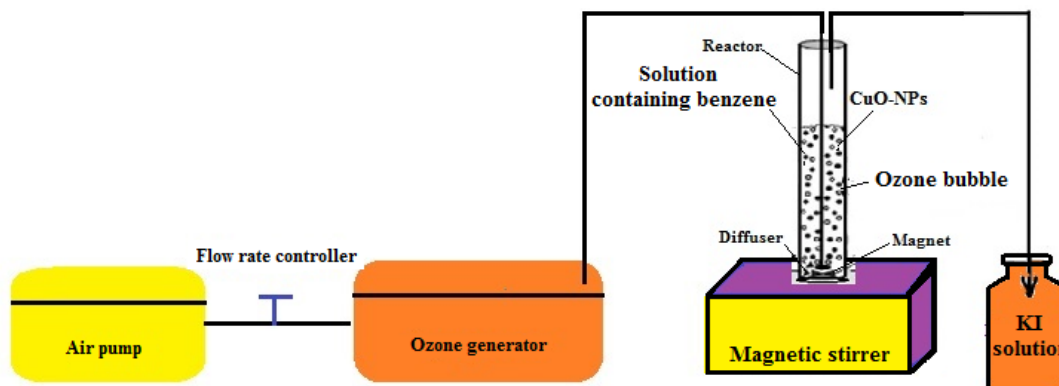


Fig. 1: Schematic design of the catalytic ozonation reactor

Table 3: Analysis of variance (ANOVA) results and adequacy of the quadratic models for benzene removal by catalytic ozonation process (COP/CuO-NPs)

Source	SS <sup>a</sup>	DF <sup>b</sup>	MS <sup>c</sup>	RMS <sup>d</sup>	Prob > F, (p value)	
Model	1241.16	4	310.29	42.92	< 0.0001	Highly significant
pH	11.54	1	11.54	1.60	< 0.0001	Highly significant
Dose (mg/L)	227.99	1	227.99	31.54	< 0.0001	Highly significant
Time, min	256.27	1	256.27	35.45	< 0.0001	Highly significant
Conc. (mg/L)	745.36	1	745.36	103.10	< 0.0001	Highly significant
Residual	180.74	25	7.23	-	-	-
Lack of fit	155.49	20	7.77	1.54	0.3348	Not significant
Pure error	25.25	5	5.05	-	-	-
Cor Total	1421.90	29	-	-	-	-

Adeq Precision= 88.891, R<sup>2</sup> Adjusted= 0.9946, R<sup>2</sup> Predicted= 0.9893<sup>a</sup> Sum of squares. <sup>b</sup> Degree of freedom. <sup>c</sup> Mean square. <sup>d</sup> Ratio of mean square (F-value).

Cor Total: Total of all information corrected for the mean.

was statistically significant ( $P < 0.001$ ); however, the lack of fit was not statistically significant ( $P = 0.3348$ ,  $> 0.05$ ), which supports the fitness of the ANOVA model. According to the results, the response equation proved to be suitable for the CCD of experiments. Fitness of the model was controlled by  $R^2$ . Based on the findings of ANOVA, the model reports a high  $R^2$  value of 99.72% for the pollutant degradation process. Also, an acceptable alignment with the adjusted determination coefficient is necessary. An adjusted  $R^2$  value of 99.46% was observed in this study. The value of  $R^2$  is close to 1.0 which is a high value indicating a high correlation between the predicted values and the observed values. This shows that the model of regression provides an excellent description of the relationship between the response variables and the independent variables (Khajeh, 2011). According to the regression model, the order of priority among the main effect of impact factors can be given as initial concentration of benzene > ozonation time > CuO-NPs > pH.

Recently, application of catalytic ozonation in degradation of organic pollutants that cannot be biologically degraded has attracted a considerable attention (Moussavi *et al.*, 2009b). Results concerning the effects of pH (3, 5, 7, 9, and 13) on the single ozonation, the sole use of nanoparticles, and the catalytic ozonation processes are presented in Fig. 2. As shown in Fig. 2, by increasing pH, 30 min after the start of the process, the efficiency raised from 31 to 42.3% in the conventional ozonation process, from 10.2 to 10.23% in the sole use of nanoparticles (adsorption process) and from 59 to 71% in the catalytic ozonation process. Therefore, increase of pH has the maximum effect on the catalytic ozonation process as compared to both single ozonation process and sole use of nanoparticles. Moreover, these results show that the catalytic ozonation process outperforms the single ozonation process at all pH values (Fig. 2). Results indicated that the efficiency of benzene removal improved with the increase of pH. This can be attributed to the structure of benzene and

the structure of copper oxide nanoparticles used in the catalytic ozonation process. At high pH values, the functional groups on the surface of nanoparticles were decomposed and their nucleophilicity was enhanced and, under these conditions, the functional groups decomposed on the surface of catalyst increased the rate of ozone reaction (Bazrafshan *et al.*, 2016; Moussavi *et al.*, 2009b; Moussavi *et al.*, 2009c). In the catalytic ozonation process under acidic conditions, direct and indirect oxidations are involved in benzene removal. At pH values of less than 3, hydroxyl radicals are not produced and do not influence the decomposition of ozone and pollutants. Some researchers attribute the increase of efficiency in the catalytic ozonation process under acidic conditions to the production of radicals other than hydroxyls (Moussavi *et al.*, 2009a). Moussavi *et al.* (2009b) studied the use of magnesium oxide nanoparticles in the catalytic ozonation process to remove the reactive red 198 azo dye. They reported that the efficiency of the dye removal in the catalytic ozonation process improved with the increase of pH values. They attributed this to increase of ozone decomposition rate at high pH values and its conversion to active radicals, and added that degradation of the dye molecules took place through indirect oxidation by active radicals. Valdez *et al.* (2008) studied the application of volcanic rocks in the catalytic ozonation process for the removal of benzothiazole. They found that removal efficiency improved when pH was raised from 2 to 7. They also mentioned the high affinity of ozone for reaction with

Lewis acids and metal oxides present in volcanic rocks as the reason for this improvement. Moreover, Erol and Özbelge (2008) studied the effect of using nonpolar bonded alumina in the catalytic ozonation process for the removal of phenol from aqueous environments and reported that the removal efficiency of phenol was higher at alkaline pH values (pH=13) than at acidic pH values (pH=2.5). They attributed this to the formation of hydroxyl radicals at high pH values.

To show the interactive effects of pH and other variables (the quantity of copper oxide nanoparticles, the contact time, and the initial concentration of benzene entering the process), 2-dimensional diagrams were used. The results from these diagrams are presented in Fig. 3. Benzene removal improved with the increase of the quantity of CuO-NPs and increase of the pH level, because production of hydroxyl radicals increases under alkaline conditions. In this process, under alkaline conditions, the conditions for benzene removal improved when higher quantities of CuO-NPs were used. At pH=12, the use of CuO-NPs in an amount of >0.3 g led to removal efficiencies of higher than 68%. Moreover, as clearly shown in Fig. 3B, simultaneous increase of ozonation time and pH also increased the efficiency of benzene removal. At pH>12 and ozonation time of <30 min, increase of either of the two variables increased the removal efficiency, so that the efficiency of benzene removal reached to nearly 70% under alkaline conditions and ozonation time of 27.5 min. Moreover, as indicated in Fig. 3C,

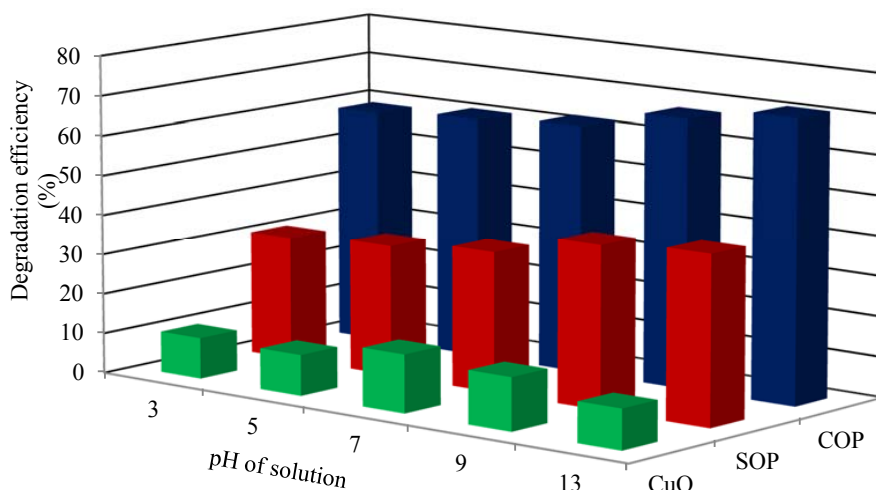


Fig. 2: The effect of pH on benzene removal efficiency

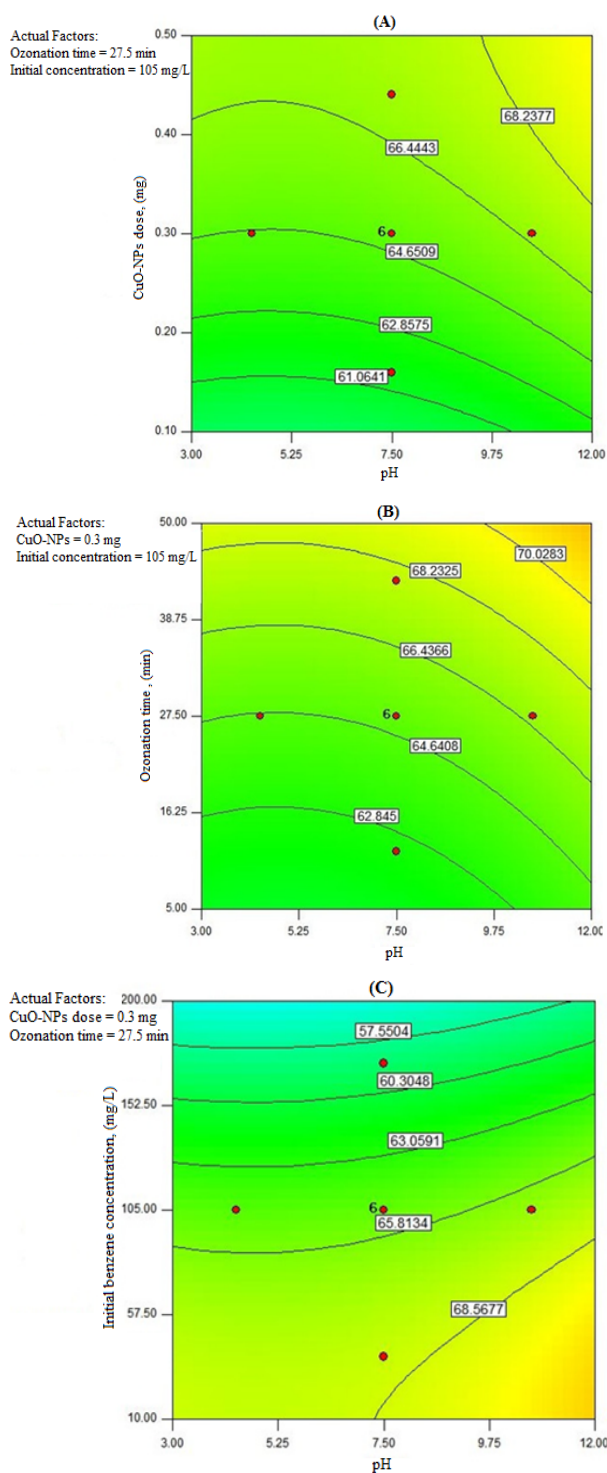


Fig. 3: (A) Interaction effects of pH and CuO-NPs dose, (B) pH and ozonation time, and (C) pH and initial concentration of benzene on benzene removal by COP/CuO-NPs

the highest removal efficiency was achieved at pH=12 and initial benzene concentration of <50 mg/L. In fact, reaction between organic compounds and ozone in the wastewater took place directly at acidic pH values or indirectly under alkaline conditions through special radicals, particularly hydroxyl radicals (Moussavi and Alizadeh, 2010). Consequently, according to Figs. 3A, 3B and 3C, the optimum pH for benzene removal by catalytic ozonation process was 12.

Fig. 4 shows the effects of contact time (5, 10, 20, 30, and 50 min) on the efficiency of benzene removal. Increase of ozonation time from 5 to 50 min raised the benzene removal efficiency by about 24% in the single ozonation process, by 20% (from 9 to 20%) in using sole nanoparticles, and by 31% in the catalytic ozonation process. Therefore, increase of ozonation time (contact time) was more effective in catalytic ozonation rather than in two other processes (Fig. 4).

As shown in Fig. 4, destruction of ozone increased simultaneously with the increase of the catalytic ozonation efficiency (from 58% to 68%) when ozonation time increased from 5 to 50 min. Moreover, as Fig. 4 indicates, benzene degradation increased with the increase of ozonation time and decrease of initial benzene concentration entering the process. In addition, according to the results, catalytic ozonation in contact time of 50 min proved to be better than single ozonation. Since in the catalytic ozonation, processes of adsorption and oxidation are either directly or indirectly involved in the removal of benzene, the catalytic ozonation process in a shorter time than ozonation will lead to greater efficiency (Valdes et al., 2008).

Fig. 5 shows the effects of catalyst dose on the efficiency of benzene removal. In catalytic ozonation process, at the contact time of 35 min, increase of the catalyst dose from 0.1 to 0.5 g raised benzene removal efficiency from 50% to 81%. Since raising the quantity of copper oxide nanoparticles to 0.3 g led to a steeper increase in the benzene removal efficiency, and this increase of efficiency was less when larger quantities of the nanoparticles were used, 0.3 g was considered as the optimum dose of catalyst to make the process cost effective.

Fig. 6 shows that increase of the dose of CuO-NPs as a catalyst from 0.1 to 0.5 g in the process of using sole nanoparticles raises benzene removal efficiency by 22%. Figure 7A indicated that benzene removal efficiency increased with the simultaneous increase

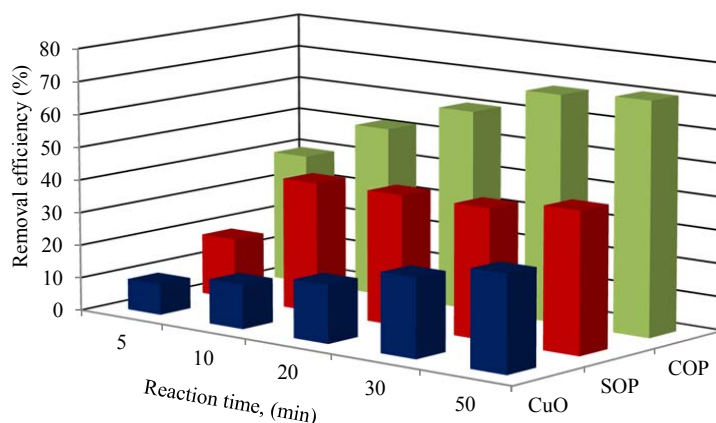


Fig. 4: The effect of contact time on benzene removal efficiency

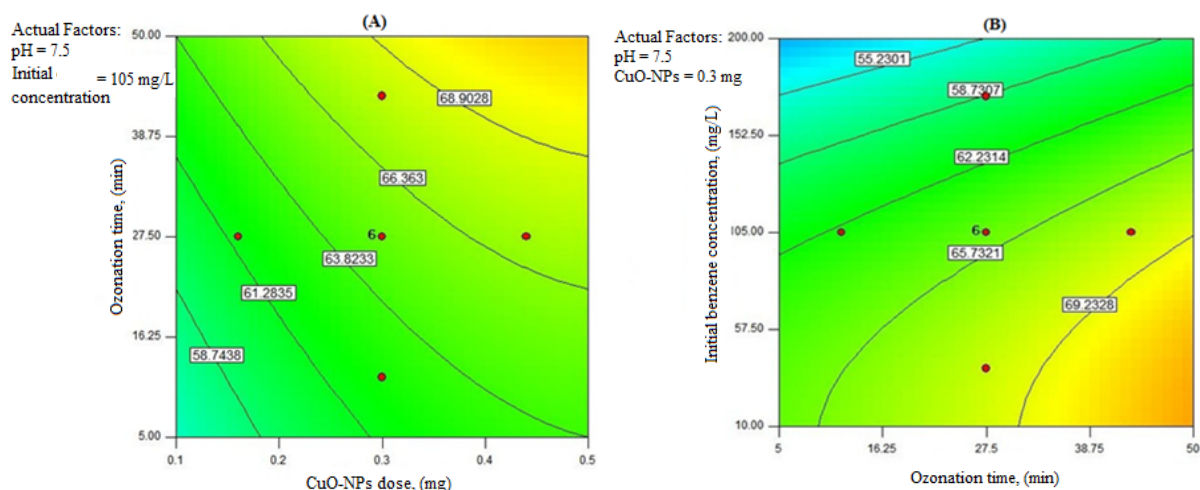


Fig. 5: (A) Interaction effects of ozonation time/contact time and CuO-NPs dose; and (B) effects of ozonation time/contact time and initial concentration of benzene

of the the quantity of CuO-NPs and ozonation time. For example, at the initial concentration of 105 mg/L, pH=7.5, and ozonation time of above 27 min, benzene removal efficiency increased to higher than 69 % when more than 0.4 g of CuO-NPs was used. At the contact time of less than 20 min, the effect of nanoparticles was less than that of ozonation time, so that benzene removal efficiency was 58% when less than 0.4 g of the nanoparticles was used at ozonation time of 11 min. Moreover, as shown in Fig. 6, benzene degradation increased when the amount of nanoparticles was raised from 0.1 to 0.5 g. Increase of benzene removal in catalytic ozonation

with the increase of the quantity of nanoparticles can be due to larger number of active sites on the surface of the catalyst where the reaction with ozone can take place. At constant flow rates, increase of catalyst concentration leads to the improvement of transition of ozone from gaseous to the liquid phase and increase of the rate of ozone degradation (Khan *et al.*, 2008). Study of the effects of catalyst dose on benzene removal using the conventional and catalytic ozonation processes showed that efficiency of benzene removal increased with the increase in the quantity of the catalyst. This increase in benzene degradation in the catalytic ozonation process



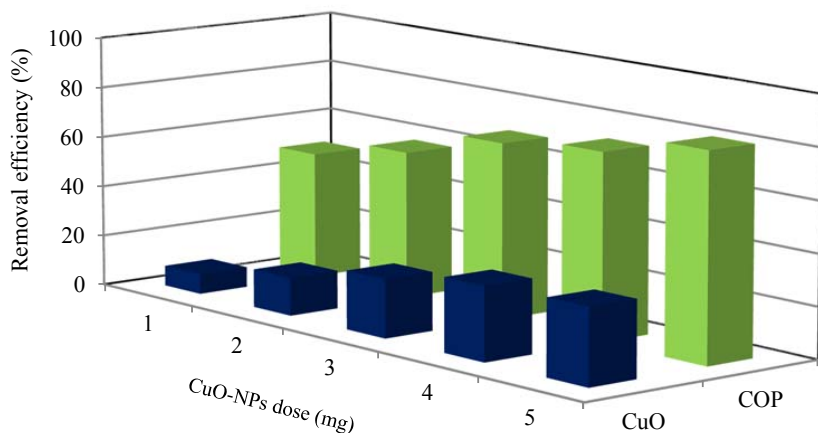


Fig. 6: The effect of catalyst dose on efficiency of benzene removal

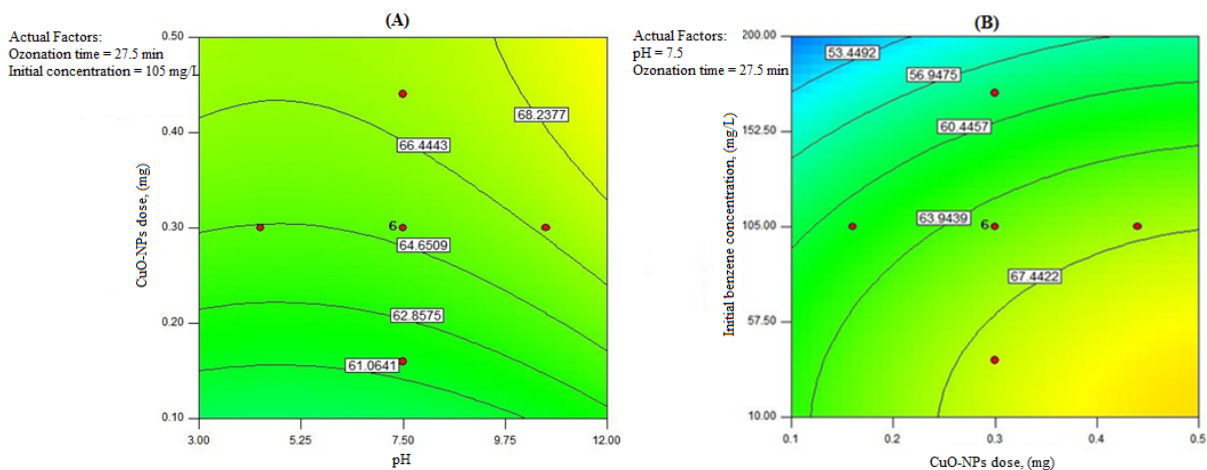


Fig. 7: (A) Interaction effects of CuO-NPs dose and pH; and (B) effects of CuO-NPs dose and initial concentration of benzene

resulted from the increased ozone decomposition on the surface of nanoparticles that led to higher concentrations of radicals on the surface of and inside the liquid (Mortazavi *et al.*, 2010). Application of the catalyst in larger quantities increased its surface area and the number of active sites leading to increased ozone absorption on the surface. This improved absorption increased surface reactions and production of radicals in the catalytic ozonation process. In a study conducted by Valdez *et al.* (2009), the effect of using volcanic rocks and natural zeolite on the rate of ozone decomposition was investigated. They found that the rate of ozone decomposition on volcanic rocks was higher as compared to natural zeolite. Moreover, considering the determination of reaction

constancy, it was noticed that reactions took place more heterogeneously and with greater intensity on the surface of the catalyst as compared to the aqueous solution (Valdés *et al.*, 2009). Furthermore, Moussavi *et al.* (2009b; 2009c) compared the efficiencies of catalytic ozonation process and activated carbon with those of catalytic ozonation together with biological process in removing phenol from salty wastewater. Results showed that the efficiency of phenol removal in 5 min increased from 50% to 97% in the presence of 2.5 to 20 g of the activated carbon catalyst, where the optimum dose of the catalyst was 20 g/L.

Fig. 8 shows the effect of initial benzene concentrations on its removal. As shown in Fig. 8, at the reaction time of 35 min, when benzene initial

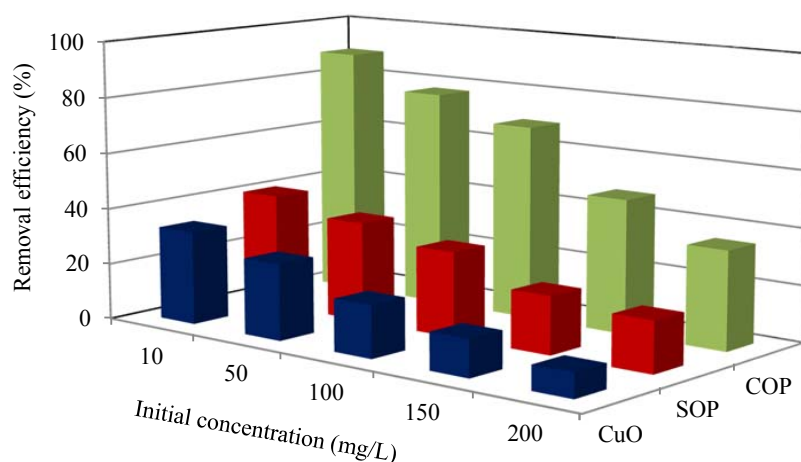


Fig. 8: The effect of initial benzene concentration on the removal efficiency

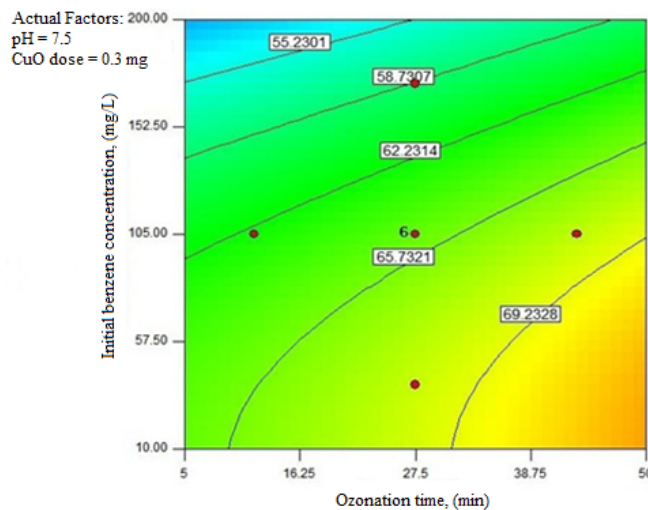


Fig. 9: Interaction effects of initial benzene concentration and contact time on benzene removal by COP/CuO-NPs

concentration was raised from 10 to 200 mg/L, its removal efficiency declined from about 40 to 18% in single ozonation, from 33 to 8% in adsorption only CuO-NPs, and from 89 to 35% in catalytic ozonation processes. Therefore, the optimum initial benzene concentration was less than 10 mg/L (Fig. 8). In addition, as presented in Fig. 9, degradation of benzene increased with the increase of ozonation time and decrease of initial concentration of benzene.

The obtained results indicated that removal efficiency declined with the increase of the initial concentration of benzene. With the increase of

benzene concentration, the molecules in the reaction environment increased. Furthermore, since the quantity of the hydroxyl radicals produced by the decomposition of ozone on the surface of the catalyst was constant, degradation of benzene molecules took place slowly at high concentrations of benzene. This problem could be resolved by increasing ozonation either through increasing the discharge in ozonation or by increasing ozonation time (Bazrafshan et al., 2016; Moussavi et al., 2009a). Results of this study showed that CuO-NPs performed well in the catalytic ozonation process for the removal of benzene.

Moreover, results indicated that benzene removal efficiency improved with the increase of the pH value of the solution, and benzene degradation took place through indirect oxidation and production of hydroxyl radicals in the reaction environment. Furthermore, benzene removal efficiency was directly proportional to the increase of contact time and dose of the catalyst and inversely proportional to the increase of the initial concentration of benzene. Therefore, considering the high efficiency of benzene removal and the ease of performing the catalytic ozonation process using copper oxide nanoparticles, this process can be used in water and wastewater treatment.

### CONCLUSION

In the current study, in summary, the application of heterogenic catalytic ozonation by CuO-NPs for the removal of benzene from synthetic solutions was studied. The degradation of benzene increased as pH of the solution, CuO-NPs dose and time of ozonation increased. The highest benzene degradation efficiency was achieved at reaction time of 50 min, pH of 12, initial benzene concentration of 10 mg/L and CuO-NPs dose of 0.5 g. Among the studied factors, the maximum contribution was made by the quantity of CuO-NPs (83%) and the minimum by the reaction time (~73%). The software predicted that the use of 0.13 g of CuO-NPs as catalyst at pH of 12 and reaction time of 5 min would lead to removal efficiency of equal to 68.4%. Finally, it was concluded that the catalytic ozonation process using CuO-NPs as catalyst was able to remove benzene from aqueous solutions, and addition of copper oxide as a catalyst together with the ozonation process, increased the efficiency of benzene removal.

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### CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

### ABBREVIATIONS

<i>ANOVA</i>	Analysis of variance
<i>Bet</i>	Brunauer–Emmett–Teller
<i>CCD</i>	Central composite design
$C_e$	Effluent concentration of benzene
$C_i$	Initial concentration of benzene
<i>CCD</i>	Central composite design
<i>Conc.</i>	Concentration
<i>COP</i>	Catalytic ozonation process
<i>Cor Total</i>	Total of all information corrected for the mean
<i>CuO-NPs</i>	Copper oxide nanoparticles
<i>DF</i>	Degree of freedom
<i>EPA</i>	Environmental Protection Agency
<i>FID</i>	Flame ionization detector
<i>g</i>	Gram
<i>GC</i>	Gas chromatography
<i>g/L</i>	Gram per liter
<i>M</i>	Molar concentration
$m^2/g$	Square meter per gram
<i>mg/L</i>	Milligram per liter
<i>min</i>	Minute
<i>MS</i>	Mean square
<i>nm</i>	Nanometer
<i>Prob &gt; F</i>	P-value
$R^2$	R-squared
<i>RMS</i>	Ratio of mean square (F-value).
<i>RSM</i>	Response surface methodology
<i>SOP</i>	Single ozonation process
<i>SS</i>	Sum of squares
$X_1$	Coded value for pH
$X_2$	Coded value for CuO-NPs dose (mg/L)
$X_3$	Coded value for time of ozonation (min)
$X_4$	Coded value for concentration of benzene (mg/L)
$X_i$	Coded values of the independent process factors which refer to “i” factor

$X_j$	Coded values of the independent process factors which refer to "j" factor.
$Y$	Predicted response
$\beta_0$	Constant coefficient
$\beta_i$	Linear coefficient
$\beta_{ii}$	Quadratic coefficient
$\beta_{ij}$	Interaction coefficient
$\mu m$	Micrometer

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#### AUTHOR (S) BIOSKETCHES

**Mohammadi, L.**, Ph.D. Candidate, Instructor, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran. Email: [lailimohamadi@gmail.com](mailto:lailimohamadi@gmail.com)

**Bazrafshan, E.**, Ph.D., Professor, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran. Email: [ed\\_bazrafshan@yahoo.com](mailto:ed_bazrafshan@yahoo.com)

**Noroozifar, M.**, Ph.D., Professor, Analytical Research Laboratory, Department of Chemistry, University of Sistan and Baluchestan, Zahedan, Iran. Email: [mnoroozifar@chem.usb.ac.ir](mailto:mnoroozifar@chem.usb.ac.ir)

**Ansari-Moghaddama, A.R.**, Ph.D., Professor, Health Promotion Research Center, Zahedan University of Medical Sciences, Zahedan, Iran. Email: [ansarialireza@yahoo.com](mailto:ansarialireza@yahoo.com)

**Khazaei Feizabad, A.R.**, Ph.D., Assistant Professor, English Department, Zahedan University of Medical Sciences, Zahedan, Iran. Email: [arkhazaei@yahoo.com](mailto:arkhazaei@yahoo.com)

**Mahvi, A.H.**, Ph.D., Assistant Professor, Department of Environmental Health, Graduate School of Public Health, Tehran University of Medical Sciences, Tehran, Iran. Email: [ahmahvi@yahoo.com](mailto:ahmahvi@yahoo.com)

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