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Removal, optimization and kinetic modeling of high concentration of methyl tertiary butyl ether from aqueous solutions using copper oxide nanoparticles and hydrogen peroxide

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ABSTRACT

This study aimed to evaluate the efficiency of a simple and cheap catalytic oxidation process for removal of MTBE in high concentration by H_2O_2/CuO process. The effects of H_2O_2, CuO and initial MTBE concentration, pH and reaction time on the catalytic oxidation were investigated. The study was performed using Design-Expert. According to statistical analyses, 2FI model has been introduced as the best model that was statistically valid. Based on the experimental design model, the most effective factors were initial MTBE concentration and CuO, respectively. The highest removal efficiency (79%) was obtained at the following condition: CuO concentrations; 19 mg_{CuO}/L_{water}, pH 7.25, reaction time 16.30 min, H_2O_2 12.5 mL/L and initial MTBE concentration 225 mg/L. The higher the MTBE and CuO concentration, the less the removal efficiency. Optimization conditions were initial MTBE concentration 225 mg/L, reaction time 16.5 min, H_2O_2 13.4 mL/L, pH 7.5, CuO 19 mg/L. Removal efficiency in the laboratory condition was obtained to be 72%. The best kinetic model for removal of MTBE was pseudo-second order (R^2 = 0.99, RMSE = 0.21). Therefore, the adsorption of MTBE on CuO catalyst was the predominant process. This is the first time that the CuO/H_2O_2 has been used as a cost–benefit, simple and effective method as well as kinetic model for removal of high concentration of MTBE during a short period of time.

Keywords: MTBE; CuO/H_2O_2; Oxidation; Kinetic model; RSM

1. Introduction

Water pollution due to oil compounds is a major problem in most societies. One of these compounds is MTBE ($C_5H_{12}O$), which is added to the gasoline for boosting of octane number [1,2]. It is a flammable and toxic matter with a high solubility in water (42 g/L). Moreover, it remains in the groundwater for a long time. MTBE enters the water resources in different ways such as accidents, spills, defective gas stations, and pipelines [3,4]. MTBE causes health, environmental and esthetic effects including taste and odor [5]. Thus, its threshold for taste and odor in drinking water is limited to 40 and 15 μg/L, respectively [6]. Likewise, California Department of Public Health (CDPH) has determined 13 and 5 g/L as the primary and secondary maximum contaminant level for MTBE, respectively [7]. Moreover, MTBE is classified as a suspected human carcinogen, a potential carcinogen [8,9].

Therefore, the removal of MTBE is essential. The conventional methods are not suitable for removal of MTBE

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[1,2,10–12] because of ether linkage and tertiary carbon in the MTBE molecular structure [13] as well as low vaporizability (Henry constant = 5.5×10^{-4} atm m^3 mol^{-1} at 25°C) [3]. For these reasons, the advanced oxidation processes (AOPs) can be a better choice for treatment of MTBE. In previous studies, advanced methods such as the adsorption using activated carbon, O_3/H_2O_2, Fenton's reaction, UV/O_2^-, $KMnO_4$, persulfate, gamma radiolysis and electrochemical oxidation of hydrogen peroxide have been used to eliminate MTBE from water. Although AOPs are fast running and cost-effective, some of them such as Fenton have been used only for low concentration of MTBE [14,15]. Besides, not only its adsorption on activated carbon is unsuitable [16] but also it is an expensive method [4,5]. Therefore, it seems that other AOPs with high potential for generation of hydroxyl radical can be more effective. These processes have some advantages and disadvantages. For example, in spite of the high production rate of hydroxyl radicals and decomposition of organic matter in AOPs [1,12], they act as a non-selective factor in reaction. For this reason, its efficiency is decreased. Therefore, the selection of these processes for removal of MTBE from the solution can be associated to some parameters such as cost-effectiveness, availability of raw material and simplicity of operation. Furthermore, co-process such as catalytic process is suggested [3,13,17]. A catalyst can reduce the activation energy and time required for optimum removal [18,19]. Catalysts have been applied in homogeneous and heterogonous phase compared with solution. There are many limitations in the homogeneous phase compared with non-homogeneous ones [14]. Thus, the use of heterogenic catalyst is cost-effective. In the meantime, nanoscale structures, especially metal oxide nanoparticles, are widely applied due to their powerful physiochemical properties. In some studies, catalysts such as iridium have been explored to increase the oxidation reaction rate [1]. However, the cost of the process and its availability are the main factors in water treatment, especially in developing countries such as Iran. Unlike most catalysts, CuO has less synthesis cost and higher absorption capacity at ambient temperatures for volatile organic compounds (VOCs) [20]. Moreover, the CuO catalysts are the most efficient in the MTBE compared with the other single steps of heterogeneous systems [15].

The main purpose of this research was to remove the MTBE from the solution using H_2O_2 and CuO in pilot scale as well as the kinetic model. Moreover, the combination of both processes is the simplicity and cost-effectiveness that can effectively remove the high concentration of MTBE. Moreover, H_2O_2 not only can generate OH radicals but also is available in Iran abundantly. On the other hand, according to literature investigations, this is the lower attention to the combination of H_2O_2/CuO for treatment of MTBE without use of any augmentation factor such as UV and sono radiation. Besides, the mathematical behavior of MTBE has not been determined in this process yet.

2. Materials and methods

2.1. Chemicals

All chemicals such as MTBE ($(CH_3)_3COCH_3$), copper oxide (CuO), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2) and sodium hydroxide (NaOH) were used from Sigma-Aldrich, USA. Moreover, the deionized water (resistivity 18 MU cm, Hack) was used as the solvent for any material. In the beginning of the experiment, pH was adjusted by H_2SO_4, 0.1 Mole/L and NaOH, 0.1 Mole/L. Synthesized CuO nano-catalyst was purchased from Sigma-Aldrich.

2.2. Batch experiments and experimental design

This study was a batch scale that was conducted in August 2017 to April 2017. During this period of time, the reactor was prepared and oxidation process was conducted and injected to gas chromatography. The reactor was cubic Plexiglas rectangular with 1 L effective volume. The reagents used were of analytical grade as expressed above. Then, they were stirred in deionized water by a stirrer. Therefore, the solution was mixed completely. The scheme of this reactor is shown in Fig. 1.

The experiments were done using Design-Expert 7.0 as Central Composite Design. Table 1 shows the variables and levels. Finally, 50 experiments were designed in DE (supplementary file 1). The catalytic oxidation process was performed at the lab temperature (25°C).

2.3. Analytical methods

All the experiments were done according to DE design. The residual MTBE was analyzed using GC-FID (Varian-CP 3800, CP-SiL5CB Made in the USA). For each experiment, the removal efficiency was calculated based on the difference between the initial and residual MTBE concentrations. MTBE was extracted with dispersible liquid–liquid micro extraction method (DLLME) [21]. DLLME is a simple, fast, valid and suitable method for extraction of organic compounds from water. In this method, first 1 mL acetonitrile was mixed with 0.2 mL hexane in a tube. Second, 10 mL of the raw sample was taken from the reactor and added to a tube. Third, the mixture of both solvents was injected to the raw sample at once. In fact, hexane and acetonitrile were used as extraction and dispersion solvents, respectively. In other words, the former solvent extracted the MTBE from raw sample and the latter dispersed the MTBE in a little solvent. Then, the solution was shaken and allowed to form a cloudy solution in a tube. After that, the sample was

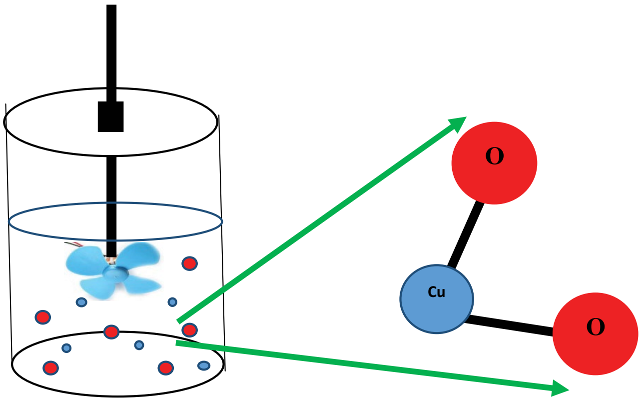

Fig. 1. Scheme of oxidation process.

Table 1
Natural and coded levels of independent variables based on the central composite design

Independent variable	Symbol	Coded level				
		–2	–1	0	1	2
		Natural level				
MTBE (mg/L)	*A*	50	225	400	575	750
H_2O_2 (mL/L)	*B*	0	12.5	25	37.5	50
CuO (mg/L)	*C*	0	19	38	56	75
pH	*D*	2	3.75	5.5	7.25	9
Time (min)	*E*	2	16.5	31	45.5	60

centrifuged at 5,000 rpm for 2 min. Finally, the supernatant was injected into GC-FID. In GC-FID, the temperature was programmed at 30°C for 5 min; then, it reached 170°C with a rate of 7°C/min. The total running time was 26 min. The detector and injector temperatures were adjusted at 250°C and 180°C, respectively. Helium was used as carrier gas with the flow rate of 3 mL/min.

Data analysis was performed using RSREG test-design software (version 7.0.0). Regression coefficients of the empirical data were generalized as a quadratic polynomial model. This model is as follows:

$$\gamma = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum \sum_{i<j=1}^{3} \beta_{ij} X_i X_j \quad (1)$$

where Y = the rate of MTBE removal; β_0 = tracking regression intercept; β_i = tracking regression linear; β_{ii} = tracking regression quadratic; β_{ij} = tracking regression interactive; X_i and X_j = dependent variables.

Furthermore, analysis of variance (ANOVA) was used to estimate the removal efficiency in different pH levels, initial MTBE concentrations, H_2O_2, and nano catalyst dosages. The significance level was 0.05 ($p < 0.05$) and the k_{value} was less than 1 ($k < 1$) for the dependent factor.

3. Results and discussion

3.1. Fitting equation and analysis of variance

The effect of initial MTBE concentrations, reaction time, pH, CuO nano-catalyst and H_2O_2 dosage on the efficiency of the oxidation process and optimization of these variables was investigated by RSM. According to central composite rotatable design (CCRD), the number of runs was 50 with 8 central points designed. The average, the lowest and highest MTBE oxidation efficiencies were 66.9%, 56% and 79%, respectively. These results are more similar to catalytic process such as Fe_3O_4 in which MTBE removal efficiency was 48% [22].

In order to measure the desirability of the tested model, the parameters F-value, R^2, *p*-value, and lack of fit were used. Table 2 summarizes the results of the statistical analysis for selecting a model at 95% confidence level.

According to the statistical analysis of the models (Table 2), the two factor interaction model (2FI) was suggested as the best model for MTBE removal (*p*-value = 0.0002, *p*-value for lack of fit = 0.1575, R^2 = 0.9727 and predicted R^2 = 0.9331). Because the obtained *p*-value (0.0002) indicated that there was 0.02% chance that two large F-values could take place due to the noise in the experiment.

Moreover, in Table 3, the results of ANOVA for important operational factors in the residual amount of MTBE performed using DE (Demo v. 7, Stat-Ease, Inc.) are shown.

ANOVA was used to determine the adequacy of the model and significant factors. Moreover, the amount of residual MTBE was predicted using the suggested regression model. In this model, the high *F*-value (80.64) and low *p*-value ($p < 0.05$) indicated that they were statistically significant. The *F*- and *p*-value indicated that the possibility of noise and pure error was 0.01% and 15.75%, respectively. As the R^2 of 2FI model can express about 97.27% of the total of response variations, it was the most appropriate model for the design of surface response [23]. Furthermore, the *F*-value of 2FI vs. linear was 5.11 for the residual MTBE that expressed the significance of the model at the 5% level. The *p*-value and *F*-value of the studied parameters show that the MTBE concentration and CuO dosage are the most efficient parameters in the catalytic oxidation process of MTBE (Table 3). Moreover, Adeq precision = 36.433 indicates an adequate signal because it measures the signal noise ratio and the ratio more than 4 is desirable. Therefore, this model can be used to navigate the design space. The proposed model based on the significant parameters is presented in Eq. (2) for predicting the catalytic oxidation values of MTBE.

$$\text{MTBE} = 132.44 + 58.66A - 5.11B - 8.27C + 14.73D - 1.1E \quad (2)$$

where A—MTBE; B—pH; C—time; D—CuO; E—H_2O_2.

Based on Eq. (2), by raising the concentration of MTBE and CuO and decreasing pH, time and H_2O_2, the residual MTBE in oxidation process is increased. Furthermore, based on the coefficients of the parameters, the effect of the initial MTBE concentration was more than the others.

Table 2
Statistical analysis of the models for modeling of MTBE removal

Source	SD	R^2	Adjusted R^2	Predicted R^2	PRESS	–
Linear	15.84	0.9315	0.9237	0.9081	14,810.36	–
2FI	11.38	0.9727	0.9606	0.9331	10,787.06	Suggested
Quadratic	11.37	0.9767	0.9607	0.9215	12,654.96	–
Cubic	8.33	0.9940	0.9789	0.9052	15,281.62	Aliased

Table 3
ANOVA of the reduced response surface 2FI model to predict removal of MTBE

Source	Source of squares	*Df*	Mean square	*F*-value	*p*-value prob > *F*	–
Model	1.568E + 005	15	10,450.65	80.64	<0.0001	Significant
A-MTBE	1.376E + 005	1	1.376E + 005	1,061.91	<0.0001	***
B-pH	1,043.56	1	1,043.56	8.05	0.0076	–
C-Time	2,738.86	1	2,738.86	21.13	<0.0001	–
D-CuO	8,675.09	1	8,675.09	66.94	<0.0001	*
E-H_2O_2	48.82	1	48.82	0.38	0.5435	–
AB	929.56	1	929.56	7.17	0.0113	–
AC	3.12	1	3.12	0.024	0.8776	–
AD	626.31	1	626.31	4.83	0.0348	–
AE	1,373.54	1	1,373.54	10.60	0.0026	–
BC	100.29	1	100.29	0.77	0.3852	–
BD	3.35	1	3.35	0.026	0.8733	–
BE	1,687.95	1	1,687.95	13.02	0.0010	–
CD	1,049.16	1	1,049.16	8.10	0.0075	–
CE	84.66	1	84.66	0.65	0.4246	–
DE	770.97	1	770.97	5.95	0.0201	–
Lack of fit	3,921.3	27	145.23	2.10	0.1575	Not significant
Pure error	485.12	7	69.30	–	–	–
Cor total	1.612E + 005	49	–	–	–	–
SD	11.38	–	–	–	–	–
Mean	132.44	–	–	–	–	–
CV%	8.6	–	–	–	–	–
Residual	4,406.42	34	129.60	–	–	–

* It was not very significant (p = 0/05).
***The most important factor on residual MTBE.

The proportion of the predicted values and the actual values obtained from the experiments for residual MTBE is shown in Fig. 2.

The actual values are data for the square root of the runs and the predicted values are produced by the model. In Fig. 2, the coefficient for the actual and predicted values of MTBE removal was acceptable. The proportion of predicted to actual values indicated that there was more correlation and fewer differences between them. Furthermore, the difference between the adjusted determination coefficient (Adj R^2) and the predicted determination coefficient (Pred R^2) have not to be more than 0.2 [24]; based on Table 3, the difference was 0.0275 and the model was adequate.

3.2. Effects of variables and their interactions

In this study, the effects and interactions of the variables in a specific point was calculated by the perturbation plot. The major perturbation was simulated by Eq. (1), and the effects of the important parameters on the amounts of residual MTBE are shown in Fig. 3.

According to Fig. 3, the most effective factors on residual MTBE were the MTBE concentration and CuO dosage, respectively. Therefore, increasing the initial concentration of MTBE and CuO dosage increased the residual MTBE. In fact, the generated reactive radicals degrade MTBE in the oxidation process, but in higher concentrations of MTBE, these radicals are consumed completely. Besides, MTBE can be absorbed on the surface of CuO due to the presence of the ether functional group that provides weak polarity (relative polarity = 0.124) [41]. Furthermore, oxygen is transferred between the catalyst surface and the MTBE during a redox mechanism [42]. Thus, CuO promotes the catalytic activity for MTBE oxidation as well as increasing the affinity between MTBE and catalyst when MTBE is adsorbed. However, the removal efficiency of MTBE decreases when the concentration of MTBE exceeds from the capacity of the catalyst's active holes. In brief, the most important factor is the initial concentration of MTBE, as shown in Fig. 3.

3.3. Simultaneous effect of various parameters on the initial MTBE concentration

Fully coupled CCD and RSM techniques have been simultaneously employed to investigate its desirability performance during oxidation process and thus to optimize them.

3.3.1. Simultaneous effect of pH and initial MTBE concentration

3D response surface plot of the simultaneous effect of different pH levels and initial MTBE concentrations is shown in Fig. 4.

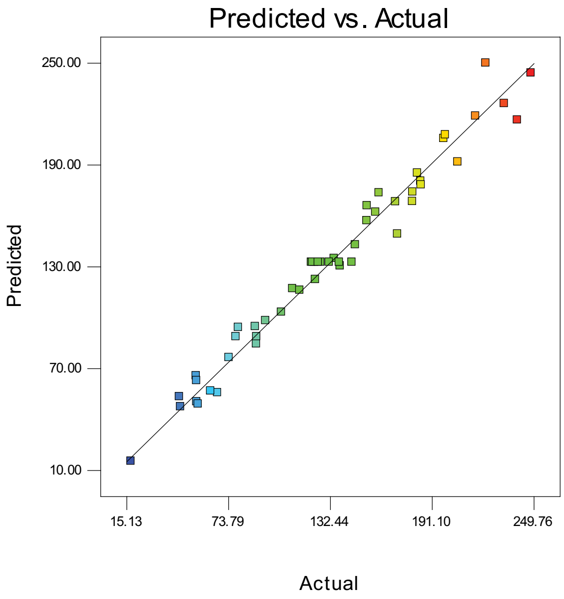

Fig. 2. Predicted vs. actual experimental results for MTBE catalytic oxidation efficiency.

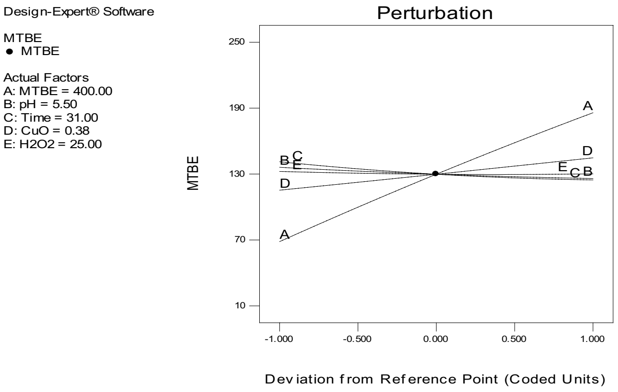

Fig. 3. Effects of the main parameters including the concentration of MTBE (a), pH (b), time (c), CuO (d) and H_2O_2 (e).

Increasing the initial MTBE concentration and pH enhanced the removal efficiency of MTBE. However, when the initial MTBE exceeded 400 mg/L, the effect of pH was negligible. The trend of pH and initial MTBE concentration was consistent with Dong et al. [22] and Hu et al.'s [17] studies. In the catalytic processes, the pH variations affect removal efficiency [25], which depends on the types of contaminants and catalysts [26]. In spite of the higher removal efficiency and stability in the operation, the structure and function of the catalysts were observed at neutral pH [17,22], Under acidic condition, not only the hydrolysis of MTBE was catalyzed by acid [27] but also the electron flow was facilitated from the valence band to the conduction band. As a result of this reaction, O_2 molecules of the solution adsorb the excited electron and reduce it to $O_2^{\bullet}$. This compound acts as a reactive production that can degrade the MTBE [40]. Otherwise, at alkaline pH, the catalyst surface is negatively charged due to the presence of OH^-. In this condition, the electron–hole with positive charge moved from the depth to the surface of the catalyst. This reaction is observed at the lower concentrations of MTBE, but at higher concentrations, more intermediates were formed that compete with the MTBE in the oxidation process [17]. Consequently, the effect of pH on the residual MTBE is associated to the initial concentration of MTBE. With regard to the importance of the initial MTBE concentration, the study and optimization based on this factor is more suitable.

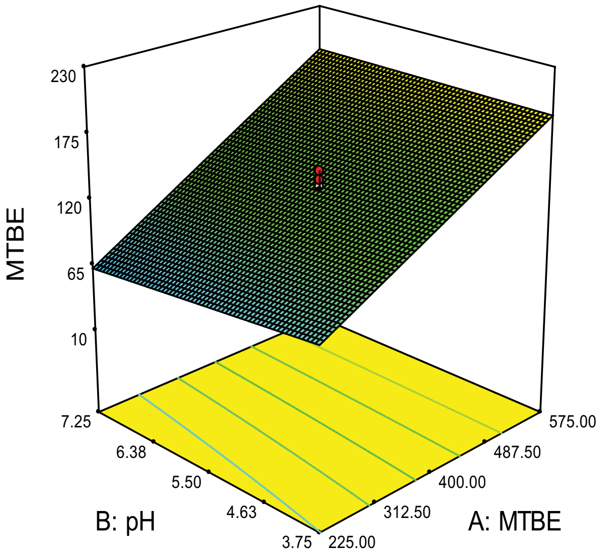

Fig. 4. Surface plot for interactive effect of pH and initial MTBE (mg/L).

3.3.2. Simultaneous effect of CuO concentrations and initial MTBE

CuO nanoparticle is a catalyst that binds to organic molecules due to adsorption capacity and a relative polarity. There are both characteristics of MTBE, but the simulation effect of the initial MTBE and CuO has not been investigated yet. The simultaneous effect of various concentrations of CuO and initial MTBE on oxidation efficiency is shown in Fig. 5.

By increasing the initial MTBE concentration, the oxidation efficiency decreases due to decreasing at $OH^{\bullet}$ concentration for all CuO concentrations (Fig. 5). Moreover, the performance and adsorption on CuO depend on the morphology, condition of the experiment and use of H_2O_2 [28] that is a factor effective on production rate of $OH^{\bullet}$ and $O_2^{\bullet}$. Therefore, the increased concentration of CuO adversely affects the removal of MTBE [29]. A few researchers have reported that increasing the TiO_2 dosage leads to decreased removal rate of MTBE [17]. On the other hand, CuO is less expensive than other catalysts used for degradation of MTBE. Moreover, it had an important role in the transport of ions that created active sites in heterogeneous oxidation processes [10,30,31]. As such, the lower dosages of CuO nano-catalyst are more appropriate and cost-effective, and with regard to the results of this study, the use of lower concentration of CuO is suggested.

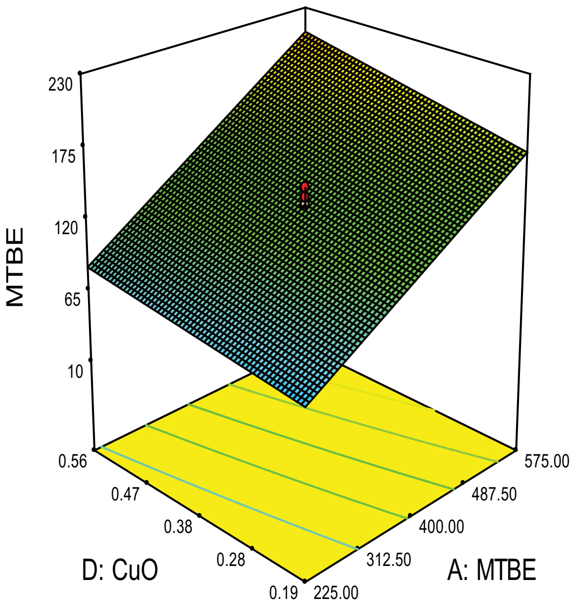

Fig. 5. Surface plot for interactive effect of CuO and initial MTBE concentration (mg/L).

3.3.3. *Simultaneous effect of reaction time and initial MTBE concentration*

The removal efficiency of MTBE has oscillatory response during the variation in the reaction time. In Fig. 6, the simulation effect of reaction time and initial MTBE concentration is shown.

As shown in Fig. 6, the oxidation efficiency of MTBE in the presence of CuO and H_2O_2 increased by increase in the oxidation time from 16 to 45.5 min, but its effect was negligible when the reaction time exceeded 45.5 min. The main mechanisms for increased removal efficiency were oxidation, absorption and volatilization of MTBE. If there is enough time, these mechanisms enhance the effectiveness [17]. However, by continuous increase in the initial MTBE concentration, the residual MTBE concentration was increased and the reactive hole of CuO was saturated. Then, outbreak of the nanocatalyst occurred. With regard to these results, the optimum point for reaction time was 45.5 min, but it seems that the cost–benefit analysis for selection of reaction time is essential.

3.3.4. *Simultaneous effects of H_2O_2 concentrations and initial MTBE*

H_2O_2 is an effective variable on the AOP process. H_2O_2 has some advantages such as being commercially accessible, thermally stable and infinitely soluble. Simultaneous effects of different levels of H_2O_2 and initial MTBE concentrations on residual MTBE are displayed in Fig. 6.

However, as the initial MTBE concentration rises, the oxidation efficiency decreases; the effect of H_2O_2 was related to the variation of initial MTBE concentration. This relationship was reverse at MTBE concentration under 400 mg/L. Otherwise, when H_2O_2 dosage was increased, the removal efficiency of MTBE was increased as well at MTBE above 400 mg/L. Although H_2O_2 is identified as a weak acid, it is a strong oxidizing agent, so that it produces $OH^{\cdot}$ that can break down MTBE (Eq. (3)). But the removal efficiency may vary depending on the reaction, reagents, energy sources and some other parameters [29,32]. For example, the reaction rate proceeds slowly due to high concentrations of MTBE. On the other hand, not only the degradation of MTBE decreased due to the balance between H^+ and OH^- ions [25] but also MTBE was unstable at alkaline pH, so it was decomposed rapidly by bicarbonate buffer system [17]. Likewise, when H_2O_2 concentration exceeds a certain limit, the self-quenching reaction of OH that acts as a radical scavenger occurs. As a consequence, the radical scavenger competes with $OH^\bullet$ in the oxidation process and reduces the oxidation rate (Eq. (3)) [17]. In fact, the certain limit is related to the type of contaminant, as it was 12.5 mL in this study.

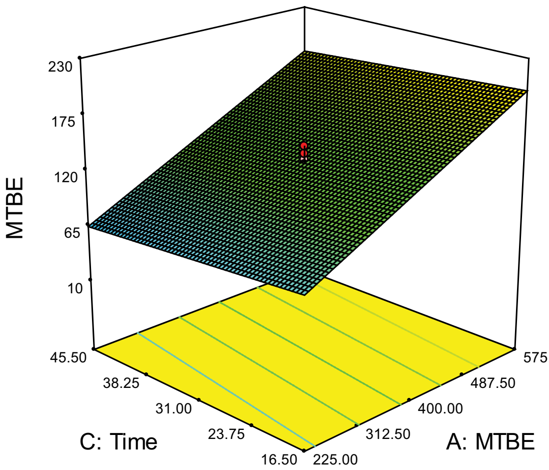

Fig. 6. Surface plot for interactive effect of reaction time and initial MTBE concentration (mg/L).

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O \tag{3}$$

Some other limitations for application of H_2O_2 are experimental conditions, H_2O_2-MTBE weight to weight ratio, and H_2O_2 added frequency [25]; the continuous addition was more effective in eliminating MTBE [32].

In brief, although the H_2O_2 generates hydroxyl radical that oxidizes the MTBE, high concentration of H_2O_2 and initial concentration of MTBE can be investigated as a limiting factor because the higher concentration of MTBE consumes the $OH^\bullet$ completely. Likewise, the high dosage of H_2O_2 acts as a radical scavenger. Both factors reduce the removal efficiency of MTBE, using H_2O_2 and CuO nanocatalyst.

3.3.5. *Simultaneous effects of H_2O_2 concentrations and CuO dosage*

Both H_2O_2 and CuO are effective factors on oxidation of organic matter, but little attention has been paid to their simulation effect. Therefore, the main goal of this study was to investigate the simulation oxidation of MTBE, using H_2O_2 and CuO. Fig. 8 shows the simulation effect of CuO and H_2O_2.

As the dosage of the CuO and H_2O_2 increased, the residual MTBE was decreased (Fig. 8). Similar results were obtained in other studies, so that combination of H_2O_2 and UV or H_2O_2 and SO_3 improved the oxidation reaction [18,25]. Because there are more reactive sites involved for the adsorption of MTBE in this condition [29]. Besides, the oxidation of MTBE can be associated to production of hydroxyl radical, using H_2O_2 [32,13]. Moreover, $OH^{\bullet}$ increases the polarity of hydrocarbons. On the other hand, H_2O_2 not only generates the active radical ($OH^{\bullet}$) for degradation of MTBE but also improves its adsorption on the surface of CuO. For these reasons, the simulation effect of CuO and H_2O_2 improved the efficiency removal of MTBE.

3.4. Process optimization and model validation

The optimization of experimental results was calculated for the determination of energy and material costs. The first step in the optimization process is the screening of most of the parameters by estimating their optimal levels [33]. In the current study, optimization of variables was performed to maximize the removal of MTBE from aqueous solutions, using the 2FI model. Optimal predicted conditions by the RSM were shown in Fig. 9 and the MTBE removal rate was predicted to be 76.4%.

As shown in Fig. 9, the optimum removal rate took place in the following condition:

MTBE initial concentration 225 mg/L, time 16.5 min, H_2O_2 13.4 mL/L, pH 7.5, CuO 19 mg/L.

To validate the model, experiments were carried out in optimal predicted conditions and removal efficiency in the experimental conditions was 72%. Also, desirability of the model was 0.932 that indicates the suitability and high accuracy of the model.

The kinetics of MTBE decomposition under optimal conditions was calculated by the first-order model, which is shown in Eq. (4).

$$C = C_0 e^{-Kt} \qquad (4)$$

where C = MTBE concentration (µg/L); C_0 = initial MTBE concentration (µg/L); K = first order constant (1/min); t = reaction time (min).

According to Eq. (4), K = 0.077 min^{-1} was obtained that is higher than the photocatalytic process [34] and sonolytic decomposition [35]). Although in this study only catalytic oxidation was used, the degradation rate was reasonable. These results indicate that the CuO/H_2O_2 process is suitable for the removal of high concentrations of MTBE.

3.5. Kinetic modeling

The kinetics of the decomposition of MTBE was done by CuO/H_2O_2 in a batch system. In Fig. 10, the kinetics of MTBE decomposition is represented by zero order, first order, pseudo-first order, second and pseudo-second order models at ambient temperature.

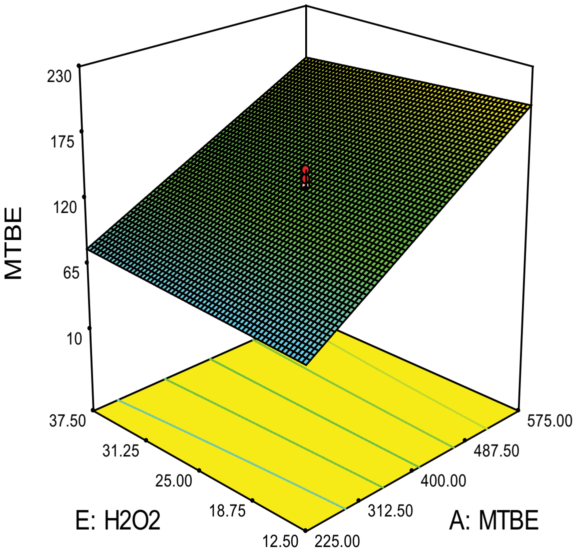

Fig. 7. Surface plot for interactive effect of H_2O_2 dosage and initial MTBE concentration (mg/L).

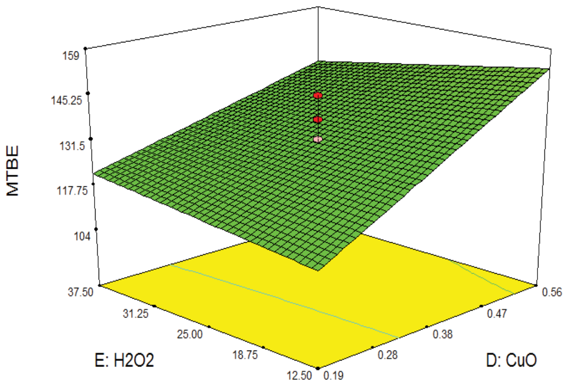

Fig. 8. Surface plot for interactive effect of H_2O_2 and CuO dosage (mg/L).

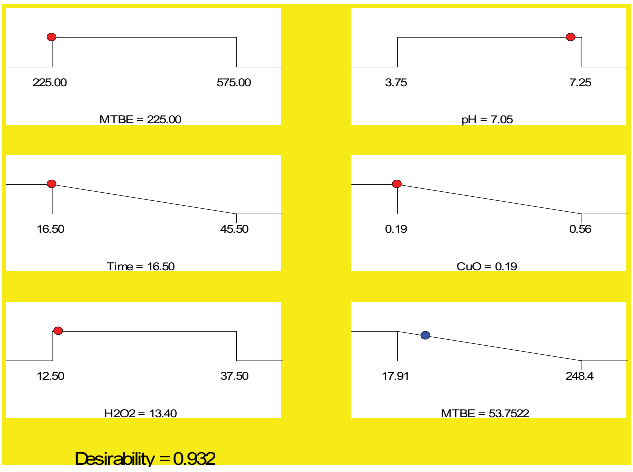

Fig. 9. Desirability ramp for optimization of initial MTBE concentration (mg/L), CuO dosage (mg/L), H_2O_2 dosage (mL/L), time (min) and pH.

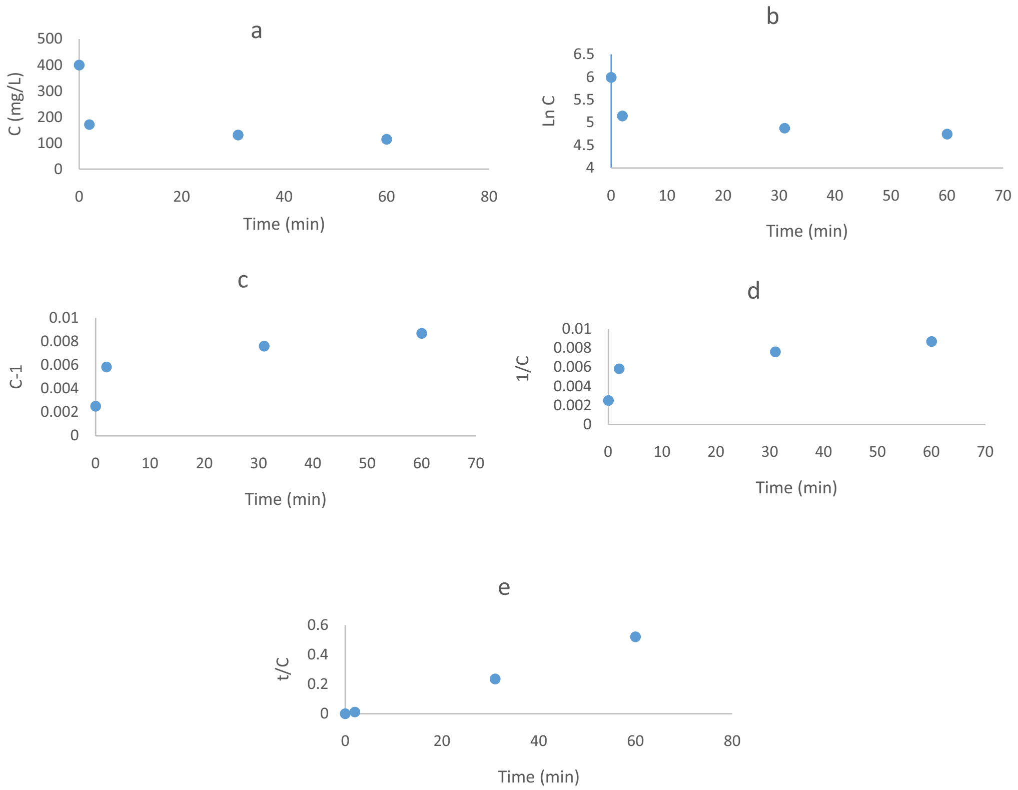

Fig. 10. Mathematical model of MTBE decomposition kinetics. (a) Zero order, (b) first order, (c) pseudo-first order, (d) second order, (e) pseudo-second order.

As shown in Fig. 10, increased retention time leads to a rise in the MTBE decomposition rate. In this study, several kinetics models were used to determine the governing equations of MTBE decomposition. In Table 4, the constant rates of kinetics (K_0, K_1, K_1', K_2 and K_2'), Half-Life ($T_{1/2}$) and correlation coefficient (R^2) were estimated for each model.

According to Table 4 in the zero-order model, the kinetic coefficient and required time were more than the others to decompose half of the MTBE. Also, the little kinetic coefficients in the first-order equation, pseudo-first, second and pseudo-second show the dependency of the model on the characteristics of the experimental operations and the lower impact of the initial pollutant concentration. According to the results shown in Table 4, the R^2 and RMSE in the pseudo-second order equation were more and less than the others, respectively (R^2 = 0.99, RMSE = 0.21). Therefore, the pseudo-second order model is suggested as the best model for MTBE decomposition in high concentrations using CuO/H_2O_2 because in this process (CuO/H_2O_2) both oxidation and adsorption of MTBE occurred. In study of Zhang et al. [28], the MTBE removal using ZSM-5 zeolite was pseudo-second order. As the pseudo-second order model is considered as the best model, it can be concluded that the predominant process for removal of MTBE using CuO/H_2O_2 is its adsorption on the surface and inter-holes of CuO. In contrast, attention to decomposition kinetics of MTBE and determination of the trend of its rate is reasonable. In Table 5, the parameters of decomposition kinetics were compared with those

Table 4
Kinetic modeling of MTBE decomposition by CuO/H_2O_2

	Kinetic
Zero-order	$C_t = 279.03–3.2t$
K_0	3.2
$T_{1/2}$	62.5
R^2	0.47
First-order	LnC = 5.54–0.0151t
K_1	0.0151
$T_{1/2}$	45.9
R^2	0.59
Pseudo-first order	$C_t = 0.0039\ (1–e^{0.0151t})$
K_1'	0.0151
$T_{1/2}$	45.9
R^2	0.59
Second-order	$1/C = 0.0025 + 8E\text{-}5t$
K_2	8E-5
$T_{1/2}$	31.25
R^2	0.73
Pseudo-second-order	$C_t = \frac{1,376t}{1+3.44t}$
K_2'	0.0086
$T_{1/2}$	0.29
R^2	0.99

Table 5
Parameters of MTBE decomposition by various removal processes

Process	Model	Initial MTBE (mg/L)	K	$T_{1/2}$ (min)	E%	R^2	References
Adsorption (ASM-5 zeolite)	Pseudo-second order	300	0.03	34.84			[28]
Ultrasonic + O_3	Pseudo-first order	4.4	0.18	3.7	7.3		[35]
Ultrasonic + O_3	first order	88.15	0.024	10			[35]
TiO_2-ZnO-CoO/UV	Pseudo-first order	30.58	0.0497	13.9		0.99	[36]
H_2O_2/nZVI/ultrasonic	Pseudo-first order	50	0.1	3	89.5	0.93	[37]
Natural removal in groundwater	First order	1	0.01	7.3*	99		[38]
CuO/H_2O_2	Pseudo-second order	400	0.0086	0.29	71.21	0.99	This study

*Month.

of the other studies for removing MTBE from the aqueous solutions.

According to Table 5, the decomposition constant, overall decomposition rate and MTBE removal efficiency using pseudo-second model were more than those in other studies. However, the half-life of this model is lesser. Hence, the decomposition rate of MTBE using CuO/H_2O_2 is higher and the process is more cost-effective.

3.6. Cost–benefit of this method compared with others

In this study, the cost–benefit of CuO/H_2O_2 process for removal of 1 g MTBE was estimated. The cost–benefit was calculated based on the cost of the catalysts used in optimization condition compared with other studies. The detail of this analysis is shown in Table 6.

As shown in Table 6, the cost of CuO/H_2O_2 process for removal of 1 g MTBE from solution was lower than others. Likewise, the reaction time for removal of 74% MTBE using this process was a little. Therefore, the cost–benefit of this process was more than other catalytical processes.

3.7. Fate of CuO

Finally, the CuO catalysts were reused from solution by filtering and reduced. Although the efficiency of CuO was decreased, it could be used for removal of organic matters. In brief, it is another effectiveness for removal of MTBE using this reaction.

Also, this study was conducted at higher concentrations than the other studies, and similar results have been rarely observed [39]. All in all, the catalytic oxidation by CuO/H_2O_2 is more suitable and cost-effective than adsorption and photocatalytic processes for removal of MTBE from aqueous solutions.

4. Conclusion

This study aimed to evaluate the MTBE removal efficiency under catalytic oxidation process, using the H_2O_2/CuO. According to statistical analyses performed by DE software, the 2FI model was introduced as the best model in the MTBE removal (p-value = 0.0002, p-value for lack of fit = 0.1575 and F = 80.64). High F-value and low p-value ($p < 0.05$) indicate that it is statistically significant. Moreover, whereas F-value = 5.11 and the lack of fit were not significant (2.1), the 2FI model was suitable and significant for RSM design at 5% level. The value of R^2 (0.9727) indicates that the model can express 97.27% of the variations in the response. The proportion of the predicted values vs. the actual values indicated that there were higher correlation and lower difference between them. Furthermore, the difference between Adj R^2 and Pred R^2 was 0.0275, indicating that the model was acceptable. The most effective factor in the amount of residual MTBE was the initial concentration of MTBE and then the CuO dosage; there was an inverse linear relationship between them. Other factors such as pH, time and H_2O_2 had little effect. Optimization step was done using DE software by which MTBE = 225 mg/L, time = 16.5 min, H_2O_2 = 13.4 mL/L, pH = 7.5, CuO = 19 mg. Predicted removal efficiency by software was 76.4%, but in the laboratory it

Table 6
Cost benefit of CuO/H_2O_2 process for removal of 1 g MTBE

Method	Initial concentration of MTBE (mg/L)	Reaction time	Removal efficiency (%)	Cost of catalyst (USD) for removal of 1 g MTBE*	References
Fe_2O_3/ ZnO/H_2O_2	89.14	–	70	3.7	[26]
Ag_2O/fly ash	1	120 min	71	14,000	[43]
Fenton/H_2O_2	88	–		17.5	[44]
Fe/H_2O_2	2	–	78	8.5	[45]
Permanganate	122	500 h		7.7	[46]
CuO/H_2O_2	225	16.5 min	74	3.4	This study

*The cost of raw material calculated based on its cost in Iran.

was 72%. Therefore, this model is approved for removal of MTBE. The decomposition kinetic constant (K) was 0.077 min^{-1} at the optimization condition. Although the overall removal efficiency was 59%–79%, it was lower than many other methods. The best kinetic model for decomposition of MTBE using CuO/H_2O_2 was pseudo-second order ($R^2 = .99$, RMSE = 0.21). As a consequence, the adsorption of MTBE using CuO nano-catalyst was the predominant reaction. This method can be used as one of the most suitable methods for removal of high concentration of MTBE in aqueous solution because it is a cost-effective method for removal of high concentration of MTBE. Moreover, MTBE was removed effectively during a short period of time. Other superiority of this study in comparison with other studies is the use of combination process including H_2O_2/CuO for the first time without any wave's amplifier such as UV, sono-wave or the other catalysts. Therefore, this process can be used as an appropriate method for contaminated water in full-scale.

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