

Removal of Iron from Groundwater by Ozonation: The Response Surface Methodology for Parameter Optimization

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ABSTRACT

This research studied the possibility of using ozone to remove iron from groundwater. The optimum conditions were investigated using a Box-Behnken experiment design with statistical analysis by response surface technique. The three parameters investigated, pH (6.0-8.0), hardness (300-500 mg/L as CaCO₃) and removal time (10 to 60 min) were independent parameters of iron removal. Data was examined for optimal conditions and included main effects and their interactions. Analysis of variance indicated that the proposed quadratic model successfully interpreted the experimental data with a coefficient of determination (R²) of 98.83% and adjusted R² of 96.72%. Through this model, it could predict the iron removal efficiency under variable conditions. Furthermore, the optimum conditions were pH 6.99, hardness of 300 mg/L as CaCO₃, and 10 min of reaction time. The predicted iron removal efficiency obtained from the model under the optimum conditions was 99.00%. The experiment confirmed that the optimum condition which validated the model's accuracy of iron removal efficiency was 98.45%. The results showed that ozone can remove iron from groundwater.

1. INTRODUCTION

Iron, the fifth most abundant element of the Earth's crust, easily contaminates groundwater (Das et al., 2007). Iron is an essential mineral for humans; however, its presence in groundwater above a certain level makes water unusable, mainly for aesthetic considerations such as giving reddish color, metallic taste, odor, and turbidity. Iron oxides which are formed in reservoirs upon aerial oxidation of dissolved iron can promote the growth of micro-organisms in water. Therefore, the World Health Organization (WHO) has set a guideline value of 0.3 ppm of iron in drinking water (WHO, 1984; Chaturvedi and Dave, 2012).

There are many conventional methods for the detection and removal of iron from water such as adsorption, complexation, ion exchange, water softening, and electrocoagulation (Das and Nandi, 2019; Thaweechai and Kaewvilai, 2019). These methods are expensive for domestic applications (Choothong et al., 2013; Das and Nandi, 2019). Another effective water treatment is the oxidation

method, which involves the transfer of electrons from iron(II) to iron(III). The most common chemical oxidants in water treatment are chlorine and potassium permanganate. Chlorination is widely used for oxidation of divalent iron. However, the formation of trihalomethane (THMs) in highly colored water can create a problem (Ellis et al., 2000). In contrast, potassium permanganate is normally more expensive than chlorine and must be carefully controlled. Furthermore, the former can form precipitates that cause mudball formations on filters that are difficult to remove and compromise filter performance. Alternatively, a low-cost method of providing oxidation by adding oxygen and reducing the use of chemicals and operating attention is often used. However, this method is not effective for iron in water with complex humic materials or other large organic molecules due to its inability to break strong complexes formed between iron and large organic molecules (Chaturvedi and Dave, 2012).

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Ozone may provide a suitable catalyst for iron oxidation and leaves no environmentally harmful residues. The parameters that affect iron removal by ozone are time, pH, and hardness. Iron(II) can be easily oxidized by ozone, which is shown in Equation 1 (Araby et al., 2009).



In many studies, the optimization parameters are still based on trial and error, such as changing one factor at a time. This is an experimental technique based on varying a single factor while fixing the remaining parameters at a certain set of conditions. However, the single-dimensional factor of the experiment is a time-consuming technique and the attained optimum conditions are not accurate due to the neglect of the interaction between the operating variables (Tayeb et al., 2018). To solve this problem, the response surface methodology (RSM) has been suggested to define the effects of individual parameters.

RSM is an assortment of statistical and mathematical tools that have proven valuable for multifactor optimization of various processes. (Aljundi, 2011) Box Behnken design (BBD) is a widely exploited form of RSM, particularly tailored for three levels (-1, 0, and +1). BBD is more efficient than other factorial designs including Central Composite Design (CCD) and requires fewer experiments (Kumar et al., 2016). Recently, RSM has been extensively used in the optimization of operating parameters in combined systems (Qiu et al., 2014).

For this reason, the objective of this study was to investigate the optimum condition of iron removal from groundwater with ozonation by using RSM. Factors affecting ozonation including pH, time and hardness were studied. The results from this research, which exhibit achievements of the utilization of ozonation, can be applied to the oxidation of iron present in groundwater.

2. METHODOLOGY

2.1 Materials

All reagents used in this experiment, including sodium hydroxide (NaOH), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), potassium iodide (KI), nitric acid (HNO_3) and sulfuric acid (H_2SO_4) were analytical grades. Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) was used to quench residual ozone. Potassium iodide (KI) was used to

determine ozone concentration and to trap unreacted ozone. Groundwater was derived from a groundwater well with a depth of approximately 80 meters. The groundwater had a reddish color, an odor, and an initial pH of 7.5. The groundwater sample was preserved by adding 6 M of nitric acid until the pH was 2 in order to stabilize the metal in solution form and prevent precipitation (Rice et al., 2017).

2.2 Groundwater characterization, ozonation, and analysis

Iron concentration in groundwater was analyzed by inductively coupled plasma optical emission spectrophotometer (ICP-OES, Perkin model optima 2100 DV). Hardness was analyzed by following standard methods for water and wastewater treatment (Rice et al., 2017). The ozone generation rate measured by iodometric method was 0.57 mg/min. Ozonation experiments were carried out in batch mode using a cylindrical reactor. Ozone was generated by a laboratory ozone generator (ZON027) using oxygen from an air pump (CS-51). The ozone flow was introduced into the reactor via air diffusers. Aliquot samples of 50 mL were collected at the specified time. Ozone concentration was measured by standard iodometry (Rice et al., 2017). A few drops of sodium thiosulfate solution were added to quench the residual ozone. All experiments were performed in triplicates.

Ozone generation rate was measured with the iodometric method using 2% KI solution in the absorption of ozone gas, then subsequently titrated against sodium thiosulfate titrant. The total iron concentration and pH of groundwater before and after ozonation was analyzed by ICP-OES (Perkin model optima 2100 DV) and pH meter (Eutech Model CyberScan pH1100). The detection limit of ICP-OES was 0.1 µg/L. The instrument was calibrated by standard solutions for obtaining a curve with regression coefficient $R^2=0.9999$. Deionized water was used as a blank. The efficiency of iron removal was calculated and analyzed by using BBD and statistical analysis.

2.3 Box-Behnken design and statistical analysis

To analyse the problem and to achieve a model, the researcher used BBD, a RSM which is a collection of mathematical and statistical techniques. To investigate the optimum of the response, this study focused on three significant independent variables: (1) Time; (2) pH; and (3) Hardness as shown in Table 1.

Table 1. Levels of each factor for Box-Behnken design

Parameters	Code levels		
	-1	0	1
Time (min)	10	30	60
pH	6	7	8
Hardness (mg/L as CaCO ₃)	300	400	500

Each variable was manipulated independently over three levels between -1 and +1, at the determined ranges, based on a set of preliminary experiments. To reduced possible bias, experimental order was randomized. Considering that there are only three levels for each factor, the appropriate model was identified as the quadratic model as shown in Equation 2.

$$y = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum_i x_i \sum_{<j=2}^k \beta_{ij} x_i x_j + e_i \tag{2}$$

Where; y is the response; x_i and x_j are the variables; β is the regression coefficient; k is the number of factors studied and optimized in the experiment; and e is the random error. The optimum condition for iron removal was analyzed by RSM with different variable combinations according to the BBD.

3. RESULTS AND DISCUSSION

3.1 Groundwater characterization, ozonation, and analysis

The groundwater sample had a reddish color and odor. The chemical properties of groundwater were examined as shown in Table 2.

Iron found in the groundwater was 109 mg/L, which was higher than the permissible concentration standard for iron in drinking water (0.3 mg/L) (Araby et al., 2009). The groundwater sample was considered very hard water with a hardness of 304 mg/L as CaCO₃. The most common sources of iron in groundwater occur naturally from weathering of iron-bearing minerals and rocks. Water hardness in natural water can be up to 100 mg/L as CaCO₃, depending on the associated sources. The concentration of iron and hardness in the groundwater was high due to minerals leached from surrounding soil releasing their constituents, including iron, calcium or magnesium carbonate into the source well (Pentamwa et al., 2011). The high iron and hardness of the groundwater sample not only effects health but also contributed to inefficient and costly operation resulting from scale deposition in the distribution system.

Table 2. Chemical properties of groundwater

Chemical properties	
Iron (mg/L)	109
pH	7.5
Hardness (mg/L as CaCO ₃)	304

3.2 Box-Behnken design and statistical analysis

A model suitability analysis was performed to explain the change in the efficiency of iron removal, resulting from ozonation at different lengths of time (min). The initial pH and hardness of the groundwater were analyzed using four models: (1) Linear model; (2) Linear + square model; (3) Linear + interaction model; and (4) Quadratic model as shown in Table 3.

Table 3. Statistical summary for each model

Model	S	R ² (%)	R ² (adj) (%)
Linear	2.04572	85.49	81.54
Linear + square	1.07718	97.07	94.88
Linear + interaction	2.24922	87.25	77.68
Full quadratic	0.86253	98.83	96.72

Note: S is standard deviation; R² is coefficient of determination; R² (adj) is adjusted coefficient of determination

According to Table 3, the quadratic model had the lowest standard error (0.8625) and the highest adjusted decision coefficient R² (adj) (96.72 %). This shows that the Quadratic model is the most suitable to explain the results when it is compared to all the others. It might be indicated that the quadratic model was fit to data which explained that some parameters

are twice as effective for iron removal with ozone. On the other hand, the linear models did not provide suitable data of iron removal (high standard error with low R²) with ozone due to results that showed the y parameter did not change equally to the x parameter in the equation.

Table 4. Estimated coefficients and analysis of variance with coded units suggesting a quadratic model for removal of iron by ozone

Term	Coef	SE Coef	t	p
Constant	33.3286	26.9029	1.239	0.270
pH	29.6853	6.5518	4.531	0.006
Hardness	-0.2046	0.0474	-4.316	0.008
Time	-0.3900	0.1484	-2.628	0.057
pH × pH	-1.8513	0.4489	-4.124	0.009
Hardness × hardness	0.0002	0.0000	5.171	0.004
Time × time	0.0011	0.0007	1.512	0.191
pH × hardness	-0.0049	0.0043	-1.148	0.303
pH × time	0.0401	0.0173	2.325	0.068
Hardness × time	0.0002	0.0002	0.870	0.424

Note: Coef is coefficients; SE Coef is the standard error of the coefficients; t is t-value; p is p-value

According to [Table 4](#), regression coefficient, initial pH and hardness showed t significant factors in the removal of iron. The efficiency of iron removal at 95% confidence level with the p-value was less than the significance level ($p < 0.05$). The p-value of time was not significant because it was greater than the p-value ($p > 0.05$), indicating that the initial pH, groundwater and hardness significantly influenced iron removal efficiency at 95% confidence level. Considering the second influence (square terms) in [Table 4](#), which was pH × pH (pH^2), hardness × hardness (hardness^2) and time × time (time^2), the possibility of the square terms was $p = 0.005$. It can be interpreted that at least one independent variable influenced the efficiency of iron removal. The p-value of pH^2 and hardness^2 was less than 95%. This implied that these factors had a significant effect on iron removal efficiency at 95% confidence level. However, the fact that the p-value of time^2 was significantly greater than the p-value > 0.05 indicates that time^2 had no effect on the removal efficiency. When examining the interaction terms in [Table 4](#), it was found that pH × hardness had a p-value of 0.303 and pH × time had a p-value of 0.068, which were greater than the significance level ($p > 0.05$). Meanwhile hardness × time had a p-value of 0.424, which was greater than the significance level ($p > 0.05$). In other words, the change in time has no influence on iron removal in the groundwater.

The equations for predicting the iron removal efficiency in groundwater obtained from statistical analysis using RSM from the Quadratic model, showed the relationships among the independent variables (pH, hardness, and removal time) with iron

removal efficiency, which can be shown as Equation 3.

$$\begin{aligned} \text{Remove efficiency (\%)} & \quad (3) \\ & = 33.3286 + 29.6853 - 0.2046 \text{ hardness} - 0.3900 \text{ time} - \\ & \quad 1.8513 \text{ pH} \times \text{pH} + 0.0002 \text{ hardness} \times \text{hardness} + 0.0011 \\ & \quad \text{time} \times \text{time} - 0.0049 \text{ pH} \times \text{hardness} + 0.0401 \text{ pH} \times \text{time} \\ & \quad + 0.0002 \text{ hardness} \times \text{time} \end{aligned}$$

According to Equation 3, iron removal efficiency could be predicted by inserting values of hardness, pH and time. However, the range of each factor was limited (pH 6-8, hardness 300-500 mg/L, time 5-60 min). For this reason, Equation 3 may provide unexpected results for data outside these ranges.

3.3 Response surface optimization of iron ozonation

The determination of the optimum condition for iron removal was performed according to the BBD featuring different variable combinations. To determine the optimum level of independent variables, three-dimensional surface plots were constructed as shown in [Figure 1](#).

The effect of time and pH on iron removal at a fixed hardness at 300 mg/L as CaCO_3 clearly showed that iron removal favored high pH. According to previous studies, under alkaline pH conditions, iron(II) oxidized to iron(III) and subsequent formation of ferric hydroxide ([Abraham et al., 2020](#)). In the ozonation process, high pH is attributed to the decomposition of ozone and consequently the generation of the hydroxyl radicals (OH^\bullet), which was a very powerful radical and reacted with iron ([Sukmilin et al., 2019](#)). For these reasons, at pH 8 with ozone applied to oxidized iron from the groundwater, the removal efficiency of iron was almost 100 %.

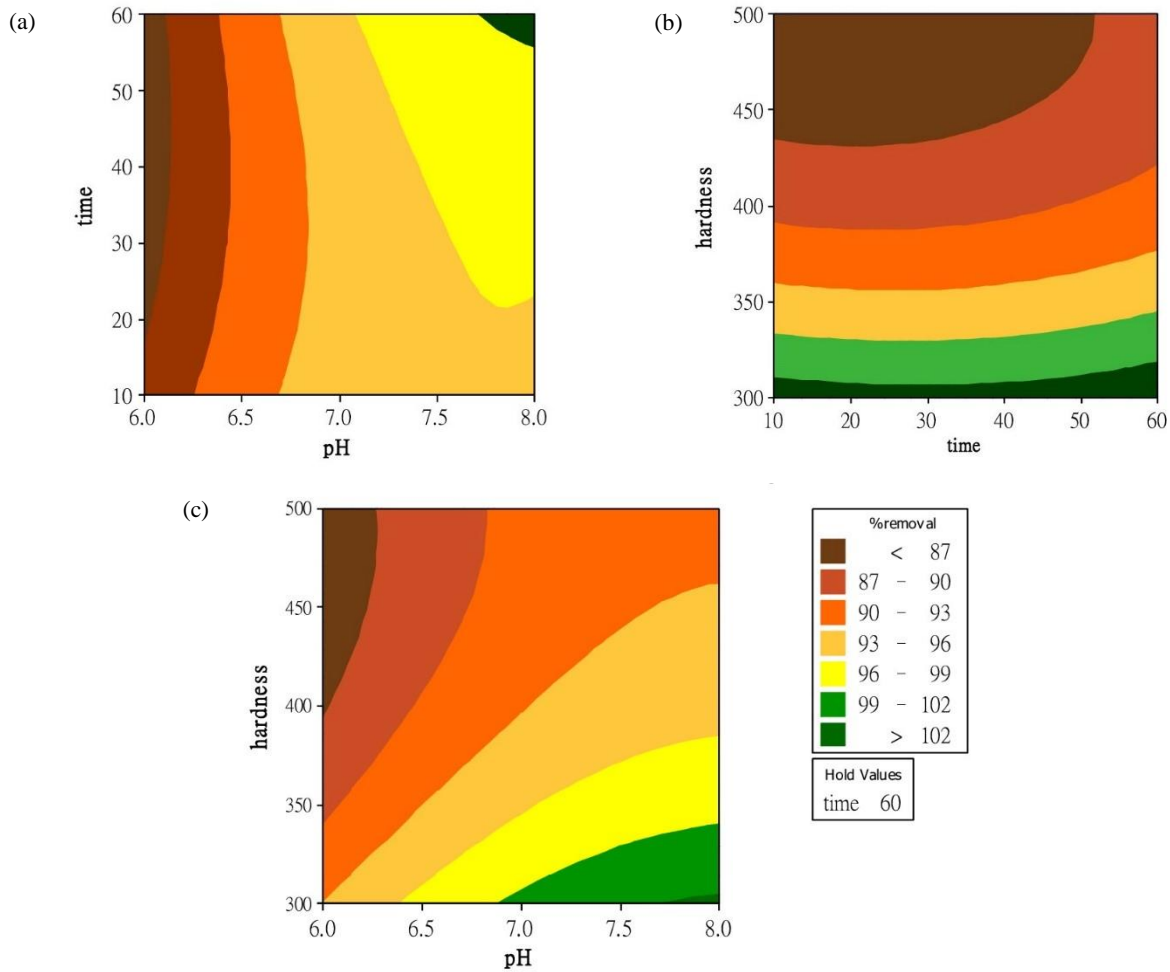


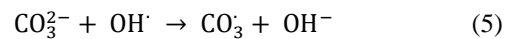
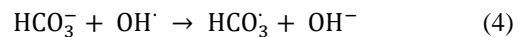
Figure 1. Contour plot of iron removal on variable affected (a) pH vs time; (b) time vs hardness; and (c) pH vs hardness (Experimental conditions: O_3 generation=0.57 mg/min, iron concentration=109 mg/L).

The effect of time and pH on iron removal at a fixed hardness at 300 mg/L as $CaCO_3$ clearly showed that iron removal favored high pH. According to previous studies, under alkaline pH conditions, iron(II) oxidized to iron(III) and subsequent formation of ferric hydroxide (Abraham et al., 2020). In the ozonation process, high pH is attributed to the decomposition of ozone and consequently the generation of the hydroxyl radicals (OH^\bullet), which was a very powerful radical and reacted with iron (Sukmilin et al., 2019). For these reasons, at pH 8 with ozone applied to oxidized iron from the groundwater, the removal efficiency of iron was almost 100 %.

The reaction time did not affect iron removal by ozonation due to ozone acting as a strong oxidant. Ozone could rapidly oxidize iron(II) to iron(III). For this reason, reaction time had no effect on iron removal by ozonation.

When the hardness in the groundwater was increased, the oxidation of iron decreased. The results showed that at 60 minutes, as the hardness as $CaCO_3$

increased from 300 to 500 mg/L, the removal efficiency of iron decreased. According to a previous study Araby et al. (2009), carbonate and bicarbonate can act as ozone radical scavengers as shown in Equation 4 and Equation 5.



From Equation 4 and Equation 5, bicarbonate and carbonate are strong scavengers for hydroxyl radicals (Hachemi et al., 2013). Therefore, the ozonation process with high hardness could slow down decomposition of ozone in the groundwater. For this reason, at hardness 300 mg/L as $CaCO_3$, the removal efficiency of iron was nearly 100%. It might suggest, when the hardness increased, the oxidation of iron decreased. Conversely, when pH increased, iron removal increased. The results showed that high efficiency of removing iron occurred at high pH and

low hardness. In other words, high pH and low hardness could remove iron almost 100%.

3.4 Condition optimization and confirmation test

The compared results between experimental data and the predicted data, calculated using Equation 3, is shown in Table 5.

Table 5 showed the maximum predicting iron removal percentage was about 99% at an initial iron concentration of 109 mg/L, initial solution pH of 6.99, contact time 10 min, hardness 300 mg/L as CaCO₃ and ozone concentration 0.57 mg/min. The optimum conditions were calculated from Equation 3. The optimum conditions were 10 min, pH 6.99 and hardness 300 mg/L. The optimum iron removal

efficiency of the experiment was 98.45%, which was close to the target iron removal efficiency (99%). The percentage of error was 0.558%. Therefore, the Quadratic model was accurate. According to a previous study, the optimum condition to remove iron from simulated groundwater was a pH between 9-10. The percentage of removal iron was 96% (Araby et al., 2009) which was close to the test results. This showed that the RSM model could be effectively used to predict the optimal conditions for iron removal in real groundwater. Therefore, the ozonation process was efficient for removal of iron from groundwater as a pre-treatment process before continuing to other processes such as filtration and ion-exchange in the water treatment.

Table 5. Experimental design matrix and iron removal from the experimental data compared to the predicted values.

Order	Time (min)	pH	Hardness (mg/L)	Iron removal efficiency (%)		% Error
				Experiment	Predict	
1	10	6.00	400	86.95	87.450	0.575
2	10	7.00	300	99.95	99.011	0.939
3	10	7.00	500	88.65	88.976	0.367
4	10	8.00	400	91.35	91.827	0.522
5	35	6.00	300	92.65	93.088	0.472
6	35	6.00	500	84.89	84.428	0.544
7	35	7.00	400	91.35	91.48	0.142
8	35	7.00	400	91.26	91.48	0.241
9	35	7.00	400	91.83	91.48	0.381
10	35	8.00	300	100.00	100.46	0.46
11	35	8.00	500	90.26	89.821	0.486
12	60	6.00	400	87.26	86.782	0.547
13	60	7.00	300	99.56	99.598	0.038
14	60	7.00	500	89.76	90.689	1.034
15	60	8.00	400	95.67	95.17	0.522
Optimum condition	10	6.99	300	98.45	99.0	0.558

4. CONCLUSION

The ozonation process, of which the optimum condition was identified by the BBD with the RSM, was successfully applied to remove iron from the groundwater. Furthermore, the quadratic model was proven suitable to describe the relationship between pH and hardness. The model fitted the experimental data well, with a coefficient of determination (R^2) of 98.83 % and an Adj- R^2 of 96.72%. In addition, the p-value of this model was less than 0.05, which indicates that the model was statistically significant. At the optimum condition of pH 8 and hardness of 300 mg/L, removal efficiency of iron reached 99.00%. Moreover,

the experiment revealed that iron removal was 98.45%. It can be concluded that ozonation was able to effectively oxidize iron in the groundwater as predicted by the model constructed according to the BBD. Future research is required to investigate more effective pilot-scale treating. In addition, the efficiency of disinfection and economic aspects such as operation cost and investment cost should be investigated.

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