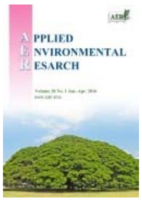
App. Envi. Res. 39 (1): 1-10

Applied Environmental Research

Journal homepage : http://www.tci-thaijo.org/index.php/aer



Manganese Removal from Aqueous Solution by Ozonation Process Designed by Box-Behken Design (BBD)

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Article History
Submitted: 8 September 2016/ Accepted: 11 November 2016/ Published online: 15 February 2017

Abstract

The aim of this research was to investigate interactions in the removal of manganese from contaminated water by oxidation through an ozonation process. The manganese oxidation was used to oxidize manganese ions (Mn^{2+}) in solution to manganese dioxide (MnO2) in its brown solid form, in order to reduce levels of manganese ions in the water to below the acceptable limit for drinking water (0.05 mg/L). In this study, the independent effects such as the initial concentration of manganese (5, 10 and 15 mg/L), initial pH of solutions (3, 4 and 5) and ozone concentrations (10.970, 21.945 and 32.920 mg/L) designed Box-Behnken Design (BBD) as a one of the design of experiments were examined for optimal conditions and including main effects and their interactions. The ozone concentration in the reactor was increased with increasing operating time of an ozone generator and linearly increased at the rate about 2.194 mg O_3/L min. The experimental results indicated that all factors significantly affected manganese removal rate. Initial manganese concentration was negatively correlated, while pH and ozone concentration were both positively correlated with removal percentage. Main, square and interaction effects were significant on percent manganese removal. Additionally, percent removal was reduced with increasing ozone concentrations because at higher ozone levels, MnO_2 in solid form was converted to MnO^{4-} and re-dissolved into solution-a process known as over-oxidation. The maximal condition, the removal efficiency of manganese in oxidation reaction by ozonation process in initial manganese concentration 5 mg/L, pH 4.0 and ozone concentration 21.945 mg/L was appeared more than 100%. The present study indicates that manganese ions can be effectively removed from drinking water by ozonation.

Keywords: Manganese removal; Oxidation reaction; Box-Behnken Design (BBD); O_3; Over-oxidation

Introduction

Manganese (Mn) is frequently found as a contaminant in natural water resources, and is highly stable in the environment. Manganese is an abundant element, comprising about 0.1% of the earth's mass [1]. Divalent manganese (Mn^{2+}) is highly soluble and enters sources of potable water though soil water, surface water and ground water. Although Mn is important for human health, e.g. in the function of certain enzymes, higher levels of exposure are toxic to humans; the World Health Organization (WHO) has set the maximum Mn concentration in drinking water at 0.05 mg/L [2-3].

Considerable research has been undertaken to identify effective means of Mn removal to below maximum permissible limits, including physiological, biological and chemical methods. However, each method was suffered drawbacks; for example Dalai et al. [4], who developed a physiological methodology, studied adsorption of iron (Fe) and Mn by using activated carbon prepared from rice husk, and reported 100% removal of Fe and Mn. Moreover, Goher et al [5], who studied removal of aluminum, Fe and Mn by using granular activated carbon (GAC) reported 79.05% removal of Mn. Additionally, Mariana et al. [6] studied the thermodynamics and kinetics of Mn removal by adsorption on white rice husk ash (WRHA). This group showed that WRHA was an effective as well as inexpensive adsorbent for Mn. However, regeneration of adsorbent was very difficult and expensive. Burger et al. [7], using *Leptothrix discophora* sp-6 microorganisms to remove Mn, achieved 90% removal of Mn from solution. However, this biological process suffered from the disadvantages of rapid achievement of equilibrium adsorption, and difficulty in controlling the operating system. Ion exchange was widely used in industry to remove Mn from raw water. Kononova et al. [8] examined the exchange of chromium and Mn ions on resin. They found that Mn can be removed to below the maximum permitted level of 0.1 mg/L (99.8% removal); however, a regeneration process was needed once the resin became saturated [9]. Nowadays, chemical precipitation achieves high efficiency of removal. The oxidation reaction process was also widely applied to remove contaminated heavy metals by using oxidizing chemicals such as oxygen (O_2) [10], potassium permanganate (K_2MnO_4) [11-12], chlorine (Cl_2), hydrogen peroxide (H_2O_2), chlorine dioxide (ClO_2) and ozone (O_3), etc. [13-14]. Ozone is known as a strong oxidant for heavy metals, and can decompose some organic pollutants. Although ozone is unstable in water, it is easily produced by activation of oxygen under high voltage conditions. Nevertheless, the retention time of ozone in aqueous solution is sufficient to allow an oxidation reaction with Mn ions. The ozone generation can be explained by Eq.1 and Eq.2 [15]. Briefly, an oxygen molecule in gaseous phase has a bond broken to create an oxygen radical, which then reacts with oxygen to form ozone gas.

$$O_2 + energy \rightarrow O + O \qquad \text{(Eq.1)}$$

$$O + O_2 \rightarrow O_3 \qquad \text{(Eq.2)}$$

Hence, the oxidation process to remove pollutants from water is of considerable potential and eh subject of much research. The strongly oxidization properties of ozone gas allows its use as a disinfectant, to remove heavy metals and decompose toxic organic pollutants. In the ozonation process, heavy metals produce a sediment that is then easily filtered from the water. Additionally, the short lifetime of ozone in water is advantageous; ozone is quickly decomposed to oxygen, which presents no health or environmental risks. Eq.3 shows the oxidetion reaction of soluble Mn ions to Mn dioxide in solid form, which is easily separated from the aqueous phase.

$$Mn^{2+}_{(aq)} + H_2O + O_3 \rightarrow MnO_{2\,(s)} + 2H^+ + O_2 \quad \text{(Eq.3)}$$

Recently, several groups of researchers studied removal of Mn by oxidation using ozonation process. For examples, Zahra et al. [16] investigated the efficiency of advance oxidation processes (AOPs) by ozone as an oxidant with Mn^{2+} to make solid Mn dioxide (MnO_2). They reported that ozonation at a suitable concentration can remove Mn^{2+} to about 97.2%; however, higher concentrations had a negative effect on Mn removal. Martin et al. [17] achieved a removal rate of 82%, while Araby et al. [18] found that removal of Mn and Fe by ozone addition was about 83% at an ozone concentration of 3 mg/L and reaction temperature of approximately 20°C.

The aim of this study was to explore removal of Mn ions from aqueous solution by the ozonation process. The independent variables such as initial Mn concentration, solution pH and ozone concentration were examined in a one liter batch reactor designed by Box-Behnken design (BBD) based on the Response Surface Methodology (RSM). The main effects and interaction terms were discussed and optimal conditions identified. The results of this work will contribute as a pre-treatment of raw groundwater before continuing to other processes in drinking water treatment plants.

Materials and Methods

All chemical reagents used were analytical grade. Mn nitrate at a purity of more than 97% ($Mn(NO_3)_2 \cdot 4H_2O$), used as the pollutant, was purchased from AppliChem Panreac, Germany. The stock Mn pollutant, at about 1,000 mg/L, was prepared by dissolving in 1% of HNO_3 solution then analyzed by a 5-point external standard ($R^2 > 0.995$) using an Atomic Adsorption Spectrophotometer (AAS, Perkin Ermer 300 AAnalyst, USA). Sodium hydroxide (NaOH) and 65% HNO_3 was supplied from Ajax Finechem Pty Ltd, Auckland, New Zealand and RCL Labscan Limited, Thailand, respectively. Ozone was synthesized from the air using the plasma discharge method. The ozone concentration was analyzed by using potassium iodide (KI) and sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) reagents obtained from Ajax Finechem Pty Ltd, Auckland, New Zealand. Deionized water was used in all experiments.

The experiments were conducted in a batch reactor to study the effects of independent variables such as initial Mn concentration (5–15 ppm), initial solution pH (3–5) and ozone concentration (10.970–32.920 ppm). This Mn concentrations span its concentrations found in groundwater from the northeast of Thailand. The acidic pH range was selected to prevent precipitation of Mn hydroxide. The system consists of an ozone generator (MMS Engineering CO., LTD, Thailand), an ozone injector, an air vent, glass laboratory bottle with volume of 1,000 mL, and magnetic stirrer (Figure 1). The ozone was injected into the solution in the reactor and mixed using the magnetic stirrer at room temperature. Samples were collected for each reaction time then filtered by nylon fiber filter (0.45 μm) before analyzing the level of Mn ions remaining in solution using an Atomic Absorption Spectrophotometer (AAS, Perkin Ermer 300 AAnalyst, USA).

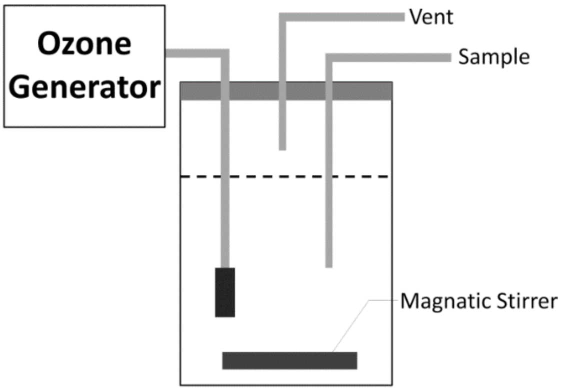

Figure 1 Experimental unit.

Mn removal by ozonation was performed by examining as independent variables the initial Mn concentrations (X_1), initial solution pH (X_2) and ozone concentrations (X_3) designed by BBD. The low (-1) and high (+1) levels of factors are shown in Table 1. About 30 order runs (2 replications) were created by BBD to test in this experiment.

The percentage of Mn removal was used as a response value in this work computed by Eq.4. Where, C_i was initial Mn concentration (mg/L) and C_f was final Mn concentration (mg/L). Then, the coefficient terms for the full quadratic equation (Eq.5) were calculated by using least square of error technique.

$$Y(\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad \text{(Eq.4)}$$

$$Y(\%) = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{i \neq j}^{3} \beta_{ij} X_i X_j \qquad \text{(Eq.5)}$$

Here, Y was percentage of Mn removal (%), X_i was independent variables. $ß_0$, $ß_i$, $ß_i^2$ and $ß_{ij}$ were coefficient terms and was the error term.

Table 1 Parameters and levels used for the experimental design in Mn oxidation process

Parameters	**Level**		
	-1	**0**	**+1**
Initial Mn concentrations (mg/L), X_1	5	10	15
Initial solution pH, X_2	3	4	5
Ozone concentrations (mg/L), X_3	10.970	21.945	32.920

Results and Discussion

Firstly, the Mn removal, tested at initial concentration of 15 mg/L, initial pH of solution of 4, can be removed to 100% at 20 min of reaction time and ozone concentration of 43.880 mg/L. So, ozone concentrations were reduced in order to be elucidate the effect of independent variables on Mn removal (10.970–32.920 mg/L). Next, in the optimization study, Mn removal of all experiments as calculated by Eq.4 were shown in Table 2. Next, the coefficient can be calculated using least square of error technique (Table 3). Additionally, these terms could be articulated as a full quadratic equation (Eq.6); a predicted Mn removal rates computed using this equation are presented in Table 2.

The standard errors of every run were calculated from predicted and experimental results. Histogram and normal probability plots were used to check the accuracy of experimental results are displayed in Figure 2 and Figure 3, respectively.

$$\begin{aligned} Y = {} & 98.893 - 13.634X_1 + 4.462X_2 + 11.564X3 - 6.301X_1^2 - 3.467X_2^2 - 10.52X_3^2 \\ & + 3.72X_1X_2 + 9.57X_1X_3 - 7.774X_2X_3 \qquad \text{(Eq.6)} \end{aligned}$$

Table 2 Percent Mn removal for every run order designed by Box-Behnken design (BBD)

Run	Initial Mn concentration (mg/L)	Initial solution pH	Ozone concentration (mg/L)	Percentage of Mn removal (%)	
	X_1	X_2	X_3	Experimental results	Predicted results
1	15	5	21.945	86.10	83.67
2	10	4	21.945	98.99	98.89
3	15	3	21.945	69.90	67.31
4	15	4	32.920	86.67	89.57
5	10	4	21.945	98.70	98.89
6	15	4	32.920	86.04	89.57
7	10	4	21.945	98.99	98.89
8	10	4	21.945	98.70	98.89
9	10	4	21.945	98.99	98.89
10	5	5	21.945	100.00	103.50
11	5	4	32.920	100.00	97.69
12	15	4	10.970	44.99	47.30
13	10	5	32.920	92.16	93.15
14	10	4	21.945	98.99	98.89
15	15	4	10.970	44.99	47.30
16	15	5	21.945	85.28	83.67
17	10	3	32.920	99.46	99.78
18	10	3	10.970	59.83	61.10
19	10	3	32.920	99.51	99.78
20	5	4	10.970	96.61	93.70
21	5	3	21.945	100.00	102.02
22	10	5	10.970	83.92	85.57
23	10	5	10.970	87.80	85.57
24	10	5	32.920	96.53	93.15
25	15	3	21.945	71.72	67.31
26	10	3	10.970	59.98	61.10
27	5	4	10.970	97.22	93.70
28	5	4	32.920	100.00	97.69
29	5	3	21.945	100.00	102.02
30	5	5	21.945	100.00	103.50

Table 3 Estimated regression coefficients (β) for percentage of Mn removal

Parameters	Percentage of Mn removal	
	Coefficients (β)	P_{Value}
Constant	98.893	0.000
X_1	−13.634	0.000
X_2	4.462	0.000
X_3	11.564	0.000
X_1^2	−6.301	0.000
X_2^2	−3.467	0.003
X_3^2	−10.527	0.000
X_1X_2	3.720	0.001
X_1X_3	9.570	0.000
X_2X_3	−7.774	0.000

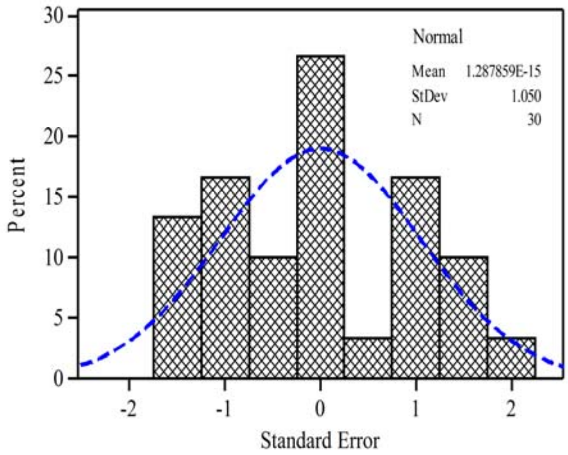

Figure 2 Histogram plot of standard error.

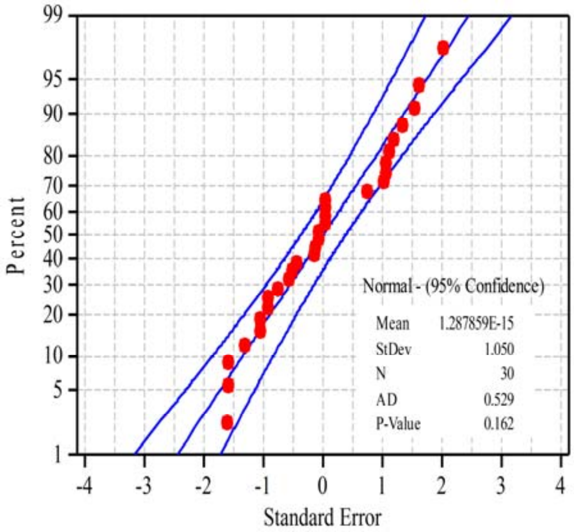

Figure 3 Normal probability plot of standard error.

The standard errors were found in normal curve type in the histogram plot (Figure 2) and lies on a straight line in the normal probability plot (Figure 3). At 95% confidence, P_{value} was about 0.162, i.e. higher than 0.05. It can be concluded that the experimental results for every run were free of significant error. Thus, the results can be utilized to explain the significant terms of all effects on percentage of Mn removal and the full quadratic equation can be also used to calculate Mn removal percentage. Surprisingly, all coefficient terms were significant on Mn removal at 95% confidence ($P_{value} < 0.05$). The initial Mn concentration was negatively correlated (–13.634) on percentage of Mn removal, while initial solution pH and ozone concentration were positively correlated (4.462 and 11.564, respectively) for main effects. Explained by Figure 4, Mn removal percentage decreased with increasing initial Mn concentrations, whereas percentage of Mn removal increased with increasing initial solution pH and ozone concentration. Another study [18] reports that Mn ions can be exceptionally removed from a high pH solution (pH 10–12). The square terms were shown to be negatively correlated for all variables. The result can be explained by the change in oxidation reaction of Mn from 2+ (Mn^{2+}) to 4+ (MnO_2). Then, at higher ozone concentration, the Mn oxide can be further oxidized from 4+ (MnO_2) to 7+ (MnO_4^-) [18]- a process known as over–oxidation of Mn ions. Oxidation of Mn has been easily achieved in high solution pH as well. [18-20] Additionally, the interaction term between initial solution pH and ozone concentration was found to be negatively correlated with percentage of Mn removal.

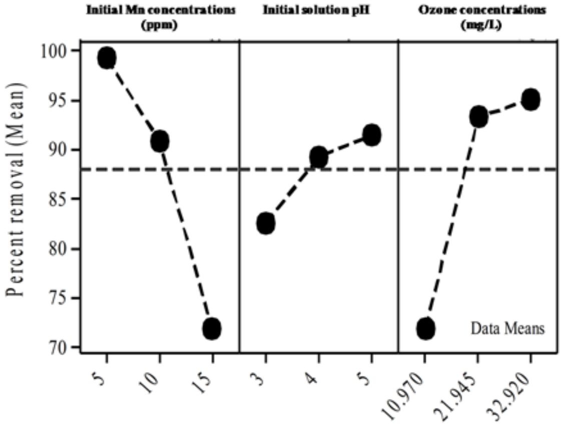

Figure 4 Main effect of independent variable plot for percent removal.

The coefficient of determination, denoted R^2, between predicted and experimental results was used to confirm the accuracy of Eq.6 displayed in Figure 5. R^2 was about 0.98, which closed to 1.00. It can be concluded that this Eq.6 can be used to predict percent Mn removal in the ozonation process.

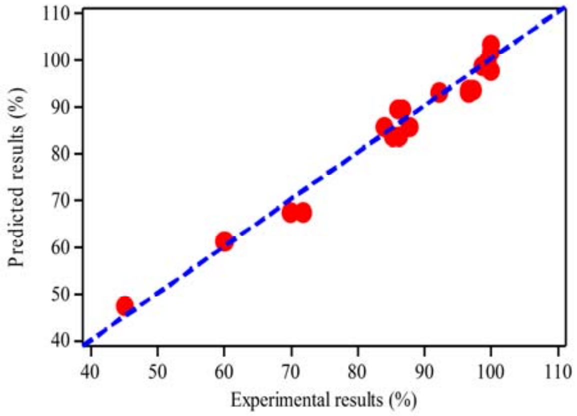

Figure 5 Scatter plot of predicted and experimental results of Mn removal.

The analysis of variance (ANOVA) method was used to test the precision of this study in terms of the F_{Value} shown in Table 4. At 95% confidence, all variables significantly affected percentage of Mn removal by comparing F_{Values} with $F_{Critical}$. $F_{Critical}$ of main, square and interaction terms was about 3.098 ($F_{(0.05,3,20)}$), which was lower than F_{Values} of main, square and interaction (236.05, 46.96 and 57.66, respectively), as confirmed by $P_{Value} < 0.05$. However, lack of fit (LOF) was displayed in significant term ($F_{Values} = 38.74$) because of a higher than $F_{Critical}$ ($F_{(0.05,\ 3,\ 17)} = 3.196$). Although some predictions showed above than 100% Mn removal as shown in Table 2 (Run order 10, 21, 29 and 30), the R^2 was close to 1.00, so that both accuracy and precision can be confirmed. The predicted equation (Eq.6) can be used to calculate percentage of Mn removal. Comparing the F_{Value} of main, square and interaction terms, the main term ($F_{Value} = 236.05$) gives the highest effect, while square term ($F_{Value} = 46.96$) shows the lowest effect on Mn removal in the ozonation process. Moreover, initial Mn concentration ($F_{Value} = 387.70$) had the highest effect on percent Mn removal and next ozone concentration ($F_{Value} = 278.94$), while initial solution pH ($F_{Value} = 41.52$) had the lowest effect on Mn removal percentage.

Table 4 ANOVA for Mn removal percentage

Sources	DF	Adjusted MS	F_{Value}	P_{Value}	Results
Regression	9	871.10	113.56	0.000	Significant
Linear	3	1810.79	236.05	0.000	Significant
X_1	1	2974.07	387.70	0.000	Significant
X_2	1	318.53	41.52	0.000	Significant
X_3	1	2139.76	278.94	0.000	Significant
Square	3	360.24	46.96	0.000	Significant
X_1^2	1	293.19	38.22	0.000	Significant
X_2^2	1	88.78	11.57	0.003	Significant
X_3^2	1	818.39	106.69	0.000	Significant
Interaction	3	442.28	57.66	0.000	Significant
X_1X_2	1	110.71	14.43	0.001	Significant
X_1X_3	1	732.68	95.51	0.000	Significant
X_2X_3	1	483.45	63.02	0.000	Significant
Residual Error	20	7.67			
Lack-of-Fit	3	44.61	38.74	0.000	Significant
Pure Error	17	1.15			
Total	29				

The interaction effects among all variables are shown in Figures 6-8. Figure 6 presents the interaction between ozone concentration and initial solution pH. The coefficient term of the interaction between ozone concentration and initial solution pH is found in negative effect on Mn removal. However, increasing initial solution pH at high ozone concentration was found to decrease of efficacy of Mn removal. MnO_2 can be easily oxidized to MnO_4^- at high solution pH; a Pourbaix-type diagram for Mn was used to determine the thermodynamically predicted range for Mn dioxide (MnO_2) and used to prevent further oxidation to soluble permanganate (MnO^{4-}) [17]. Briefly, solid Mn oxide was dissolved to soluble permanganate back to aqueous solution in over–oxidation conditions. Therefore, the concentrations of ozone in oxidation reaction have to control to prohibit over–oxidation of Mn to permanganate, which is more toxic than the original pollutant.

Figure 7 shows the interaction between initial solution pH and initial Mn concentrations. The coefficient term of the interaction between initial solution pH and initial Mn concentrations is found in positive effect. The results can be seen that percentage of Mn removal increased with increasing solution pH. Figure 8 indicates the interaction between ozone concentration and initial Mn concentrations. The coefficient term of the interaction between ozone concentration and initial Mn concentrations is found to be positive. Although the increasing of ozone concentration increased Mn removal percentage, the initial Mn concentration (–13.634) had been more negative effect on percentage of Mn removal than positive effect of ozone concentration (11.564). Besides, the over–oxidation of Mn in low Mn concentration condition was observed at the highest ozone concentration because of re–solution of MnO_2 [16].

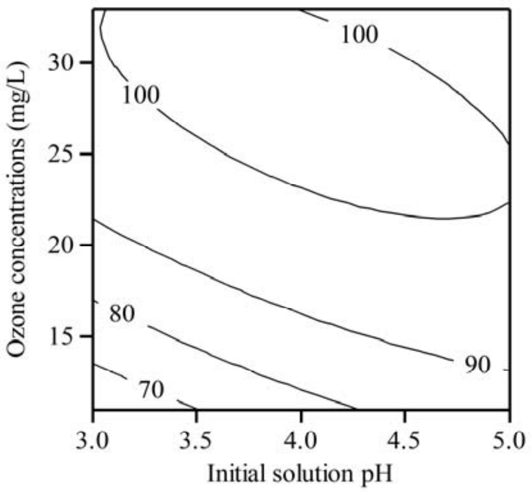

Figure 6 Contour plot of removal percentage versus ozone concentrations and initial solution pH at 10 ppm of initial Mn concentration.

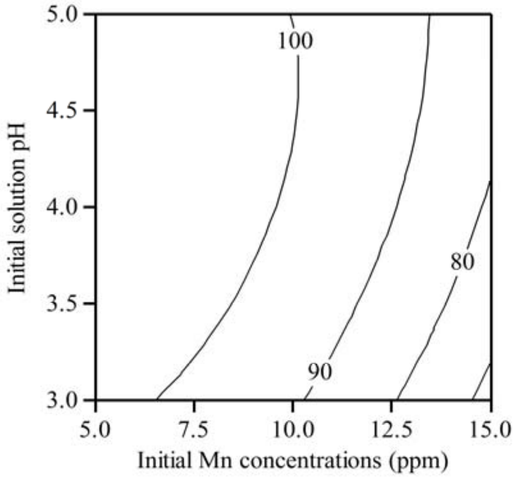

Figure 7 Contour plot of removal percentage versus initial solution pH and initial Mn concentrations at 21.945 ppm of ozone concentration.

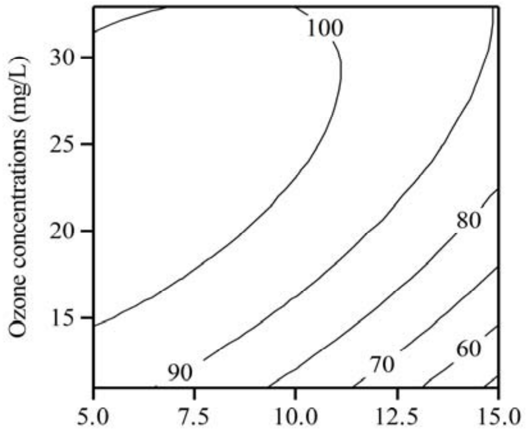

Figure 8 Contour plot of removal percentage versus ozone concentrations and initial Mn concentrations at initial solution pH at 4.

The maximum predicted Mn removal percentage was about 106% at initial Mn concentration of 5 mg/L, initial solution pH of 4.01 and ozone concentration about 22.94 mg/L- above the maximum 100% possible. Thus, validation of the equation was performed at an initial Mn concentration of 15 mg/L, initial solution pH of 4.0 and ozone concentration of 21.95 mg/L. The calculated result was about 79%, while the experimental result was about 88±5%. The higher Mn removal percentage of experimental results and predicted result was about 4–13%. The optimum condition for Mn removal can be decreased in solution to below the standard value and final solution pH was found about 3.2 from 4.0. Hence, the ozonation process was used to efficiently remove Mn ions from aqueous solution to solid MnO_2 in the pre-treatment process before continuing to other processes such as filtration and ion-exchange in the purification plant.

Conclusions

The aim of this present research was to investigate the feasibility of ozonation in removing Mn ions from aqueous solution by an oxidation reaction. The results found that soluble Mn was oxidized to brown solid MnO_2 by ozone to below the standard permitted concentration in drinking water (<0.05 mg/L). The independent variables all had a significant effect on Mn oxidation rates. Initial Mn concentration was negatively correlated effect, whereas initial solution pH and ozone concentration were positively correlated on percent Mn removal. Not only was the main effect significant; the square and interaction effects were also significant for percent Mn removal. Obviously, the higher ozone concentration was found to be a dissolution of MnO_2 to MnO_4^- in aqueous solution through over–oxidation. The optimal condition for Mn removal was a lowest Mn concentration and initial solution pH and an ozone concentration of about 4 and 22.94 mg/L, respectively. Next, the coagulation and filtration process were continuously studied in further of this work.

Acknowledgements

The authors would like to thank the Research Center for Environmental and Hazardous Substances Management (EHSM) of the Faculty of Engineering of Khon Kaen University for support throughout this research.

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