



## Analysis of Environmental Performances of Ferritization Method for the Treatment of Copper-Ammonia Wastewater under the Optimized Condition via RSM

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### Abstract

Copper-ammonia wastewater from industrial processes is an important form of hazardous waste that can contaminate water resources. The conventional hydroxide precipitation method used to remove copper complexes produces a large volume of unstable precipitates which still require further treatment. Ferritization is a powerful technique to remove bivalent cations from wastewater in the form of metal ferrites. This method is highly efficient in removal of metal complex ions; in addition, sludge resulting from this method is stable. The objective of this study was to investigate optimum conditions for ferritization using Response Surface Methodology (RSM). After optimal conditions were determined, the environmental performance of ferritization compared with hydroxide precipitation was compared using Life Cycle Assessment (LCA) methodology. The IMPACT 2002+ method was used to calculate midpoints and damage levels. The experiment found that the model obtained from RSM was accurate and reliable with  $R^2=98.37$ ,  $Adj-R^2=96.91$ ,  $Pred-R^2=91.40$ ,  $S=1.45$  and  $PRESS=110.859$ . The optimal conditions for the pH, reaction temperature, and reaction time were found to be 10.8, 69 °C, and 115 min, respectively. In addition, the actual experiment showed that the efficiency of copper-ammonia removal was  $98.41\pm 3.18\%$ . The LCA results indicate that hydroxide precipitation shows more impact at midpoint levels than ferritization, except for aquatic acidification and global warming effects. On the other hand, the endpoint analysis showed that the ferritization has a higher performance in regard to human health, ecosystem quality, and resource consumption. Ferritization had a greater impact on climate change than hydroxide precipitation because the process requires electricity. Without the use of recycling sludge as catalyst, the endpoint of natural resources from ferritization could be higher than for hydroxide precipitation. In conclusion, ferritization demonstrated better performance both in terms of its efficiency of copper-ammonia removal and its environmental performance.

**Keywords:** Ferritization; RSM; Copper-ammonia wastewater; Optimization; Environmental performances; Life cycle assessment

## Introduction

Natural rehabilitation of ecosystems cannot keep pace with the increasing rate of dumping of industrial wastes into the environment. In the last decade, major environmental problems in Thailand were caused by excessive industrial waste dumping [1]. Industries that use copper metal often discharge toxic wastewater that can be hazardous to aquatic animals. In turn, people who ingest contaminated food may accumulate high and potentially dangerous levels of copper in their bodies. High copper levels can stimulate excess adrenaline production, which in turn has many possible health impacts such as anxiety, panic, overstimulation, and insomnia [2]. Treatment of copper contamination in industrial wastewater is therefore subject to strict legal control.

Unfortunately, some forms of copper ions are difficult to remove from wastewater. Copper-ammonia wastewater is highly stable in solution and cannot be effectively treated by conventional methods such as hydroxide precipitation, ion exchange, reverse osmosis or nanofiltration [3-5].  $\text{Cu}^{2+}$  ions can react with ammonia to form  $\text{Cu}(\text{NH}_3)_4^{2+}$  due to strong interaction between the heavy metal ions and the binding ligands [6]. This chelated metal-ammonia complex is generated from tannery, timber and explosive industries, in which ammonia is often used as a leaching agent to extract heavy metal [3].

The ferritization method was proposed by Katsura et al. (1977) to remove bivalent cations from wastewater in forms of metal ferrites [7].

This method can enhance co-precipitation of  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  ions by using alkaline reagents. The  $\text{Fe}^{2+}$  ions react to form hydroxide ions, and are then partially oxidized to  $\text{Fe}(\text{OH})_2$ . In the oxidized state, copper ferrite formation takes place. The result of co-precipitation generates crystalline copper ferrite according to the following Eq. 1 [8-9].

This method has been proposed as a promising approach for copper-ammonia wastewater treatment using a strong oxidizing agent. Moreover, sediment generated from the reaction is amenable to separation [10]. After treatment, purified water can be reused. In a study of the ferritization method, Heuss-Aßbichler et al. (2016) used ferritization to purify copper-rich wastewater and studied copper recovery as a secondary resource [11]. John et al. (2017) proposed a 2-step ferritization method that can recover silver and gold from industrial wastewater at efficiencies exceeding 99.99% [12]. Ferritization has also been applied to arsenic treatment, achieving removal rates of more than 99%. In addition, recovery of arsenic ferrites has potential for commercial application as catalysts [13]. Previous studies have found that the important parameters for ferritization process are the mole ratio of the metal ion ( $\text{M}^{2+}$ ) to  $\text{Fe}^{2+}$ , reaction temperature, pH, and reaction time [14-16]. Some studies indicate that operating ferritization treatment at high temperatures can result in a sludge with useful magnetic properties [17-18].



Determining optimal reaction conditions requires multiple replications and conventional techniques can be expensive. More recently, statistical experimental design methods have proven useful in optimizing process parameters, having the advantage of enhancing

our understanding of interactions among the parameters, which in turn contributes to more useful statistical models. A range of design tools such as Taguchi, full/fractional factorial design (FFD), and central composite design (CCD) are available. The Taguchi methods do

not have a statistical basis, which poses some computational problems, while the full/fractional factorial design (FFD) requires a large set of experimental factors [19]. The RSM method is based on the central composite design (CCD) technique used for determination of effective factors and statistical analysis. Moreover, it is a powerful technique to develop a model for optimized process conditions for copper removal efficiency [20], using only a limited number of experiments. It can illustrate the influence of various test variables and the influence of interactions between variables via 3D images [21-23].

The LCA method has also been used widely to assess the environmental impact of various applications including wastewater treatment systems and waste management options [1, 24-25]. Renou et al. (2008) studied the value of LCA-based impact assessment methods to assess wastewater treatment systems through a case study at a full-scale plant; five life cycle impact assessment (LCIA) methods were used and compared in this study [26]. Tabesh et al. (2018) evaluated LCA of wastewater treatment plants (WWTPs) in Tehran, Iran. They suggested that the availability of sufficient and reliable data is an important role for LCA [27]. This dataset is referred to as the original life cycle inventory (LCI) dataset for the study.

Although the ferritization method has been known for some years, extant literature on statistical optimization of process conditions for ferritization is very limited, and few studies have focused on LCA for ferritization. This study addresses this gap by investigating optimal conditions for removal copper complex ions using the ferritization method. Based on the optimal conditions determined, the environmental performances of ferritization was compare with conventional hydroxide precipitation was compared using LCA methodology.

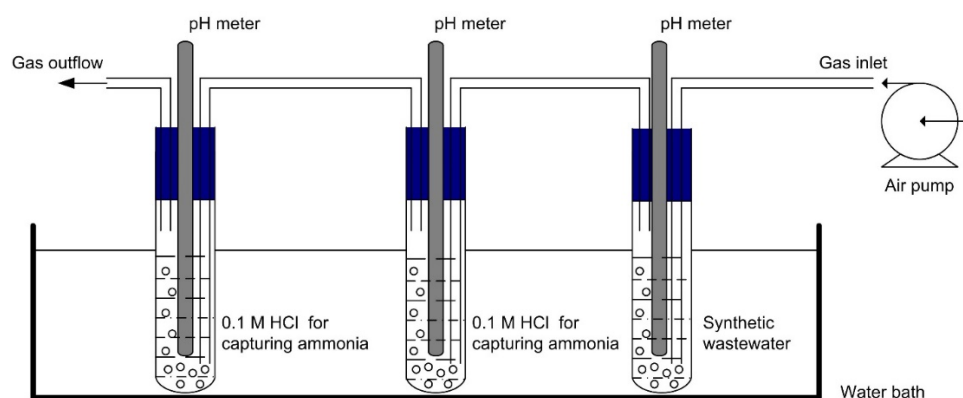
## Materials and methods

### 1) Treating synthetic wastewater by the ferritization process

To prepare synthetic wastewater, 30% w/w of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) was added to a  $2 \text{ mgL}^{-1}$  standard copper solution to achieve a  $\text{Cu}^{2+}:\text{NH}_4\text{OH}$  molar ratio of 1:4, afterwards diluting to 100 mL with deionized water. Standard analytical grade solutions of Cu ions and all chemical reagents were source from Merck, Germany.

First, 50 mL of synthetic wastewater was added into a 100 mL cylinder reactor connected to an automatic temperature controller. After that, a certain amount of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was added and dissolved into the synthetic wastewater. Sodium hydroxide ( $\text{NaOH}$ ) was used to adjust pH of the solution. A water bath with thermostat was used to maintain constant temperature. The pH of the solution was measured continuously using a pH meter (Metrohm model 827). Air was continuously supplied at constant flow rate as shown in Figure 1. To capture the ammonia gas ( $\text{NH}_3$ ) resulting from the chemical reaction, 0.1 M of hydrochloric acid ( $\text{HCl}$ ) was added into the cylinder reactor.

To study the effect of pH and temperature, pH synthetic wastewaters were adjusted to 8, 9, 10, 11, and 12, and temperatures were set to 43, 50, 60, 70, and 77 °C. In addition, the effect of reaction time was also studied. After 73, 90, 115, 140, and 157 min, the suspensions were cooled down to room temperature and then filtered in a crucible filter. The collected solid was dried at 105 °C for 24 h. The toxicity characteristic leaching procedure (TCLP) test was applied to the collected solid. The concentration of Cu in aqueous solution was determined by Flame Atomic Absorption Spectrophotometer (FASS SpectrAA-200, Perkin Elmer).



**Figure 1** Schematic diagram of the ferritization process.

The FAAS applied in this study uses eight turret lamps emitting in the 190-900 nm spectral region with a deuterium-arc background corrector. The parameters were set as follows: bandwidth 2.7/0.8 nm with 1.0 filter factor and deuterium arc background correction. The time of integration was set at 7.0 s at 15.0 mA lamp current. Detection of analytes was performed at 324.8 nm. Due to the specific characteristic of copper-ammonia wastewater, analysis of its concentration using FAAS needs to be adjusted at specific conditions according to previous studies [28].

## 2) Experimental design

In order to determine the parameters that influence the efficiency of ferritization process, a Central Composite Design (CCD) was used. In this research, CCD employed three independent factors: pH of the synthetic wastewater ( $X_1$ ), operating temperature ( $X_2$ ) and reaction time ( $X_3$ ), using Design-Expert software (Stat-Ease Inc., Minneapolis, MN, USA, ver 7.0.0). The coded levels in the CCD consisted of five experimental levels ( $-\alpha$ ,  $-1$ ,  $0$ ,  $1$ , and  $\alpha$ ). Each parameter was coded as shown in Table 1. In this design, 20 experimental runs were conducted with three replications at the

central point for estimating the purely experimental uncertainty variance. Analysis of Variance (ANOVA) and regression analysis were applied to predict and evaluate the optimal process conditions.

## 3) The empirical model validation and variable optimization

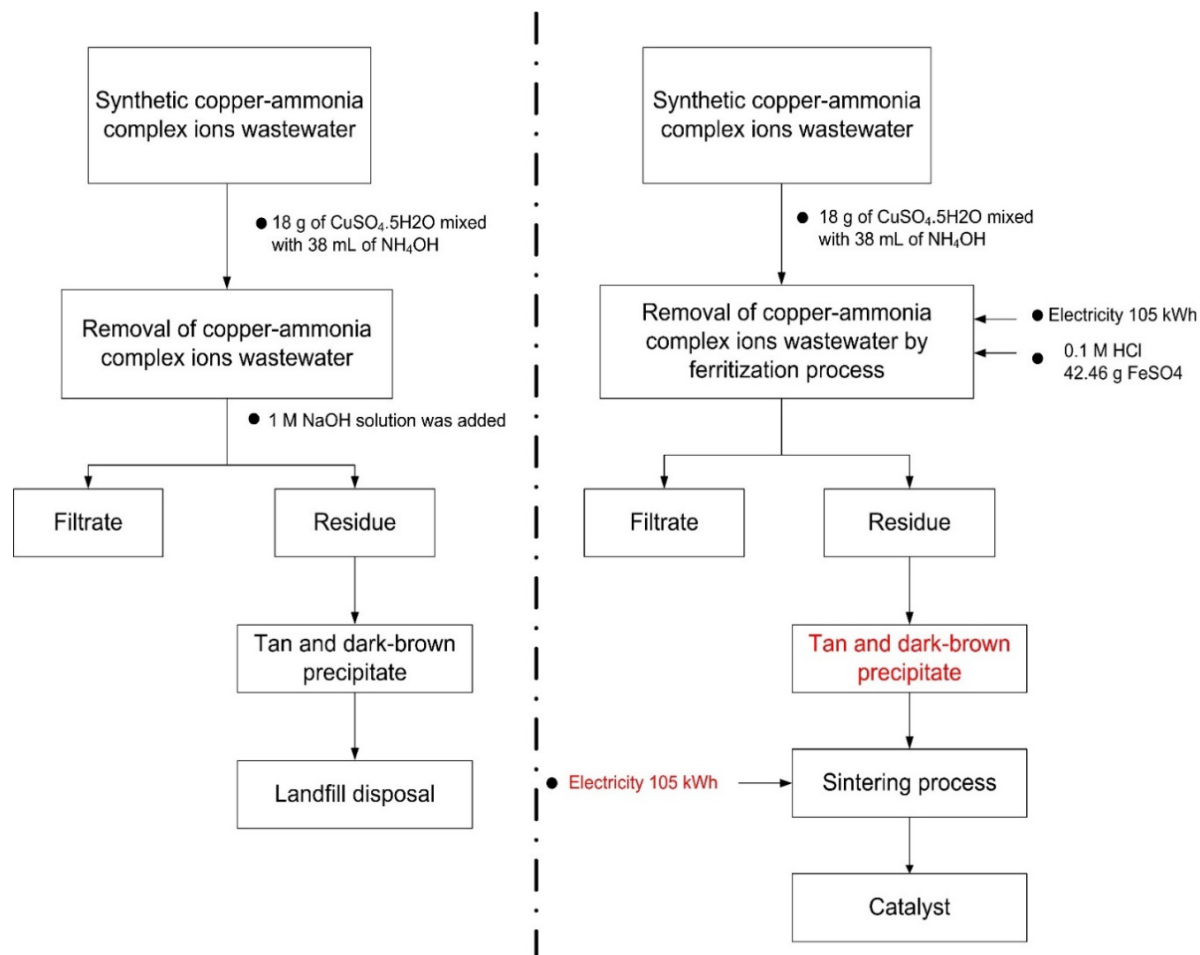
The statistical model obtained from CCD was validated by the experimental results. The efficiency of Cu removal based on the theoretical values was compared with the experimental results. Design-Expert software was used to predict the result and optimized the independent variables.

## 4) Analysis of environmental performance

After determining the optimal condition as described above, the environmental performance of ferritization and the precipitation method was compared. The functional unit was based on 1 liter of chelated wastewater. The system boundary system was defined as from cradle to gate, which included extraction of raw materials, energy consumption, and emissions during the treatment process. The system boundary is shown in Figure 2.

**Table 1** Coded level in each parameter for CCD

Parameters	Code	Coded level				
		$\alpha$	-1	0	1	$\alpha$
pH	$X_1$	8	9	10	11	12
Operating temperature ( $^{\circ}\text{C}$ )	$X_2$	43	50	60	70	77
Reaction time (min)	$X_3$	73	90	115	140	157

**Figure 2** Boundary system for comparing environmental impact of precipitation and ferritization processes.

The quantity of chemical reagents (NaOH,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{NH}_4\text{OH}$ , HCl, and  $\text{FeSO}_4$ ) used in the experiment was calculated. Also, the electricity consumed during the ferritization process and other applications was recorded. The LCI for raw material acquisition was obtained from the Ecoinvent v3.0 database and calculated through SimaPro 8.40 software. The LCI of conventional NaOH precipitation

and ferritization methods is shown in Supplementary Material (SM) 1.

The environmental impact from mass input – mass output of each treatment was calculated at the midpoint and damage levels by using the IMPACT2002+ method. The results obtained from the impact assessment were interpreted to compare the environmental performance of the treatment methods.

## Result and discussion

### 1) Treatment of copper in synthetic wastewater

Table 2 shows the effects of pH, temperature and reaction time on the accuracy of the empirical model for treating chelated copper synthetic wastewater by ferritization. Copper removal efficiencies in the range of 69.14-99.32% were obtained. As a result, the best performance was occurred in run order #8 with 99.32% of observed efficiency value and 100.11% of predicted efficiency value.

### 2) Coefficient determination of the prediction model

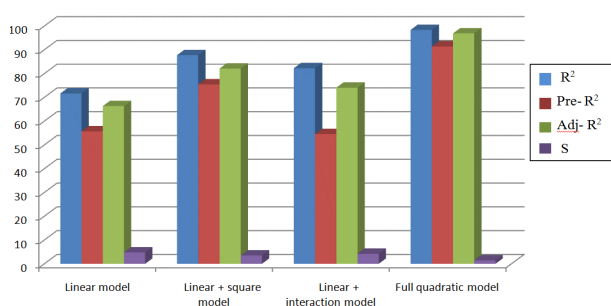
In this study, the coefficient of determination ( $R^2$ ) was determined as the quality of the fit

polynomial model. The  $R^2$  value shows the measurement of variance of the observed response from experimental and interactive factors. An  $R^2$  value closer to 100% indicates stronger models and better predictions of the responses. To provide an unbiased estimate of the population  $R^2$ , the adjusted determination of coefficient (Adj- $R^2$ ) was examined. When the adjusted  $R^2$  value is high and close to the  $R^2$  value, the polynomial model is considered consistent with the experimental data. In addition, the predicted R-squared (Pre- $R^2$ ) was applied to indicate how well a regression model predicts responses for new observations.

**Table 2** Experimental design of CCD compared with observed efficiency

Run order	pH	Temp	Time	Observed efficiency value	%Predicted efficiency value	%Error
1	11	50	90	86.67	85.56	1.30
2	10	60	115	98.95	97.63	1.35
3	10	60	157	98.88	98.58	0.30
4	10	60	115	96.77	97.63	-0.88
5	10	60	115	95.15	97.63	-2.54
6	10	77	115	98.69	99.13	-0.44
7	9	50	90	69.14	69.86	-1.03
8	11	70	90	99.32	100.11	-0.79
9	10	60	115	98.17	97.63	0.55
10	10	60	115	98.45	97.63	0.84
11	9	70	140	97.90	98.78	-0.89
12	8	60	115	86.04	86.57	-0.61
13	10	60	115	98.37	97.63	0.76
14	9	50	140	90.82	89.80	1.14
15	10	43	115	79.45	79.40	0.06
16	10	60	73	83.13	83.76	-0.75
17	9	70	90	91.11	89.46	1.84
18	11	50	140	92.46	93.88	-1.51
19	12	60	115	99.16	98.96	0.20
20	11	70	140	98.74	97.80	0.96
Optimal	10.8	69	115	98.25	101.48	3.18

The values of  $R^2$ ,  $\text{Adj-}R^2$ , and  $\text{Pre-}R^2$  for each variable in the quadratic empirical model are shown in Figure 3. The predicted results from the full quadratic model showed that the  $R^2$  value was 98.37%, indicating that the actual and the predicted responses were almost the same. In addition, the  $\text{Adj-}R^2$  and the  $\text{Pre-}R^2$  followed the same trend. Moreover, the standard of variation (S) was 5.37%, indicating good precision. On top of that, the predicting sum of square (PRESS) was low, indicating that the full quadratic model fit every point consistently and that it was able to explain the experimental variables and their interactions well.



**Figure 3** Coefficient of the predicting model obtained in this study.

### 3) Analysis of Variance (ANOVA) on the empirical model

The results of ANOVA on the full quadratic model for the prediction of the residual copper level are shown in Table 3. The F-value and P-value parameters explain the effect intensity of each term factor i.e. main factors and their interaction. In this study, the full quadratic model had an F-value of 67.26 and P-value of 0.000 ( $P < 0.05$ ) showing that it was a good model for predicting the experimental results. The lack of fit of the model (0.474) was more than 0.05 and highly non-significant. The

equation of the final empirical model for treatment of residual copper is shown in Eq. 2.

As shown in Table 4, the main effects (pH, temperature, time), square effects (pH \* pH, temperature \* temperature, time \* time), and interaction effects (pH \* temperature, pH \* time, pH \* time) were considered statistically significant terms for the efficiency of copper removal due to each factor having a P value  $< 0.05$ .

### 4) Determination of the accuracy of the empirical model

The accuracy of the empirical model was verified by using 4 types of residual plots (Supplementary material 2) such as normal probability, histogram, residuals versus the order of the data, and residuals versus the fitted values plots. As shown in Supplementary material 2 (upper left), it is evident that the residuals are uniformly distributed around the zero point and fall along the straight line. This suggests that the model is adequate to predict copper removal efficiency for various conditions. The histogram of residuals (lower left of Supplementary material 2) indicates a normal distribution of data. In addition, the distribution of the residuals versus the fitted value has no clear pattern (upper right of Supplementary material 2), indicating that the data is stable in variance. In this study, the experiments are related to time. Therefore, the independence of the data must be verified by plotting the residuals versus the observation order (as shown in lower left of Supplementary material 2). It was found that the residuals are indeed independent because the distribution has both positive and negative values, without any discernible pattern.

$$R = 15519.4 - 2321.3\text{pH} - 93.8\text{Temp} + 15.2\text{Time} + 98.1\text{pH}^2 + 0.5\text{Temp}^2 + 4.2\text{pH} \cdot \text{Temp} + 0.8\text{pH} \cdot \text{Time} - 0.1\text{Temp} \cdot \text{Time} \quad (\text{Eq.2})$$

Where, R: residual copper (%), pH: pH of solution, Temp: reaction temperature ( $^{\circ}\text{C}$ ), and Time: reaction time (min).

**Table 3** Analysis of variance (ANOVA) of the fitted quadratic polynomial model

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	9	1,267.46	1,267.46	140.829	67.26	0.000
Linear	3	922.83	347.00	115.667	55.24	0.000
pH	1	185.15	99.85	99.845	47.69	0.000
Temperature	1	472.59	174.90	174.895	83.53	0.000
Time	1	265.08	216.35	216.352	103.33	0.000
Square	3	207.71	207.71	69.235	33.07	0.000
pH*pH	1	22.84	42.75	42.750	20.42	0.001
temp*temp	1	109.54	127.15	127.153	60.73	0.000
Time*time	1	75.33	75.33	75.327	35.98	0.000
Interaction	3	136.93	136.93	45.643	21.80	0.000
pH*temp	1	12.80	12.80	12.802	6.11	0.033
pH*time	1	67.63	67.63	67.628	32.30	0.000
Temp*time	1	56.50	56.50	56.498	26.98	0.000
Residual error	10	20.94	20.94	2.094		
Lack-of-Fit	5	10.79	10.79	2.159	1.06	0.474
Pure Error	5	10.14	10.14	2.029		
Total	19	1,288.40				

**Note:** DF refers to Total Degrees of Freedom, Seq SS refers to Sequential Sums of Squares, Adj SS refers to Adjusted Sums of Squares, Adj MS refers to Adjusted Mean Squares, F refers to F-value, and P refers to P-value.

### 5) Optimization by using response surface methodology (RSM)

The relationships among the three variables, pH, temperature and reaction time, were determined using the response surface for the quadratic model according to Eq. 2. Three-dimensional surface responses (3D) and contour chart of the dependence of copper removal efficiency were plotted to elucidate the relationships between the responses and variables (Figure 4).

The results of the regression analysis revealed that copper removal efficiency was clearly affected by interactions between pH, temperature and reaction time. When the

reaction time was fixed at 115 min (Figure 4a), the 3D response surface showed the best efficiency for the elimination of copper which was achieved at a high pH of 11 and a high temperature of 70°C. The 3D plot also indicated that the decomposition rate of  $\text{Cu}(\text{NH}_3)_4^{2+}$  rapidly increased when the pH was raised from 8 to 11. The higher pH can facilitate entry of  $\text{Cu}^{2+}$  into the ferrite crystal lattice [18]. However, at pH above 11, entry of  $\text{Cu}^{2+}$  ions into the ferrite crystal lattice was reduced due to excessive oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . This phenomenon indicates that this alkaline pH produced a goethite precipitate and so the ferrous ions did not change into ferrite.



**Table 4** Comparison of midpoint levels

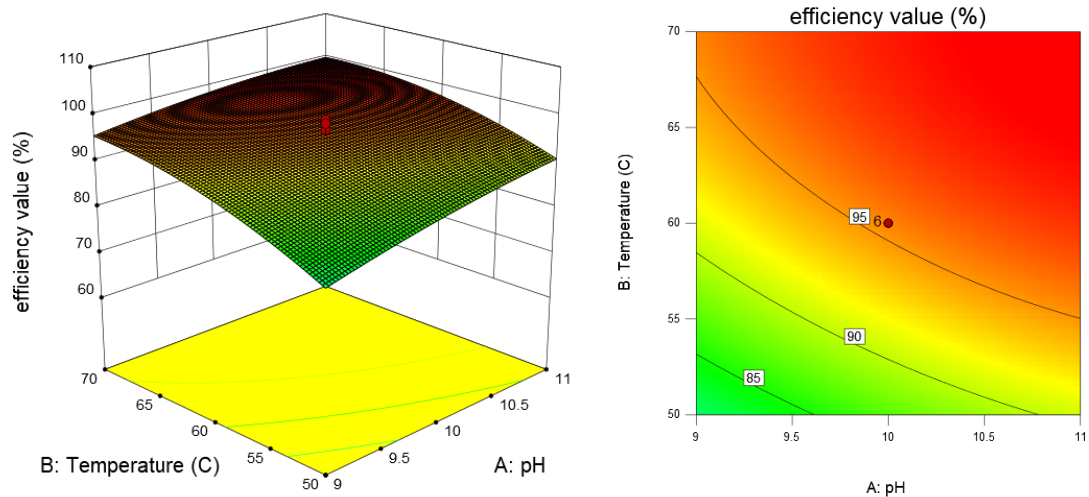
Impact category	Unit	Hydroxide precipitation	Ferritization
Carcinogens	kg C <sub>2</sub> H <sub>3</sub> Cl eq	0.2845099	-14.8779476
Non-carcinogens	kg C <sub>2</sub> H <sub>3</sub> Cl eq	27.84621918	-65.6744248
Respiratory inorganic	kg PM2.5 eq	0.051293157	-1.13719744
Ionizing radiation	Bq C-14 eq	520.62208	-812.638116
Ozone layer depletion	kg CFC-11 eq	8.66943E-06	-0.00015346
Respiratory organics	kg C <sub>2</sub> H <sub>4</sub> eq	0.02237748	-0.10665645
Aquatic eco-toxicity	kg TEG water	15795869.46	1230788.913
Terrestrial eco-toxicity	kg TEG soil	773.4362566	-97990.1163
Terrestrial acid/nutrient	kg SO <sub>2</sub> eq	1.519789737	-13.7903718
Land occupation	m <sup>2</sup> org.arable	1.473862867	-9.0478144
Aquatic acidification	kg SO <sub>2</sub> eq	145.3658631	269.0952166
Aquatic eutrophication	kg PO <sub>4</sub> P-lim	0.004942558	-2.32840346
Global warming	kg CO <sub>2</sub> eq	1000.804042	1695.458084
Non-renewable energy	MJ primary	1099.406506	-2299.09919
Mineral extraction	MJ surplus	87.78301604	-1090.64968

Thus, a pH close to 11 was considered optimal for removal of copper ions from synthetic wastewater. In addition, a reaction temperature between 43-50 °C caused hydroxide and ferrite to precipitate together, but a temperature between 50-70 °C caused precipitation of ferrite alone [29]. A hydroxide precipitate is less desirable than a ferrite precipitate because a hydroxide precipitate may suffer from leaching of heavy metal [30] as it settles to the bottom of the water body. Accumulation of biodegradable organic matter reduces the pH of the wastewater [31].

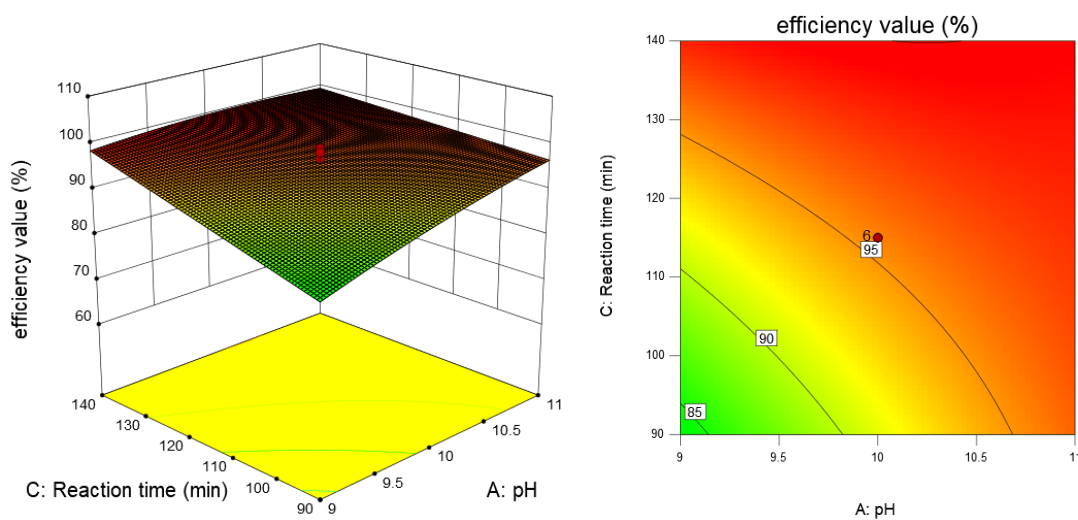
Figure 4b shows the 3D plot of the percentage of efficiency of copper removal versus reaction time and initial pH with the reaction temperature at a constant 60°C. The 3D response surface displays the percentage of efficiency of copper removal over 90% at an

initial pH of 10.5 and reaction time of 100 min. Figure 4a and 4b show that the pH close to 11 was optimal for removal of copper ions. When the initial pH was 10.5 and the reaction time between 40-80 min, efficiency was not reduced, most probably due to the presence of both hydroxide and ferrite precipitation. At a reaction time from 80-105 min, precipitation was mostly entirely composed of ferrite. The longer reaction time would not increase removal efficiency due to excessive Fe<sup>2+</sup> reacting with excess oxidizing agent to give goethite instead of ferrites.

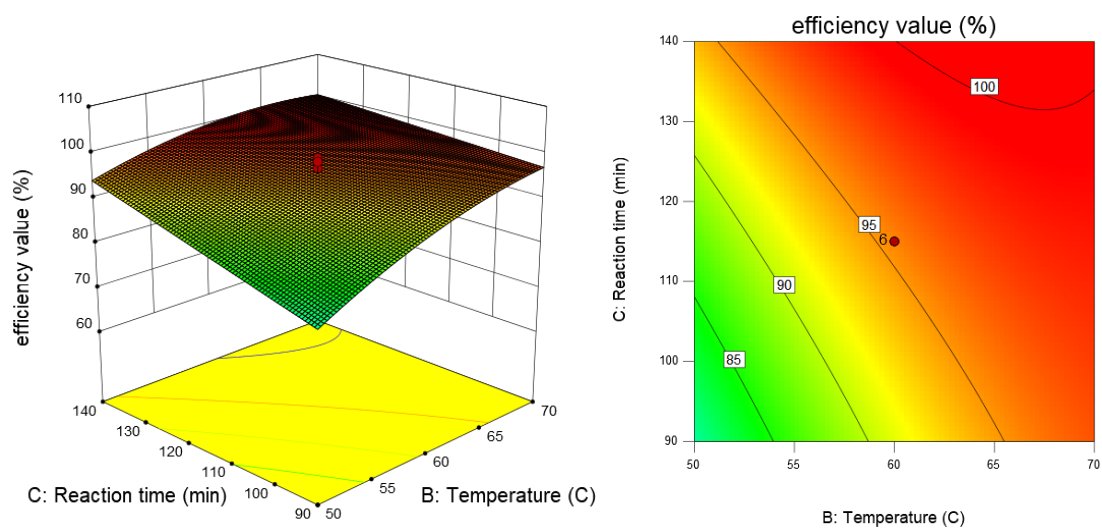
Figure 4c plots efficiency of copper removal against temperature and reaction at an initial pH of 10. The 3D response surface shows a removal efficiency of more than 90 percent at a reaction temperature of 65 °C and reaction time of 100 min.



(a) The effect of reaction temperature and initial pH on % efficiency of copper removal.



(b) Effect of reaction time and initial pH on % efficiency of copper removal.



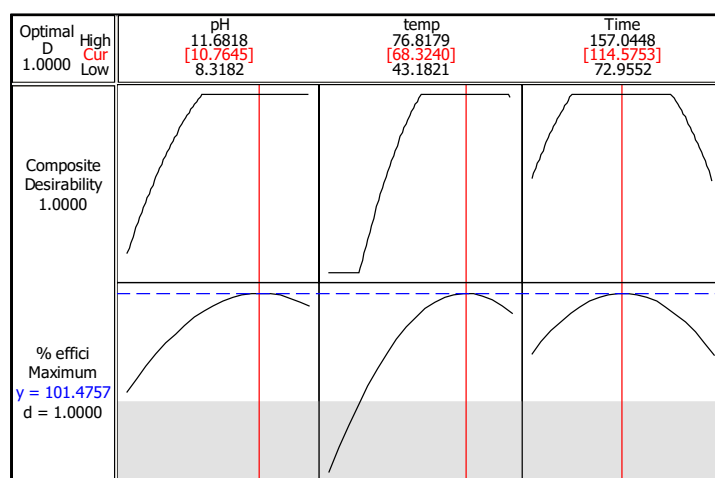
(c) Effect of temperature and reaction time on % efficiency of copper removal.

**Figure 4** The 3D Surface and contour plots for treating of copper-ammonia synthetic wastewater by ferritization.

## 6) Results of optimization plot

The ranges of optimum conditions for copper removal were found to be as follows: pH 8-12, reaction temperature of 43-77 °C and reaction time of 73-157 min. Single values of every tested condition were computed using MINITAB software. The output from the software for 99.5% of copper removal efficiency is shown in Figure 5. This output had a composite desirability value (D) of 1, confirming that the calculated conditions were truly optimal.

Batch experiments were conducted to confirm the validity of the statistical prediction by MINITAB software. The experiments were repeated 10 times under these optimal conditions. The confirming experimental results shown in Table 3 indicate that the percentage of efficiency of copper removal was  $98.25 \pm 3.18$  under these predicted optimum conditions, hence it was concluded that these numerical results from the empirical model were reasonably good at predicting the efficiency of copper removal.



**Figure 5** Response optimization plot for the maximum removal of copper-ammonia in wastewater using ferritization method.

## 7) Comparison of environmental impact between hydroxide precipitation and ferritization method

### 7.1) Results at midpoint category level

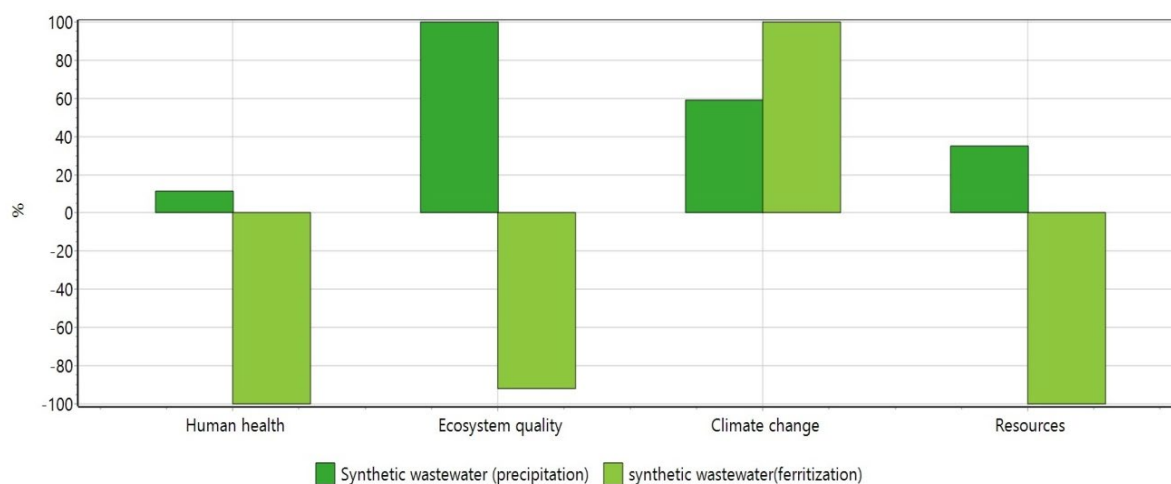
Table 4 shows a comparison of midpoint levels between hydroxide precipitation and ferritization methods. It can be seen that the impact of midpoint levels from hydroxide precipitation was higher than ferritization, except for aquatic acidification and global warming effects. This is because ferritization consumed a significant amount of electricity for operating the process, as compared with hydroxide precipitation. The impact of using electricity is however compensated by aquatic acidification and global warming effects.

### 7.2) Damage categories

Damage characterization factors of any substance can be obtained by multiplying the midpoint characterization potentials with the damage characterization factors of the reference substances. Four damage categories (human health, ecosystem quality, climate change, and resources) were linked with these results. As shown in Figure 6, it demonstrated that three damage categories (human health, ecosystem quality, and resources) from the ferritization method show lower damage than the hydroxide precipitation. On the other hand, climate change from ferritization shows a higher level of impact than hydroxide precipitation.

With this result, reducing electricity consumed during ferritization is important in mitigating climate change impact. Using electricity generated from renewable sources would neutralize this impact. In this study, we consider sludges from ferritization as a catalyst. Conversion of sludge to producing a catalyst involves high energy consumption in

the sintering process. However, we can recycle some metal ore with this process to produce a catalyst which resulted in reducing natural resource use. Without this, the damage of using natural resources from the ferritization method may be higher than for hydroxide precipitation.



**Figure 6** Comparison of damage analysis between hydroxide precipitation and ferritization methods.

## Conclusions

The present study aimed to optimize the main process parameters of the ferritization method for treating copper-ammonia wastewater. We also evaluated the environmental performance of ferritization compared with conventional methods to confirm that ferritization is not only the better method for removal copper-ammonia in the wastewater but also shows better environmental performance than conventional methods. The trial design trials was based on a statistical design in order to determine optimal conditions for removing copper to the lowest possible level and to provide an empirical model for predicting the efficiency of copper removal by ferritization. The results demonstrated that the empirical model was highly accurate for prediction at the 95% confidence interval. The empirical model was accepted because the residuals were normally and independently distributed.

Additionally, the predicted data on the residual copper from the empirical model was quite close to the experiment data, indicating that the empirical model is able to capture effectively the connection between the copper treatment variables and responses.

In the case of environmental performance, it can be concluded that ferritization method shows better performance than hydroxide precipitation. Although the climate change damage generated from ferritization method was much higher than for hydroxide precipitation due to the electricity consumption for ferritization, three damage categories from ferritization were found to be lower than for hydroxide precipitation. It could be stated that the reason for the disadvantage of hydroxide precipitation in terms of environmental performance arises largely from the many reagents required.

Copper complexes contaminated in wastewater result from many industrial processes such as textile manufacture, paint manufacturing, electronic plating, wire drawing, and printed circuit board manufacturing. The optimal conditions for removal of copper complexes as determined in this study using synthetic wastewater could be applied to real industrial wastewater. However, real industrial wastewater also typically contains other inorganic and organic matter [32]. Other metal ions and metal complex ions may affect the efficiency of removal copper complex ions by preventing the formation of ferrite sludge [33]. Therefore, the optimized condition obtained in this study could be used only as a guideline for initial conditions for treating copper complex removal using ferritization. The specific characteristics of each type of wastewater will depend on source of generation, requiring case-by-case investigation.

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