Polynomial Regression Analysis for the Removal of Heavy Metal Mixtures in Coagulation/Flocculation of Electroplating Wastewater

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Abstract: *Wastewater produced from the electroplating industry generally consists of heavy metal mixture and organic materials that need to be treated before it can be discharged to the environment. Thus, the present investigation was focused on the selective removal of heavy metal mixtures that consist of Copper (Cu), Cadmium (Cd), and Zinc (Zn). Several operating conditions, including the effect of pH and coagulant ($FeCl_3$) dosage, were varied to find the best performance of heavy metal removal. Results showed that the efficiency of heavy metals removal for 2 types of wastewaters were both approximately 99%. The experimental data on the treatment of synthetic wastewater was plotted using polynomial regression (PR) via Excel software. The value of the adjusted R^2 obtained for the final concentration of Cu, Zn, and Cd after treatment were 0.6884, 0.9676, and 0.9283, respectively, which showed that the data were acceptably fitted for Cu and very well fitted for Zn and Cd. The coagulation/flocculation process performed on actual wastewater showed that the lowest final concentration of Cu, Zn, and Cd after treatment were 0.487, 1.232, and 0 mg/L respectively, at pH 12.*

Keywords: *hydroxide precipitation; metal removal; coagulation-flocculation; electroplating wastewater; polynomial regression*

INTRODUCTION

The fast emergence of urbanization and the development of industrial sectors, including metal coating manufacturing and electroplating industries, have led to environmental degradation in terms of industrial pollution. Wastewater produced from these industrial activities may consist of a variety of toxic substances, hence, becoming major environmental concerns if it is not properly treated [1-5]. The subsequent water from the acid pickling process, alkaline cleaning, plating, and rinsing activities are discharged in large quantities as wastewater, which contains heavy metals at high concentrations [6-7]. The metallic ions discharged from industries will remain suspended in water for an extended time [8]. The most common toxic heavy metals that are of concern in the treatment of industrial wastewater are zinc (Zn), copper (Cu), mercury (Hg), nickel (Ni), cadmium (Cd), lead (Pb), and chromium (Cr) [9-14]. These heavy metals are toxic to the environment and may cause illness if consumed even at low concentrations. Each of these heavy metals is known to have significant effects on the health of individuals as well as impacts on the neurological system, and some of them are even carcinogenic [15]. The consequences are also severe to the aquatic ecosystem, even at low concentrations, because heavy metals are not degradable and will remain in the water for a long period of time [16-17]. Industries are facing challenges in treating their wastewater as the Department of Environment (DOE) is stringent on discharge concentration of heavy metals in wastewater via regulation, namely the Environmental Quality (Industrial Effluents) Regulation 2009 under the Environmental Quality Act (EQA) 1974 [18].

The nature of wastewater is a crucial consideration in suggesting the suitable treatment method for heavy metal removal from wastewater [13]. Researchers have explored several treatment technologies to remove heavy metals from industrial wastewater. These treatment approaches can be classified into three main categories: physical, chemical, and biological treatment, which includes adsorption [19-20], membrane filtration [21-22], ion exchange [23], coagulation-flocculation [24], up-flow anaerobic sludge blanket (UASB) [25], and electrochemical treatment technologies [26-28].

Hydroxide precipitation is a common method used for chemical precipitation [29]. Hydroxide precipitation is a process of removal of soluble metal ions from solution in the form of metal hydroxide precipitate. Metal hydroxide is formed when hydroxide ion (OH^-) bonds to the metal ion (Me^{2+}) in the solution at a specific pH. The reaction involved in hydroxide precipitation is [30]:

$$Me^{2+} + 2OH^- \rightleftharpoons Me(OH)_2 \quad (1)$$

The optimum pH for metal precipitation is selected at a minimum solubility concentration of the heavy metals [31-32]. Generally, metals such as Ag, Cd, Cu, Ni, Pb, and Zn are soluble in acidic conditions, but their solubility decrease towards alkaline pH. The optimum pH at minimum solubility is different for each of the heavy metals.

The coagulation/flocculation process was typically performed along with metal precipitation to enhance the destabilization of the suspended solid and enable the co-precipitation of heavy metals to create larger agglomerates or flocs. Thus, additional chemicals including ferric chloride ($FeCl_3$) or alum (PAC) as coagulants and surface charged polymers such as polyacrylamide (PAM) as flocculants are required to initiate the sedimentation of sludge containing heavy metals [33]. In coagulation/flocculation treatment, a coagulant is mainly used to destabilize colloids and form micro flocs, while flocculants function as a bridging agent for the micro flocs to form bigger flocs, dense enough to be able to settle in the sedimentation process [13,34]. This treatment process was found to be cost-efficient, easy to operate, and requires less energy compared to other treatment methods [35-36].

Recent studies mainly focus on single metal removal from synthetic wastewater via the coagulation/flocculation process. Results showed that an excellent removal rate was achieved via this treatment method [37]. However, actual wastewater typically consists of multi-metals. Since the optimum pH at minimum solubility is different for each of the heavy metals [38], it is a challenge to determine the optimum pH for the metal precipitation process. Several researchers have worked on the removal of heavy metal mixture from wastewater by metal precipitation [39]. Generally, the actual wastewater is substantially challenging to treat since the heavy metal content in the waste usually fluctuates as the industrial processes are being altered [40]. Therefore, some significant controls are necessary for the treatment process to achieve maximum removal of heavy metals.

Statistical analysis approaches such as polynomial regression (PR) can predict the effectiveness of a treatment process through mathematical equations [41]. These equations can generate the expected value of response in regards to the interrelated data of the treatment parameter [41-42]. This method has been implemented mostly in the chemical industries and other fields such as physics, engineering, biology [42]. Therefore, a statistical analysis study is important to verify the significant factor that influences the treatment of heavy metal mixture in actual wastewater. The optimization of the coagulation-flocculation process can be initiated by polynomial regression. By implementing statistical analysis, the time consumed on experimental work can be reduced, improving the cost of operation. Optimum conditions can be achieved after simulating the relationship between parameters such as initial pH of wastewater, initial heavy metal concentration, coagulant dosage, alkaline dosage, and flocculant dosage.

A study on synthetic wastewater is introduced to analyze the effect of parameters without the presence of any interference substance that can affect the statistical analysis. This study was performed to evaluate the performance of heavy metal mixture removal using hydroxide precipitation with co-precipitation via the coagulation/flocculation treatment process. The treatment was performed for synthetic wastewater and actual wastewater. The synthetic wastewater was an imitation of wastewater from electroplating industries, which consists of heavy metal mixtures of Cu, Zn, and Cd. The parameter studies involved were the effect of metal concentration, operating pH, and coagulant dosage on the performance of multi-metals removal. Polynomial regression (PR) analysis via Excel Software was used to analyze and verify the relationship between the percentage of metal removal response with parameters studied for the treatment of synthetic wastewater. The predicted results obtained from PR analysis were compared with the treatment of actual wastewater to evaluate the reliability of the mathematical expression in predicting the removal of heavy metals from wastewater.

■ EXPERIMENTAL SECTION

Materials

The actual wastewater was collected from the raw wastewater of the electroplating industry. The synthetic wastewater was prepared from metal salts such as Cadmium(II) Nitrate Tetrahydrate ($CdN_2O_6·4H_2O$), Copper(II) Nitrate Trihydrate ($CuN_2O_6·3H_2O$), and Zinc(II) Nitrate Hexahydrate ($ZnN_2O_6·6H_2O$) purchased from Sigma Aldrich, Malaysia. The other reagents used were the industrial grade of Ferric Chloride ($FeCl_3$), Polyacrylamide (PAM), Sodium Hydroxide (NaOH), and Sulfuric Acid (H_2SO_4).

Instrumentation

The metal concentration was analyzed using Furnace Atomic Absorption Spectroscopy (Model HITACHI Z-2000). The percentage of the removal of heavy metals (%R) can be calculated by using the equation:

$$\%R = \frac{(C_0 - C_f)}{C_0} \times 100\% \qquad (2)$$

where C_0 is the initial concentration of heavy metal and C_f is the final concentration of heavy metal after treatment.

Procedure

Sample collection and characterization

The characterization of actual wastewater was collected at two different interval dates to determine the fluctuation of heavy metals in actual wastewater. Then, these samples were characterized for the heavy metal concentration, specifically focused on Cu, Zn, and Cd. The pH condition of both samples of actual wastewater was also checked simultaneously.

Preparation of synthetic wastewater

Characterization results from actual wastewater were the basis for the preparation of synthetic wastewater. The synthetic wastewater containing Cu, Zn, and Cd were prepared by dissolving the respective heavy metal salts, namely cadmium(II) nitrate tetrahydrate ($CdN_2O_6·4H_2O$), copper(II) nitrate trihydrate ($CuN_2O_6·3H_2O$), and zinc(II) nitrate hexahydrate ($ZnN_2O_6·6H_2O$) in deionized water. The pH and metals concentration were prepared based on results obtained from the characterization of actual wastewater.

Jar test

The jar test experiments were carried out at room temperature. The initial pH was adjusted by using H_2SO_4. The jar test was set at 120 rpm and 5 min for rapid mixing; 60 rpm and 15 min for slow mixing. The hydroxide precipitation was conducted by adjusting operating pH via the addition of NaOH in the range of 8 to 12 with an interval of 0.5. Next, the coagulation process was done by adding $FeCl_3$ coagulant into the solution until pH 8 was obtained. Both the hydroxide precipitation and coagulation process were performed under rapid mixing. For the flocculation process, PAM at a concentration of 40 mg/L was added into the solution under slow mixing to promote the formation of larger flocs. Residual metal concentration was determined after settling for 40 to 60 min. Fig. 1 presents a flowchart of the treatment process.

The jar test experiments were conducted for synthetic and actual wastewater. For synthetic wastewater, two sets of samples were prepared according to the characterization results of actual wastewater obtained during sample collection and characterization.

Polynomial regression via excel software

Polynomial regression was performed to analyze and verify the relationship between the final concentration of heavy metals as response and the studied

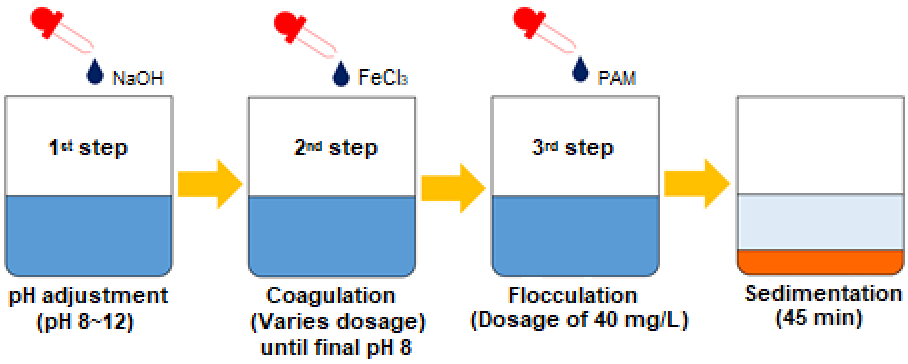

Fig 1. Flowchart of the treatment process

parameter as factor. The factors and responses are listed as follows:

y_1 = Final concentration of Cu (mg/L)
y_2 = Final concentration of Zn (mg/L)
y_3 = Final concentration of Cd (mg/L)
x_1 = Initial concentration of Cu (mg/L)
x_2 = Initial concentration of Zn (mg/L)
x_3 = Initial concentration of Cd (mg/L)
x_4 = pH for hydroxide precipitation
x_5 = volume of $FeCl_3$ (mL)

RESULTS AND DISCUSSION

Characterization of Actual Wastewater

The samples obtained at two different interval dates were labeled as Sample 1 (S1) and Sample 2 (S2). Table 1 presents the characteristics of the actual wastewater for both samples. From this table, the actual wastewater was determined to be acidic and consisted of a high concentration of Cu, followed by Zn and Cd, which exceeded the allowable discharge limit as stipulated in IER2009.

Effect of the pH of Hydroxide Precipitation on Heavy Metals Removal

The removal of Cu, Zn, and Cd from two sets of synthetic wastewater (S1 and S2) via hydroxide precipitation followed by coagulation/flocculation process was conducted by adjusting the pH of the hydroxide precipitation between 8 to 12 through the addition of NaOH and reduced to neutral pH of 7.5 to 8 by addition of $FeCl_3$ as co-precipitator and coagulant. The results are presented in Fig. 2. It is observed that Cu achieved the highest percentage removal, followed by Zn and Cd for both S1 and S2. This is due to the capability of metal mixtures to produce metal hydroxide precipitates at a certain pH. The tendency of a metal to produce precipitate via hydroxide precipitation increase with the decrease of metal solubility concentration. The metal solubility concentration decreased in the sequence of Cu < Zn < Cd as the pH increased from 9 to 10.5 [38]. Therefore, the tendency of Cu to form hydroxide precipitation is higher than Zn and Cd, hence resulting in the highest removal of Cu as compared to Cd and Zn. The removal of metal mixtures for S1 at pH 9 was 99.56% for Cu, 88.58% for Zn, and 99.34% for Cd. As for S2, the Cu removal was 99.34%, followed by Zn (78.60%) and Cd (30.37%).

Theoretically, the solubility concentration of metal hydroxide decreases as pH increases until it achieves its minimum solubility concentration. Further increase of pH will cause the metal hydroxide to resolubilize, hence increase the metal solubility concentration in aqueous

Table 1. Characteristics of actual wastewater

Sample	Initial pH of solution	Initial COD value (mg/L)	Initial TSS Value (mg/L)	Turbidity (mg/L)	Concentration of heavy metal (mg/L)		
					Cu	Zn	Cd
Sample 1 (S1)	1.5	318	9.5	4.8	80	10	1
Sample 2 (S2)	1.5	276	8.2	4.1	40	20	2
Standard B*	5.5–9.0	200	100	-	1.0	2.0	0.02

*Allowable Discharge Limit by DOE [14]

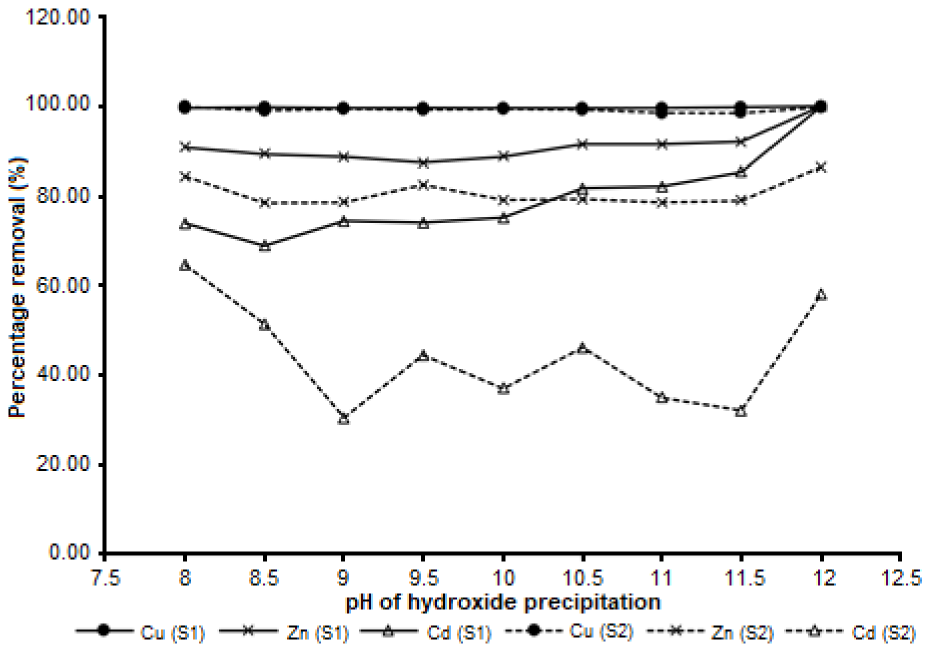

Fig 2. Percentage removal of Cu, Zn, and Cd for S1 and S2

solution. The metal solubility concentration decreased in the sequence of Cd < Cu < Zn as the pH increased from 10.8 to 12 [38]. It is theoretically predicted that Cd would achieve higher removal compared to Cu and Zn at pH between 11 to 12. However, Fig. 2 shows that Cu obtained the highest removal at pH 8 to 12 for both S1 and S2. This finding is resulted from the competitive hydroxide precipitation between Zn and Cd with the hydroxide ion due to the ionization energy factor. The ionization energy of different metals shows different reactiveness that attributable to the removal of an electron from its outer orbital [43]. The reactivity of elements in removing electrons to produce stable compounds increases with the decrease of the first ionization energy. The first ionization energy increase in the sequence of Cu > Cd > Zn at 745, 868, and 906 kJ/mol, respectively [43]. The hydrolysis of Cu, Cd, and Zn in aqueous solution creates competition with hydroxide ions (OH^-) for the precipitation of metal ions at certain pH. Thus, the efficiency of selective metal removal depends on the relative concentration of the anions (OH^-) in the solution and is consequently pH-dependent [44]. In this study, Cu has the lowest ionization energy compared to Cd and Zn; hence tends to form hydroxide precipitate better than Zn and Cd. Also, the concentration of Cu was 80 and 20 times higher than the concentration of Cd for S1 and S2, respectively. The presence of a high concentration of Cu will hinder the Cd ion from reacting with hydroxide ion, hence decreasing the potential for Cd ions to produce $Cd(OH)_2$, even at its optimum pH of hydroxide precipitation. The highest removal of metal mixtures was obtained at pH 12 for both S1 and S2. The removal of Cu, Zn, and Cd was 99.91%, 99.91%, and 99.97%, respectively for S1. For S2, the sequence of metal removal was Cu (99.71%) > Zn (86.45%) > Cd (58.11%). Johnson et al. [45] and Hargreaves et al. [16] observed similar findings where the removal of Cu was higher than Zn by using $FeCl_3$ as the coagulant.

It was also observed that the removal of metal mixture for S1 was higher than S2. This phenomenon is due to the different initial metal concentrations used in the experiments. The concentration ratio for Cu:Zn:Cd was 80:10:1 and 20:10:1 for S1 and S2, respectively. The presence of a high concentration of Cu in S1 required a high amount of NaOH for pH adjustment. This resulted in a higher concentration of hydroxide ion in S1, hence increasing the tendency of more metal ions to form hydroxide precipitate compared to S2.

Fig. 3 presents the comparison of metal concentration after the coagulation/flocculation process

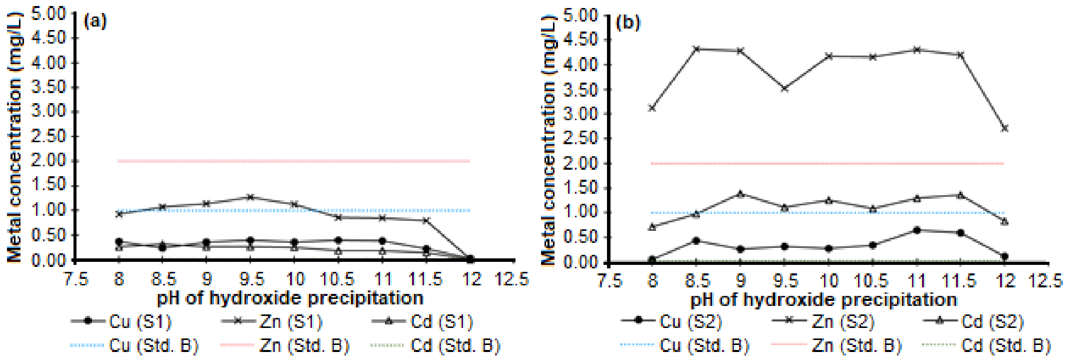

Fig 3. Comparison of metal concentration for (a) S1, and (b) S2 after the coagulation/flocculation process with Standard B of IER 2009

with Standard B of IER 2009 under EQA 1974 for S1 and S2. It can be observed that the concentration of Cu and Zn complied with Standard B. Meanwhile, the Cd concentration only complied at pH 12 for S1. From these findings, it can be concluded that the metal precipitation for multi-metals is influenced by metal solubility concentration and adequate dosing of NaOH to ensure complete hydroxide precipitation of multi-metals in aqueous solution. Therefore, a study on data verification using a mathematical model is useful in predicting the concentration of metals after coagulation/flocculation treatment at various initial metal concentrations.

Polynomial Regression Analysis on Heavy Metals Removal

A polynomial regression analysis via Excel Software was used to analyze and verify the relationship between the final concentration (Cu (y_1), Zn (y_2), and Cd (y_3)) and the parameters studied in this research. The selected parameters were the initial concentration (Cu (x_1), Zn (x_2), and Cd (x_3)), pH for hydroxide precipitation (x_4), and volume of $FeCl_3$ (x_5).

The best mathematical expression obtained for the prediction of the final concentration of metals Cu (y_1), Zn (y_2), and Cd (y_3) can be expressed as:

$$\begin{aligned} y_1 &= (8.620\times10^{-2})x_4^3 - 2.427x_4^2 + 0.139x_5^2 + \\ &(7.549\times10^{-3})x_2^2x_5 - (4.356\times10^{-2})x_4^2x_5 + \\ &(2.843\times10^{-2})x_1x_2x_4 + (4.67\times10^{-3})x_1x_4x_5 - 70.647 \end{aligned} \quad (3)$$

$$\begin{aligned} y_2 &= (2.863\times10^{-2})x_5^3 - (2.85\times10^{-3})x_4^2x_1 - \\ &(7.83\times10^{-3})x_4^2x_2 - (4.885\times10^{-2})x_5^2x_2 + \\ &(6.592\times10^{-3})x_1x_2x_4 + (2.762\times10^{-3})x_1x_2x_5 - 21.681 \end{aligned} \quad (4)$$

$$\begin{aligned} y_3 &= -(2.598\times10^{-4})x_4^2x_1 - (6.829\times10^{-3})x_5^2x_2 + \\ &(3.615\times10^{-4})x_1x_2x_4 + (3.834\times10^{-4})x_1x_4x_5 - 0.698 \end{aligned} \quad (5)$$

The regression statistics and ANOVA for the expression above are presented in Table 2. From this table, it is depicted that for Cu, Zn, and Cd, the significance F, and the P-value reported for intercept and all independent variables are less than 0.05; showing that the results are quite reliable and the variable is statistically significant [46-47]. The adjusted R^2 obtained for Zn and Cd were 0.9676 and 0.9283, respectively, indicating that the data were very well fitted. Meanwhile, for Cu, the obtained adjusted R^2 was 0.6884, which shows that the data were acceptably fit, although it was slightly lower than the adjusted R^2 of Zn and Cd.

It is evident from Eq. (3), (4), and (5) that all independent variables or parameters depend on each other significantly except for the initial concentration of Cd (x_3). The x_3 is also insignificant to the final concentration of Cu (y_1), Zn (y_2), and Cd (y_3). The concentration of Cd used in this study is considered very low; hence Cd does not influence the competitive hydroxide precipitation of multi-metals.

Fig. 4 shows the comparison between the experimental and predicted value of the final concentration of Cu (y_1), Zn (y_2), and Cd (y_3). It is clearly shown that the scatter plots of Zn and Cd are denser at around the 45-degree lines which indicates that the experimental data were close to the predicted value calculated from the mathematical expression. Meanwhile, several Cu scatter plots are distant from the

Table 2. Regression statistics and ANOVA for the percentage of the final concentration of Cu, Zn, and Cd

Regression statistics and ANOVA			
	Cu	Zn	Cd
Multiple R	0.9037	0.9895	0.9722
R Square	0.8167	0.9790	0.9452
Adjusted R Square	0.6884	0.9676	0.9283
Standard Error	0.0896	0.2889	0.1337
Observations	18	18	18
Significance F	0.0048	1.383×10^{-8}	4.5271×10^{-8}
P-value for intercept	0.0275	0.0376	0.039
P-value for x_5^3	-	0.0190	-
P-value for x_4^3	0.0213	-	-
P-value for x_4^2	0.0234	-	-
P-value for x_5^2	0.0052	-	-
P-value for $x_2^2x_5$	0.0470	-	-
P-value for $x_4^2x_5$	0.0233	-	-
P-value for $x_4^2x_1$	-	0.0092	2.9590×10^{-8}
P-value for $x_4^2x_2$	-	0.0459	-
P-value for $x_5^2x_2$	-	0.0005	0.0061
P-value for $x_1x_2x_4$	0.0254	0.02179	1.0774×10^{-6}
P-value for $x_1x_2x_5$	-	0.0076	-
P-value for $x_1x_4x_5$	0.0371	-	0.0117

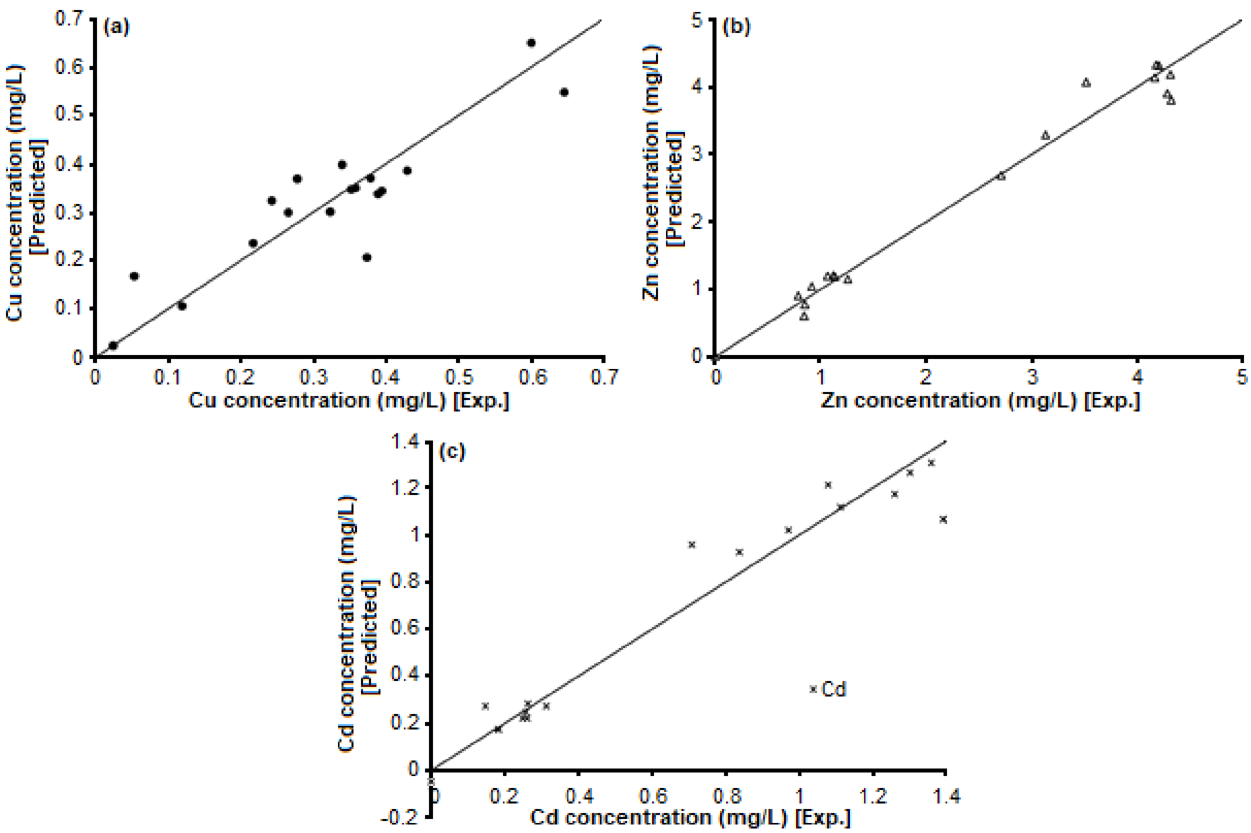

Fig 4. Comparison between the experimental and predicted value of the final concentration of (a) Cu, (b) Zn, and (c) Cd

Table 3. Results of the heavy metal mixture before and after treatment for actual wastewater

pH of hydroxide precipitation	Volume of $FeCl_3$ (mL)	Initial metal concentration (mg/L)			Final metal concentration (mg/L)		
		Cu	Zn	Cd	Cu	Zn	Cd
9.50	0.07	78.89	10.23	0.89	1.06	1.85	0.28
10.00	0.07	78.89	10.23	0.89	1.17	1.36	0.18
10.50	0.16	78.89	10.23	0.89	0.96	1.13	0.18
11.00	0.67	78.89	10.23	0.89	0.87	1.15	0
11.50	1.29	78.89	10.23	0.89	0.61	1.26	0
12.00	3.43	78.89	10.23	0.89	0.49	1.23	0

45-degree line, which is in agreement with the results of adjusted R^2 obtained in Table 2.

Treatment of Actual Wastewater from the Electroplating Industry

The treatment of actual wastewater from the electroplating industry was experimentally conducted via coagulation/flocculation method, while Eq. (3), (4), and (5) were used to predict the final concentration of Cu, Zn, and Cd for this treatment. Results for the final concentration of multi-metals obtained after treatment (Table 3) were compared with the predicted value and presented in Fig. 5. It is noticeable from this figure that the final concentration of multi-metals decreased with the increase of pH for hydroxide precipitation. The lowest final concentration of Cu, Zn, and Cd after treatment was 0.487, 1.232, and 0 mg/L respectively at hydroxide precipitation pH of 12, which complied with Standard B, of IER 2009. This finding is in good agreement with results obtained for coagulation/flocculation of synthetic wastewater. It is also evident from this finding that the presence of organic and other constituents in the actual wastewater does not influence the efficiency of the coagulation/flocculation process in multi metals removal. It is also observed from Fig. 5 that most of the final concentrations of Zn and Cd obtained from the predicted value were almost similar with error distribution between 2% to 19%, except for Cd at pH 11 to 12, whereby Cd was completely removed at this condition. Most of the final concentrations of the multi-metals obtained from the experiments were found to be lower than the predicted value, especially for Cu. Therefore, it can be concluded that the mathematical expression of Eq. (3), (4), and (5) are useful in predicting the final concentration of multi-metals for the coagulation/flocculation process.

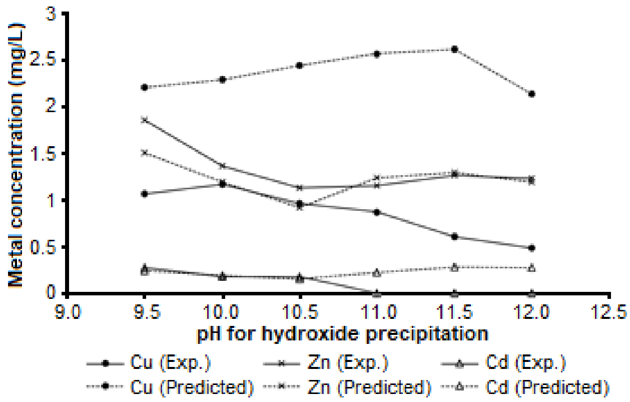

Fig 5. Final concentration of Cu, Zn, and Cd obtained from experiments and the predicted value for coagulation/flocculation treatment of actual wastewater

■ CONCLUSION

The removal of synthetic multi-metals that consisted of Cu, Zn, and Cd was investigated in this study via coagulation/flocculation method using NaOH as the source of (OH^-) ions and $FeCl_3$ as the coagulant or co-precipitator. This method was found to be significantly capable of removing up to 100% of the multi-metals concentration in aqueous solution to meet the requirement as stipulated in the Environmental Quality (Industrial Effluent) Regulation (IER) 2009 under Environmental Quality Act (EQA) 1974. The highest removal achieved for S1 was 99.75% of Cu, 99.91 of Zn, and 99.98% of Cd, while 99.71% of Cu, 86.45% of Zn, and 58.11% of Cd removal were obtained for S2 at hydroxide precipitation pH of 12. The final concentration of Cu, Zn, and Cd after coagulation/flocculation treatment were verified in this study by using polynomial regression (PR) via Excel software. It was proven from the ANOVA analysis that the data were acceptably fitted for Cu and very well fitted for Zn and Cd. The significance F and probability value obtained for all variables were less than 0.05, which proved that the mathematical expression obtained from polynomial regression could be used to predict the final concentration of Cu, Zn, and Cd obtained after coagulation/flocculation treatment. The actual wastewater was successfully treated via the coagulation/flocculation method. The lowest final concentration of Cu, Zn, and Cd was0.487, 1.232, and 0 mg/L respectively, at hydroxide precipitation pH of 12, which complied with Standard B, of IER 2009. The mathematical expression obtained from PR was proven to be useful in predicting the final concentration of multi-metals for the coagulation/flocculation process. Future works may focus on the optimization of hydroxide precipitation on the operating cost of the treatment process, including the disposal of sludge produced from treatment.

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