Removal of Heavy Metal Mixtures from Wastewater of Electroplating Industry.

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Abstract— ***Heavy metals from wastewater of electroplating industry have caused major hindrance to inland water pollution. Heavy metals are currently removed by the coagulation-flocculation process. This method had been chosen due to low operational cost and high removal efficiency. The present investigations mainly focused on single element treatment. However, in the actual wastewater, there were complexes of multi-metals present. Therefore, the research work is focused on removal multi-metals which included Copper (Cu), Cadmium (Cd), and Zinc (Zn) from two different characteristic of synthetic wastewaters which prepared according to the actual characteristic of wastewater from electroplating industries. Jar test was conducted by using two different methods known as Method A and Method B. The parameters of the study were initial pH adjustment and Ferric Chloride ($FeCl_3$) dosage. Results shows the optimum removal condition obtained from Method A for both wastewaters type I and type II is at pH 10 of pH adjustment and $FeCl_3$ dosage of 140 mg/L and 100 mg/L respectively. The efficiency of heavy metals removal for both wastewater characteristics were approximately 99%. The selected data obtained were fitted using multilinear regression via Microsoft Excel. The regression analysis shows adjusted R^2 obtained for all metals from wastewater type I are above 90% which indicate the best fitting data. The ANOVA analysis proved that the mathematical expression can be used to predict the removal of multi-metals from wastewater solution.***

Keywords— Heavy metals; hydroxide precipitation; coagulation-flocculation; wastewater; multilinear regression; electroplating.

I. INTRODUCTION

Water contaminations and inadequate sources of clean water are becoming major environmental adversity which is caused by the demolition of natural inland water. With the fast emergence of urbanization and industrial sectors, for instance, metal coating manufacturing, manure production industries, paper industries, textiles, and others have indicated a variety of toxic substances released to the environment which can cause severe complication later on [1-2]. The trace of metal elements normally carried away by rivers and shifted to the coastal marine system through bays. The common toxic heavy metals of particular concern in the treatment of industrial wastewater are zinc (Zn), copper (Cu), mercury (Hg), nickel (Ni), cadmium (Cd), lead (Pb) and chromium (Cr). Heavy metal species such as Cr, Ni, and Zn normally discharged in wastewater from the source of wastewater in automobile coating industry [3]. In the manufacturing of mirror, silver (Ag) is used as a coating material and subsequent residual majorly discharged in drained spray solution which later causes emission [4]. Cd commonly found in battery processing industries, stabilizers, and alloy industries [5]. Meanwhile, Cr usually generated from latter industries, tanning and electroplating industries [5-6]. Plating industries mostly implemented metal to a surface of a material through the electroplating process to make it corrosion resistance [7]. Most of the elements used in the electroplating process were including brass, Zn, Ag, gold (Au), Ni, Cu, iron (Fe), aluminium (Al), Pb, tin (Sn), platinum (Pt) and Cr as plating material [8–10]. The subsequent water from acid pickling process, alkaline cleaning, plating, and rinsing activities discharged as wastewater in large quantities which contain heavy metals at high concentration [7, 11]. All the heavy metals listed are toxic to environment which resulting in illness if consumed even at low concentration. Each of the heavy metals lead to significant effects to the healthiness of individual as well as impact to neurological system and some of them even carcinogenic [12].

There is a condition where the metallic ions discharged from industries or other sources which will remain suspended in water for an extended of time [13]. Due to the existence of resistance properties of the heavy metals, researchers have suggested alternative solutions for the removal of heavy metals [6]. Different nature of wastewater required an evaluation in order to eliminate the heavy metals inside the solution [6]. The treatment approach can be classified into three categories mainly physical, chemical and biological treatment including adsorption, membrane filtration, ion exchange, chemical precipitation, electrochemical treatment technologies, and others [5]. Nowadays, researchers were obligated on heavy metals removal from waste effluent because even at low concentration, the consequences are severe to aquatic living and environment due to no degradation occurs over a period of time [14].

Hydroxide precipitation is a common method used for metal precipitation [15]. Hydroxide precipitation is a process of removal of soluble metal ions from solution and forms metal hydroxide precipitates. Metal hydroxides are formed when a hydroxide ion (OH^-) bonds to the metal ion in the solution. The operating pH of treatment process affecting the solubility of metals since most of them was soluble in acidic condition. Based on Fig. 1, the solubility of heavy metals such as Ag, Cd, Cu, Ni, Pb, and Zn decreases toward alkaline pH [16]. The solubility of Cu and Zn increase in acidic solutions due to increment formation of Cu^{2+} and Zn^{2+} ions [17]. Meanwhile, in alkaline solution, these two metals tend to form insoluble copper hydroxide ($Cu(OH)_2$) and zinc hydroxide ($Zn(OH)_2$) precipitates.

The ionization energy of different metals shows different reactiveness which can be related to removal of electron from its orbital [18]. The lowest the first ionization energy, the reactive the element to remove electron to produce stable compound. The

hydrolysis of Cu, Cd, and Zn in aqueous solution creates competition between hydroxide for the precipitating metal ions. The first ionization energy increasing in the sequence of Cu>Cd>Zn at 745 kJ/mol, 868 kJ/mol and 906 kJ/mol respectively [18]. Thus, the efficiency of selective metal removal depends on the relative concentration of the anions in solution and is consequently pH dependent [19]. The decrement in pH or hydroxide ions in the solution cause the metals to become more soluble in water. However, there are certain limitations toward the application of hydroxide precipitation in wastewater treatment due to amphoteric properties of heavy metals. The amphoteric properties of heavy metals can cause problem when the treatment is run at one optimum pH condition of one metal. This condition may put another metal back into solution. The metal precipitation also cannot be formed when the pH of the wastewater undergoes pH alteration due to the fluctuation of wastewater sources.

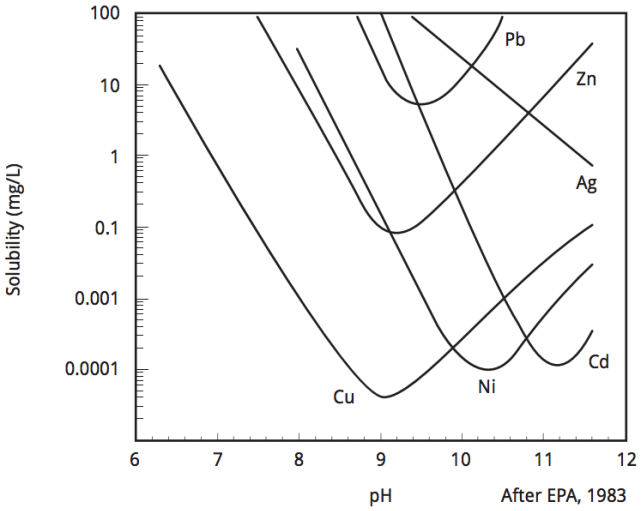

Fig 1. Graph of Theoretical Solubility of Metal Precipitation vs pH *(Source :* American Public Health Association, American Water Works Association, 2014 [16]*)*

Coagulation-flocculation was typically performed along with metal precipitation by help to destabilizes suspended solid containing heavy metals to create larger agglomerates. Thus, an additional chemical such as coagulants including ferric chloride ($FeCl_3$) or alum (PAC) and also surface charges polymer such as polyacrylamide (PAM) to initiate the sedimentation of sludge containing heavy metals [20]. Therefore, it became most popular method for wastewater treatment [21]. In coagulation-flocculation treatment, coagulant mainly used for separation of small molecules or suspended solid contents from solution by destabilizing the particles bond between water [22,6]. This treatment process was found to be efficient in cost saving, easy operational, and require less energy compared to other treatment method [23].

Recently, a number of studies have been reported in the literature in the usage of single metal solutions as wastewater in coagulation-flocculation process. This is because single metal solution can be easily treated at an optimum condition without having to consider the presence of other elements. Therefore, the highest removal rate was achieved in this method [24]. Some researchers conduct research on multi-metals solution as wastewater in order to evaluate the potential of heavy metals removal by metal precipitation [25]. In previous studies, actual wastewater generally used and only a few utilized the synthetic or modeled wastewater for their treatment process. This is because the actual wastewater was considered complex to treat since the heavy metals content in the water usually fluctuate as the industrial processes have been altered [26]. Therefore, some significant controls are necessary in the treatment process in order to achieve maximum removal of heavy metals.

Multiple linear regression is a statistical method which is used to prove the reliability of treatment process by generate mathematical equation that relates to the expected value of a response. This method has been implemented mostly in chemical industry, and also in another fields such as physical, engineering, biological and others [27]. Optimization of coagulation-flocculation process can be initiated by multiple linear regression. This can reduce the time consumed on experimental work, cost of operation, as well as capable to achieve optimum condition after simulate the relationship between parameters including initial pH of wastewater, coagulant dosage, flocculant dosage and others.

The objective of this research is to carry out the experimental study of parameters affecting the multi-metals removal from two types of synthetic wastewater characteristic which imitated the actual wastewater with mainly combination of metals Cu, Cd, and Zn. Jar test was conducted by coagulation-flocculation process which consisting of two method known as Method A and Method B. The parameters in this study were effect of initial pH of wastewater, and effect of coagulant dosage on performance of multi metals removal. Then, this study was to perform a multiple linear regression to develop a mathematical model to indicate the removal process as well as to compare the effectiveness of each treatment method for heavy metals removal.

METHODOLOGY

A. Materials

The materials used in this research were actual wastewater collected from electroplating company at Industrial Area, Selangor. 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 ($ZnN_2O_6.6H_2O$) which were purchased from SIGMA-Aldrich Malaysia. The other reagents used were industrial grade $FeCl_3$, PAM, 7.5% Sodium Hydroxide (NaOH), and 4% Sulfuric Acid (H_2SO_4).

B. Analysis Instruments

The instruments used to characterize pH of wastewater in this study was Handheld Water Resistance pH Meter (HANNA HI-8424). To characterize concentration of heavy metals inside wastewater, Furnace Atomic Absorption Spectroscopy, AAS (HITACHI Z-2000) was used. A Jar Test Flocculator (Stuart SW6) was used to run jar test experiment.

C. Experimental Procedure

Industrial wastewater sampling and characterization

10 L the actual wastewater collected from source of discharged at electroplating company. Then, the wastewater was characterized for pH and metal content in the solution.

Synthetic modeled wastewater preparation

The preparation of synthetic wastewater was conducted by dissolving laboratory standard heavy metal salts powder that are soluble in water. The solution concentration for each heavy metals

was prepared based on results obtained from characterization of actual wastewater obtained from electroplating industry. Each metal salts were measured according to formulation to imitate the concentration of actual wastewater. The measured salts powder was diluted with distilled water in a 2 L of volumetric flask. The prepared wastewater model was characterized for pH and metal concentration.

Jar Test Experiment

i. Method A

The coagulation-flocculation jar test experiments were carried out on the synthetic modeled wastewater at room temperature at constant volume of 200 mL in each beaker. To imitate the pH of actual wastewater, 2200 mg/L of H_2SO_4 is used for each beaker until the pH of modeled wastewater is similar to the actual wastewater (pH 1.5). The flocculator or was automatically set to two different agitation speed which were 120 rpm for rapid mixing and 60 rpm for slow mixing. In the first parameter, the coagulation and hydroxide precipitation process was conducted by adjusting the initial pH of wastewater of range between 7 to 12 with interval of 0.5. The process was stirred at rapid mixing mode. The selection of pH was based on minimum solubility of each metal at certain pH [15]. The dosage of $FeCl_3$ was kept constant for each different pH at 200 mg/L. The final pH of treated water was adjusted to pH 8 with additional of NaOH or H_2SO_4. Then, for flocculation process, a constant volume of PAM added to each beaker at 40 mg/L and conducted at slow mixing mode. The sedimentation process was set to 45 minutes for each beaker before the supernatant treated water was characterized for metals removal by AAS. The optimum pH can be obtained from the lowest solubility of each metals in the solution after treatment process. In second parameter, the coagulation and hydroxide precipitation was operated at similar manner to first parameter. However, the dosage of $FeCl_3$ was differ between 20 mg/L to 200 mg/L. The pH of wastewater treatment was kept constant based on optimum condition obtained from experiment in first parameter. The sequence of process for Method A is shown in Fig. 2 below.

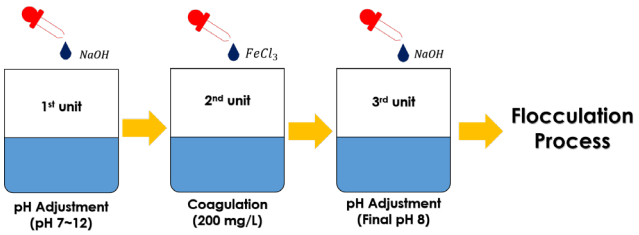

Fig 2. Flowchart of Treatment Process for Method A

ii. Method B

Next, the experiment was conducted based on industrial method which simultaneously run both parameters of initial pH of wastewater and also coagulant dose. The coagulant in this method is used to coagulate the microflocs form from pH adjustment process as well as to adjust the pH to pH 8. The similar flocculator operating condition used as the Method A. The PAM dosage was kept constant at 40 mg/L. Then, supernatant was collected for analysis of remaining concentration of metals by AAS. The flowchart of treatment process for Method B is illustrated in Fig. 3 below.

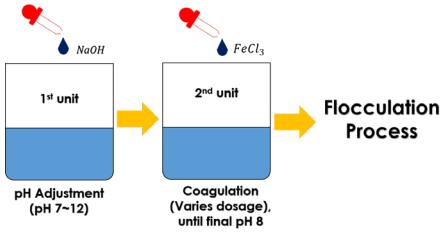

Fig 3. Flowchart of Treatment Process for Method B

Statistical analysis of metals removal by multiple linear regression

Multiple linear regression is carried out to develop a regression model by considering the data from the jar test experiment. Choosing independent and dependent variables in a multiple linear model by using waste water factor. Removal percentage of Cu, Cd and Zn was chosen as dependent variable. Meanwhile, the dosage of NaOH and $FeCl_3$ were chosen as independent variables. The general equation proposed for multilinear regression modelling was formulated as follows,

$$Y = aX_1 + bX_2 + cX_1X_2 + dX_1{}^2 + eX_2{}^2 + fX_1{}^2X_2 + gX_2{}^2X_1 \quad \textbf{(1)}$$

Where Y = Metal Removal Percentage (%), X_1, X_2 were NaOH dosage and $FeCl_3$ dosage.

II. RESULTS AND DISCUSSION

A. Characterization of Wastewater and Synthetic Wastewater Preparation

The characterization of effluent from the electroplating industry is carried out according to Standard Methods for the Examination of Water and Wastewater [16]. The modeled wastewater is prepared with the same initial metals concentration of actual wastewater to imitate the real condition before being treated by the coagulation-flocculation process. Based on Table 1, the concentration of Cu, Cd, and Zn of the modeled wastewater to be imitated according to characterization of actual wastewater were 80 mg/L, 10 mg/L and 1 mg/L respectively.

Table 1. Characteristic of Modelled Wastewater Type I

Type of Heavy Metals	Initial Concentration of Actual Wastewater (mg/L)	Standard B Allowable Discharge Limit by DOE (mg/L)
Copper	80	1.00
Zinc	10	2.00
Cadmium	1	0.02

Initial pH of wastewater = 1.5

Based on Table 2, the concentration of heavy metals inside wastewater was altered which to compared the effectiveness of heavy metals removal by previous treatment process. The Cu, Cd and Zn were altered to 40 mg/L, 20 mg/L and 2 mg/L respectively.

Table 2. Characteristic of Modelled Wastewater Type II

Type of Heavy Metals	Initial Concentration of Actual Wastewater	Standard B Allowable Discharge Limit by DOE

	(mg/L)	(mg/L)
Copper	40	1.00
Zinc	20	2.00
Cadmium	2	0.02

Initial pH of wastewater = 1.5

B. Effect of Initial pH of wastewater on heavy metals removal

The efficiency of multi-metals removal from modeled wastewater significantly affected by the pH of the solution. By varying the pH solution during pH adjustment process between pH 8 until pH 12 with an interval of 0.5 and at constant coagulant dosage of 200 mg/L and constant flocculant dosage of 40 mg/L, the graph of final multi-metals concentration is plotted against pH of wastewater as well as the percent multi-metals removal against pH of the wastewater. Then, the optimum pH of modeled wastewater for removal of multi-metals was obtained.

Fig. 4 shows the effect of the initial pH of wastewater on the removal of three different metals which were Cu, Cd, and Zn in the coagulation-flocculation process from wastewater type I. Based on Fig. 4, as the pH of wastewater solution increased from pH 8.0 to pH 10.0, the removal of multi-metals increased and the final concentration of multi-metals decreases toward minimum concentration. Based on Fig. 1, the lowest solubilities of Cu is at pH 9.0, Zn at pH 9.2, and Cd at pH 11.2. The lower the solubility the highest the $Cu(OH)_2$, $Zn(OH)_2$ and $Cd(OH)_2$ formed. However, in this treatment process, as the pH of wastewater increased more to pH 12.0, the multi-metals removal efficiency is decreased. The deionization of metal ions did take place at pH increased to 12, but the solubility of each metal inside water increase. This is because hydroxide precipitation can no longer eliminate the metals ion by forming precipitates due to competition between each metals ions and the other ions present in the water [19]. The final concentration of Cu, Cd, and Zn at maximum removal efficiency are 0.0450 mg/L, 0.0052 mg/L and 0.0014 mg/L respectively. It is shown that the optimum pH for wastewater treatment is at pH 10.0 due to maximum removal of heavy metals. The percent removal was 99.93 %, 99.38%, and 99.98% respectively.

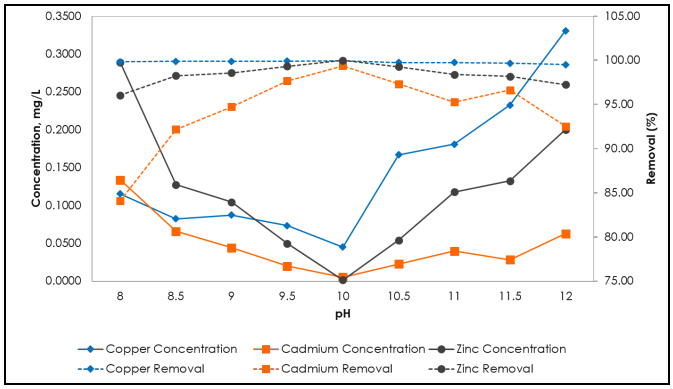

Fig 4. Effect of Initial pH of Wastewater on Heavy Metals Removal (Method A for Wastewater Type I)

Fig. 5 shows the effect of initial pH of wastewater on heavy metals removal for wastewater type II. Based on Fig. 5, as the pH of wastewater increased from pH 8.0 to 10, the removal of heavy metals approaching maximum removal. However, when the pH increased more toward pH 12.0, the concentration of heavy metals inside the wastewater increase. This is because, the solubility of each metals depending on the different optimum condition of metals (Cu = pH 9.0, Cd = pH 11.2, Zn = pH 9.2). Since there were multi-metals presence in the wastewater solution, the competition between metals ion take place in order to ionized with (OH^-) presence to produce metal hydroxide salt precipitation. The optimum condition in the experiment 2 was at pH 10.0. The final concentration of Cu, Cd and Zn were 0.0401 mg/L, 0.0000 mg/L and 0.0044 mg/L respectively. These values give removal percentage of 99.90%, 100.00% and 99.97% respectively

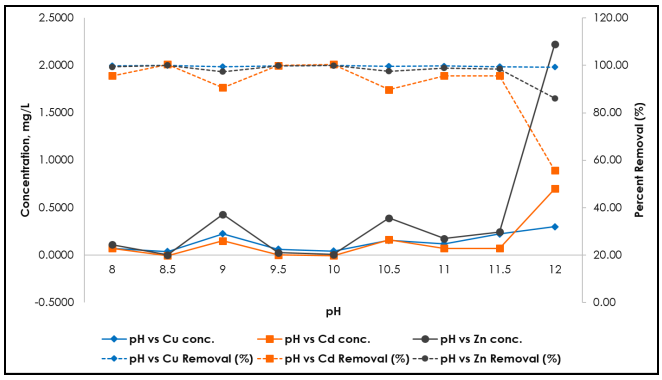

Fig 5. Effect of Initial pH of Wastewater on Heavy Metals Removal (Method A for Wastewater Type II)

C. Effect of coagulant dosage on heavy metals removal

The efficiency of multi-metals removal from modeled wastewater significantly affected by a dosage of coagulant into the wastewater. By varying the coagulant dose between 20 mg/L until 200 mg/L with interval of 20 mg/L and at constant optimum pH of 10.0 and constant flocculant dosage of 40 mg/L, the graph of final multi-metals concentration is plotted against pH of wastewater as well as the percent multi-metals removal against coagulant dose into the wastewater. Then, the optimum coagulant dose for maximum removal of multi-metals was obtained.

Fig. 6 shows the effect of the $FeCl_3$ dosage on the wastewater type I on the removal of three different metals in the coagulation-flocculation process. Based on Fig. 6, as coagulant dosage increased from 20 mg/L to 200 mg/L, the removal of multi-metals increased. The final concentration of multi-metals decreases toward minimum concentration. The trend shows the increment of coagulant dosage at a certain amount can enhance the removal of heavy metals inside the wastewater. However, as the coagulant dosage was low, the efficiency of heavy metals removal decrease as the pH of wastewater still at alkaline condition due to the hydroxide group present in wastewater. The alteration of pH by NaOH can cause the metals inside the water to ionized into metals ions which were considered stable in water. These metals ions considered hard to eliminate by a little amount of $FeCl_3$ dose. Therefore, the solubility of the metals inside the water increases at this point. It is shown that the optimum coagulant dose for wastewater treatment is at 140 mg/L. The final concentration of Cu, Cd, and Zn at maximum removal efficiency are 0.0073 mg/L, 0.0023 mg/L and 0.0077 mg/L respectively. Meanwhile, the removal percentage was 99.99%, 99.73%, and 99.89% respectively.

Fig. 7 shows the effect of $FeCl_3$ dosage on heavy metals removal from wastewater type II. Based on Fig. 7, the effectiveness of heavy metals removal increases as the dosage of $FeCl_3$ from 20 mg/L to 200 mg/L. It is shown that the optimum coagulant dose for wastewater treatment is at 100 mg/L. The final concentration of Cu, Cd, and Zn at 100 mg/L $FeCl_3$ are 0.0510 mg/L, 0.0198 mg/L and 0.0494 mg/L respectively. Meanwhile, the removal percentage

was 99.87%, 98.74%, and 99.69% respectively. Although the heavy metals removal at 140 mg/L of $FeCl_3$ approaching 100.00%, the dosage of chemical is considered costly since 100 mg/L of $FeCl_3$ can already remove the heavy metals go beyond the permissible standard limit set by Deparment of Environment Malaysia (DOE).

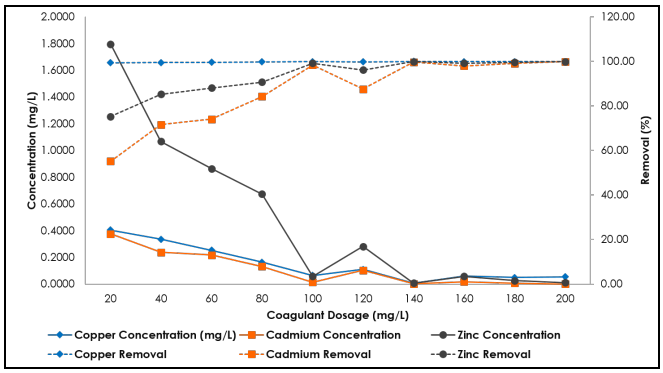

Fig 6. Effect of Coagulant Dosage on Heavy Metals Removal (Method A for Wastewater Type I)

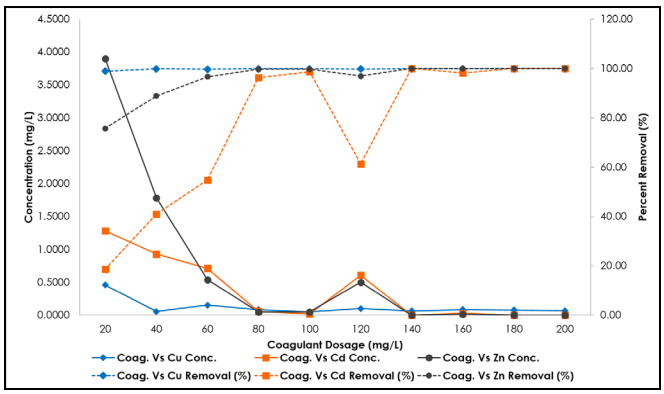

Fig 7. Effect of Coagulant Dosage on Heavy Metals Removal (Method A for Wastewater Type II)

D. Effect of both initial pH adjustment and Coagulant Dosage on heavy metals removal

Treatment process by Method B was conducted by adjusting initial pH to a range between 8 to 12 by addition of NaOH and reduced to neutral pH of 7.5 to 8 by addition of $FeCl_3$. Based on Fig. 8, the removal of heavy metals increased as initial pH of wastewater type I increase. The dosage of $FeCl_3$ gradually increase parallel to these increment. The concentration of metal ions cause competition to the hydroxide ions to precipitate them into metal hydroxides. Therefore, the rate of ionization of metals inside the wastewater increase in the sequence of Cu>Cd>Zn. The maximum removal condition observed at the initial pH of wastewater of 12 with 978 mg/L $FeCl_3$ dosage, the final concentration of Cu, Cd and Zn was 0.0230 mg/L, 0.0002, and 0.0092 mg/L respectively. The percent removal at pH 12 was 99.97%, 99.98% and 99.87% respectively.

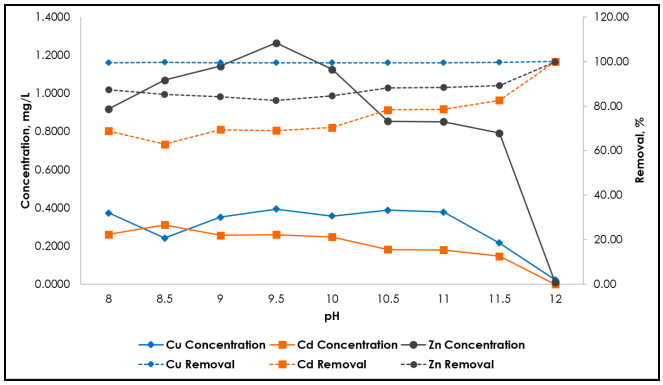

Fig 8. Effect of Initial pH adjustment and coagulant dosage (Method B for Wastewater Type I)

The effect of Method B on heavy metals removal from wastewater type II is shown in Fig. 9 above. Based on Fig. 9, the trend of removal percentage was dissimilar toward each metals. This is because, the dosage of NaOH and $FeCl_3$ play important part in removal process by ionization of metals ion with (OH^-) ions to produce metal hydroxide ions. The higher the dosage of NaOH and $FeCl_3$ the higher the removal due to ionization process. The optimum condition for Method B treatment process was at pH 12.0 with dosage of 482 mg/L $FeCl_3$ and 3195 mg/L of NaOH dosage. The final concentration of Cu, Cd and Zn after treatment process were 0.1178 mg/L, 0.8378 mg/L, and 2.7102 mg/L respectively. The removal percentage were recorded 99.71%, 46.80%, and 83.10% respectively.

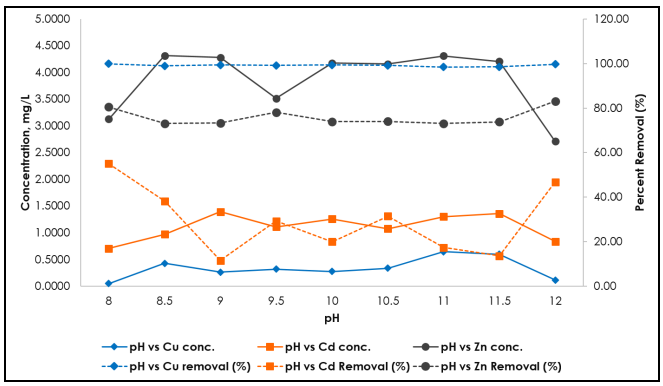

Fig 9. Effect of Initial pH adjustment and coagulant dosage (Method B for Wastewater Type II)

Table 3. Comparison between Treatment Method A and Method B (For Wastewater Type I)

Comparison Between Method	**Method A**			**Method B**		
Optimum pH of treatment	10			12		
Dosage, mg/L	**NaOH**	**$FeCl_3$**	**H_2SO_4**	**NaOH**	**$FeCl_3$**	**H_2SO_4**
	4688	140	-	6251	970	-
Removal (%)	**Cu**	**Cd**	**Zn**	**Cu**	**Cd**	**Zn**
	99.99	99.73	99.89	99.97	99.98	99.87
Final Concentratio	**Cu**	**Cd**	**Zn**	**Cu**	**Cd**	**Zn**

n of Heavy Metal (mg/L)	0.0073	0.0023	0.0077	0.0230	0.0002	0.0092
Treatment Unit		3			2	

Based on Table 3, the removal of Cu, Cd, and Zn from wastewater type I by using both treatment Method A and Method B yield the same removal efficiency since all of the metals removed was approximately above 99%. However, different dosage of chemicals used in both experiment lead to dissimilar of treatment costing. The NaOH dosage in Method A was about 4688 mg/L and in Method B was 6251 mg/L respectively. Meanwhile, the $FeCl_3$ dosage for optimum condition used in Method A was 140 mg/L and for Method B, the $FeCl_3$ dosage was 970 mg/L. The treatment unit for both experiment also different. In the Method A, three unit of treatment required to remove heavy metals inside wastewater. Meanwhile, the Method B only requires two unit of treatment which lessen the costing of treatment operation.

Table 4. Comparison between Treatment Method A and Method B

(For Wastewater Type II)

Comparison Between Method	**Method A**			**Method B**		
Optimum pH of treatment		10			12	
Dosage, mg/L	**NaOH**	**$FeCl_3$**	**H_2SO_4**	**NaOH**	**$FeCl_3$**	**H_2SO_4**
	3825	100	-	3195	482	-
Removal (%)	**Cu**	**Cd**	**Zn**	**Cu**	**Cd**	**Zn**
	99.87	98.74	99.69	99.71	46.80	83.10
Final Concentration of Heavy Metal (mg/L)	**Cu**	**Cd**	**Zn**	**Cu**	**Cd**	**Zn**
	0.0510	0.0198	0.0494	0.1178	0.8378	2.7102
Treatment Unit		3			2	

Based on Table 4, the removal of Cu, Cd, and Zn from wastewater Type II by Method A yield highest removal efficiency since all of the metals removed was approximately and above 99%. However, removal by treatment Method B yield lower percentage. This is because, at pH 12, all metal solubility inside water became increase. Thus, in order to counter the solubility of metals, high dosage of NaOH and $FeCl_3$ required. In the treatment process, the dosage of NaOH for Method A and Method B are about 3825 mg/L and 3195 mg/L respectively. The dosage for treatment Method B is considered insufficient to remove Cd and Zn since the highest removal achieved is only for Cu at this dosage. Meanwhile, the $FeCl_3$ dosage for optimum condition of Method A treatment method was 100 mg/L and for the Method B the $FeCl_3$ dosage was 482 mg/L. Therefore, treatment with Method A may be extra effective for heavy metals removal compared to Method B although there are additional of treatment unit for Method A. The final concentration of heavy metals for Method A is passed according to maximum allowable concentration as stipulated by Environmental Quality (Industrial Effluent) Regulation 2009.

E. Multiple linear regression analysis on heavy metals removal

Multiple linear regression analysis is performed to analyse the relationship between Cu removal (Y_1), Cd removal (Y_2), and Zn removal (Y_3) due to several variables such as initial pH of NaOH dosage (X_1), and $FeCl_3$ dosage (X_2) in the treatment process. The regression analysis conducted based on experiment of treatment Method B by using Excel Software. The coefficient of determination (*Adjusted R^2*) determines the goodness of fit and only value of *adjusted R^2* is need to be concerned in this study since the statistical analysis involve two different variables. The range of *adjusted R^2* varies from 0.0 to 1.0. If the value of *adjusted R^2* too small, it can be concluded that no linear relationship exists between variables. If the value of *adjusted R^2* is approaching 1, all points lie exactly on the straight line without scatter. If the X variable is known, Y variable can be perfectly predicted. The probability value below 0.05 indicates the reliable of model to predict the responses.

Table 5. Regression Statistic

Regression Statistic	**Cu**	**Cd**	**Zn**
	Wastewater Type 1		
Multiple R	1.00000	0.96861	0.98042
R Square	0.99999	0.93821	0.96123
Adjusted R Square	0.99994	0.91762	0.92245
	Wastewater Type II		
Multiple R	0.83020	0.70748	0.98699
R Square	0.68923	0.50052	0.97415
Adjusted R Square	0.58564	0.33403	0.89660

Table 5 shows the regression statistic for heavy metals removal by treatment Method B for concentration based on actual wastewater Type 1 and wastewater Type II. Based on Table 5, the value of *adjusted R^2* for multiple regression of Cu, Cd, and Zn for wastewater Type I were 0.9999, 0.9176, and 0.9225 which show that the predictor variables are correlated to removal of heavy Cu, Cd, and Zn by 99.99%, 91.76%, and 92.25% respectively. The *adjusted R^2* values listed indicated the data are well fitted. Meanwhile for the wastewater Type II, the value of *adjusted R^2* for multiple regression of Cu, Cd, and Zn were 0.5856, 0.3340, and 0.8966. The *adjusted R^2* values listed for wastewater type II indicated the data are not fitted well. The predictor variables for wastewater type II correlated with removal of Cu, Cd and Zn at less percent of Cu = 58.56%, Cd = 33.40%, and Zn = 89.66 %. Based on both experiment, it can be concluded that the coefficient of determination from wastewater type I seem to have stronger relationship between independent and dependent variables due to value of *adjusted R^2* approaching 1. The ANOVA for regression for each metal were presented in Table 6 and Table 7 below. It is depicted from Table 6, the significance F of each regression are nearly or less than 0.05. This shows that the data and results from treatment process by Method B onto the wastewater type I are quite reliable.

Table 6. Analysis of Variance (ANOVA) – Wastewater Type I

Metal		***df***	***Significance F***
Cu	*Regression*	7	0.00576
	Residual	1	
	Total	8	

Cd	*Regression*	2	0.00024
	Residual	6	
	Total	8	
Zn	*Regression*	4	0.00439
	Residual	4	
	Total	8	

Meanwhile in wastewater type II, the value of significant of *F* for Cu was less than 0.05 whereas for Cd and Zn the value were more than 0.05 which 0.12461 and 0.07556 respectively. The *significance F* value should be smaller than 0.05 so that the significant probability that regression output is not by random chance or by null hypothesis. For Cd, the output of regression was obtained by random chance or null hypothesis only accounted about 12.46%.

Table 7. Analysis of Variance (ANOVA) – Wastewater Type II

Metal		***df***	***Significance F***
Cu	*Regression*	2	0.03001
	Residual	6	
	Total	8	
Cd	*Regression*	2	0.12461
	Residual	6	
	Total	8	
Zn	*Regression*	6	0.07556
	Residual	2	
	Total	8	

The coefficients of model and the coefficient are listed in Table 8 and Table 9 for each heavy metals.

Table 8. Model Parameters (For Wastewater Type I)

Metals		***Coefficients***	***P-value***
Cu	*Intercept*	-3757.29	0.0097
	X1	624.73	0.0095
	X2	-1304.05	0.0323
	X1X2	160.53	0.040375
	X1^2	-25.30	0.0095
	X2^2	-22.31	0.0210
	*X1^2*X2*	-4.46	0.0475
	*X2^2*X1*	0.19	0.0500
Cd	*Intercept*	-527.23	0.0296
	X1	77.76	0.0237
	X1^2	-2.41	0.0344
Zn	*Intercept*	2674.27	0.0493
	X1	-392.32	0.0541
	X2	31.17	0.0432
	X2^2	-12.81	0.0562
	X1^2	14.79	0.0545

Table 9. Model Parameters (For Wastewater Type II)

Metals		***Coefficients***	***P-value***
Cu	*Intercept*	99.59	2.93E-15
	X2	-2.37	0.0167
	X2^2	1.01	0.0122
Cd	*Intercept*	39.01	0.0019
	X2	-58.41	0.0868
	X2^2	25.64	0.0630
Zn	*Intercept*	-9099.06	0.0484
	X1	2448.81	0.0473
	X2	-1932.14	0.0397
	X2^2	-162.45	0.0470
	X1^2	2641.54	0.0678
	*X1^2*X2*	29.10	0.0400
	*X2^2*X1*	-320.50	0.0677

The reliability of significant coefficient including intercept value can be determined from *P-value*. When the P-value less than 0.05 means that the greater the probability of that regression output were not obtained by random chance or null hypothesis. Based on Table 8, the value of *P-value* for regression of each metals were less and approaching 0.05. This means that the values of coefficient can be used to determine the regression output which in this study to identify the removal percentage of metal Cu, Cd and Zn. Meanwhile, for wastewater Type II, the *P-value* for regression of each metals also approaching 0.05. Some of *P-value* for metal Cd and Zn are more than 0.05. However, it was still considerable since it was not exceeding 10.00%. The coefficient and intercept values can still be used to identify the regression output because only small percent of probability of these output may be obtained by random chance. Therefore, mathematical model equation can be equated to illustrate the regression output. From these coefficients listed in Table 8, the equation for the model is constructed. By applying the data of the unstandardized coefficients listed in Table 8, the multiple linear regression modelling for heavy metals removal was stated as follow,

$$Y_1 = -4.46{X_1}^2X_2 + 0.19{X_2}^2X_1 - 25.30{X_1}^2 - 22.31{X_2}^2 + 160.53X_1X_2 + 624.73X_1 - 1304.05X_2 - 3757.29 \quad \textbf{(2)}$$

$$Y_2 = -2.41{X_1}^2 + 77.76X_1 - 527.23 \quad \textbf{(3)}$$

$$Y_3 = 24.79{X_1}^2 - 12.81{X_2}^2 - 392.32X_1 + 31.17X_2 + 2674.27 \quad \textbf{(4)}$$

Thus, the equation 2, 3 and 4 were the best and acceptable multiple linear model for illustrating the profile of heavy metals removal by treatment method B. It was apparent from mathematical modelling that the $FeCl_3$ dosage give insignificant effect on Cd removal. However, $FeCl_3$ give significant impact to both Cu and Zn removal. From the coefficients listed in Table 9, the equation for the model is constructed. The multiple linear regression modelling for heavy metals removal for altered initial concentration of heavy metals was stated as follow,

$$Y_4 = 1.01{X_2}^2 - 2.37X_2 + 99.59 \quad (5)$$

$$Y_5 = 25.64{X_2}^2 - 58.41X_2 + 39.01 \quad (6)$$

$$Y_6 = 29.10\,{X_1}^2X_2 - 320.50{X_2}^2X_1 - 162.45{X_1}^2 + 2642.54{X_2}^2 + 2448.41X_1 - 1932.14X_2 - 99.09.06 \quad (7)$$

Meanwhile for wastewater Type II, the best and acceptable multiple linear regression model that can illustrate the profile of heavy metal removal by coagulation process was illustrated as equation 5, 6 and 7. It can be conclude that the $FeCl_3$ dosage give significant effect on Cu and Cd removal. However, for Zn removal, $FeCl_3$ and NaOH both significant effect on removal percentage. Based on the mathematical model obtained from regression, the mathematical model for experiment 1 give dissimilar model compared to experiment 2. This is because, different nature of wastewater required different treatment method and different dosage of chemicals to achieve the permissible limit as stipulated by IER2009. Therefore, the changes made to the initial concentration would give different regression model.

III. Conclusion

Hydroxide precipitation with aid of coagulation-flocculation for removal of Cu, Cd, and Zn from aqueous solution was investigated. The treatment process by Method A was study on effect of initial pH of wastewater and $FeCl_3$. It has shown that the maximum removal of multi-metals achieved from wastewater Type I was at pH 10 and 140 mg/L respectively. The removal obtained from this method for Cu, Cd, and Zn were 99.99%, 99.73% and 99.89% respectively. Meanwhile, after some changes made to initial concentration of heavy metals inside wastewater, the optimum condition for treatment process was achieved at pH 10 and 100 mg/L of $FeCl_3$ dosage. The removal obtained for Cu, Cd, and Zn from wastewater Type II were 99.87%, 98.74%, and 99.69%. These findings confirm that the solubilities of each metals differ at any pH. Hydroxide precipitation cannot completely remove all metals inside aqueous solution due to competitiveness between metal to ionize with hydroxide ions to produce metal precipitates. For treatment Method B, both experiment give same optimum pH condition at pH 12 with different $FeCl_3$ dosage of 970 mg/L and 482 mg/L respectively. Based on data obtained from Method B treatment process, the mathematical expression was developed from data fitting by multilinear regression via Excel software. The value of *adjusted* R^2 for wastewater type I gives the best fit of data above 90% and for wastewater type II consist of scattered data. The ANOVA analysis of mathematical expressions proved that the developed expression can be used to predict the removal of Cu, Cd and Zn at NaOH dosage between 0 mg/L to 6300 mg/L and $FeCl_3$ dosage between 0 mg/L to 1000 mg/L at initial pH of wastewater at 12 for wastewater Type I. Meanwhile, for wastewater type II, the ANOVA analysis of mathematical expressions can be used to predict the removal of Cu, Cd and Zn at NaOH dosage between 0 mg/L to 3200 mg/L and $FeCl_3$ dosage between 0 mg/L to 500 mg/L at initial pH of wastewater at pH 12, However, the mathematical model for both wastewater Type I and Type II are reliable to predict the outcomes. However, the mathematical expression can only be used for that particular initial concentration of heavy metals and operating condition.

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