

Removal of Copper from Acid Mine Drainage (AMD) or Acid Rock Drainage (ARD)

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Abstract

Acid mine drainage is wastewater from a mine having a low pH and an elevated level of dissolved heavy metals. These metals are harmful to aquatic, animal and human life. This paper looks at the removal of copper from acid mine drainage using ion exchange to less than 1 mg/l. A weak acidic cation resin was used. Spectrophotometric determination of copper with sodium diethyldithiocarbamate was used to determine the copper concentrations in the treated water. Using regression analysis, the experimental results gave a correlation coefficient of 0.977 and a coefficient of determination of 99.5%. Results indicated that the higher the flows rate the shorter the period after which the copper concentration in the treated water reaches 1 mg/l. At pH 3.85 and 5.09, the resin performed better and at pH above 6.62 and between pH 3.0 and below the resin's does not perform well. The higher the resin height the greater is the resin exchange capacity and the longer it takes for the copper concentration to reach 1 mg/l in the treated water. The higher the wastewater copper concentration the shorter the time it takes the resin to reach 1 mg/l. The results for this experiment indicated that acid mine drainage can be treated well by ion exchange resins, but it is also very important to establish suitable operating conditions.

Keywords

Acid Mine Drainage, Copper, Ion Exchange, Resin and Spectrophotometry

1. Introduction

Acid mine drainage (AMD) is mine wastewater usually at low pH that has elevated levels of heavy metals and sulphides. Drainage acidity arises from oxidation of pyrite, the crystalline form of iron sulphide and copper pyrite. The contaminated water is often reddish-brown in color, indicating high levels of oxidized iron. Mining disturbs pyrite and, as a result, pyrite weathers and reacts with oxygen and water in the environment [1] [2].

Mine drainage is formed when pyrite, an iron sulfide, is exposed and reacts with air and water to form sulfuric acid and dissolved iron. Some or all of this iron can precipitate to form the red, orange, or yellow sediments in the bottom of streams containing mine drainage. The acid runoff further dissolves heavy metals such as copper, lead, mercury, lead, zinc, etc. into ground or surface water [3] [4].

Due to the low pH and the presence of heavy metals, AMD is toxic to aquatic and human lives, destroys the ecosystem, corrodes infrastructure and reduces fresh water supply [5] [6]. Due to the persistent nature in the natural ecosystem and successive accumulation in the biological chain, heavy metals can cause acute and chronic diseases in humans. The toxicity or poisoning of heavy metals results from disruption of metabolic functions and inhibition of the absorption of vital nutritional minerals. Once the heavy metals accumulate in vital organs and glands such as the heart, brain, kidneys, bone and liver they disrupt important functions of these organs. Once the vital mineral nutrients are inhibited, their biological functions are hindered.

Plants undergo oxidative stress upon exposure to heavy metals that lead to cellular damage and disturbance of cellular ionic homeostasis, thus disrupting the physiology and morphology of plants [7] [8]. Excessive copper levels can cause anemia, liver and kidney damage, stomach and intestinal irritation in humans and in plants, it can inhibit photosynthesis, plant growth and reproductive process; decrease thylakoid surface area [9] [10] [11]. Copper like other heavy metals like cadmium, lead, and zinc are severely toxic to aquatic life. Acute exposure (short-term, high concentration) of these metals can kill organisms directly, whereas chronic exposure (long-term, low concentration) can result in either mortality or non-lethal effects such as stunted growth, reduced reproduction, deformities, or lesions [12].

Zambia is one of the major copper mining countries. And its copper mining history dates back to the early 1900s. Most old mines are still operation while some old mines have been abandoned and new mines continue to be opened. As a result of this copper mining, a lot of mine waste rock and tailings have also been dumped on the surface. Abandoned old copper mines, new mines, waste rock dumps and tailings dam may contain appreciable amount of copper. The Zambian copper mostly occurs as charcoal pyrite. And when the pyrite comes in contact with water and air (O₂) it is oxidized producing sulphuric acid and an iron hydroxide precipitate. The acid in turn dissolves the copper and other heavy

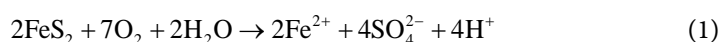
metals like gold, cobalt, zinc, lead, etc. This could bring about acid mine drainage which if not treated and controlled could be a serious environmental issue. The copper and other heavy metals alluded to are toxic and could be dangerous to human, animal and plant lives that are highly dependent on the water that comes into contact with these heavy metals.

The objective of this study was to contribute to the existing literature on the removal copper ions from acid mine drainage to less than 1 mg/l so as to render the wastewater less toxic. A sample collected from a copper mine in Lioaning Province of China is used in the presence of a weak acid cation resin to remove copper ions from acid mine drainage. While the study area is China, it is envisioned that the outcome of this study will be adopted and tailored provide solutions to the African environment, and specifically Zambian, where such a study has never been done.

2. Literature Review

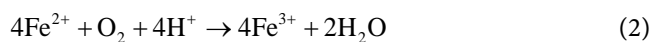
2.1. Acid Mine Drainage Chemistry

First, confirm that you have the correct template for your paper size. This template has been tailored for output on the custom paper size (21 cm × 28.5 cm). The overall oxidation of pyrite is a complex process that can involve a number of reactants and products under varying conditions. The oxidation of pyrite from the exposure to atmospheric conditions is well documented by many researchers and scientists and can be summarized by Equations (1.1) to (1.6) [2] [13] [14]. The first reaction in the weathering of pyrite includes the oxidation of pyrite by oxygen in the presence of water as expressed in (1). Sulfur is oxidized to sulfate and ferrous iron is released. This reaction generates two moles of acid for each mole of pyrite oxidized.



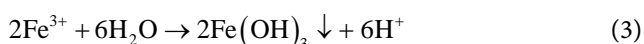
Pyrite + Oxygen + Water → Ferrous Iron + Sulfate + Acidity

The oxidation of ferrous ions to ferric ions is the rate determining step. It consumes one mole of acid for each mole of ferrous ions present. Certain bacteria increase the rate of this pH dependent reaction. Under acid conditions (between pH of 2 and 3), with no bacteria present, the reaction proceeds slowly. However, at pH around 5, the reaction proceeds at a rate which is several orders of magnitude faster. The reaction is expressed as in



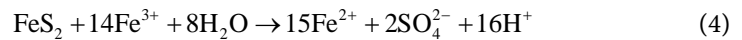
Ferrous Iron + Oxygen + Acidity → Ferric Iron + Water

Hydrolysis of iron then occurs, splitting the water molecule and generating more acid, and above pH 3.5, ferric hydroxide will precipitate. The formation of ferric hydroxide precipitate (solid) is pH dependant. Solids form if the pH is above about 3.5 but below pH 3.5 little or no solids will precipitate.



Ferric Iron + Water → Ferric Hydroxide (yellowboy) + Acidity

Ferric iron is then capable of oxidising additional pyrite. The reaction is rapid and continues until either the ferric iron or the pyrite is depleted.

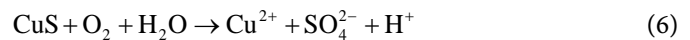


Pyrite + Ferric Iron + Water → Ferrous Iron + Sulfate + Acidity

Thus, as shown, significant acid is generated by the overall reaction.



Pyrite + Oxygen + Water → “Yellowboy” + Sulfuric Acid



This acid is then available to dissolve other minerals to liberate their contained metals. One of the major metals released by this chemistry is copper. Copper is toxic to many life forms and therefore must not be allowed to enter the environment.

2.2. Research Work in Acid Mine Drainage Treatment

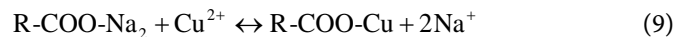
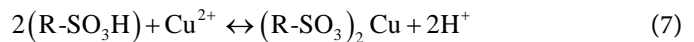
Several methods such as chemical treatment, passive treatment, membrane technology, functionalized membrane processes and ion exchange have been used before and currently [2] [14] [15]. In chemical treatment the acidity is buffered by the addition of alkaline chemicals such as calcium carbonate (limestone), calcium hydroxide (hydrated lime), sodium hydroxide (Caustic Soda), sodium carbonate (Soda ash), or anhydrous ammonia. These chemicals raise the pH to acceptable levels and decrease the solubility of dissolved metals. Precipitates that form are settled from the solution. The heavy metals will actually form as precipitate [2]. Passive acid mine drainage treatment technologies include Aerobic wetland, compost or anaerobic wetland, open limestone channels, diversion wells, limestone drains, vertical flow reactors, etc. [14]. Microporous liquid membrane extraction systems have been used to recover copper and other metals [15]. Silica-based ion exchange resins for the recovery of metal ions from acid drainage solutions. A range of ion exchange resins, normally either based on polystyrene-divinyl benzene or acrylic backbones have been developed for the recovery of metal [3].

2.3. Weak Acid Cation Resin

In a weak acid resin the ionizable group is a carboxylic acid (COOH) as opposed to the sulfonic acid group (SO₃H) used in strong acid resins. These resins behave similarly to weak organic acids that are weakly dissociated. Weak acid resins exhibit a much higher affinity for hydrogen ions than do strong acid resins. This characteristic allows for regeneration to the hydrogen form with significantly less acid than is required for strong acid resins. The degree of dissociation of a weak acid resin is strongly influenced by the solution pH. Consequently, resin capacity depends on solution pH.

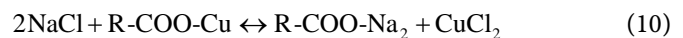
2.4. Basic Mechanisms of Cation Exchanges in Resins

Cation exchangers resins remove cations from solution, exchanging them for Hydrogen ions in the Hydrogen cycle (7) and (8) or Sodium ions in the Sodium cycle (9). Equations (7), (8) and (9) represent the Copper ions removal process where R indicates the organic portion of the resin and SO_3 is the immobile portion of the ion active group.



In this way, Cu^{2+} ions are retained on the resin and a soft effluent is produced. This soft effluent mainly contains sodium salts or acids depending on which cycle has been employed.

When the exchange capacity of the resin is exhausted the resin must be regenerated. Prior to regeneration, the column must be backwashed to remove solid deposits. Regeneration consists of passing through the column either a brine solution or an acid solution depending on the cycle employed. This is achieved by using the expression in (10) for the Sodium Cycle and expressions (11) and (12) for the Hydrogen Cycle.



As indicated in (7), (8) and (9) above regenerant consists of cation salts. Following regeneration the exchanger bed is rinsed with water to remove residual regenerant [16].

3. Methodology/Experimental Procedure

3.1. Abbreviations and Acronyms

Having known the mass (m) and absolute density (ρ) of each ion exchange resin to be used, the volume (V) of the resin to be used was estimated using equation (13).

$$V = \frac{m}{\rho} \quad (13)$$

Having estimated the resin volume, the diameter (D) of the column was assumed and the cross section area (A) of the column calculated. And making H_r the subject of the formula in (14), the height of the column was estimated.

$$V = A \cdot H_r \quad (14)$$

Therefore,

$$H_r = \frac{V}{A} = \frac{14V}{11D^2} \quad (15)$$

And assuming a free space factor (β) allowing for cleaning, backwashing and bed expansion, the height of the column was estimated using Equation (16)

$$H_c = \beta H_r \quad (16)$$

Table 1.

3.2. Apparatus

The apparatus (see examples **Figure 1**) used in the experiment included but not limited to the ion exchange resin column, spectrophotometer, pH meter, erlenmeyer flasks and beakers, graduated cylinders, burets, volumetric flasks, test tubes, spatula, safety goggles, thermometer, pipets, pipet bulbs, analytical balance, pure water, gloves, universal pH Indicator paper, wash bottle, rubber tubing, cotton wool, funnel, magnetic stirrer, stop watch and clips.

Table 1. Resin sample D401 (for $D = 25$ mm, $\rho = 0.75$ g/ml and $\rho = 10\%$).

Parameter	Unit	Value
Mass (m)	g	200
Density (ρ)	g/ml	0.75
	ml	266.7
Volume (V)	l	0.2667
	m ³	0.0002667
Column Diameter (D)	m	0.0250
Diameter Squared (D^2)	m ²	0.0006
Resin Depth (H_r)	m	0.5430
Factor (β)	%	10.00
	m	0.5973
Column Height (H_c)	cm	59.73
	mm	597.3

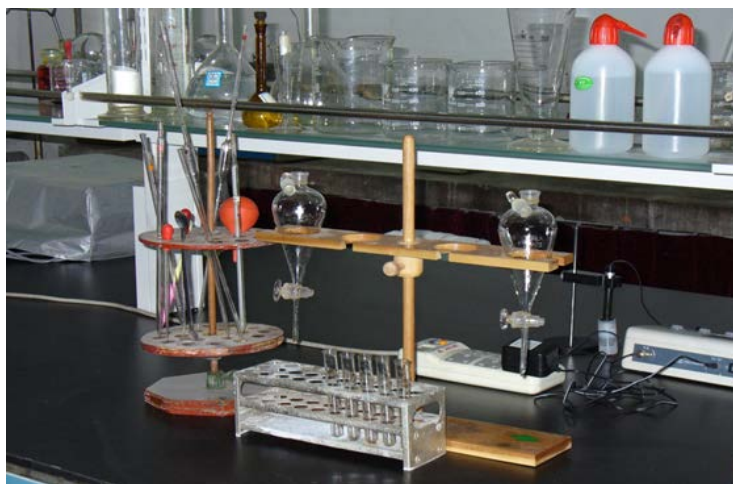


Figure 1. Some of the apparatus used in this study.

3.3. Standards Used

The maximum allowable concentration in industrial wastewater discharge into the environment is 1 mg/l. This is threshold limit value recommended by the WHO and most developed countries. The International Standard (UDC 614.777: 543.42:546.56, GB 7474-87) was used in the determination of copper in wastewater. This standard uses sodium diethyldithiocarbamate and spectrophotometric methods to determine copper concentrations in wastewater or water samples [17].

3.4. Reagents Used

The reagents used in this study, some of which are shown in **Figure 2**, include: Copper (II) Sulphate Pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), pure water, Hydrochloric acid (HCl), Sulphuric acid (H_2SO_4), Diethyldithiocarbamate (DDTC), Carbon Tetrachloride (CCl_4), Ammonium Chloride (NH_4Cl), Ammonium Hydroxide (NH_4OH), Sodium Chloride (NaCl), Sodium hydroxide (NaOH) and Resin Sample D401.

3.5. Pretreatment of Resin Sample D401

50 g of resin sample D401 was weighed and put in a clean beaker, pure water was heated to about 78°C and 150 ml (three times as much as the resin) of the heated pure water was added to the resin, then the mixture was stirred using the magnetic stirrer for 15 minutes and the water removed. The two steps above were repeated for a total of 5 times. Again the above step was repeated for another two times, but this time stirring for 30 minutes each time. 1M of HCl and three times the resin's volume was passed through the resin. The resin was rinsed with pure water to pH 5 and 5% NaCl having three times the volume of the resin was passed through the resin. 1M of NaOH was passed through the resin. The resin was rinsed with pure water to pH 9. 1M of HCl having 4 times the resin volume was passed through the resin. Bring the resin to the hydrogen form. The resin was rinsed with pure water to pH 6 and this process was repeated all the time a fresh sample D401 of resin was used. Note that this is a weak acid cation resin and it is dependent on pH. Its capacity is affected by changes in pH.



Figure 2. Some of the reagents used in this study.

3.6. Regeneration of Resin Sample D401

1M of HCl and three times the resin volume was passed through the resin. This was done until all the blue coloring on the resin was removed. The acid elutes the collected ions and converts the bed to the hydrogen form. The resin was then washed with pure water until it reached pH 6. The column was put back to work.

3.7. Preparation of Wastewater (Acid Mine Drainage) Sample

Copper (II) Sulphate Pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, M.W. = 249.68 g) was used to prepare the wastewater. Notice that there is 64 g of copper in every 249.68 g of Copper (II) Sulphate Pentahydrate. To make 100 mg Cu^{2+}/L , we need to add 100 g of copper to every liter of pure water. Therefore using direct proportion, 0.390125 g of Copper (II) Pentahydrate is needed to get 100 mg of copper to dissolve in one liter. To make the wastewater acidic, drops of H_2SO_4 were added to the Copper (II) Sulphate Pentahydrate solution little by little and each time testing the pH using either the pH meter until the required acid pHs of 2.5, 3.0, 3.85, 4.37 and 5.09 were reached.

3.8. Preparation of Standard Wastewater Solutions

Standard solution with copper concentrations of 0.00, 0.12, 0.24, 0.36, 0.48 and 0.60 mg/l were prepared by initially preparing 1 liter of copper concentration 10 mg/l using 0.0390 g of Copper (II) Sulphate Pentahydrate. Calculated amounts (in ml) of the 10 mg/l solution were first put in each of the 50 ml capacity flasks and then diluted with pure water to the mark. This calculation is based on the formula below;

$$M_i V_i = M_f V_f \quad (17)$$

where M_i is the initial concentration of the solution in mg/l, V_i is the initial volume of the solution in ml, M_f is the final concentration of the solution in mg/l and V_f is the final volume of the solution in ml.

With the initial concentration known and the final volume and concentration fixed, the volume to be added to each flask (initial volume) was calculated as in

$$V_i = \frac{M_f V_f}{M_i} \quad (18)$$

Table 2 gives the values of the initial and final concentrations.

Table 2. Standard wastewater solutions.

Parameter	Quantity					
Final volume (ml)	50	50	50	50	50	50
Final concentration (ml/l)	0.00	0.12	0.24	0.36	0.48	0.60
Initial concentration (mg/l)	0	10	10	10	10	10
Initial volume (ml)	0.00	0.60	1.20	1.80	2.40	3.00
Volume to be added						

3.9. Reagent Preparation

The reagents were prepared as follows:

- **Diethyldithiocarbamate**—The Diethyldithiocarbamate (DDTC), was prepared by putting 0.2000 g of DDTC, measured using the analytical balance, in a clean beaker. Pure water was gradually added to the beaker while stirring until all the DDTC crystals had dissolved. The solution was then put in a 100 ml flask and diluted to the mark.
- **Ammonium Chloride and Ammonium Hydroxide**—First 70 g of Ammonium Chloride (NH_4Cl) was weighed and put in a clean beaker. Pure water was gradually added while stirring until all the Ammonium Chloride crystals had dissolved. The solution was put in a 1l flask. Next 570 ml of Ammonium Hydroxide was measured using a measuring cylinder and added to the Ammonium Chloride solution in the 1l flask. The solution was then diluted to the mark.
- **Carbon Tetrachloride (CCl_4)**—Carbon Tetrachloride (CCl_4) was used to extract the copper ions from the wastewater and was handled with great care.

3.10. Standard Sample Reacted With Reagents

Diethyldithiocarbamate (DDTC) has been used as a chelating agent in the determination of metal ions by UV/vis spectrophotometry. However, DDTC metal complexes are water insoluble and therefore a solvent-extraction step is necessary. Sensitivity of spectrophotometric methods for the determination of low concentrations of metal ions in water samples is insufficient. Consequently, a pre-concentration and matrix elimination step is usually required. The most widely used techniques for the separation and pre-concentration of trace amounts of Cu are liquid-liquid extraction (LLE), CCl_4 , was used for this purpose [18] [19].

Sample 1 of the standard sample was poured in a reaction bottle (see examples **Figure 3**) 50 ml of NH_4Cl and NH_4OH and 5 ml DDTC were added. The bottle was shaken for few seconds and put back in the clamp. After 5 minutes 10 ml of



Figure 3. Treated water reacted with reagents.

CCl₄ was added. The bottle was shaken for three minutes. The product of the reaction is denser, so it collects below and the other mixture on top. The product was then extracted into a test tube ready to be taken for the measurement of its absorbance. In this way all the standard solutions were reacted and their products measured for their absorbance using the Spectrophotometer set at 440 nm wavelength.

3.11. Calibration Curve

Table 3 shows the concentration values (X_i) and absorbance values (Y_i) use in the regression analysis to estimate the calibration curve and regression equation for calculating the concentrations of the treated water. Figure 4 shows the plot of the concentrations in mg/l against the absorbance.

From Table 3, the Pearson correlation, r , and coefficient of determination, r^2 , are derived as in the following.

SS_X : Sum of Squared Deviations for X_i values

$$SS_X = \sum X_i^2 - \frac{(\sum X_i)^2}{n} = 0.252 \tag{19}$$

SS_Y : Sum of Squared Deviations for Y_i values

$$SS_Y = \sum Y_i^2 - \frac{(\sum Y_i)^2}{n} = 0.162 \tag{20}$$

Table 3. Calibration curve.

Sample	X_i	Y_i	X^2	Y^2	XY
1	0.000	0.028	0.000	0.001	0.000
2	0.120	0.112	0.014	0.013	0.013
3	0.240	0.233	0.058	0.054	0.056
4	0.360	0.339	0.130	0.115	0.122
5	0.480	0.408	0.230	0.166	0.196
6	0.600	0.501	0.360	0.251	0.301
Sum	1.800	1.620	0.790	0.600	0.690

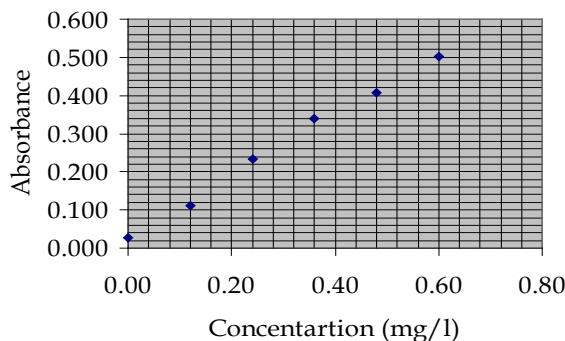


Figure 4. Concentration (mg/l) vs absorbance using Beer’s Law.

SS_{XY} : Sum of Co-deviations for paired values X_i and Y_i

$$SS_{XY} = \sum X_i Y_i - \frac{\sum X_i \sum Y_i}{n} = 0.202 \quad (21)$$

Correlation coefficient (r)

$$r = \frac{SS_{XY}}{\sqrt{SS_X \cdot SS_Y}} = 0.997 \quad (22)$$

The r value is positive while the coefficient of determination, r^2 is 0.995 (99.5%) indicating a strong positive correlation between the concentration (X) and the absorbance (Y).

Then the regression equation is derived as follows. The regression line is illustrated in **Figure 5**.

$$\bar{X} = \frac{\sum X_i}{n} = 0.300 \quad (23)$$

$$\bar{Y} = \frac{\sum Y_i}{n} = 0.270 \quad (24)$$

$$Y = \beta_1 X + \beta_0 \quad (25)$$

$$\beta_1 = \frac{SS_{xy}}{SS_x} = 0.800 \quad (26)$$

$$\beta_0 = \bar{Y} - \beta_1 \bar{X} = 0.030 \quad (27)$$

$$Y = 0.800X + 0.030 \quad (28)$$

Making X the subject of the formula, we get

$$X = 1.25Y - 0.038 \quad (29)$$

with a variance S^2 of

$$S^2 = \frac{SS_y - \beta_1 SS_{xy}}{n - 2} = 0.0002 \quad (30)$$

and standard deviation S of

$$S = \sqrt{S^2} = 0.015 \quad (31)$$

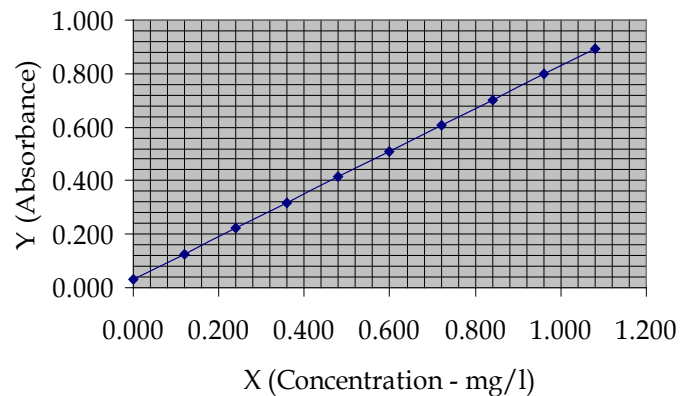


Figure 5. Plot of the regression line.

3.12. Determination of the Effect of Flow Rate

Keeping the resin height constant at 90 mm (50 g), wastewater with copper concentration at 100 mg/l and wastewater pH 4.58, the experiment was done for five times each time changing the wastewater flow rate. During the experiment 20 ml of treated water was collected at each specified time interval and later diluted to 50 ml. The 50 ml was reacted with 50 ml of Ammonium Chloride and Ammonium Hydroxide solution (buffering media), 5 ml DDTC and 10 ml carbon tetrachloride (extractor).

3.13. Determination of the Effect of pH

Keeping the resin height constant at 110 mm (60 g), wastewater copper concentration at 150 mg/l and wastewater flow rate at 24.5 m/h, the experiment was done five times each time changing the pH of the wastewater by adding H₂SO₄ until the desired pH is obtained.

3.14. Determination of the Effect of Resin Height

Keeping the wastewater flow rate at 24.5 m/h, wastewater with copper concentration at 150 mg/l and wastewater pH 5.09 constant, the experiment was done for five times each time changing the resin height.

3.15. Determination of the Effect of Copper Concentration of the Wastewater

Keeping the other factors constant, *i.e.* resin height at 110 mm, pH at 5.09, 24.5 m/h, and varying the copper ion concentration of wastewater, the experiment was also repeated five times.

3.16. Acid Mine Drainage from the Mine

Two 2.5 liters of acid mine drainage Samples 1 and 2 with contaminants as shown in **Table 4** were treated using ion exchange resins and the effluent was detected for copper ions using Spectrophotometric methods. The spectrophotometer was set at 440 nm wavelength during the testing. 40 g of resin with a height of 90 mm in the column was used. Initially before the wastewater (AMD) was treated it was allowed to settle and the suspensions were removed. In order to completely remove the suspended solids the wastewater was also filtered using cotton wool as a filter. After this the wastewater was ready for treatment with the resin and 2 liters was used in each of two experiments.

Table 4. Acid mine drainage samples before and after treatment.

Sample	Before treatment					
	pH	Suspensions (mg/l)	Copper (mg/l)	Zinc (mg/l)	COD (mg/l)	Cadmium (mg/l)
1	6.28	Not checked	1.539	13.880	165.456	0.027
2	6.62	113.000	0.657	6.990	39.832	0.044

4. Results and Discussions

4.1. Effect of Flow Rate

The results of the effect of flow rate are shown in **Table 5** and **Figure 6**. From **Figure 6** it can be seen that at a flow rate of 33.1 m/h it takes 2.5 minutes for treated wastewater to reach 1 mg/l, at 28.2 m/h it took 7 minutes, at 24.5 m/h it took 14.5 minutes, at 20.8 m/h it took about 20.5 minutes and at 16.5 m/h it took

Table 5. The effect of flow rate

Time (min)	Flow Rate				
	16.5 m/h	20.8 m/h	24.5 m/h	28.2 m/h	33.1 m/h
1				0.074	0.108
2		0.083	0.086	0.283	0.668
3	0.055			0.368	1.199
4		0.096	0.139	0.505	1.802
5				0.536	3.058
6	0.093	0.136	0.336	0.730	
7				1.018	
8		0.255	0.393	1.286	
9	0.127				
10		0.327	0.527		
12	0.183	0.402	0.699		
14		0.468	0.924		
15	0.258				
16		0.643	1.289		
18	0.368	0.727			
21	0.589				
24	0.886				
27	1.327				
30	1.974				

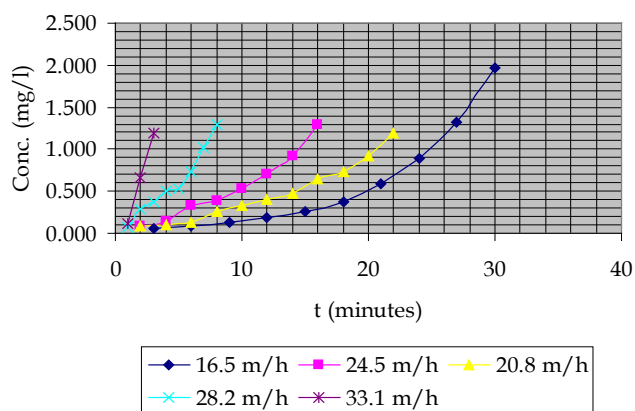


Figure 6. The effect of flow rate.

25 minutes. So we notice here that the higher the flow rate the shorter the period after which the copper concentration in the treated water reaches 1 mg/l and the opposite is the truth.

4.2. Effect of pH

The experiment results are shown in **Figure 7** and **Table 6**. It can be seen that at pH 5.09 it took 14.75 minutes for the treated water to reach 1 mg/l, at pH 4.37 it took 14.25 minutes, at pH 3.85 it took 13.25, at pH 3.0 it took 6.25 minutes and at pH 2.5 it was greater than 1 mg/l with the first 1 minute. Therefore for pH 5.09, 4.37 and 3.85 it was in the time range of 13.25 to 14.75 minutes for the

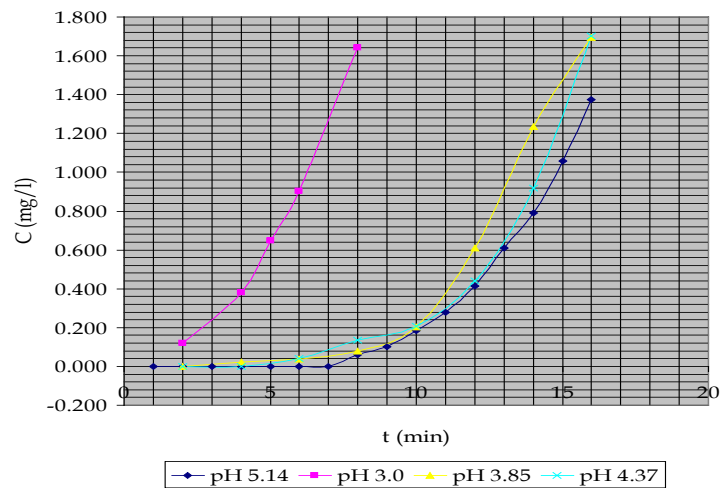


Figure 7. The effect of pH.

Table 6. The effect of pH.

Time (min)	pH 5.09	pH 4.37	pH 3.85	pH 3.00	pH 2.50
1	0.000				>1
2	0.000	0.000	0.000	0.121	
3	0.000				
4	0.000	0.000	0.024	0.380	
5	0.000			0.649	
6	0.000	0.043	0.036	0.902	
7	0.000				
8	0.058	0.136	0.080	1.643	
9	0.102				
10	0.183	0.205	0.202		
11	0.280				
12	0.414	0.439	0.611		
13	0.611				
14	0.789	0.918	1.236		
15	1.058				
16	1.374	1.700	1.696		

copper concentration of the treated water to reach above 1 mg/l. This tells us that at between pH 3.85 and 5.09 the resin capacity is not affected much by changes in pH and at pH 3.0 and below the resin's exchange capacity is affected there by not performing well. This is seen when the pH is further reduced to 2.5 when its performance is even reduced more.

4.3. Effect of Resin Height

The experiment results are shown in **Figure 8** and **Table 7**. With resin height 70

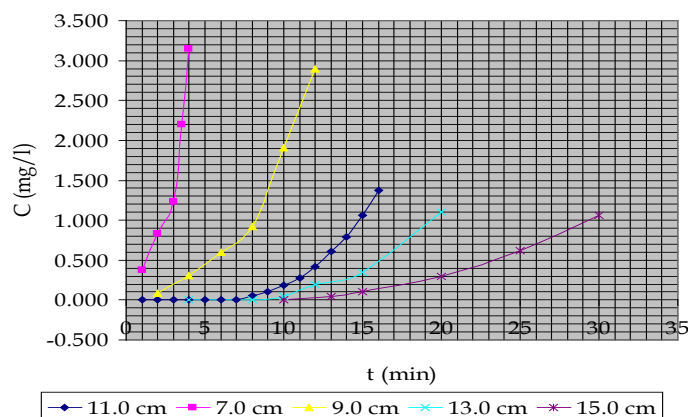


Figure 8. The effect of resin height.

Table 7. The effect of resin height.

Time (min)	Resin Height				
	70 mm	90 mm	110 mm	130 mm	150 mm
1	0.375		0.000		
2	0.830	0.083	0.000		
3	1.230		0.000		
3.5	2.199				
4	3.146	0.308	0.000	0.000	
5			0.000		
6		0.599	0.000		
7			0.000	0.000	
8		0.924	0.058		
9			0.102		
10		1.911	0.183	0.049	0.000
11			0.280		
12		2.899	0.414	0.199	
13			0.611		0.049
14			0.789		
15			1.058	0.349	0.108
16			1.374		
20				1.099	0.299
25					0.618
30					1.058

mm, it took 2.5 minutes for the copper concentration in the treated water to reach 1 mg/l, 8.25 minutes for 90 mm resin height, 14.75 minutes for 110 mm resin height, 19.5 minutes for 130 mm resin height and 29.5 minutes for a 150 mm resin height. So the higher the resin height the greater is the resin exchange capacity and the longer it takes for the copper concentration to reach 1 mg/l in the treated water and the opposite is the truth.

4.4. Effect of Copper Concentration of Wastewater

The results for the effect of Copper concentration of wastewater are shown in **Figure 9** and **Table 8**. It can be seen that for 200 mg/l wastewater copper concentration it took about 1.25 minutes for the copper concentration in the effluent (treated water) to reach 1 mg/l, 5 minutes for 175 mg/l, 14.5 minutes for 150

Table 8. The effect of Copper ion concentration of wastewater.

Time (min)	Copper ion concentration of wastewater				
	50 mg/l	100 mg/l	150 mg/l	175 mg/l	200 mg/l
1			0.000	0.199	0.699
1.5					1.049
2			0.000	0.349	1.321
2.5					1.830
3			0.000		2.302
4			0.000	0.821	
5		0.000	0.000	0.964	
6			0.000	1.205	
7			0.000		
8			0.058		
9			0.102		
10		0.039	0.183		
11			0.280		
12		0.149	0.414		
13			0.611		
14		0.339	0.789		
15			1.058		
16		0.658	1.374		
18		0.799			
20		1.099			
30	0.000				
35	0.230				
40	0.499				
45	0.739				
50	1.058				

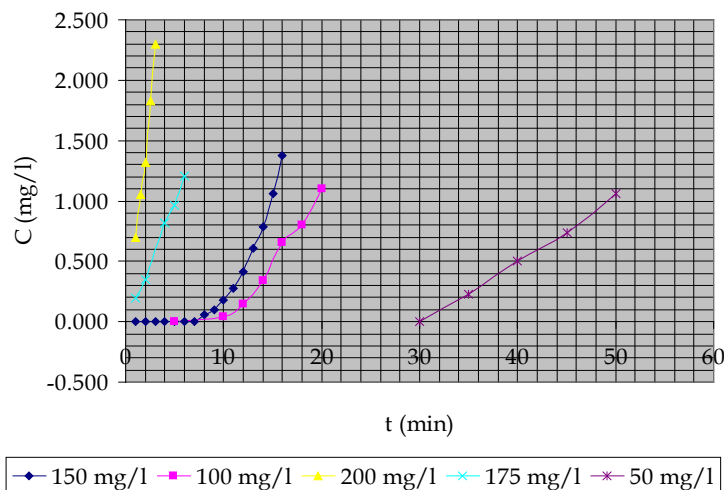


Figure 9. The effect of Copper ion concentration of wastewater.

Table 9. Acid mine drainage samples after treatment.

Time	Acid mine drainage concentration	
	1.539 mg/l	0.657 mg/l
3	0.077	0.019
6	0.270	0.023
9	0.298	0.048
12	0.302	0.075
15	0.306	0.101
18	0.310	
19		0.120
21	0.313	
22		0.131
25	0.318	
26		0.142

mg/l, 19.5 minutes for 100 mg/l and 49 minutes for 50 mg/l wastewater. The higher the wastewater copper concentration the shorter the time it takes the resin to reach 1 mg/l. So the higher the concentration the quicker the resin is exhausted to its capacity and vice versa. So if the influent copper concentration is too high it calls for pretreatment. Then it can be treated using the resin.

4.5. Acid Mine Drainage from the Mine

The results for acid mine drainage from the mine are shown in **Figure 10** and **Table 9**. The pH for Samples 1 and 2 were measured and found to be pH 6.28 and pH 6.62 respectively. It took 25 minutes to treat 2 litres of Sample 1 and it took 26 minutes to treat 2 litres of Sample 2. The rates of flow of the effluent (treated water) were 24.4 m/h and 23.5 m/h respectively. For sample 1, 82%

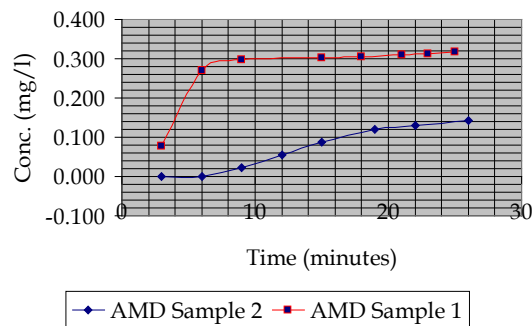


Figure 10. Acid mine drainage sample concentrations for Samples 1 and 2.

copper removal on average was achieved and for sample 2, 89.5% removal was achieved. These results indicate that acid mine drainage can be well treated by ion exchange resins, but it is also very important to determine optimum conditions for the experiment.

5. Conclusions and Recommendations

5.1. Conclusions

This study has demonstrated that acid mine drainage and other forms of wastewater can well be treated using ion exchange resins optimum conditions, in terms of pH, flow rate and copper ion concentration. For resin sample D401 the optimum conditions were established as follows:

- **pH**—The optimal pH was established at between pH 3.85 and pH 6.62. At pH 6.62, a removal of 89.5% was achieved for the acid mine drainage Sample 2 from Hongtoushan Mine. At pH lower than 6.62, the copper ions would precipitate as hydroxides making ion exchange of no use. At pH higher than 3.0, resin sample D401's exchange capacity was affected and did not perform well. This is attributed to the fact that hydrogen in the acid at pH below 3.85 has more affinity to the resin than the copper ions resulting into more copper ions going into the effluent.
- **Flow rate**—Optimal flow rate is required in order to get best treatment results. Too low a flow rate might result into long treatment periods and consequently demand for more treatment and labor hours. So in practical a more suitable flow rate must be established.
- **Copper ion concentration**—The lower the copper ion concentration of the wastewater, the longer it takes for treated water to reach the required standard concentration. And the opposite is the truth in the above case. Therefore wastewater concentration must be well measured before the start of the treatment process. Too high copper ion concentration requires pretreatment first or a higher resin height. Low concentrations might require reduced resin height.

5.2. Recommendations

- It is recommended here that after establishing the pH of the Acid Mine Drainage to be treated and if its pH is low or too high and would affect the ex-

change capacity of the ion exchange resin, the wastewater pH must be brought higher by adding NaOH until it reaches a pH which falls within the range that is known not to affect the resins capacity.

- The lower the flow rate the longer it takes for the treated water to reach the set standard and vice versa.
- Explore the use of ion exchange resins in terms of putting up a pilot plant on some copper mines where acid mine drainage is a problem currently especially in the mines in Northwestern Province of Zambia.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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