



Research article

Monitoring the extraction of copper from chicken dung leachate using an aluminium electrode as an indicator

Peterson Mutembei Kugeria^{a,*}, Isaac Waweru Mwangi^b, Jackson Wachira Muthengia^a, Peter Waithaka Njoroge^c^a Physical Sciences, University of Embu, P. O. Box 6 - 60100, Embu, Kenya^b Chemistry Department, Kenyatta University, P. O. Box 43844-00100, Nairobi, Kenya^c Department of Physical Sciences, Murang'a University, P. O. BOX 75 -10200, Murang'a, Kenya

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ABSTRACT

Copper is found in several minerals in the earth's crust with varying the elemental and mineralogical composition. Several techniques of extraction have been investigated all in the effort of obtaining a cheaper and viable method. This paper reports on further works done on copper extraction using a wet chemical method. According to the method, reduction of copper (II) ions using hydrazones from chlorinated chicken waste leachate was stoichiometrically driven. The chicken dung leachate used was an impure bio-material in which the concentration could not be determined. It was, therefore, difficult to quantify the stoichiometric ratios of species in that reaction. This paper reports on a method of monitoring the extent of copper reduction by chlorinated chicken dung leachate using an aluminium electrode as an indicator. Mineral rocks were obtained from Maragwa Location in Tharaka Nithi County in Kenya. The samples were ground into a fine powder of 250 micro millimeters. The samples were then subjected to mineralogical analysis using X-ray diffraction (XRD). Chemical analysis was done using atomic absorption spectroscopy (AAS) and X-ray fluorescence spectroscopy (XRFS). Ground samples were leached using 1.0 M hydrochloric acid. The resulting leachate was treated with chicken dung leachate prepared from chicken dung in which chlorine gas was bubbled at a constant temperature of 28 °C. The pH of the resultant chicken dung leachate was adjusted from 4 to 12 using 1.0 M sodium hydroxide and then used as an electrolyte. An electrochemical cell was set up consisting of aluminum and graphite rods. The aluminum electrode was found not to corrode at pH above 11 while it was able to displace available copper ions. This property of the aluminum electrode was used to monitor when all copper ions were displaced. The recovered copper was analyzed using XRFS. The copper recovery rate from the samples ranged from 7.0 to 20.0 at level A and 7.4–26.8% at level B with a purity range of 84.9 level A to 88.6% level B. An overall positive potential in the reduction process confirmed the greater the tendency of copper reduction without an external source of electricity. The corrosion of the aluminium electrode in the process was not observed and therefore does not require frequent replacement. Therefore, a large scale extraction process needs to be investigated.

1. Introduction

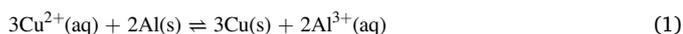
Copper metal has an industrial and economic application such conduction of electricity to power industries and the making of currency coins [1]. It is obtained from its ore by reduction using a hydrometallurgical process that involves the use of electricity as well as fossil fuel. The reduction process is expensive and contributes to global warming [2]. The recovery of metallic copper from the copper leach solution by the cementation process using aluminum disc has been reported by

Ahmet and co-workers (2012) [4]. In their study, the leaching of malachite was done using acetic acid. In their results, they observed that the cementation rate increased with increasing mass of the ore. The rate was also affected by temperature in a direct proportion and inversely proportional to the pH of the solution [4]. The extraction of copper by a wet chemical method has also been reported by Kugeria and co-workers. In their method, the electrolyte was made using a strongly alkaline media of chlorine-treated chicken dung leachate (chicken waste leachate) [5]. In that study, the complexation of copper (II) in a basic aqueous

* Corresponding author.

E-mail address: mutembei.kugeria@gmail.com (P.M. Kugeria).

environment at a suitable temperature was optimized and subsequent reduction of the metal ion was achieved. The reduction process was stoichiometrically driven with a reaction ratio of chlorinated chicken dung leachate to copper leachate which was 100ml: 30ml respectively. The copper metal obtained depended on the concentrations of the *insitu* prepared hydrazones in chicken dung leachate. However, the hydrazones were formed from a biomaterial whose concentration could not be verified. This, therefore, could not enable a calculation of the species reduced. But, aluminum is known to reduce copper in solution [4]. The Eq. (1) below shows the reduction process.

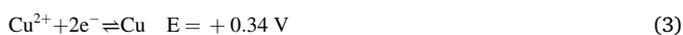


The equilibrium constant for the equation can be expressed as shown in Eq. (2) below.

$$K_c = \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3} \quad (2)$$

The K value determines the direction of the reaction. Thus, if less than one the reaction will move to the left and if the K value is greater than one the reaction will move to the right. The magnitude will, therefore, be dependent on the concentration of the reacting species. When the copper (II) ions have been depleted in the solution, Kc will be infinitely high.

In the redox process shown in Eq. (1), there exist two half-cells due to both reduction and oxidation reactions that involve a transfer of electrons as shown in Eqs. (3) and (4).



In an ideal situation and considering a standard cell given in Eqs. (3) and (4), the resultant potential between the cathode and anode is +2.01 V if the concentrations are unit based on Eq. (5) shown below. Eq. (3) relates the content of species involved with the electrode potential, E, of each half-reaction and its standard electrode potential, E⁰ [7].

$$E = E^0 - \frac{RT}{nF} \ln \frac{[\text{Red}]}{[\text{Ox}]} \quad (5)$$

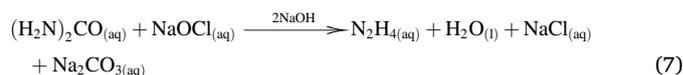
The higher the difference in the electro potential the higher the tendency of electron transfers. This results in a spontaneous heterogeneous reaction taking place in the galvanic cell. Due to the different potentials between the solutions, the migration of electrons occurs which leads to the generation of electrical energy. This leads to a different electrochemical potential, E, being developed that is associated with the chemical reactions in the respective cell. The amount of chemical change is proportional to the electricity generated as demonstrated by Nernst Eq. (5) [6]. Therefore the potential difference of the cell can give a measure of the number of species involved in the reaction as shown in Eq. (5).

This study exploited that property to investigate the number of copper ions in solution by measuring the change in potential across an electrochemical cell. The cell was made of chlorinated chicken dung leachate as an electrolyte. In the study, therefore, the aluminum electrode was used to detect when all copper (II) ions were reduced by the hydrazones in the chlorinated chicken dung leachate and none is available to oxidize aluminum. In that case, it was expected that there would be no copper ions to interact with the aluminum electrode thus no cementing. In this study unlike the work done by Ahmet and co-workers, where the aluminum disc was being corroded [4], it was observed that the corrosion of aluminum rod was minimal due to the pH of the reaction chamber. This factor reduces the cost of depletion of aluminum.

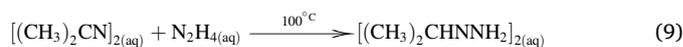
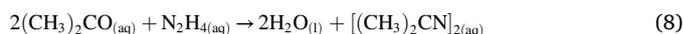
The oxide of aluminum is known to offer a protective oxide layer that creates a kinetic barrier that inhibits oxidation of aluminum. In aggressive environments that contain anions such as chloride, Cl⁻, the thin oxide film is broken down and enables oxidation [8]. Aluminum oxide being amphoteric, the stable protective layer of the oxide occurs at a pH range of

7.0–9.0. The oxide has been found to deteriorate in chloride environments at pH region below 7 and greater than 9 [9]. On the other hand, when copper ions are introduced in the environment containing the hydrazones reducing agents, they are converted to zero-valent [5, 10].

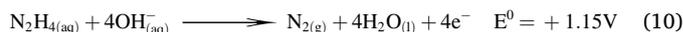
The study explored the reaction chamber is maintained at a working pH above 12.0 of chlorinated chicken dung leachate and using aluminum and graphite rods as electrodes. The study involved dispersing the copper ions in a chlorinated chicken dung leachate in which sodium hypochlorite had been formed *in situ*. This introduces chloride radicals that inhibit the formation of the aluminum oxide layer on the aluminum rod during the reduction of copper ions formed by hydrazones. Hydrazones are simple and suitable for reducing agents in a wet chemical form. Therefore, they can be prepared by interacting ammonia, urea or chicken dung leachate with chlorine in basic media as given by Eqs. (6) and (7) [5, 11, 12, 13].



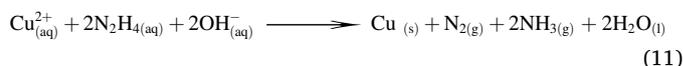
Hydrazine produced in Eqs. (6) and (7) is found to react further with alkanones and hydrazones to form other forms of hydrazones which are also strong reducing agents as shown in Eqs. (8) and (9) [14].



The reduction potential of hydrazine in a basic environment occurs as shown in Eq. (10).



Hydrazones are known to reduce some metal ions to elemental state as shown by Eq. (11) [5, 7].



Nitrogen in chicken dung is found in the form of amide bound protein, amino acids, or other forms of organic compound [5, 15, 16, 17]. In this study, amide and amino acid compounds were obtained from decomposed chicken dung. The dung was used to prepare the electrolyte as a reducing agent for copper ions in an electrochemical cell and aluminum rod acted as an indicator for the redox process.

2. Materials and methods

Analytical grade sodium hydroxide, hydrochloric acid, hydrazine, chlorine gas, starch, nitric acid, boric acid, and deionized water were supplied by Kobian (K) Ltd, an outlet of Sigma Aldrich Company. These chemicals were used to make all the solutions used in this study. Aluminum was procured from East African Cables Company. Chicken dung was obtained randomly from local poultry farmers from Thika in Kenya. Mineral rocks were obtained from Maragwa location in Tharaka North Sub - County in Tharaka Nithi County at locations 0°18'S38°08'E and 0°21'S38°11'E from three quarries which were about 1.5 km from each other. The three quarries were coded as 3230, 3234 and 3238. From each place, one kilogram of mineral rock was collected at a depth of 30 cm and 100 cm below the ground surface level respectively. The samples were packed in plastic bags labeled 3230A, 3234A, and 3238A. Another set of samples was obtained at about 100 cm depth (level B) and labeled as 3230B, 3234B and 3238B. The samples were then transported for analysis. The ore samples from each site were dried at 105 °C for 9 h in an oven. The dry samples were pulverized to 250 micro millimeters size and used for XRD, AAS and XRF analysis.

2.1. Mineralogical and chemical analysis

Mineralogical analysis of the samples was carried out using X-ray diffraction (XRD) and chemical composition was carried out using atomic absorption spectroscopy (AAS) and X-ray fluorescence spectroscopy [5, 18].

2.2. Copper leachate

To obtain copper leachate, 100.0 ml of 1.0 M of HCl was added into a 200-ml beaker containing 5.0 g of the mineral sample. The content was stirred and left to react for 3 h. The samples were filtered using Whatman filter paper number 110 mm. The residue was washed using distilled water and the filtrate transferred into a 100 ml volumetric flask and made to the mark using distilled water [5].

2.3. Preparation of chicken dung leachate

1 kg of chicken dung was placed in a desiccator. 2000 ml of water added and stirred for 5 min to ensure a uniform mixture was achieved. The content was covered and left to equilibrate for 15 days. The contents were filtered using 300-micron sieve to obtain the chicken dung leachate. To 100 ml of chicken dung leachate, chlorine gas was bubbled into at a flow rate of 0.5–0.7 cm³ per second for three minutes to form chlorinated chicken dung leachate [5].

2.4. Characterization of chicken dung leachate

The chicken dung leachate was characterized using the FT-IR spectrophotometer model Alpha 1005 4238 from Bruker. The instrument was initialized and calibrated by conducting a background scan. The resulting background spectrum was compared to a reference spectrum provided in the manufactures manual. The hydrazine hydrate solution was injected into a liquid cell for analysis the same manner samples of chicken waste leachate were done. A comparison of the absorption bands obtained in the spectra of the sample chicken waste with that of the hydrazine hydrate was used for data interpretation.

2.5. Reduction of copper

100 ml of copper leachate solution was introduced into a 500-ml beaker (cell 1) containing 100 ml of chlorinated chicken dung leachate solution. The initial pH and temperature of the resulting solution were taken. The content was allowed to react until all copper ions were reduced. At the same time, a second cell containing 100 ml of the chlorinated chicken dung leachate was done. A clean aluminum electrode of the thickness of 0.4 cm was weighed and introduced into cell 1 and then

connected to a digital multimeter (model 6000 Counts TRMS from Neoteck Company). The meter was then externally connected to a graphite electrode in cell 2 using a copper wire. The two cells were then connected using another copper wire with two graphite electrodes in each cell as shown in Figure 1. The reaction was monitored until no further displacement of copper on the electrode was observed. The copper obtained was filtered and dried in the oven at 40 °C. The dry extract was weighed and the percentage calculated from the original mass of the ore. The copper extract was later analyzed using XRFs for the percentage purity. The aluminum rod was reweighed after every experiment and results recorded.

2.6. The pH optimization

The procedure 2.5 was repeated by adjusting the pH values in both cells from 4.0 to 14.0 using 1.0 M NaOH at an interval of 2. The temperature of the solutions was maintained at room temperature of 28 °C during the reaction. The resulting precipitates obtained were filtered and dried in the oven at 40 °C and later analyzed using XRFs.

2.7. Temperature optimization

Procedure 2.5 was repeated while varying the temperature from 30 to 70 °C at an interval of 10. The pH was maintained at the optimized value of 12.0. The resulting copper precipitates at every varied temperature were filtered and dried in the oven at 40 °C and later analyzed using XRFs. The aluminum rod was reweighed at the end of every experiment and the difference obtained was recorded.

2.8. Rates of copper ions reduction

Procedure 2.7 was repeated by measuring the change in potential against the time taken. The volume of the chicken dung leachate used remained as 100 ml. The pH was maintained at 12. The voltage produced by the cell was recorded for 150 min at an interval of 25 min. The copper produced at every time interval was filtered and dried in the oven at 40 °C and later analyzed using XRFs.

3. Results and discussion

3.1. Mineralogical and chemical composition

The results for mineralogical analysis are as presented in Figure 2. From Figure 2; A- represent Albite, C – Chalcopyrite, Q – Quartz, M – Microcline, Ma – Magnetite, X – Magnesiohornblende, S – Sodium praeodymium sulphite.

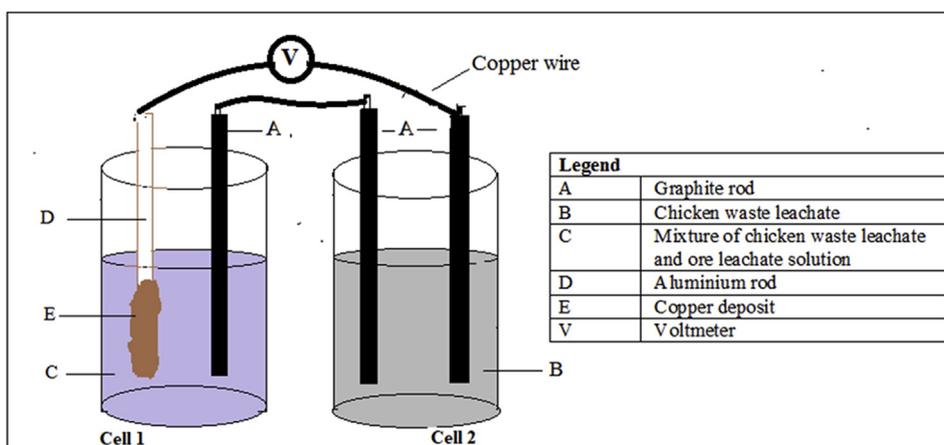


Figure 1. Diagrammatical presentation of an electrochemical cell.

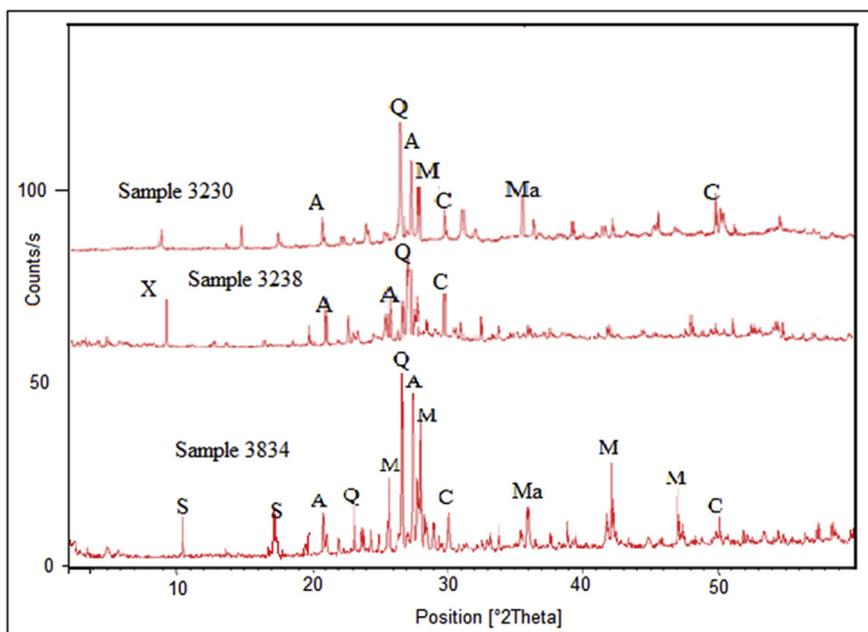


Figure 2. Minerals found in sample 3234, 3238 and 3230.

The results show that the deposits contain chalcopyrite mineral (CuFeS₂), as evidenced by a peak at an angle 2θ of 30° and 50°, albite (angle 2θ of 27.5°, 21°, and 24.5°) and quartz (angle 2θ of 27.0° and 23.0°). However various mineral deposits have different mineralogical composition. For instance, Magnetite (angle 2θ of 35.5°, 63° and 43.5°) and microcline (angle 2θ of 27.5°, 42.0°, and 50.5°) were found in sample 3834 and 3230. Sodium praseodymium sulfite mineral (angle 2θ of 10.5°, 17.5°, and 19.8°) was only found in sample 3834. This shows that mineral deposits in Tharaka North Sub County have varied mineral composition. Chemical composition was carried out on the samples and the results given in Tables 1 and 2. Statistical analysis of the two methods was done and the results given in Table 3.

The values of the mean given with superscript "a" against each column show that there is no significant difference in results obtained using AAS and XRFS methods. This shows that any of the two methods can be used for the analysis of the samples. The p-values obtained from the two methods show no significant difference in mineralogical composition from the three quarries (p > 0.05 at 95% confidence level). The results show well-distributed minerals in all quarries and their composition varies with the depth geologically. The percentage composition of Cu in samples 3230 3234 and 3238 ranges from about 2 and 10%. These compositions are better than those from the ores mined from other countries. For instance, Chile is one of the largest copper producers from ores containing 0.4–1.0 percent copper [19]. In Zambia, all copper mines contain an average ore composition of 0.5–2.3 percent copper [22]. In East Africa, copper mining has been going on in Uganda since the 1950s–1980s from ores with compositions ranging between 0.48 to 2.0 percent Cu [20]. From this observation, it implies that ores

from Tharaka Nithi County are viable for economic extraction. Since these copper deposits are yet to be exploited economically, this study investigated a possible alternative method for the extraction of these minerals. The method investigated was the one that could minimize impurities of silica, alumina, iron, and calcium which are the dominant impurities in the ore.

3.2. Synthesized hydrazones

The chicken waste samples were studied to show the presence of the various functional groups. The results from FTIR-characterization of the unchlorinated and chlorinated chicken waste leachate were as presented in Figure 3A, 3B, and 3C respectively [5].

The results show that before chlorination, the chicken waste samples contain OH, 1°&2°NH (amines), and C–H groups due to the bands found within the range from 3000 and 3500 cm⁻¹, SH group at 2494.9 cm⁻¹, carbonyl group stretching at 1634 cm⁻¹, CN triple bond stretch at 2100 cm⁻¹, and CH group are found at 1355 cm⁻¹. The spectra show that the same functional groups were found in pure hydrazine hydrate solution that was available in the chlorinated sample solutions. Before chlorination, the spectrum of chicken waste has no peak at around 1090–1020 cm⁻¹. However, after chlorination, a signal appeared at 1080.16 cm⁻¹, at the same position as that found in the hydrazine sample. The emergence of that band at 1080.16 cm⁻¹ could be due to induced vibration excitation of N–N covalent bonds [5, 21]. This shows that a reducing agent either symmetrical or unsymmetrical hydrazones were produced [13]. Since C=O and NH₂ groups are found in amines and amides compounds, then the same compounds are found in chicken waste solution. These

Table 1. Chemical composition of the mineral ores at level A and B analyzed using AAS.

Oxides Sample Reference	SiO ₂ Mean ± SE	Al ₂ O ₃ Mean ± SE	K ₂ O Mean ± SE	Na ₂ O Mean ± SE	CaO Mean ± SE	TiO ₂ Mean ± SE	MnO Mean ± SE	Fe ₂ O ₃ Mean ± SE	Cu Mean ± SE	CuO Mean ± SE	MgO Mean ± SE
3230 A	41.53	8.16	7.69	12.81	2.28	1.00	0.11	3.81	9.60	12.00	5.81
3230 B	37.53	6.28	6.95	13.75	5.00	0.98	0.17	4.39	7.16	8.95	6.91
3234 A	35.86	3.56	0.69	12.15	23.67	0.66	0.27	13.13	1.96	2.45	4.12
3234 B	34.84	2.84	1.00	8.39	18.4	0.45	0.31	19.80	1.58	1.97	5.14
3238 A	42.44	10.79	2.68	13.15	10.63	1.70	0.33	10.06	4.43	5.54	1.93
3238 B	45.86	7.26	4.38	17.75	11.05	1.58	0.35	5.46	6.61	8.26	3.67

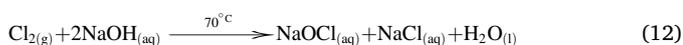
Table 2. Chemical composition of the mineral ores at level A and B analyzed using XRFs.

Oxides Sample Reference	SiO ₂ Mean ± SE	Al ₂ O ₃ Mean ± SE	K ₂ O Mean ± SE	Na ₂ O Mean ± SE	CaO Mean ± SE	TiO ₂ Mean ± SE	MnO Mean ± SE	Fe ₂ O ₃ Mean ± SE	Cu Mean ± SE	CuO Mean ± SE	MgO Mean ± SE
3230 A	41.58	8.18	7.76	12.89	2.28	1.01	0.11	3.82	9.66	12.07	5.85
3230 B	36.6	6.24	6.95	13.84	4.90	0.96	0.13	4.35	7.19	8.94	6.89
3234 A	35.87	3.59	0.69	12.13	23.67	0.61	0.20	13.09	1.93	2.41	4.16
3234 B	34.3	2.85	1.04	8.37	18.4	0.46	0.36	19.82	1.59	1.97	5.17
3238 A	42.47	10.78	2.71	13.08	10.61	1.71	0.52	10.07	4.40	5.51	1.84
3238 B	44.9	7.24	4.13	16.95	11.17	1.56	0.33	5.44	6.60	8.25	3.61

Table 3. Statistical analysis of the means of AAS and XRFs methods at 95% confidence level.

	SiO ₂ Mean ± SE	Al ₂ O ₃ Mean ± SE	K ₂ O Mean ± SE	Na ₂ O Mean ± SE	CaO Mean ± SE	TiO ₂ Mean ± SE	MnO Mean ± SE	Fe ₂ O ₃ Mean ± SE	Cu Mean ± SE	CuO Mean ± SE	MgO Mean ± SE
Mean using AAS	39.67 ± 1.75 ^a	6.48 ± 1.21 ^a	3.89 ± 1.21 ^a	13.0 ± 1.23 ^a	11.84 ± 3.28 ^a	1.06 ± 0.20 ^a	0.25 ± 0.04 ^a	9.45 ± 2.55 ^a	5.22 ± 1.28 ^a	6.52 ± 1.6 ^a	4.59 ± 0.71 ^a
P-Value using AAS	4.498	3.103	3.116	3.153	8.43	0.519	0.1	6.55	3.298	4.123	1.836
Mean Using XRFs	39.28 ± 1.74 ^a	6.48 ± 1.2 ^a	3.88 ± 1.21 ^a	12.87 ± 1.13 ^a	11.83 ± 3.29 ^a	1.05 ± 0.20 ^a	0.28 ± 0.06 ^a	9.43 ± 2.55 ^a	5.23 ± 1.29 ^a	6.53 ± 1.62 ^a	4.59 ± 0.73 ^a
P-Value Using XRFs	4.468	3.091	3.118	2.909	8.454	0.523	0.165	6.552	3.324	4.152	1.872

compounds are potential sources for making hydrazones when reacted with suitable oxidizing agents as shown in Eq. (12) [3, 5].



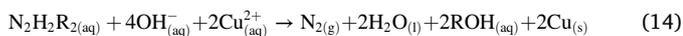
The produced sodium hypochlorite oxidizes amines and amides to hydrazones as given in Eq. (13) [5, 12, 14].



3.3. Copper reduction and oxidation of aluminium

The results on the effect of pH on the relationship between the reduced copper and sacrificed aluminium are presented in Figure 4.

The results show that at pH values 6.5–9.0, there was a decrease in the mass of copper obtained. This is because, at that pH environment, the oxide of aluminium on the aluminium electrode is stable thus reducing its deterioration. Also, there were no significant hydrazones produced for the reduction of copper ions. The mass of aluminium sacrificed is high in a strongly acidic environment due to both displacements of copper and hydrogen ions in solution. At pH values below 6.5, the copper reduction is as a result of oxidation of aluminium. Even when all copper ions have been reduced, aluminium continues to undergo oxidation. This is due to the presence of hydrogen ions in the solution. This explains why aluminium corrodes at low pH and the rate of corrosion decreases with an increase with the pH. Above the pH value of 11, all the copper ions are reduced by hydrazones as shown in Eq. (14).

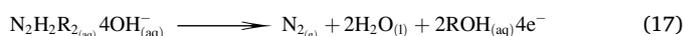


From Figure 4, there is little or no corrosion of aluminium electrode yet displacement of copper occurs on the electrode as shown in Eqs. (15) and (16).



Oxidation of hydrazones in the alkaline environment is known to occur as shown in Eq. (8). Therefore the produced hydrazones in cell 2

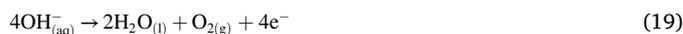
will occur the same way thus providing with electrons that recharge the oxidized aluminium electrode as shown by Eqs. (17) and (18) [5, 10, 11].



(Where R is an alkyl group or halogen group)



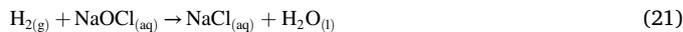
This explains why the aluminium electrode does not corrode. This property of the aluminium electrode makes it an indicator of the presence of copper ions during the redox process. Other reactions that occur in the electrodes are as follows; the hydroxide ions in cell 1 migrate to the graphite electrode where they undergo oxidation on as shown in Eq. (19).



The produced electrons flow to the next graphite electrode (cell 2), where they reduce available hydrogen ions from the solution to hydrogen gas as shown in Eq. (20).



The produced hydrogen gas is immediately oxidized to water by sodium hypochlorite in the electrolyte, Eq. (21).



The graphite bridge was created to ensure a balanced flow of ions in chicken chicken dung leachate, as well as that of electrons in the cells.

3.4. Effect of temperature on the reduction of copper

The effect of temperature at the optimal pH value of 12.0 was investigated and the results obtained recorded in Figure 5.

The results of the regression analysis from the two curves show that r^2 is less than 0. The reaction shows that change in temperature of chlorinated chicken dung leachate has no effect on the reduction of copper ions and oxidation of aluminium at a pH greater than 12. The hydrazones in the chicken dung leachate react with all copper (II) at a given temperature to zero valences. An increase in temperature though increases the collision energy of hydrazones with copper (II), the total mass of copper

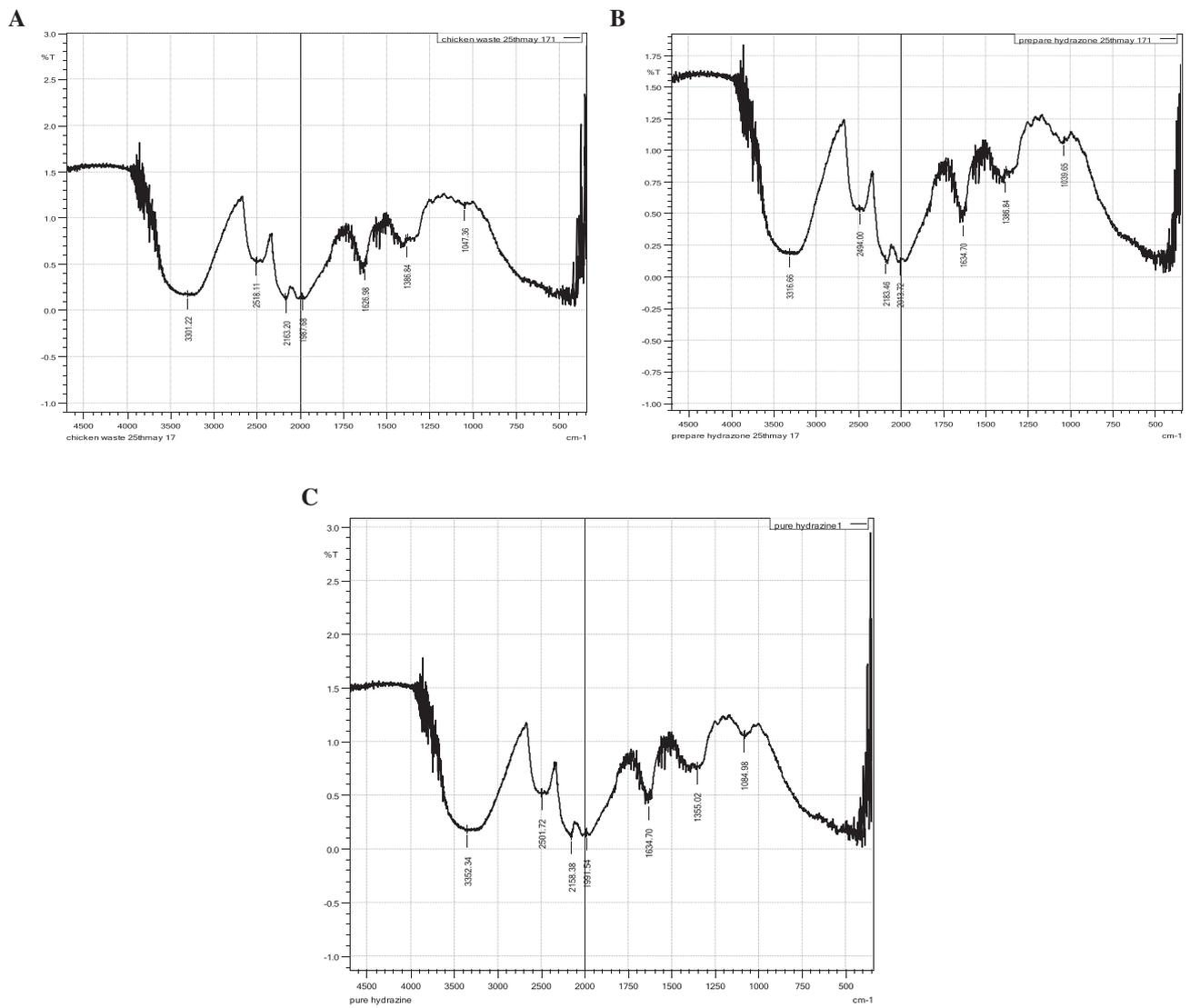


Figure 3. FTIR Spectra (A) before and (B) after chlorination and (C) hydrazine samples.

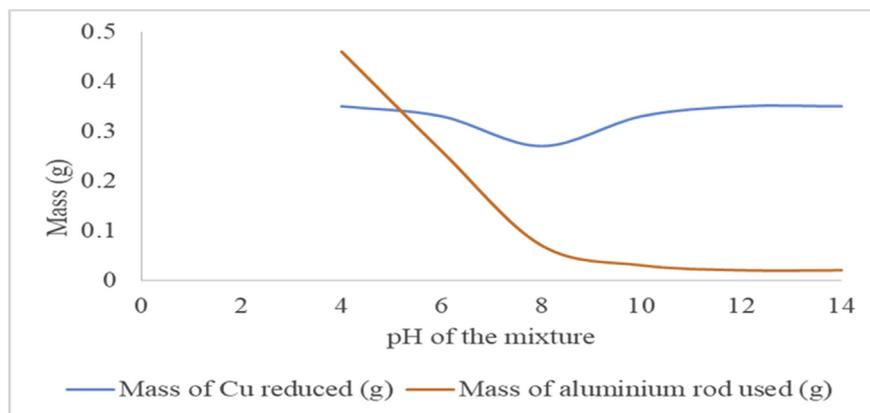


Figure 4. Effect of pH on the reduction of copper and oxidation of aluminum.

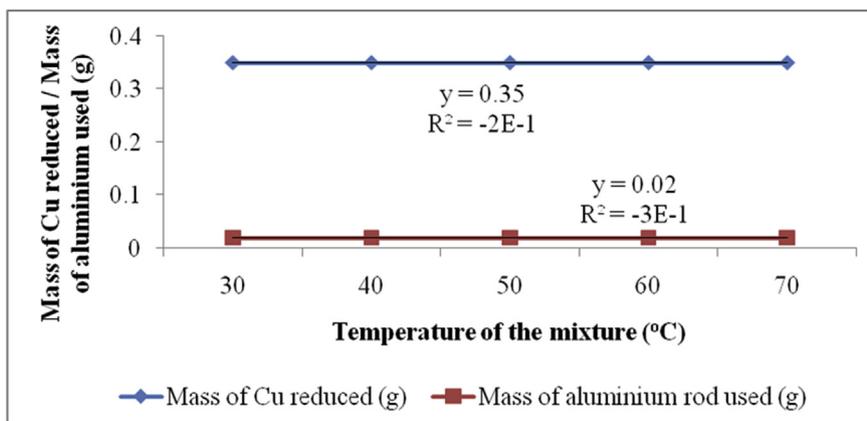


Figure 5. Relationship between temperatures, copper reduced and mass of used aluminum.

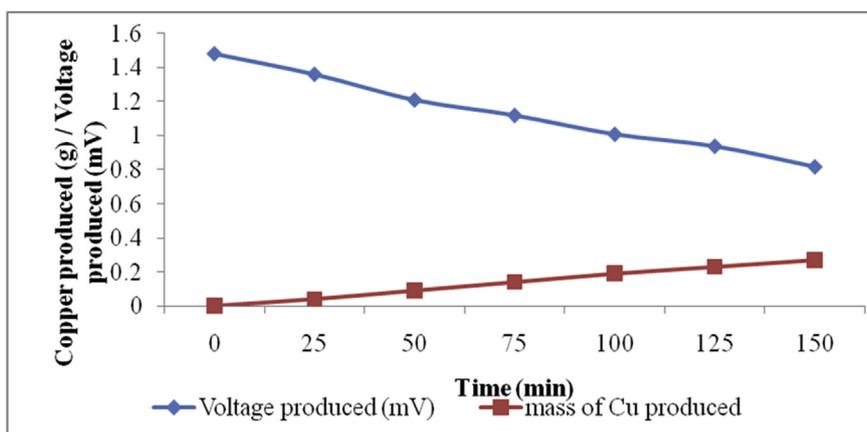


Figure 6. Effects of potential on time.

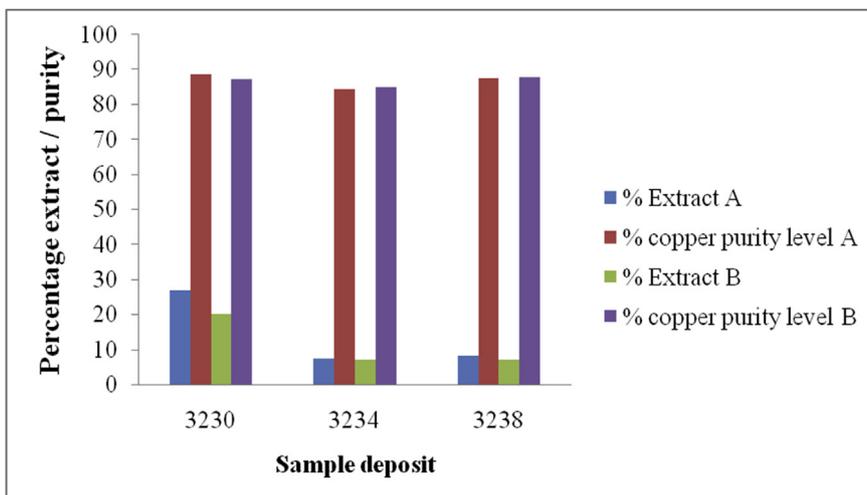


Figure 7. Percentage extract and purity of reduced copper.

produced remains the same. An increase in temperature did not influence an aluminum electrode.

3.5. Relationship between rates of copper ions reduction with potential

The relationship between the rates of copper ion reduction against the potential produced by the reaction was investigated and results given in

Figure 6. In the same Figure 6, a plot of the amount of copper produced with time was given.

Based on Figure 6, the time taken for the complete reduction of Cu ions by hydrazones in the leachate mixture is inversely proportional to the potential produced by the reaction. This follows the first-order reaction where there is a decrease in the concentration of copper ions in the chicken dung leachate with an increase in time as shown in Eq. (22).

Table 4. Mean copper extract in both level A and B.

	Mean \pm SE	p-value
% Extract level A	0.56 \pm 0.37	0.6312
% Extract level B	0.71 \pm 0.51	0.5999

$$\text{Rate} = -d[A]/dt = k[A] \quad (22)$$

The "rate" is the reaction rate (in units of molar/time) and k is the reaction rate coefficient (in units of 1/time) [24]. The potential obtained also decreases with a decrease in the concentration of copper ions with time. In other words, the higher the concentration of copper ions in solution, the higher the potential produced during the redox process. Since in the cementation process, the reduction of copper ions and oxidation of aluminum metal occurs as given by Eqs. (1) and (2) above, the high positive potential difference creates a spontaneous redox reaction. Therefore the chlorinated amine and uric acid in chicken waste produced a current that was used to recharge the number of electrons used from aluminum during the oxidation process. The change of potential with the concentration of copper ions can be explained by Eqs. (23), (24), and (25).

$$E - E^0 = \frac{RT}{nF} \ln Q \Rightarrow \Delta E = \frac{RT}{nF} \ln Q \quad (23)$$

The equation can be written as

$$\Delta E = \frac{RT}{nF} \ln \frac{\text{Reduced}}{\text{Oxidised}} \quad (24)$$

For this case

$$\Delta E = \frac{RT}{nF} \ln \frac{[Cu^{2+}(aq)]}{[Cu^0(s)]} \Rightarrow \Delta E = \frac{RT}{nF} \ln [Cu^{2+}(aq)] \quad (25)$$

This implies that as the electro process continues, the value of ΔE proportionally decreases with a decrease in Cu^{2+} ions in Cell 1 (Figure 6). Eventually, when $\Delta E = 0$, no more copper ions are available for the reduction and there was no copper displacement observed on the aluminum electrode. In this method of copper extraction, the aluminum electrode becomes a suitable method of determining when all copper ions are reduced.

After optimization, reduction of copper ions from the mixture of ore leachate and chlorinated chicken dung leachate was done on samples 3234, 3238 and 3230. The aluminum electrode was used to monitor when all copper ions were displaced from the leachate mixture. The results obtained are given in Figure 7. The results of the statistical mean extract for both level A and B are given in Table 4.

From the table, P-value was greater than 0.05. This shows that the amount of copper extract at level A and B did not differ significantly. The copper extract from the three ores ranged from 7.0 to 20.0% at level A and 7.4–26.8% at level B with purity range from 84.9% level A to 88.6% level B. The results show that the method of monitoring using aluminum electrode could be viable for copper extraction from ores.

4. Conclusion

The monitoring of copper ions reduction by hydrazones in chlorinated chicken dung leachate using an aluminum electrode was successful. In the study, there was minimal corrosion of the aluminum electrode. Therefore, further investigations on large scale production should be done for economic extraction. This will minimize the cost of using electricity for electrolysis as well as buying aluminum metal for replacement. The preparation of the chlorinated chicken dung leachate

on large scale and mixing with copper leachate using the investigated ratios can be adopted and used for copper extraction from ores.

Declarations

Author contribution statement

Isaac Waweru Mwangi: Conceived and designed the experiments.
 Peterson Mutembei: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
 Jackson Muthengia: Contributed reagents, materials, analysis tools or data.
 Peter Waithaka: Analyzed and interpreted the data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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References

- [1] Copper Development Association, Copper and Copper Alloys. Compositions, Applications, and Properties, Publication No 120. 5, Grovelands Business Centre, Hertfordshire, 2004.
- [2] E.A. Godwin, F.A. Usenobong, The contribution of energy consumption to climate change: a feasible policy direction, *Int. J. Energy Econ. Policy* 2 (1) (2012) 21–33.
- [3] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, second ed., Butterworth-Heinemann Publisher, 1997.
- [4] E. Ahmet, T. Mehmet, D. Nizamettin, Investigation of copper cementation kinetics by rotating aluminum disc from the leach solutions containing copper ions, *Physicochem. Probl. Miner. Process.* 48 (2) (2012) 355–367.
- [5] P.M. Kugeria, I. Mwangi, J. Wachira, P. Njoroge, Copper extraction by wet chemical method, *J. Sustain. Min.* (2018).
- [6] M. Karavasteva, Kinetics and deposit morphology of copper cementation onto zinc, iron, and aluminum, *Hydrometallurgy* 76 (1) (2005) 149–152, 8549.
- [7] P. Atkins, P. Julio de, in: *Physical Chemistry for the Life Sciences*. (J. C. Oxford University) & J. F. (W. H. F. and Company), second ed., Oxford University Press, New York, 2011.
- [8] R. Ambat, E.S. Dwarakadasa, Studies on the influence of chloride ion and pH on the electrochemical behavior of aluminum alloys 8090 and 2014, *J. Appl. Electrochem.* 24 (1994) 911–916.
- [9] P.M. Natishana, W.E. O'Grady, Chloride ion interactions with oxide-covered aluminum leading to pitting corrosion: a review, *J. Electrochem. Soc.* 161 (9) (2014) C421–C432 (2014).
- [10] J.P. Chen, L.L. Lim, Key factors in chemical reduction by hydrazine for the recovery of precious metals, *Chemosphere* 49 (2002) 363–370.
- [11] P. Bourdauducq, J.P. Schirmann, Hydrazine. *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2002.
- [12] R. Adams, B.K. Brown, Hydrazine sulfate, *Org. Synth. Collect. 1* (1941) 309.
- [13] K. O'Neill I, R.C.V. Borstel, C.T. Miller, J. Long, H. Bartsch, N-Nitroso Compounds: Occurrence, Biological Effects, and Relevance to Human Cancer, IARC Scientific Publication No. 57, Oxford University Press, Lyon, 1984.
- [14] A.C. Day, M.C. Whiting, Acetone hydrazones, *Org. Synth.* 50 (1988) 10–12.
- [15] E.L. Barbin, T.C. Santos, J.C.E. Spano, L.F. Guimaraes, J.D. dan Pecora, Solvent action on sodium hypochlorite on bovine pulp and physio-chemical properties of resulting liquid, *J. Braz. Dent.* 12 (3) (2001) 154–179.
- [16] A. Bono, K.B. Yeo, S.L. Goh, *Mineralized Organics in Compressed Bricks*, CONTEC 2003, October 2003, Kota Kinabalu, Sabah, 2003.

- [17] J.E. McMurry, Organic Chemistry, third ed., Wadsworth, Belmont, 1992.
- [18] P.K. Mutembei, J.W. Muthengia, N.T. Muriithi, Iron enrichment in laterites soils from selected regions in Kenya using magnetic separation, IOSR J. Eng. 4 (3) (2013) 42–48.
- [19] P.H. Kuck, Nickel: US Geological Survey Mineral Commodity Summaries 2014.Gov/publication/70100414, 2014, pp. 108–109.
- [20] R. Cox, An Assessment of the Current Status and Potential of the Mineral Industrial in Uganda, Project UGA/8, 9/001, Department of Geological Survey and Mines, 1993.
- [21] P.A. Giguère, I.D. Liu, Infrared spectrum of hydrazine, J. Chem. Phys. (1952).
- [22] D. Haglund, Zambia Mining Sector Fiscal Benchmarking and Assessment, Oxford Policy Management, 2013, p. 7.
- [24] R.H. Petrucci, W.S. Harwood, G.E. Geoff E Herring, J. Madura, General Chemistry: Principles and Modern Applications, ninth ed., Pearson Education Inc, New Jersey, 2007.