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Research paper

Copper extraction by wet chemical method

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ARTICLE INFO ABSTRACT Keywords: In many countries large deposits of copper with no locally established copper based industries occur because Hvdrazones known methods for extraction are prohibitively expensive and unaffordable. This study reports on an affordable In situ and sustainable method for the extraction of copper. This was achieved through the use of a wet chemical Reduction method which makes use of hydrazones prepared in situ from chicken dung leached solution. The method Zero valence involves the reduction of copper (II) ions leached from copper ore to zero valence using chlorine treated solution Chicken dung prepared from chicken droppings at a temperature range of 60-70 °C. The ore samples were pulverized to 250 micro millimetres and leached with hydrochloric acid to obtain leachate containing copper ions. The dissolved copper was reduced to copper metal and obtained by filtration. It was confirmed by XRFS analysis that, the metal purity was found to range between 60 and 80% depending on the ore used. In another experiment, chicken waste solution was used to extract copper from the ore. To the mixture, chlorine gas was then bubbledthrough a glass delivery tube to prepare the hydrazone in situ at a temperature range of 60-70 °C and a pure copper metal was obtained. The findings from this study have shown that there is great potential for the production of copper at low cost and this could be applied in both small-scale cottage industries and large industries using readily available resources such as chicken dung.

1. Introduction

Kenya is well endowed with a bulk of mineral resources some of which are yet to be exploited (Republic of Kenya, 2001). Among these resources, copper is found in several minerals with varied elemental compositions. Examples of such compositions occur as chalcopyrite (CuFeS₂), bornite (Cu₅FeS₄), chalcocite (Cu₂S), covellite (CuS), cuprite oxide (Cu₂O), and malachite (Cu₂CO₃(OH)₂) among many other minerals (Greenwood & Earnshaw, 1997). Malachite and sulphides are major deposits in Kenva, with elemental composition of 2.3% Cu found at Macalder in South Nyanza-Kenya (Ogola, 1987). According to DuBois and Walsh (1970) 4-6% Cu mineral deposits have been reported at Kitere near Kisii and 3-4.55% Cu at Kipkomo near Kapenguria. More copper minerals were identified near Voi Hill where the assaying content was found to be 8.2% (DuBois & Walsh, 1970). Other deposits containing chalcopyrite minerals have also been identified in Tharaka with 0.35-5% copper (DuBois & Walsh, 1970). Despite the presence of such rich copper deposits, their extraction has not yet been exploited for economic growth.

Currently the extraction of copper is performed using a

pyrometallurgical process that involves the use of electricity as well as coal, both of which are expensive. The use of fossil fuels in extraction produces carbon dioxide which contributes to global warming. The other method used is solvent extraction followed by electro-winning (SX-EW). This method is applied in Zambia, the Democratic Republic of Congo and in Uganda (Kasese Cobalt Company Ltd., 2007; Wills, 2011; Yager, 2016). The pyrometallurgical process involves the thermal treatment of minerals and metallurgical ores and concentrates (after froth flotation). The net result is a physical and chemical transformation of minerals to pure metals, intermediate compounds or alloys which are suitable as feed for further processing (Adalbert, 2005). The methods are capital intensive and require suitable technologies.

To overcome these issues, this study aims to offer solutions to the demand for copper at reduced cost. In order to achieve this, the use of a suitable reducing agent was investigated. This involved reducing copper ions using selective reducing agents that were prepared using readily available materials to produce hydrazones and then to use them as reducing agents in a wet chemical process. Such derivatives are prepared by interacting ammonia or urea with chlorine in basic media, as shown in equations (1) and (2) (O'Neill et al., 1984; Adams & Brown,

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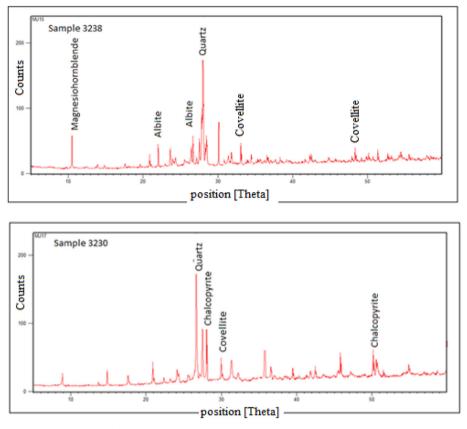


Fig. 1. Mineralogical analysis of sample 3238 and 3230.

1941; Bourdauducq & Schirmann, 2002).

$$2NH_3 \xrightarrow{\text{NaOCl}} 0^{\circ}C \quad H_2NNH_{2(aq)} + H_20_{(l)} + \text{NaCl}$$
(1)

$$(H_2N)CO_{(aq)} + NaOCl_{(aq)} \xrightarrow{2NaOH} H_2NNH_{2(aq)} + H_2O_{(l)} + NaCl_{(aq)} + Na_2CO_{3(aq)}$$
(2)

The hydrazine produced was found to react further with alkanones and hydrazones to form other forms of hydrazones, which are also strong reducing agents as shown by equations (3) and (4). (Day & Whiting, 1988).

$$(CH_3)_2CO_{(aq)} + H_2NNH_{2(aq)} \rightarrow [(CH_3)_2CN]_{2(aq)} + 2H_2O_{(l)}$$
 (3)

$$[(CH_3)_2CN]_{2(aq)} + H_2NNH_{2(aq)} \xrightarrow{100^{\circ}C} (CH_3)_2CNNH_{2(aq)}$$
(4)

10000

The reduction potential of hydrazine in a basic environment occurs as shown in equation (5) below.

$$H_2NNH_{2(aq)} + 4OH^{-}_{(aq)} \rightarrow N_{2(aq)} + 4H_2O_{(l)} + 4e^{-} E^{0} = +1.15 V$$
 (5)

This shows that hydrazine can effectively be employed in the reduction of various metal cations to their elemental state. This was reported by Chen and Lim (2002) while investigating the recovery of precious metals of silver and copper in synthesized wastewater in batch reactors. In their study they used hydrazine as the reducing agent as shown by reactions 6 and 7 below (Chen & Lim, 2002).

$$2Cu^{2+}_{(aq)} + H_2NNH_{2(aq)} \rightarrow 2Cu_{(s)} + N_{2(g)} + 4H^+_{(aq)}$$
(6)

$$2Cu^{2+}_{(aq)} + H_2NNH_{2(aq)} + 2OH^{-}_{(aq)} \rightarrow Cu_{(s)} + N_{2(g)} + 2NH_{3(g)} + 2H_20_{(l)}$$
(7)

In this study uric acid, amine and amide compounds obtained from decomposing chicken droppings (herewith referred to as biomass) were used to prepare the hydrazone derivative reducing agent. The chlorination of the chicken waste biomass leached solution in alkaline media produced compounds capable of reducing copper ions to zero valence. The nitrogenous uric compounds in the biomass are suitable ligands that are capable of forming complexes with all forms of copper in the ore and make it soluble and thus available for the reduction of the metal. This method has an advantage in that cupric ion, when compared to others, forms very stable complexes with amino acids when the reaction mixture is heated to a temperature above 60 °C (Kurtz, 1949). This is unlike other metals which are oxidised to higher insoluble states allowing a separation of copper with other transition metals to occur. This is reported by Kurtz (1949) who stated that copper has the ability to mask a-amino groups from reagents which attack unprotected amino functional groups elsewhere in the molecule. This method forms copper complexes in alkaline media, as the ligand is protonated in acid solutions (Lampeka & Gavrish, 1990). This enables dissolved copper to be reduced to copper metal and recovered by filtration, in this study.

2. Methodology

2.1. Materials and reagents

All reagents were of analytical grade and Millipore water was used to make all the solutions in this study, unless otherwise stated. Chicken dung was obtained from poultry farmers in Thika, Kenya. Chlorine was supplied by BOC Nairobi-Kenya. All other chemicals and reagents were of analytical grade from Sigma Aldrich (London, UK).

2.2. Sampling

The samples were obtained from the Maragwa location and Kamwathu sub-location, Tharaka North Sub-County of Tharaka Nithi County at locations 0°18′S38°8′E and 0°21′S38°11′E respectively. Samples were chosen at random from ten quarries which were within

Sample reference	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	TiO_2	MnO	Fe_2O_3	Cu	CuO	MgO
3227	48.34 ± 0.03	8.39 ± 0.02	7.76 ± 0.07	5.21 ± 0.02	13.85 ± 0.06	0.63 ± 0.04	0.25 ± 0.02	+1	$4.04\ \pm\ 0.02$	5.06 ± 0.02	2.13 ± 0.01
3230	41.48 ± 0.15	8.18 ± 0.04	7.76 ± 0.04	12.89 ± 0.03	2.28 ± 0.02	1.00 ± 0.03	0.11 ± 0.01	3.82 ± 0.04	9.66 ± 0.05	12.07 ± 0.06	5.80 ± 0.04
3231	45.22 ± 0.54	5.44 ± 0.02	4.87 ± 0.04	6.12 ± 0.01	19.03 ± 0.07	+1	0.83 ± 0.04	7.62 ± 0.04	4.43 ± 0.05	5.54 ± 0.06	3.75 ± 0.01
3232	42.75 ± 0.08	11.42 ± 0.04	10.49 ± 0.03	3.89 ± 0.02	2.60 ± 0.01	2.12 ± 0.13	0.14 ± 0.02	17.64 ± 0.03	2.72 ± 0.02	+1	5.48 ± 0.07
3233	25.85 ± 0.04	9.19 ± 0.03	6.81 ± 0.02	3.68 ± 0.03	1.33 ± 0.01	0.90 ± 0.04	0.23 ± 0.04	40.97 ± 0.04	4.40 ± 0.02	5.50 ± 0.02	3.16 ± 0.01
3234	35.87 ± 0.08	3.59 ± 0.03	0.69 ± 0.02	12.13 ± 0.06	23.67 ± 0.06	+1	0.20 ± 0.04	13.09 ± 0.05	1.93 ± 0.02	2.41 ± 0.02	4.16 ± 0.03
3238	42.47 ± 0.09	10.78 ± 0.01	2.71 ± 0.04	13.08 ± 0.08	10.61 ± 0.03	1.71 ± 0.02	0.52 ± 0.33	10.07 ± 0.09	4.40 ± 0.02	5.51 ± 0.03	1.84 ± 0.02
3240	74.28 ± 0.12	3.23 ± 0.02	2.43 ± 0.01	9.04 ± 0.08	1.08 ± 0.02	+1	+	1.55 ± 0.02	3.24 ± 0.06	4.05 ± 0.07	1.11 ± 0.03
3244	47.09 ± 0.06	14.70 ± 0.03	2.49 ± 0.01	16.37 ± 0.04	8.10 ± 0.04	+1	+1	0.04 ± 0.01	3.24 ± 0.07	+1	4.29 ± 0.04
3242	39.70 ± 0.09	7.68 ± 0.02	1.69 ± 0.03	5.12 ± 0.54	13.91 ± 0.02	1.05 ± 0.11	0.29 ± 0.01	20.41 ± 0.04	6.66 ± 0.03	8.33 ± 0.03	3.19 ± 0.02

elemental analysis of some selected copper deposits in Tharaka Nithi County.

Table 1

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one to 2 km from each other. A mattock was used to dig and break the rocks and a shovel was used to scoop out the soil and rocks. A kilogram of mineral samples was collected from a depth of 30 cm and another kilogram was collected from a depth of 1 m from the sample site. The samples were transported to the laboratory and pulverized to 250 micro millimetres using a ball mill.

2.3. Mineralogical analysis using XRD

A sample, 30 g of pulverized ore, was put into XRD sample holder and its mineral content was analysed using a Bruker D8 Advance Diffractometer which had data collector software. The XRD spectra obtained from the analysis before treatment was used to determine the mineralogical composition of the rock samples.

2.4. Elemental analysis using XRF

The elemental composition of solid samples was performed using the X-ray fluorescence spectrophotometer model S1Titan-Bruker. This was carried out in accordance to the test method D-6376 (ASTM, 2007). The finely ground samples of 250 μ m were each placed in the XRF cup and irradiated with an X-ray beam. The intensities of the fluorescent characteristic X-rays of the elements present were directly proportional to the concentration of each respective analyte.

2.5. Leaching of copper from its ores

A sample, 200.0 g, of the ore was weighed and placed into a 1 L beaker and 500.0 ml of 2.0 M HCl was added. The mixture was left to equilibrate for 1 h. The resulting solution was filtered and the filtrate transferred into a volumetric flask then diluted to 1 L.

2.6. Preparation for chicken waste solution

A mass of 1 kg of chicken defecate was put into a desiccator. To this, 2.0 L of water was added and the mixture stirred for 5 min to ensure a uniform mixture. The content was covered and left to dissolve the amino compounds. The mixture was filtered using a 300 μ m sieve to obtain the chicken waste solution and the functional groups in the solution were then monitored after every three days for 15 days using the FTIR Spectrophotometry model Alpha 1005 4238 from the Bruker instrument in ATR mode, in accordance with the test method D 7624-10 (ASTM, 2010).

2.7. Optimisation studies on the reduction of copper ions from leachate using chlorinated chicken waste solution

2.7.1. The pH optimisation

A solution of 100 ml of chicken waste solution was put into a 200 ml beaker. The pH and the temperature were recorded. To this solution, 30 ml of the leachate ore was then added and chlorine gas bubbled in the resulting mixture for 6 min with constant stirring. While stirring, 20 ml of chicken waste solution was slowly added until no further precipitate was observed. The chlorine flow rate was measured using a gas flow meter (model 270134.003 from TA Instruments). The resulting mixture was filtered and the percentage of copper present was later determined using XRF. The procedure was repeated by varying the pH from 7.0 to 12.7 using 1.0 M NaOH.

2.7.2. Chlorine bubbling time optimisation

After obtaining the optimal pH, the chlorination period was varied from one to 6 min before the addition of the leachate. All experiments were performed at optimal pH while ensuring all other parameters were constant. The content of the copper present was later determined.

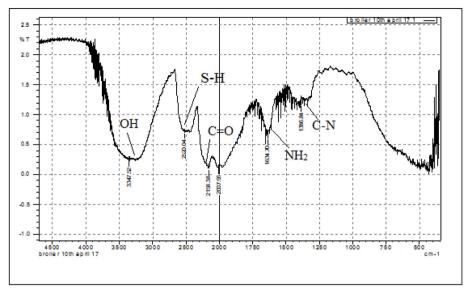


Fig. 2. Spectrum of the chlorinated chicken waste solution.

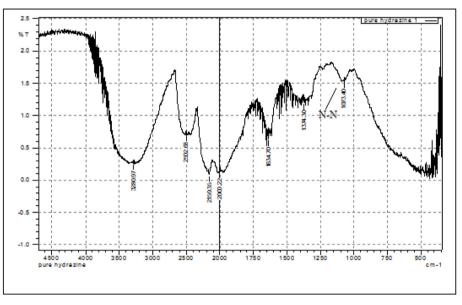


Fig. 3. Spectrum of the AR grade hydrazine solution.

2.7.3. Temperature optimisation

After establishing the optimal pH and the suitable chlorine content, the procedure was again repeated while holding the pH constant at 11.0 and the chlorine bubbling time at 3 min, but with varied temperature between 28 °C and 90 °C at intervals of 5 °C and then 10 °C. In each case, the precipitate formed was filtered and dried in an oven at 40 °C and the content of the copper was determined.

2.7.4. In situ extraction and reduction of copper

A solution, 100 ml, of the chicken waste was put in a 250-ml beaker and 1.0 g of the ore was added and the content stirred for 20 min. The content was filtered using a 300 μ m sieve. More of the chicken waste solution was added to bring the volume to 200 ml and the pH was adjusted to 11.0. The mixture was then heated at 70 °C and chlorine gas bubbled for 3 min. The content was cooled, filtered using Whatman filter paper (number 4) and the residue dried in an oven at 40 °C. The procedure was repeated using different masses of 2–10 g at intervals of 2.0 g, but the previously obtained optimal parameters were maintained. The content of the copper was then determined. The procedure was repeated whilst holding the temperature at 70 °C, the mass of the ore at 6 g and chlorine bubbling time at 3 min, but varying the time for stirring using the magnetic stirrer from one to 16 min at intervals of 2 min. The content was cooled and filtered using Whatman filter paper number 4 and the residue dried in an oven at 40 °C.

3. Results and discussion

3.1. Mineralogical analysis using XRD

A mineralogical analysis of the ore was carried out and the results obtained were as presented in Fig. 1 below.

The results show that copper minerals in Tharaka Nithi County exist mainly as chalcopyrite. A few deposits indicated the presence of covellite whose diffraction angle theta was found to be 33.0, 29.5 and 48.0 upon analysis. Other minerals that have a significant presence are silica inform of quartz whose diffraction angle was 37.0, and albite whose diffraction 38.0, 22.0 and 26.5, and hematite minerals at an angle of

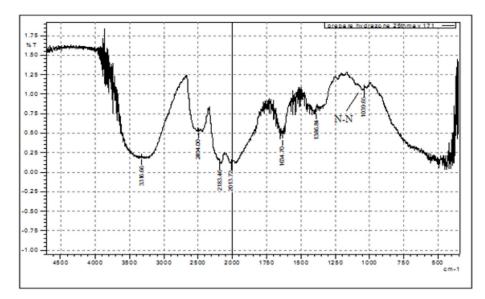


Fig. 4. Spectrum of the prepared hydrazine in the chicken waste solution.

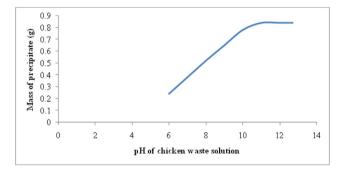


Fig. 5. Relationship between the pH of the chicken waste solution and the mass of precipitate produced.

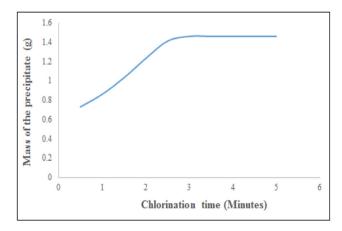


Fig. 6. Chlorination time versus mass of the precipitate produced.

33.0.

3.2. Elemental analysis using XRF

The results of elemental analysis from the ten selected deposits are given in Table 1.

The results show that copper content ranges between 1 and 9% which is better content than some of the exploited ores found elsewhere. One example is from the Democratic Republic of Congo where ores grade between 2.68 and 2.96% (Yager, 2016). In Chile copper

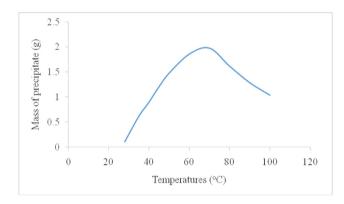


Fig. 7. Appropriate temperature for the formation of hydrazine.

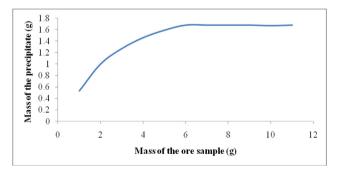


Fig. 8. Mass of the ore used against mass of the precipitate produced.

deposits range between 0.4 and 1.0% (Kuck, 2014 (pp. 108–109)) while in South Africa copper deposits grades are between 0.49 and 0.56% (Groves & Vielreicher, 2001). Botswana is another country in Africa that mines copper from ores and their average composition is between 1.3 and 1.5% copper (Discovery Metals Ltd., 2012). In Zambia all the mines have average composition of 0.5–2.3% copper (Haglund, 2013). This shows that the minerals found in Tharaka Nithi with a composition that vary between 1.93 and 9.66% are more viable for commercial extraction.

3.3. Synthesized hydrazine from the chicken waste solution

The product obtained after the chlorination of the chicken waste

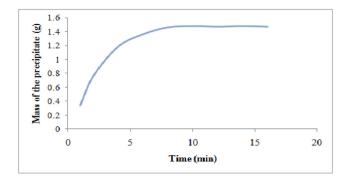


Fig. 9. Time required for the complexation of copper against the mass of precipitate produced.

Table 2

Percentage of copper extracted from leachate using chlorinated chicken waste.

Sample	Trial 1(gms)	Trial 2 (gms)	Trial 3 (gms)	Average (gms)	% Extract	% copper purity using XRF
3227	1.82	1.69	1.76	1.76	29.33	64.4
3230	3.55	3.54	3.70	3.60	59.93	62.47
3232	1.94	1.84	1.88	1.89	31.47	74.88
3234	1.68	1.62	1.63	1.64	27.40	85.22
3238	1.82	1.87	1.91	1.87	31.13	71.0
3240	1.60	1.45	1.50	1.52	25.27	65.46
3244	1.49	1.33	1.42	1.41	23.53	79.07
3242	3.08	3.02	3.01	3.04	50.67	67.08
3233	1.96	1.98	1.93	1.96	32.60	73.47
3231	2.75	2.71	2.82	2.76	46.00	57.16

Table 3

Results of in situ extraction and the reduction of copper using the chicken waste solution.

Sample	Trial 1(gms)	Trial 2 (gms)	Trial 3 (gms)	Average (gms)	% Extract	% copper purity using XRF
3227	1.63	1.57	1.59	1.60	26.62	10.61
3230	1.83	1.79	1.84	1.82	30.32	12.25
3232	1.97	2.08	2.01	2.02	33.64	4.15
3234	2.11	1.97	2.07	2.05	34.16	5.78
3238	2.91	2.88	2.82	2.87	47.83	9.08
3240	1.82	1.76	1.79	1.79	29.86	5.78
3244	1.65	1.67	1.71	1.68	27.93	9.10
3242	2.21	2.16	2.18	2.18	36.39	12.93
3233	1.52	1.49	1.47	1.49	24.88	12.08
3231	1.51	1.43	1.49	1.48	24.60	10.82

solution was analysed and the spectra obtained is given in Fig. 2.

The results show that chicken waste contain contains the –OH and –NH functional groups as evidenced by absorption of radiation at the region between 3000 and 3500 cm, –SH functional group due to the signal at 2500 cm^{-1} , carbonyl functional group due to the stretching frequency stretching between 2000 and 2200 cm^{-1} , –NH₂ group stretching at 1634 cm^{-1} , and the –CN group is found at 1334 cm^{-1} . The –C = O and –NH₂ groups are found in amine and amide compounds. These compounds found in the bio material are potential sources for making hydrazones when suitable oxidizing agents are used. For the sake of comparison, AR grade hydrazine hydrate was analysed using FTIR and the spectra is provided in Fig. 3.

Results show that the hydrazine contained all the functional groups found in chicken waste except the N-N stretch which was found at the range between 1090 and 1020 cm^{-1} . After the chlorination of chicken waste in the alkaline media a spectra was obtained and is provided in Fig. 4 below.

The results show the emergence of a band at 1090 cm^{-1} . This could

be due to induced vibration excitation of the N-N covalent bonds, as reported by Giguère and Liu (1952). This shows that a reducing agent, either symmetrical or unsymmetrical hydrazine, was produced (O'Neill et al., 1984). This product is prepared after chlorine gas reacts with sodium hydroxide as given in equation (8) (Greenwood & Earnshaw, 1979).

$$Cl_{2(g)} + 2NaOH_{(aq)} \xrightarrow{70^{\circ}C} NaOCl_{(aq)} + NaCl_{(aq)} + H_2O_{(l)}$$
 (8)

The produced sodium hypochlorite oxidises amines and amides to hydrazones, as previously shown in equations (1)–(3). Other possible products are illustrated by equation (9) below (Bourdauducq & Schirmann, 2002; Day & Whiting, 1988).

$$2RNH_2 \xrightarrow{2NaOCl} 70^{\circ}C_{RHNNRH}$$
(9)

3.3.1. Optimized results

3.3.1.1. Optimized pH of chicken waste solution. Results of pH optimisation are as presented graphically in Fig. 5.

The results show that at strongly acidic environment no copper was produced as the reduced metal was dissolved by the acid. The emergence of precipitation started at a pH of 6.0 and increased with the increase in pH up to a plateau after pH 11.0. The region between pH of 6.0–11.0, is the region where there sodium hydroxide was available, forming sodium hypochlorite. The sodium hypochlorite produced oxidises amines forming hydrazones which are a strong reducing agent. The resulting hydrazones were responsible for the reduction process. Thus the reduction was found to be best in strongly basic media.

3.3.1.2. Optimized time for the chlorination of the chicken waste solution. The appropriate time for the chlorination of the chicken waste solution was investigated and the results obtained are presented in Fig. 6.

The results show that bubbling chlorine gas into the chicken waste for 3 min was a sufficient period of time for the formation of the hydrazones required to reduce the copper ions in the solution. After that interaction period, the mass of the product remains constant because all the copper ions have been depleted.

3.3.1.3. Optimal temperature for the formation of hydrazones from chicken waste solution. Hydrazones are temperature sensitive compounds. The temperature of the chlorination process was therefore monitored and the results obtained are presented in Fig. 7.

The results show that as the temperature increases to 70 °C, the kinetic energy of the particles increases. This results in the increase of collisions between particles, therefore leading to the formation of hydrazones. Temperatures above 70 °C lead to decreased precipitate formation. This shows that the amino compounds present in chicken dung become denatured at temperatures above 80 °C, hence affecting the formation of hydrazine which is responsible for the reduction of the metal in the ore.

3.3.1.4. Optimal masses for the in situ reduction of ore using chicken waste solution. Copper from varying masses of different ore was extracted and reduced in situ. The results obtained are presented in Fig. 8.

A graph of mass of the ore used in the extraction against mass of the precipitate produced. The results show that the amines and uric acids in chicken waste can complex copper ions from ores just like the acid leached solution. Therefore the copper ions obtained from 6.0 g of the ore were later reduced by hydrazones species prepared in situ. However, the mass of the ore used varied depending on the composition of copper in the ore.

3.3.1.5. Kinetics of the extraction and in situ reduction of copper using chicken waste solution. After establishing that 6.0 g was a suitable mass for the stoichiometric reduction of the copper ions, this study

investigated the rate of reduction and the results obtained are given in Fig. 9.

The results show that 8 min was sufficient time for 100 ml of chicken waste solution to complex copper into ions from 6 g of the ore sample and subsequently reduce copper to zero valence as shown in equations (10) and (11) below (Chen & Lim, 2002).

$$2Cu^{2+}_{(aq)} + N_2H_{4(aq)} \rightarrow 2Cu_{(s)} + N_{2(g)} + 4H^+_{(aq)}$$
(10)

$$Cu^{2+}_{(aq)} + N_2H_{4(aq)} + OH^{-}_{(aq)} \rightarrow 2Cu_{(s)} + N_{2(g)} + 2NH_3^{+}_{(g)} + 2H_2O_{(l)}$$
(11)

After optimisation of the various parameters, the method was applied for the extraction of copper from different acid leached ores and the results obtained are presented in Table 2.

The results show that a high percentage of copper was first obtained from acid digested ores and this was then reduced to zero valence using chlorinated chicken waste solution. The leachate had less contamination of alumina, phosphorous, calcium and silica. This is why all copper produced had high purity of over 60% copper. The *insitu* extraction procedure was also applied for the extraction of copper and the results obtained are presented in Table 3.

In this experiment, the percentage of copper extracted using in situ extraction and the reduction method was low. The fact that some of the hydrazones acted as a ligand to extract the copper from ore into solution to make it available for reduction contributed to this fact. However, copper extracted from this method was found to have a high percentage of impurity compared to the acid leached ore. The reason for high purity may be due to the fact that oxides of aluminium and silicon did not dissolve during the in situ/reduction method. The low percentage purity of copper was also attributed to the formation of amine mesoporous silica nanoparticles (amine-MSN) with the formula (SirOxCvNHz) (Batista et al., 2016). This interaction between silica and amines introduces impurities to the reduced copper. Equally, amines formed a complex with phosphorous pentoxide, CaO and Fe, hence introducing impurities to the copper extracts. Although the percentage of the extract was low, the purity of copper was high. This proves that chicken waste can produce a purer quality of extracted copper, but with lower content.

4. Conclusions

The study successfully converted leachate from chicken waste into hydrazones by treating it with chlorine. The resulting product was then applied to reduce copper in a solution leached from its ore. It was found that the reduced zero valent copper was 60–85% pure. This confirms that the chlorine treated chicken dung leached solution has potential for the extraction of copper from its ores at low cost. This would create awareness around the fact that waste products, such as chicken waste, can be applied to extract copper from ores with a percentage content of between 1 and 9%. The method was investigated in a laboratory scale, but can be up scaled to produce copper for industrial use.

Conflict of interest

None declared.

Ethical statement

Authors state that the research was conducted according to ethical standards.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.jsm.2018.07.003.

References

- Adalbert, L. (2005). Copper. In B. Elviers (Ed.). Ullmann's encyclopedia of industrial chemistryWeinheim: Wiley-VCH Verlag GmbH & Co. KgaA. https://doi.org/10.1002/ 14356007 (doi:10.1002/14356007.a07_471).
- Adams, R., & Brown, B. K. (1941). Hydrazine sulfate. Organic Syntheses, 1, 309–411. https://doi.org/10.15227/orgsyn.002.0037.
 ASTM (2007). D1762–D1784 standard test method for chemical analysis of wood charcoal.
- ASTM (2007). D1762–D1784 standard test method for chemical analysis of wood charcoal. West Conshohocken, PA: ASTM International2.
- ASTM (2010). ASTM D7624–10 standard test method for condition monitouring of nitration in-service petroleum and hydrocarbon-based lubricants by trend analysis using fourier transform infrared (FT-IR) spectrometry. West Conshohocken, PA: ASTM International 2010.
- Batista, A. P. L., Zahariev, F., Slowing, I., Braga, A. A. C., Ornellas, F. R., & Gordon, M. S. (2016). Silanol-assisted carbinolamine formation in an amine-functionalized mesoporous silica Surface: Theoretical investigation by fragmentation methods. *Journal of Physical Chemistry B*, 120(8), 1660–1669. https://doi.org/10.1021/acs.jpcb.5b08446.
- Bourdauducq, P., & Schirmann, J. P. (2002). Hydrazine. In B. Elviers (Ed.). Ullmann's encyclopedia of industrial chemistryWeinheim: Wiley-VCH Verlag GmbH & Co. KgaA.,
- Wiley-VCH. https://doi.org/10.1002/14356007 doi: 10.1002/14356007.a13_177.
 Chen, J. P., & Lim, L. L. (2002). Key factors in chemical reduction by hydrazine for recovery of precious metals. *Chemosphere*, 49(4), 363–370. https://doi.org/10.1016/ S0045-6535(02)00305-3.
- Day, A. C., & Whiting, M. C. (1988). Acetone hydrazone. Organic Syntheses, 6, 10–12. https://doi.org/10.15227/orgsyn.050.0003.
 Discovery Metals Ltd (2012). Plutus ore reserves increased. Discovery Metals Ltd. December
- Discovery Metals Ltd (2012). Plutus ore reserves increased. Discovery Metals Ltd. December 11. Retrieved 11 December 2012 from http://www.discoverymetals.com/files/ media/20121205_sbs_gds_asx_release_plutus_ore_reserves_v7_pdf.
- DuBois, C. G. B., & Walsh, J. (1970). Minerals of Kenya, Vol.11. Republic of Kenya: Ministry of Natural Resources.
- Giguère, P. A., & Liu, I. D. (1952). On the infrared Spectrum of hydrazine. *The Journal of Chemical Physics*, 20, 136–142. https://doi.org/10.1063/1.1700155.
- Greenwood, N. N., & Earnshaw, A. (1997). Chemistry of the elements (2nd ed.). Amsterdam: Elsevierhttps://doi.org/10.1016/C2009-0-30414-6.
- Groves, D., & Vielreicher, N. M. (2001). The phalabowra (palabora) carbonatite-hosted magnetite-copper sulfide deposit, South Africa: An end-member of the iron-oxide copper-gold-rare earth element deposit group? *Mineralium Deposita*, 36(2), 189–194. https://doi.org/10.1007/s001260050298.
- Haglund, D. (2013). Zambia mining sector fiscal benchmarking and assessment. Retrieved 10 November 2017 from https://assets.publishing.service.gov.uk/media/ 57a08a1340f0b652dd000554/Zambia_mining_sector_fiscal_benchmarking_and_ assessment.pdf.
- Kasese Cobalt Company Ltd (2007). About KCCL. Kasese Cobalt Company Ltd. Retrieved 10 November 2017 from http://www.kccl.co.ug/about.htm.
- Kuck, P. H. (2014). Nickel. In mineral commodity summaries 2014. Reston, VA: U.S. Geological Survey.
- Kurtz, A. C. (1949). Use of copper (ii) ion in masking α-amino groups of amino acids. Journal of Biological Chemistry, 180(3), 1253–1267.
- Lampeka, Y. D., & Gavrish, S. P. (1990). The effect of ligand structure on spectral characteristics and kineticsof redox reactions of copper(II) and copper(III) complexes with macrocyclic ligands containing amide groups. *Journal of Coordination Chemistry*, 21(4), 351–362. https://doi.org/10.1080/00958979009408198.
- Ogola, J. S. (1987). Mineralization in the migori greenstone belt, macalder, Western Kenya. Geological Journal, 22(52), 25–44. https://doi.org/10.1002/gj.3350220605.
- O'Neill, I.,K., Borstel, R. C. V., Miller, C. T., Long, J., & Bartsch, H. (1984). N-nitroso compounds: Occurrence, biological effects and relevance to human cancer, IARC scientific publications No. 57. Lyon: Oxford University Press.
- Republic of Kenya (2001). Promotion of extractive and mineral processing industries in the EAC, "Kenya status": A draft country brief on minerals industry in Kenya. Retrieved 10 November 2017 from:https://www.academia.edu/5954068/Republic_of_Kenya_ promotion_of_extractive_and_mineral_processing_industries_in_the_EAC_Kenya_status_ brief outline.

Yager, T. R. (2016). 2013 minearls yearbook. Reston, VA: Congo (Kinshasa): U.S. Geological Survey [Advance Release].

Wills, B. A. (2011). Wills' mineral processing Technology: An introduction to the practical aspects of ore treatment and mineral recovery (7th ed.). Butterworth-Heinemann.