Adsorption of Cu and Ni from AMD using Activated Bentonite

Freeman Ntuli, Thabo Falayi, and Panelope Molala

Abstract**—**The ability of activated bentonite to adsorb Cu and Ni was investigated. 6 % solid loading was chosen as the optimum solid loading for activated bentonite with 94.85% Cu and 92.05% Ni removal after 3 hours of agitation. The adsorption process followed the Langmuir isotherm and pseudo second order kinetic models. The maximum adsorption capacities were 0.297 and 0.235 mg/g for Cu and Ni respectively. The adsorption of Cu and Ni was thermodynamically spontaneous. Cu adsorption was endothermic whilst Ni adsorption was exothermic. Activated bentonite could be used for two cycles of adsorption without regeneration.

Keywords**—**Adsorption, bentonite, heavy metal, isotherm.

I. INTRODUCTION

ACID mine drainage (AMD) is an environmental problem associated with mining operations. AMD results from the microbial oxidation of pyrite in presence of water and air forming an acidic solution that contains toxic metal ions and it is self-sustaining in that the acidic solution can further leach minerals from mining host rock creating more AMD. AMD leads to heavy metal pollution, which is a serious and complex phenomenon since metals can bio-accumulate to higher levels in biota and are poisonous [1]. Though bentonite has been shown to be an effective adsorbent for heavy metals from aqueous solutions [2, 3, 4], bentonite has also been shown to remove less than 50% of heavy metals [5] form actual AMD solutions. Therefore activation of bentonite is necessary in-order to improve heavy metal removal from AMD and neutralise acidic AMD. Activation of bentonite by alkali and acid solutions is a well-researched area [6, 7, 8] providing for improved activity of bentonite as an adsorbent for heavy metals. Sodium exchanged bentonite activated by dry mixing of bentonite and soda ash was used in this project as an adsorbent for Cu and Ni. Batch adsorption tests were done using a thermostatic shaker at varying temperatures and residence times in order to determine the adsorption parameters.

II. EXPERIMENTAL

A. Material

Acid mine drainage was collected from a local gold mine site and analysed to find the concentration of heavy and other elements present. Activated bentonite was supplied by G&W Base Minerals. Analytical grades of $CuSO_4.5H_2O$, and $NiSO_4.6H_2O$ were supplied by Sigma Aldrich.

B. Equipment

pH was measured using Metler Toledo dual meter (Sevenduo pH/conductivity meter with a Metler Toledo InLab Pro ISM pH electrode probe). Adsorption experiments were conducted in a thermostatic shaker (Labotec OrbiShaker). An Atomic Absorption Spectrometer (Thermo scientific ICE 3000 Series) was used for metal analysis.

C. Fortification of AMD

To 100 ml of AMD, appropriate amounts of sulphate salts of Cu and Ni were added. The solution was stirred at 200 rpm for 10 min and made up to 1000 ml with raw AMD whilst stirring for further 20 min. Table I shows the AMD parameters before and after fortification.

D. Effect of solid loading

1, 3, 4, and 5 g of activated bentonite was added to four 250 ml conical flasks respectively, each containing 50 ml of the fortified AMD. The resulting solutions were agitated at 25ºC in a thermostatic shaker at 200 rpm for 3 h. After 3 h, agitation was stopped and the solutions pH was measured. The solutions were then subsequently filtered and the filtrate was acid digested in preparation for metal analysis using an AAS.

The amount adsorbed per unit mass of adsorbent at equilibrium q_e is given by

$$q_e = (C_0 - C_e) \times V/M \qquad (1)$$

Where C_0 is initial metal concentration, Ce equilibrium metal concentration (mg/l), *V* volume of solution (L) and *M* mass of adsorbent (g).

E. Effect residence time and temperature

3 g of activated bentonite was added to five 250 ml conical flasks each containing 50 ml of fortified AMD. The resulting solutions were agitated at 25ºC in a thermostatic shaker at 200 rpm for 30, 60, 90, 120 and 180 min respectively. After each time interval, agitation was stopped and the solution pH was measured. The solutions were then subsequently filtered and

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the filtrate was acid digested in preparation for metal analysis using an AAS.

The procedure was repeated at 35ºC and 45ºC to evaluate the effect of temperature on adsorption of Cu and Ni.

F. Stability of metal loaded activated bentonite

50 ml of reverse osmosis (RO) water (acidified to pH 2with HCl) was added to 3 g of metal loaded activated bentonite. The resulting solution was agitated for 3 h at 25°C in a thermostatic shaker at 200 rpm. After 3 h agitation was stopped and the solution was then subsequently filtered and the filtrate was digested in preparation for metal analysis using an AAS.

G. Re-usability test

3 g of metal loaded activated bentonite was mixed with 50 ml of fresh fortified AMD. The resulting solution was agitated for 3 h at 25°C in a thermostatic shaker at 200 rpm. After 3 h, agitation was stopped. The solution was then subsequently filtered and the filtrate was acid digested in preparation for metal analysis using an AAS. This process was repeated twice.

III. THEORETICAL BACKGROUND

A. Adsorption Isotherms

To study the thermodynamic behaviour of the adsorption process, adsorption isotherms were used. In order to find the adsorption capacities of the metals adsorbed by attapulgite, the experimental results were analysed using the Langmuir (.2) and Freundlich (3) isotherms. The following linearised equations were used for this purpose

$$\frac{C_e}{q_e} = \frac{1}{q_m.b} + \frac{C_e}{q_m} \qquad (2)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (3)$$

Where C_e (mg/L) is the metal concentration in solution at equilibrium q_e (mg/g) is the amount of metal adsorbed per unit mass of adsorbent, q_m (mg/g) is the maximum adsorption, b (L/g) is a constant related to enthalpy of adsorption, K_F and n are Freundlich equilibrium constants indicative of the adsorption capacity and adsorption intensity.

B. Adsorption Kinetics

To study adsorption kinetics the experimental data was subjected to the pseudo first order plot (4) and pseudo second order plot (5), represented by the following equations respectively

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (4)$$

Where q_t (mg/g) is the amount adsorbed at any time per unit mass of adsorbent, k_1 is the rate constant (min^{-1}). A plot of *log* $(q_e\text{-}q_t)$ vs t should be linear if the model fits the experimental data.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \left(\frac{1}{q_e}\right)t \qquad (5)$$

Where k_2 is the rate constant (mg.g^{-1}min^{-1}). A plot *of* t/q_t vs t should be linear if the model fits the experimental data.

C. Gibbs free energy

Gibbs free energy can be approximated by (7)

$$\Delta G^0 = -RT\ln b \qquad (7)$$

Where $\Delta G°$ is the standard free energy change (J/mol), R is the universal gas constant, 8.314 J/mol K, T is absolute temperature (K) and, b (L/g) is the Langmuir isotherm constant related to enthalpy of adsorption.
Equation 8 also gives a linear relationship of Gibbs free energy and temperature.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (8)$$

A plot of $\Delta G°$ versus temperature, T, will be linear and the values of $\Delta H°$ and $\Delta S°$ can be determined from the slope and intercept of the plot respectively.

IV. RESULTS AND DISCUSSION

A. AMD characterization

Table I shows the AMD parameters before and after fortification.

TABLE I
AMD PARAMETERS

Parameter	Before Fortification	After Fortification
pH	2.66	2.84
Temperature (^{0}C)	23.4	23.3
Conductivity(mS/cm)	2.62	5.77
Sulphates (ppm)	2820	3522
Ni (ppm)	Below detection limit	21.78
Cu (ppm)	Below detection limit	16.55

B. Effect of adsorbent loading

Fig. 1 shows the variation in percentage of metal removed with increase activated bentonite loading

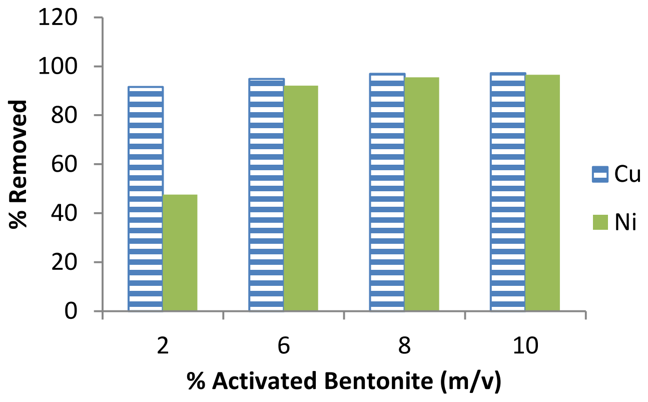

Fig. 1 Effect of activated bentonite solid loading on adsorption of Cu and Ni

There was an increase in Cu and Ni removed as the solid loading of activated bentonite increased. The increase in percent removed with adsorbent mass can be attributed to an increase in adsorption sites with increasing solid loading of adsorbent. There is no significant difference in metal removal at 6, 8 and 10% solid loading of activate bentonite. Therefore the 6 % m/v solid loading was chosen for the rest of the batch adsorption tests.

C. Variation of metal removal with pH

Fig. 2 shows the variation of pH with metal removal.

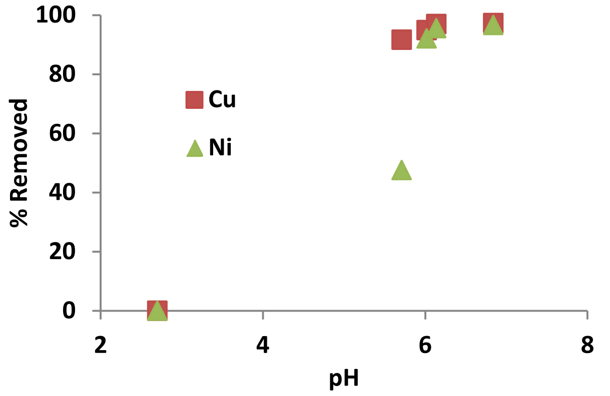

Fig. 2 Variation of metal removal with pH

An increase in pH resulted in an increase in metal removal. At low pH there is competition for adsorption sites between metal cations and the H^+ ion hence lower metal cation removal.

D. Effect of residence time

Fig.3 shows the variation of q_t with time

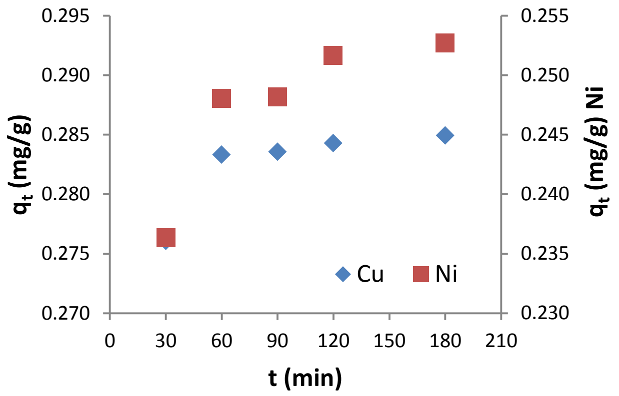

Fig. 3 Variation of q_t with time

The amount of metal adsorbed per unit mass of activated bentonite increased with time as more metal uptake took place. Equilibrium was reached after 120 min for Ni and 60 min for Cu. Adsorption of Cu and Ni is in the order Cu> Ni. Cu has a smaller radii compared to Ni, hence Cu is easily adsorbed onto the pores of activated bentonite and is preferred over Ni [9].

E. Adsorption isotherm

The experimental data fitted the Langmuir isotherm as the correlation coefficient for Cu and Ni were 1.000 and 0.9997 respectively. The correlation coefficients for the Freundlich isotherm for both metals were below 0.88. The Langmuir isotherm parameters for Cu and Ni are shown in table II.

TABLE II
LANGMUIR ISOTHERM DATA

	b (L/g)	r^2	q_{max} (mg/g)
Cu	374	1.0000	0.297
Ni	137	0.9997	0.235

F. Adsorption Kinetics

The experimental data fitted the pseudo second order kinetic model as the correlation coefficient for Cu and Ni were 0.9999 and 0.9999 respectively. The correlation coefficient for the pseudo first order kinetic model was below 0.91 for both metals. The pseudo second order kinetic model parameters for Cu and Ni are shown in Table II. Experimental and calculated q_e values are very close showing that the pseudo second order kinetic model is a good approximation of the adsorption of Cu and Ni into activate bentonite.

TABLE III
PSEUDO SECOND ORDER KINETIC PARAMETERS FOR CU AND NI

	Cu	**Ni**
k_2 (mg.g^{-1} .min^{-1})	3.78	1.64
Calculated q_e (mg.g^{-1})	0.286	0.256
Experimental q_e (mg.g^{-1})	0.285	0.253

G. Adsorption Thermodynamics

Fig. 4 shows the Gibbs free energy plots for Cu and Ni

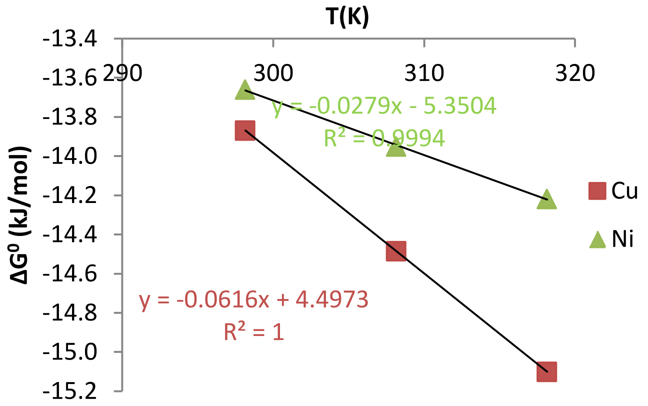

Fig. 4 Gibbs free energy plots for Cu and Ni

There was an increase in the negative value of Gibbs free energy for both Cu and Ni as the temperature was increased. This indicated that the adsorption of Cu and Ni onto activated bentonite was thermodynamically spontaneous at all temperatures. Table IV shows the thermodynamic parameters for the adsorption of Cu and Ni.

TABLE IV
THERMODYNAMIC PARAMETERS FOR CU AND NI

	ΔS(J/mol)	ΔH(kJ/mol)
Cu	61	4.5
Ni	27	-5.4

The positive entropy values for both Cu and Ni show that activated bentonite has a high affinity for Cu and Ni, whilst the adsorption of Cu is endothermic whilst that of Ni is endothermic.

H. Re-use of metal loaded activated bentonite

Fig. 5 shows the variation in metal removal with number of cycles.

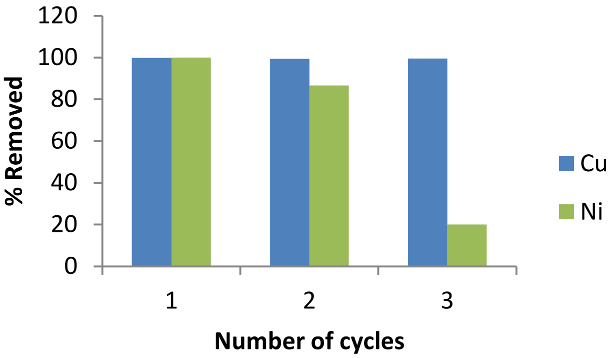

Fig. 4 Variation in metal removal with number of cycles.

The adsorption of Cu is not affected by the number of cycles as activated bentonite prefers Cu to Ni. The removal of Ni decreased to 20% in the third cycle. Therefore activated bentonite could be used in two cycles without the need for regeneration.

I. Stability of metal loaded activated bentonite

Table V shows the % metal leached from metal loaded activated bentonite

TABLE V
% METAL LEACHED FROM METAL LOADED ACTIVATED ATTAPULGITE.

	Metal leached from metal loaded activated bentonite	Metal adsorbed from AMD	% leached from metal loaded activated bentonite
Cu	0.2	17.1	1.0
Ni	3.2	15.2	21.1

1% of the adsorbed Cu was leached with acidic water and 21% of the adsorbed Ni was leached with acidic water. Metal loaded activated bentonite is therefore stable against environmental metal leaching.

J. Effect of adsorption on metal oxide composition of activated bentonite

Table VI shows the XRF analysis of activated bentonite

Activated bentonite is Na-bentonite for it has a Na/Ca ratio of 3.48. Adsorption of Ni and Cu resulted in the increase of the metal oxides in metal loaded activated bentonite accompanied by a corresponding reduction in the relative content of Na, Al and Ca oxides.

TABLE VI
XRF ANALYSIS ON BENTONITE

Component	% (m/m)	
	Activated bentonite	Metal loaded activated bentonite
Na_2O	2.960	0.850
MgO	2.630	1.910
Al_2O_3	11.80	11.90
SiO_2	80.20	77.30
P_2O_5	0.0087	0.0087
SO_3	0.0932	0.285
Cl	0.482	1.280
K_2O	0.107	0.095
CaO	0.371	0.199
TiO_2	0.241	0.272
MnO	0.0121	0.035
NiO	0.000	0.0108
CuO	0.000	0.011
ZnO	0.0328	0.0344
SrO	0.0078	0.0023
Y_2O_3	0.0124	0.0109
ZrO_2	0.0547	0.0546
Nb_2O_5	0.0179	0.0201
BaO	0.193	0.105

V. CONCLUSION

Activated bentonite can be used as an adsorbent for Cu and Ni from AMD. A 6% solid loading of activated bentonite could remove 94.85% Cu and 92.05% Ni. The adsorption process was thermodynamically spontaneous and followed Langmuir isotherm model and pseudo second order kinetic model. Activated bentonite could be used in two cycles without any need for regeneration. Metal loaded activated bentonite was stable against further leaching of metals. It is recommended to use activated bentonite with AMD from different places in order to establish its effectiveness.

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