

# Thermally activated attapulgite as an adsorbent for heavy metals

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**Abstract**—Thermal activation of attapulgite was investigated. Attapulgite calcined at 600°C was used as an adsorbent for heavy metals in AMD. The effect of solid loading, residence time and adsorption temperature was investigated. Activated attapulgite showed that it could remove more than 99% of Fe, Cu, Co and Ni from AMD. Langmuir isotherm gave the best fit for the adsorption process with maximum adsorption capacities of 8.97, 0.20, 0.32 and 0.32 for Fe, Ni, Cu and Co respectively. The adsorption of Cu and Ni was thermodynamically. The results show that thermally activated attapulgite has potential as an adsorbent for heavy metals from AMD.

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

## I. INTRODUCTION

Acid mine drainage (AMD) poses a serious threat to human health, animals and ecological systems. It is characterized by low pH and high concentrations of heavy metals contaminants, such as  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ . Adsorption using clays is one of the methods by which to remediate the environmental problems associated with AMD. A number of clay minerals have been used as adsorbents including bentonite kaolinite and attapulgite [1]. Attapulgite is a natural one-dimensional magnesium–aluminum silicate clay mineral whose diameter is between 30 and 50 nm [2]. Compared with montmorillonite and other mineral materials, the price of attapulgite is lower, therefore offering an alternative cheap low cost adsorbent for heavy metals in AMD [3]. Unactivated attapulgite at 10% (m/v) solid loading has been shown to remove at least 93% of Co, Cu, Ni and Fe whilst removing 66% Mn [4]. This research seeks to establish the effectiveness of thermally activated attapulgite as an adsorbent for heavy metals in AMD.

## 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. Attapulgite was supplied by G&W Base

Minerals. Analytical grades of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  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). Metal analysis was achieved using an Atomic Absorption Spectrometer (Thermo scientific ICE 3000 Series).

### C. Thermal activation of attapulgite

Attapulgite was calcined in an oxidizing furnace at a temperature of 600°C for 4 hours.

### D. 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 1 shows the AMD parameters before and after fortification.

### E. Effect of solid loading

Different masses of attapulgite (0.5, 0.75, 1, 1.25, 1.5, 2, 3, 3.5, 4 and 5 g) were added to 10 different 250 ml volumetric flasks each containing 50 ml of fortified AMD. The resulting solutions were agitated in a thermostatic shaker at 200 rpm for 2 h at 25°C. After 2 h, agitation was stopped and the solution pH was measured. The solutions were then subsequently filtered using a Buchner funnel and the filtrate was acid digested in preparation for AAS metal analysis.

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

$$q_e = (C_0 - C_e) \times \frac{V}{M} \quad (1)$$

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

### F. Effect residence time and temperature

3 g (6% m/v) of attapulgite was added to 6 different volumetric flasks each containing 50 ml of fortified AMD. The resulting solutions were agitated in a thermostatic shaker at 200 rpm for 15, 30, 45, 60, 90 and 120 min respectively at

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25°C. At the end of each time interval the agitation was stopped and the solution pH was measured. The solutions were then subsequently filtered using a Buchner funnel and the filtrate was acid digested in preparation for AAS metal analysis.

The procedure was repeated at 35°C and 45°C to evaluate the effect of temperature on adsorption of Cu, Co, Fe and Ni.

#### G. Stability of metal loaded activated attapulgite

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

#### H. Re-usability test

3 g of metal loaded activated attapulgite was mixed with 50 ml of fresh fortified AMD. The resulting solution was agitated for 2 h at 25°C in a thermostatic shaker at 200 rpm. After 2 h agitation was stopped and 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

#### 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

$$\frac{C_e}{q_e} = \frac{1}{q_m} \cdot b + \frac{C_e}{q_m} \quad (2)$$

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

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.

#### 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

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

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

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

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

#### Gibbs free energy

Gibbs free energy can be approximated by (7)

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

Where  $\Delta G^0$  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.

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

A plot of  $\Delta G^0$  versus temperature,  $T$ , will be linear and the values of  $\Delta H^0$  and  $\Delta S^0$  can be determined from the slope and intercept of the plot

### IV. RESULTS AND DISCUSSION

#### A. AMD characterization

Table 1 shows the AMD parameters before and after fortification.

TABLE 1  
AMD PARAMETERS

Parameter	Before Fortification	After Fortification
pH	2.66	2.84
Temperature (°C)	23.4	23.3
Conductivity(mS/cm)	2.62	5.77
Sulphates (ppm)	2820	3522
Fe (ppm)	4	532
Mn (ppm)	120	114
Ni (ppm)	Below detection limit	20.35
Cu (ppm)	Below detection limit	15.65
Co (ppm)	Below detection limit	21.25

#### B. Effect of adsorbent loading

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

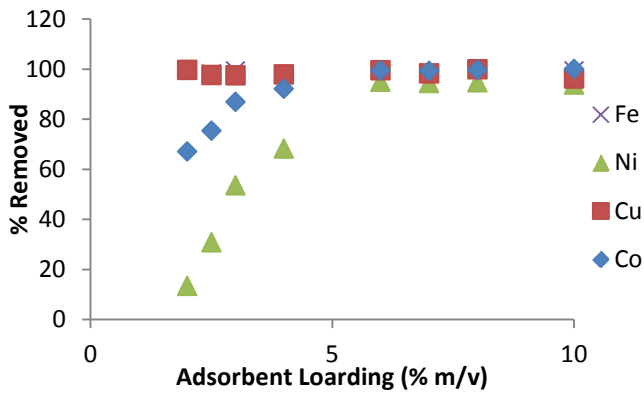


Fig.1 Effect of activated attapulgite solid loading on adsorption of Cu, Fe, Co and Ni

Metal removal increased as the solid loading increased reaching equilibrium at 6% solid loading. An increase in adsorbent solid loading is accompanied by a corresponding increase in the number of adsorption sites leading to an increase in metal uptake [5].

C. Effect of solid loading on the distribution coefficient

Fig. 2 shows the variation of distribution coefficient with solid loading.

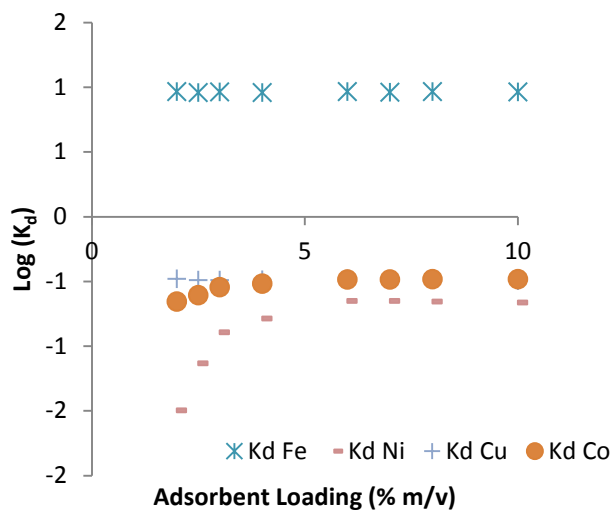


Fig. 2 Variation distribution coefficient with solid loading

The  $K_d$  values for Fe and Cu were independent of attapulgite solid loading, whilst a dependence was noticed for Co and Ni between 2 and 4 % m/v. Therefore this shows that the adsorption of Fe and Cu were more favorable than that Ni and Co. This therefore means that the activated attapulgite adsorption preference is of the order Fe>Cu>Co>Ni.

D. Effect of residence time and temperature on adsorption of heavy metals

Fig. 3 to Fig. 6 shows the effect of time and temperature on the removal of Fe, Ni, Cu and Co.

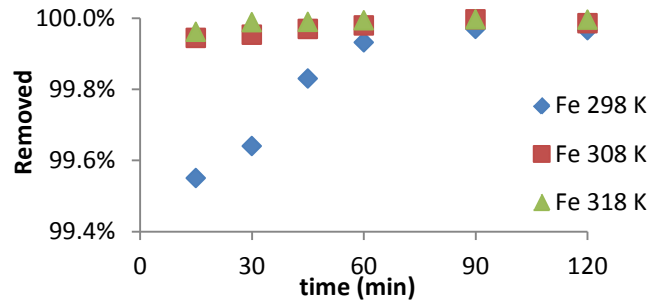


Fig. 3 Fe adsorption at different temperatures and time intervals

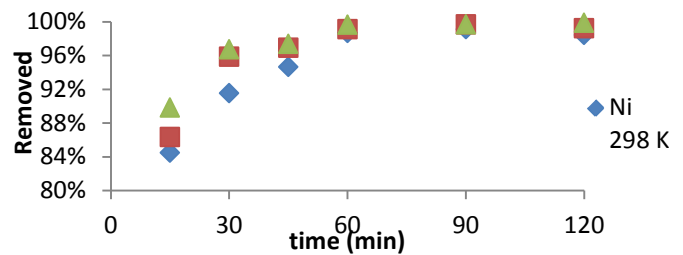


Fig.4 Ni adsorption at different temperatures and time intervals

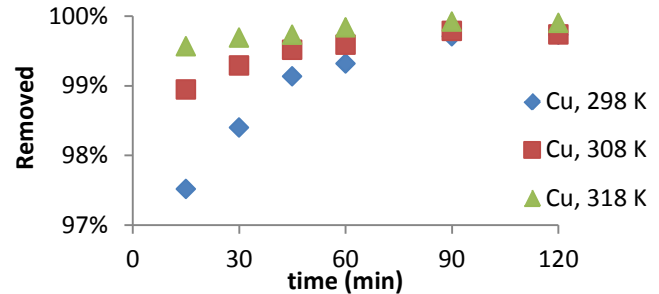


Fig. 5 Cu adsorption at different temperatures and time intervals

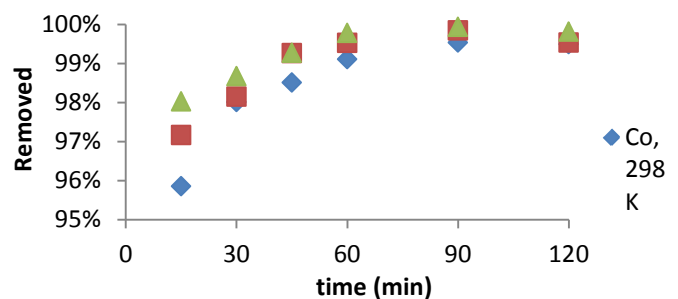


Fig. 6 Co adsorption at different temperatures and time intervals

Fig. 3 and 4 shows that increase in residence time increased the amount of Fe and Ni adsorbed onto attapulgite. The percentage removed for Fe after 15 min was 99.5 % at T= 298 K showing that the Fe removal is spontaneous, whilst after 120 minutes 100% of Fe was removed. The same trend was shown for Ni whereby the percentage removal increased from 84% to 98% at the same temperature. The increase in metals recovery with contact time was due to enough time being given to the system to reach equilibrium [6]. There was no

significant difference in metal removal rate at different temperatures from 60 min for Fe and Ni.

Fig. 5 and 6 show that increasing the temperature increased the percentage removal of the metals for Co and Cu and this might be due to an increase in the number of ions in solution due to the dissociation of the cation and hydration molecule [7].

#### E. Adsorption isotherm

The experimental data fitted the Langmuir isotherm as the correlation coefficient for all metals was above 0.9999 whereas the correlation coefficient for the Freundlich isotherm for all metals were below 0.92. The Langmuir parameters are shown in Table 2.

TABLE 2  
SUMMARY OF THE FREUNDLICH AND LANGMUIR ISOTHERMS AT DIFFERENT TEMPERATURES

Element	Temperature (K)	Langmuir		
		b (L/mg)	q <sub>m</sub> (mg/g)	R <sup>2</sup>
Fe	298	1100	8.969	1
	308	28000	9.083	1
	318	110000	9.217	1
Ni	298	23	0.199	0.9980
	308	37	0.200	0.9990
	318	76	0.215	0.9993
Cu	298	710	0.322	1
	308	2000	0.316	1
	318	15000	0.327	1
Co	298	160	0.314	0.9999
	308	430	0.318	1
	318	1200	0.324	1

#### F. Adsorption Kinetics

The experimental data fitted pseudo second order kinetic model as the correlation coefficient for all metals was above 0.999. The correlation coefficient for the pseudo first order kinetic model was below 0.91 for all metals. The pseudo second order kinetic model parameters all metals are shown in Table 3

TABLE 3  
PSEUDO SECOND ORDER KINETIC PARAMETERS FOR CU, CO, FE AND NI

Element	Temperature (°K)	Q <sub>E</sub> (mg/g)	K <sub>2</sub> (g/mg.min)	R <sup>2</sup>
Fe	298	9.2593	1.166	1
	308	9.2507	10.623	1
	318	9.2507	23.371	1
Ni	298	0.2417	1.470	0.9996
	308	0.2415	2.098	0.9998
	318	0.2417	2.532	0.9999
Cu	298	0.3318	2.660	1
	308	0.3303	22.088	1
	318	0.3310	29.363	1
Co	298	0.3287	4.670	1
	308	0.3285	7.321	1
	318	0.3290	8.376	1

#### G. Adsorption Thermodynamics

Fig. 7 shows the Gibbs free energy plots for Cu, Ni, Co and Fe. Table 4 shows the thermodynamic parameters.

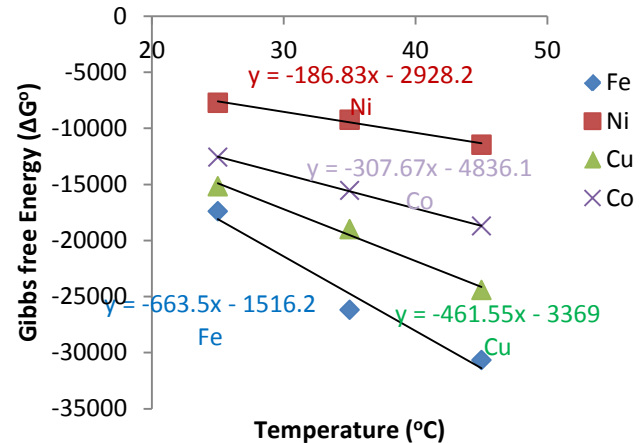


Fig. 7 Gibbs free energy plots for Cu, Co, Fe and Ni

TABLE 4  
THERMODYNAMICS PARAMETERS OF FE, NI, CU, AND CO

Element	Temperature (°C)	$\Delta G^\circ$ (kJ/mol.K)	$\Delta H^\circ$ (J/mol.K)	$\Delta S^\circ$ (J/mol.K)
Fe	25	-17.3		
	35	-26.2	-1516.2	663.5
	45	-30.7		
Ni	25	-7.8		
	35	-9.2	-2928.2	186.83
	45	-11.5		
Cu	25	-15.2		
	35	-19.0	-3369	461.55
	45	-24.4		
Co	25	-12.6		
	35	-15.5	-4836.1	307.67
	45	-18.7		

The Gibbs free energy of all metals at all temperatures was negative (Table 4) indicating that the adsorption was spontaneous. The decrease in the negative value of  $\Delta G^\circ$  with an increase in temperature indicated that the adsorption process of these ions onto attapulgite became more favorable at higher temperatures. The positive values of entropy indicated a high affinity for metal ions by activated attapulgite.

#### H. Re-use of metal loaded activated attapulgite

Fig. 8 shows the variation in metal removal with number of cycles.

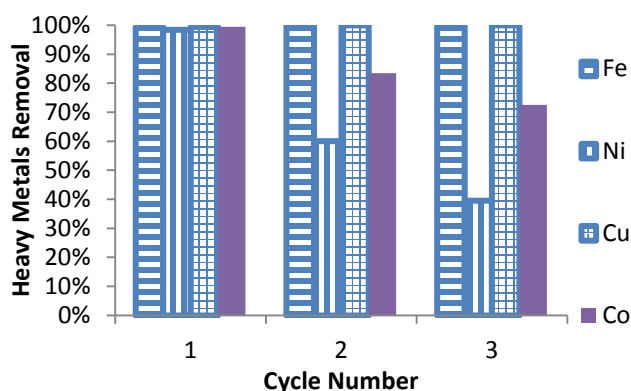


Fig. 8 Variation in metal removal with number of cycles.

Fig 8 shows that the Cu and Fe removal remained the same for all the three cycles of reuse whilst Co and Ni removal decreased in each cycle. Co decreased from 99.4% to 83.4% and then to 72.6% in the third cycle whilst Ni decreases from 98.4%, to 60% and then to 39.5%. The data suggests that attapulgite can be re-used for 3 treatment cycles without

regeneration. The decrease in metal adsorption has to do with a decrease in the number of active adsorption sites.

#### I. Stability of metal loaded activated attapulgite

Metal loaded activated attapulgite showed that it could retain adsorbed metals as only 2.2% of Co was leached after the experiments

#### J. Effect of adsorption on elemental composition of activated attapulgite

Table 5 shows the XRF analysis of activated attapulgite

TABLE 5  
XRF ANALYSIS ON ATTAPULGITE

Element	Activated Attapulgite (Mass %)	Metal loaded activated Attapulgite (mass %)
Na	0.115	0.181
Mg	7.962	7.393
Al	5.452	5.558
Si	30.895	30.521
S	0.042	0.097
K	0.479	0.506
Ca	2.966	2.773
Ti	0.339	0.332
Mn	0.049	0.200
<b>Fe</b>	<b>3.385</b>	<b>4.147</b>
<b>Co</b>	<b>0.000</b>	<b>0.017</b>
<b>Ni</b>	<b>0.015</b>	<b>0.056</b>
<b>Cu</b>	<b>0.000</b>	<b>0.072</b>

Adsorption of Ni, Co, Fe and Cu resulted in the increase of the relative content of these metals in metal loaded activated attapulgite

#### V. CONCLUSION

Activated attapulgite can be used as an adsorbent for Cu, Fe, Co and Ni from AMD. A 6% solid loading of activated attapulgite could remove 99% of all metals after 2 h of agitation. The adsorption process was thermodynamically spontaneous and followed Langmuir isotherm model and pseudo second order kinetic model. Activated attapulgite could be used in three cycles without any need for regeneration. Metal loaded activated attapulgite was stable against further leaching of metals.

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#### REFERENCES

- [1] S.E. Bailey, T.J. Olin, R.M., Bricka and D.D. Adrian, "A review of potentially low-cost sorbents for heavy metals," *Water Research*, vol 33, pp. 2469–2479, 1999.
- [2] T. Chen, H. Liu, J. Li, D. Chen, D. Chang, D. Kong, Dand R.L Frost, " Effect of thermal treatment on adsorption–desorption of ammonia and sulfur dioxide on palygorskite: Change of surface acid–alkali properties," *Chemical Engineering Journal*, vol 166, pp. 1017–1021, 2011.
- [3] F. Gan, J. Zhou, H. Wang, C. Du and X. Chen, " Removal of phosphate from aqueous solution by thermally treated natural Palygorskite," *Water Research*, vol 43, p 2907–2915, 2009.
- [4] T. Falayi and F. Ntuli, " Removal of heavy metals and neutralisation of acid mine drainage with un-activated attapulgite," *Journal of Industrial and Engineering Chemistry*, <http://dx.doi.org/10.1016/j.jiec>
- [5] A.S. Sheoran and V. Sheoran, " Heavy metal removal mechanism from acid mine drainage in wetland. *Minerals Eng*19, 105-11,2006.
- [6] W.L. Haden, "Attapulgite properties and uses," *Chemicals Philipp Corporation* vol 4, issue 5, pp. 421-42,2000.
- [7] A. Luptakovaa, S. Ubaldinib and E. Macingovaa, " Application of physical-chemical and biological–chemical methods for heavy metals removal from acid mine drainage," *Process Biochemistry*, vol, 47, pp.1633–163, 2012.