

# **Equilibrium and Kinetic Studies of Cu(II) Removal from Aqueous Solutions Using a Kenyan Micaceous Mineral.**

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## **Abstract**

*Copper (II) sorption on a Kenyan micaceous mineral (Mica-K) was studied in the batch mode. The effects of different experimental parameters such as; initial concentration, contact time, sorbent dose, pH, particle size, agitation speed, competition and temperature on the kinetics of copper removal were studied. The sorption pattern of copper onto Mica-K followed Langmuir and Freundlich isotherms. Thermodynamic parameters for copper sorption on Mica-K were also determined. X-ray photoelectron spectroscopic (XPS) analysis of metal ion-equilibrated Mica-K, demonstrated that copper, cadmium and Zinc containing nodules existed on the surface of Mica-K.*

**Key Words:** Copper, Mica-K, adsorption, equilibrium and kinetics, isotherm.

## **1.0 Introduction**

Physical and chemical properties of water make it essential to life and civilization. It is a highly efficient medium for dissolving and transporting nutrients through the soil and the bodies of plants and animals. Water therefore controls all geological and biological processes necessary for life's sustenance" (Narasimhan, 2008). Water is an important requirement in many industrial processes, which in turn generates a substantial proportion of total wastewater. If unregulated, industrial wastewater has the potential to be a highly toxic source of pollution.

Wastewater can be defined as "a combination of one or more of: domestic effluent consisting of black-water (excreta, urine and faecal sludge) and grey-water (kitchen and bathing wastewater); water from commercial establishments and institutions, including hospitals; industrial effluent, storm-water and other urban run-off; agricultural, horticultural and aquaculture effluent, either dissolved or as suspended matter (Raschid-Sally and Jayakody, 2008).

Presently, heavy metals are among the most important pollutants in source and treated water. Heavy metals are not biodegradable and tend to accumulate in the living organisms causing various diseases and disorders (Kobyas *et al.*, 2005; Asma *et al.*, 2009). Industrial and municipal waste waters frequently contain metal ions. The presence of copper, zinc, cadmium, lead, mercury, iron, nickel and other metals, has a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded (Demirbas, 2008; Mulu 2013).

Water must therefore, be used and treated in such a way that deleterious effects are minimized, both for the environment and for the next user. Methods used to remove heavy metal ions such as chemical precipitation, adsorption on activated carbon, ion exchange, solvent extraction have been found to be limited, expensive and may be associated with generation of secondary wastes (Aksu *et al.*, 2002).

This therefore calls for research efforts to develop industrially compatible technologies using low cost and locally available natural resources for the removal of heavy metal ions from water and wastewater systems. The purpose of this study is to investigate the removal of some toxic heavy metals from aqueous solution by adsorption on Mica-K, to determine the optimum removal conditions, and analyse kinetic data using suitable adsorption isotherms.

## 2.0 Materials and Methods

### 2.1 Adsorbent

Samples of Mica-K were taken from Kajiado County, Kenya. The crushed Mica-K was washed thoroughly with distilled water to remove dust and other soluble impurities. It was then dried in an electric oven at 105 °C for 24 hours and cooled before use in the adsorption studies. Dried mineral samples were further crushed using a mortar and pestle and sieved to different mesh sizes ranging from <300 to >1,200 microns. The <300µm particle size was used throughout the study except in cases where the effect of particle size was investigated.

Chemical composition and surface texture of Mica-K were determined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) before and after equilibration with divalent-metal ion solutions.

### 2.2 Reagents

All reagents used were of analytical grade. Stock solutions of  $5.0 \times 10^{-2}M$  for different heavy metal ions were prepared by dissolving appropriate weights of corresponding heavy metal salts in double distilled de-ionized water. Working solutions were prepared by appropriate dilutions of the stock solutions. Solutions of  $1 \times 10^{-1}M NaOH$  and  $1 \times 10^{-1}M HCl$  were used for pH adjustment.

### 2.3 Data Analysis

The metal ion concentration in the liquid phase was determined at the beginning ( $C_o$ ) and after equilibration

time ( $C_e$ ). The following equations were used to compute the metal ion uptake by sorbent:

$$\% \text{ Sorption} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

$$\text{Metal ions adsorbed} = \frac{(C_o - C_e) \times V}{m \times 1000} \quad (2)$$

Where;  $V$  is the volume of the aqueous phase (mL); and  $m$  is the mass of micaceous mineral used (g).

## 2.4 Adsorption Studies

Pre-weighed samples of the sorbent and measured volumes of metal ion solutions were taken in 100ml plastic vessels and the mixtures agitated for a constant time. The impeller speed was set at 200-400rpm. After the desired stirring periods, the aqueous phases were separated from Mica-K by filtration through a Whatman no. 1 filter paper and the concentrations of the metal ion in solution measured using a Varian Model AA10 Atomic Absorption Spectrophotometer and/or Varian Model Vista Pro ICP Spectrophotometer under standard operating procedures recommended by manufacturer. The experiments were carried out by varying the amount of sorbent (20-400g/L); contact time (0-3 hours); particle size (<300 - >1200 $\mu$ ); pH (1.5 to 7.5); initial metal ion concentration (1 to 100mmol/L) and temperature (293 to 333 K).

Competitive heavy metal adsorption from aqueous solutions containing  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Zn}^{2+}$  were investigated by a procedure similar to that described above. Initial concentration of the heavy metal ions, 5mmol/L from the adsorption of single, binary and ternary metal ion solutions (equal amounts of the metal ions) were used.

## 3.0 Results and Discussion

The results of whole-rock major-oxide analysis and some physical properties of Mica-K are given in Table 1.

**Table 1:** Chemical and Physical Properties of Mica-K.

Chemical Composition	% w/w	Physical Parameter Values	
SiO <sub>2</sub>	34.80	Mean Particle Diameter	200 $\mu$ m
Al <sub>2</sub> O <sub>3</sub>	17.00	pH	6.88
TiO <sub>2</sub>	2.79	Specific gravity	2.73
Fe <sub>2</sub> O <sub>3</sub>	15.30	Colour	Brown
K <sub>2</sub> O	2.44		
CuO	0.24		
CaO	1.10		
MgO	25.00		
V <sub>2</sub> O <sub>5</sub>	0.09		
Cr <sub>2</sub> O <sub>3</sub>	0.48		
NiO	0.43		
MnO	0.10		
Others	0.23		

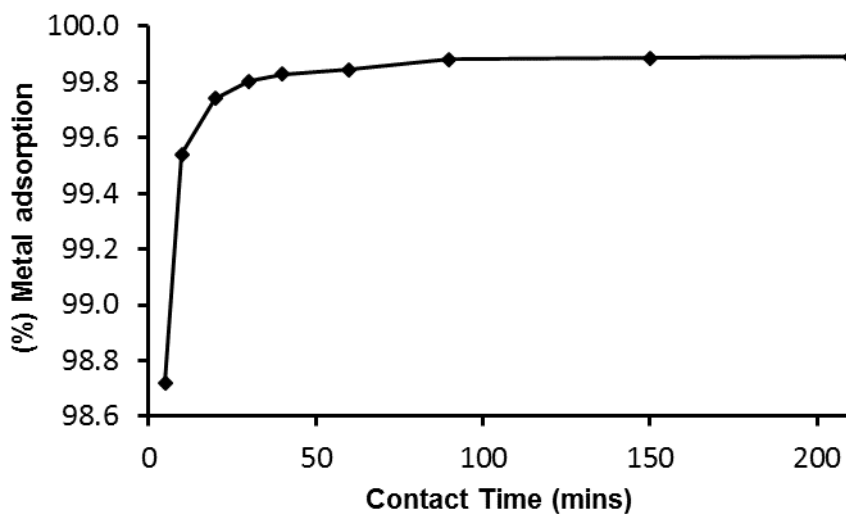
Trace element analysis of Mica-K showed that ; Major rock-forming elements ( $>10,000\mu\text{g/g}$ ) comprises of Al, Fe, K, and Mg, major ore-mineral elements, (1,000 to 9,999 $\mu\text{g/g}$ ), Ba, Ca, Cr, Ni and Ti and Trace elements, ( $>1000\mu\text{g/g}$ ); Co, Mn, Cu, P,S, Si, V, B, Hg, Li, Sr and Zn. XRD results show that the relative abundance of different minerals within Mica-K follows the order; Feldspars (22.9%), chlorite (18.3%), pyrite (15.6%), kaolinites (15.1%), dolomite (10.2%), calcite (9.0%) and quartz (8.8%).

### 3.1 Adsorption Parameters

#### 3.1.1 Effect of Contact Time.

Kinetics of metal ion sorption governs the rate, which determines the residence time, an important characteristic defining the efficiency of an adsorbent. This is necessary, especially when designing batch sorption systems. Consequently, it is important to establish the time dependency of such systems for various pollutant removal processes (Ho *et al.* 2002).

The kinetic behaviour of Cu<sup>2+</sup> ions' sorption onto Mica-K was examined using agitation times of 5 – 210 minutes, at 400rpm and at room temperature. Removal efficiency of the adsorbent for Cu<sup>2+</sup> is illustrated in Figure 1.



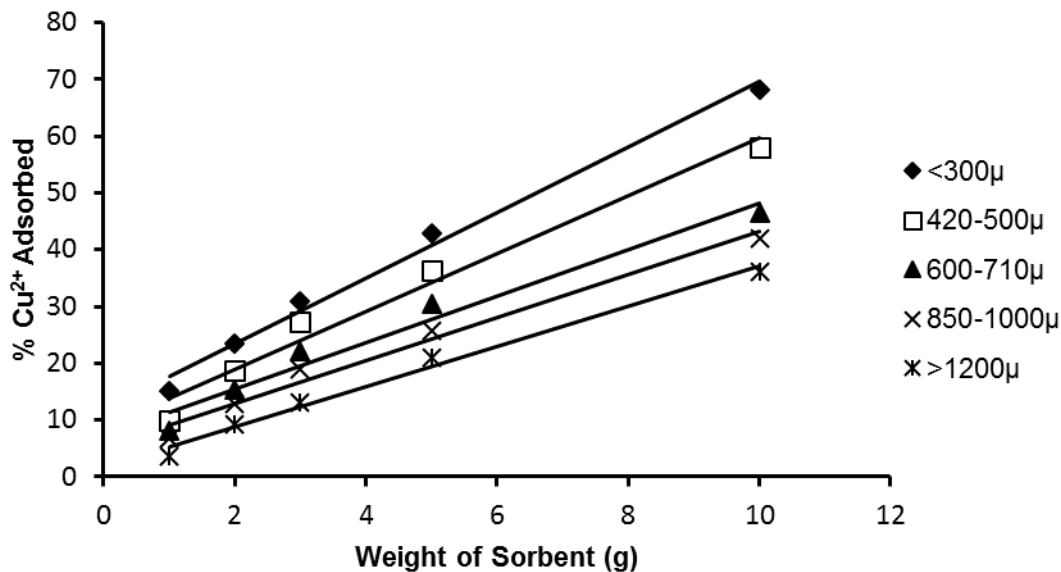
**Figure 1:** Effect of Contact Time on the sorption of  $\text{Cu}^{2+}$  by Mica-K.

Removal efficiencies of  $\text{Cu}^{2+}$  ions by Mica-K increased with contact time. The sorption was, noted to occur in two phases of fast and slow rates. The bulk of  $\text{Cu}^{2+}$  (99.7%) were removed within the first 20 min after which there was no significant increase in the removal of  $\text{Cu}^{2+}$  ions.  $\text{Cu}^{2+}$  sorption at equilibrium was thus 99.9% after the contact period of 90 min.

The initial faster rates of adsorption may be due to the availability of uncovered surface of the adsorbent, since adsorption kinetics depends on the available sorbent surface area. The decrease in removal rates, as equilibrium is approached, indicates possible monolayer formation of copper ions on the outer adsorbent surface. This may also have resulted from saturation of adsorption sites with metal ions followed by adsorption and desorption processes that occur at equilibrium.

### 3.1.2 Effect of Weight and Particle Size

Surface area of contact between sorbent and liquid phase plays an important role in sorption phenomena. Figure 2 shows adsorption of  $\text{Cu}^{2+}$  ions from aqueous solution as a function of weight of Mica-K for different particle size groups designated as; <300, 420-500, 600-710, 850-1000 and >1200 $\mu\text{m}$ . The effect of particle size and weight of Mica-K on adsorption was studied using 0.05M solutions of  $\text{Cu}^{2+}$  over a contact period of 30 minutes.

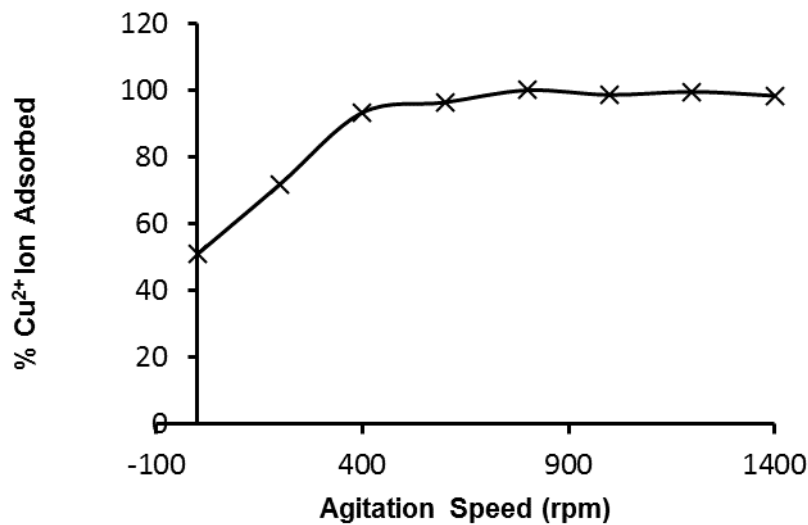


**Figure 2:** Effect of Sorbent Dose and Particle Size on Sorption of  $\text{Cu}^{2+}$  Ions.

It is clear that the amount of  $\text{Cu}^{2+}$  adsorbed after 30 minutes of contact time, increase with decreasing particle size and increase with sorbent weight. This can be attributed to the availability of more adsorption sites with increasing weight of Mica-K for the effective removal of  $\text{Cu}^{2+}$  ions from solution (Ho *et al.*, 1995) for a given initial metal ion concentration. The ratio of sorbent weight to concentration of adsorbate plays a significant role in the adsorption process. Increase in  $\text{Cu}^{2+}$  adsorption with decreasing particle size, suggests that sorption occurs by surface mechanism. Surface area for adsorption increases with decreasing particle size, hence the increased level of adsorption (Attahiru *et al.*, 2003). Consequently, Mica-K of particle size  $<300\mu\text{m}$  was used for subsequent experiments.

### 3.1.3 Effect of Agitation Speed

The influence of varying agitation speed was investigated for  $\text{Cu}^{2+}$  sorption on Mica-K. other process variables were kept constant while a series of experiments were undertaken with agitation speeds of 0, 200, 400, 600, 800, 1000, 1200 and 1400rpm. Figure 3 shows plot of  $\text{Cu}^{2+}$  ion uptake against various agitation speeds at room temperature.



**Figure 3:** Effect of Agitation Speed on the sorption of Cu<sup>2+</sup> by Mica-K.

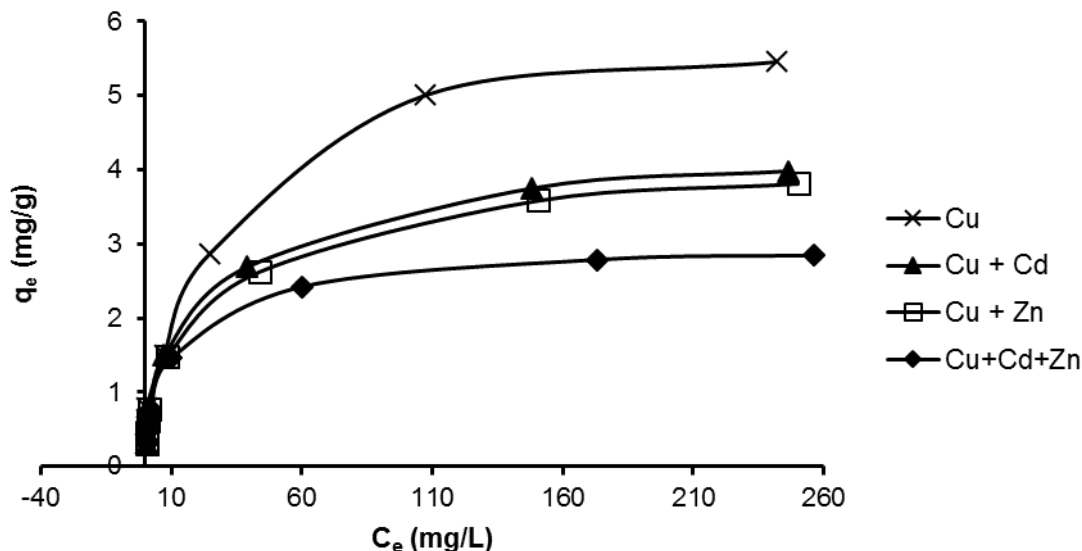
100%, of Cu<sup>2+</sup> is removed at equilibrium, with agitation speed of 800rpm. The speeds of 400, 600 and 800rpm for Cu<sup>2+</sup> assures good diffusion of the ions toward Mica-K particles (Benguella and Benaissa, 2002). This could be due to better and more uniform mixing with increasing agitation or there may possibly be some boundary layer resistance to reaction which is decreased by increasing agitation. The higher the agitation the greater is the shear on the boundary layer surrounding the particle.

For weak agitation speeds, there is reduction in Cu<sup>2+</sup> sorption by Mica-K; 50.8% in the absence of agitation and 71.75% at 200rpm. On the other hand, there is no significant increase in the amount of Cu<sup>2+</sup> removed at equilibrium with agitation speeds >800rpm. For instance 98.4% Cu<sup>2+</sup> ions are removed at 1400rpm. In this case it can be concluded that Mica-K particles are ratified and cations do not easily fix themselves on the surface. It can also be concluded that at high stirring speeds, vortex phenomena occur and the suspension is no longer homogeneous which makes the adsorption of metal ions difficult (Selatnia *et al.*, 2004).

### 3.1.4 Effect of Metal Co-ions.

Change in initial metal ion concentration and competition affects sorption. The effect of competition on Cu<sup>2+</sup> sorption (Figure 4) was investigated over metal ion (Cu<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup>) concentration ranges 0.0001–0.008 mol/L at 25±2°C and 400rpm. The contact time was maintained at 30 minutes and a sorbent dose of 2g in 25ml metal ion solution.

To account for the single and multi-component adsorption behaviour of the Cu<sup>2+</sup> ions on Mica-K, the fraction of Mica-K surface covered by metal ions was studied by plotting equilibrium sorption values ( $q_e$ ) against metal ion concentration at equilibrium ( $C_e$ ). The plots are shown in Figure 4.



**Figure 4:** Equilibrium Sorption versus Equilibrium Concentration for Single, Binary and Ternary  $Cu^{2+}$  Adsorption.

Figure 4 shows that increase in initial metal ion concentration increased the surface coverage of Mica-K until the surface was nearly fully covered with a monomolecular layer. At high concentration of metal ion, it was observed that further increase in concentration produced little change in the amount of metal ion adsorbed. Thus, increasing the initial heavy metal concentrations in the solutions decreased the removal efficiencies of the metal ions under study.

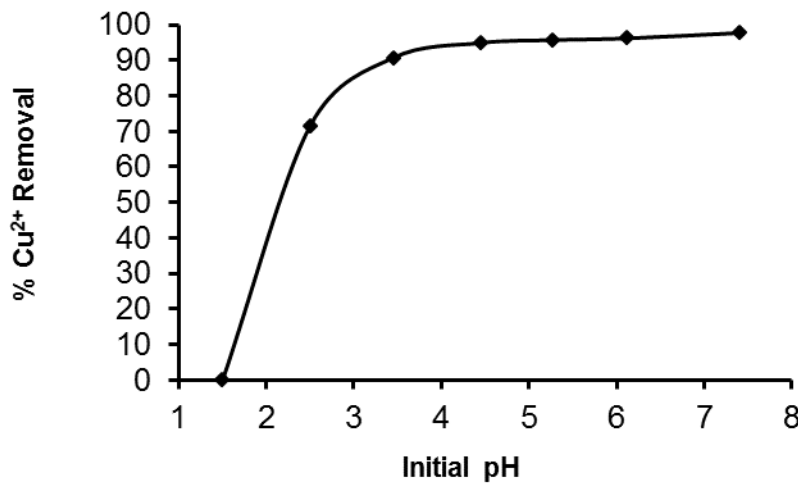
Further examination of Figure 4 reveals that adsorption of the metal ions was reduced in the presence of other competing metal ions. It is expected that a given mass of adsorbent material has a finite number of adsorption sites, and that as metal concentrations and competition increase, these sites become easily saturated. That is, there is some metal concentration that produces the maximum adsorption for a given adsorbent mass, and thereafter, adding more metal ions cannot increase adsorption because no more sites are available as all are occupied. Another possible cause of decreased adsorption of metal ions may have been a progressive decrease in the proportion of stronger interactions and an increase in the proportion of electrostatic interactions at sites with a lower affinity for heavy metals as the initial heavy metal concentrations increases.

### 3.1.5 Effect of pH.

One of the most critical parameters in the treatment of multi-component system is the effect of initial pH of adsorption medium. Solution pH determines the surface charge of the adsorbent, and the degree of ionization and speciation of the adsorbate (Heechan *et al.*, 2005; Aksu *et al.*, 2002).

The influence of pH on adsorption (Figure 5) was examined using 0.002M  $Cu^{2+}$  solution. The role of  $H^+$  ion concentration was examined from solutions at different pH of the adsorbent-adsorbate mixtures varying from 1.5 to 7.4 using 1g samples and 25mls of solution.



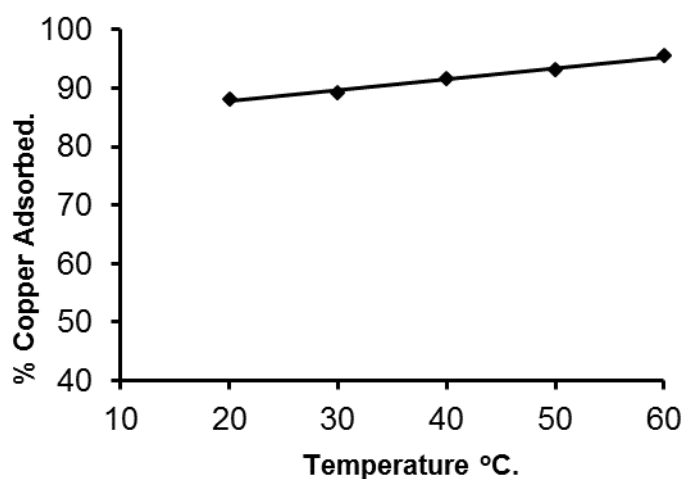


**Figure 5:** Effect of pH on Sorption of Cu<sup>2+</sup> on Mica-K.

Figure 5 shows increase in Cu<sup>2+</sup> adsorbed from almost zero at pH 1.5 to nearly 100% over the pH range of 4.45 to 7.4. The observations above leads to the conclusion that weakly acidic to neutral pH conditions are optimal for the adsorption of Cu<sup>2+</sup> ions onto Mica-K. The sorption capacity of Cu<sup>2+</sup> on Mica-K at pH 2.5 and 298 K was found to be 5.62mg/g after 24h of sorption. Similar results have been reported for goethite; 6.685 mg/g (Acemioglu and Alma, 2001).

**3.1.6 Effect of Temperature.**

The removal of Cu<sup>2+</sup> ions Mica-K was studied at 20°C, 30°C, 40°C, 50°C and 60°C. The results are presented in Figure 6.



**Figure 6:** Effect of Temperature on Sorption of Cu<sup>2+</sup> on Mica-K.

The extent of adsorption of Cu<sup>2+</sup> is found to increase with temperature suggesting that the adsorption processes are endothermic in nature. The increase in uptake of Cu<sup>2+</sup> ions with temperature may be due to

desolvation of sorbing species, change in the size of pores, and enhanced rate of intra-particle diffusion of sorbate (Knocke and Hemphill, 1981). Adsorption of  $\text{Cu}^{2+}$  from solution at  $60^\circ\text{C}$  was 95.5 % up from 88.2% at  $20^\circ\text{C}$ .

### 3.2 Adsorption Thermodynamics

Thermodynamic parameters for the adsorption process,  $\Delta H$  ( $\text{kJ mol}^{-1}$ ),  $\Delta S$  ( $\text{JK}^{-1} \text{mol}^{-1}$ ) and  $\Delta G$  ( $\text{kJ mol}^{-1}$ ), can be evaluated using the equation (Manju *et al.* 2002):

$$\ln K_d = \left( \frac{\Delta S^\circ}{R} \right) - \left( \frac{\Delta H^\circ}{RT} \right) \quad (3)$$

Where;  $K_d$  is the distribution coefficient,  $\Delta H^\circ$  enthalpy of adsorption,  $\Delta S^\circ$  entropy,  $R$  gas constant ( $8.314 \text{ JK}^{-1} \text{mol}^{-1}$ ) and  $T$  temperature (K).

The distribution coefficient  $K_d$  is given by;

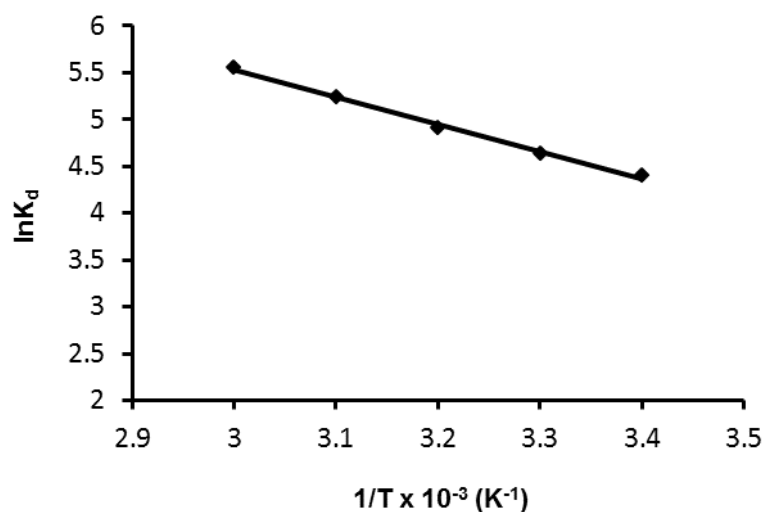
$$K_d = \left( \frac{C_o - C_e}{C_e} \right) \times \frac{V}{m} \quad (4)$$

Where;  $C_o$  is the initial concentration,  $C_e$  concentration of solution after equilibrium,  $V$  volume of solution (ml) and  $m$  is mass of sorbent (g)

The plot of  $\ln K_d$  versus  $1/T$  is linear with the slope and the intercept giving values of  $\Delta H^\circ$  and  $\Delta S^\circ$  respectively. These values can be used to compute  $\Delta G^\circ$  from the Gibbs relation;

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (5)$$

All these relations are valid when the enthalpy change remains constant in the range of temperatures considered. The plot of  $\ln K_d$  versus  $1/T$  obtained is shown in Figure 7.



**Figure 7:** Effect of Temperature on Thermodynamic Behavior of  $\text{Cu}^{2+}$  Sorption.

The results of the thermodynamic calculations, the enthalpy ( $\Delta H^\circ$ ), entropy ( $\Delta S^\circ$ ), and Gibbs free energy ( $\Delta G^\circ$ ) of activation for the single and multi-component  $\text{Cu}^{2+}$  sorption on Mica-K are shown in Table 2.

Metal Ion	$\Delta H^\circ$ kJ/mo l	$\Delta S^\circ$ J/K/mo l	$R^2$	$\Delta G^\circ$ , kJ/mol				
				293K	303K	313K	323K	333K
$\text{Cu}^{2+}$	24.11	118.32	0.995	-10.56	-11.74	-12.9 2	-14.11	-15.29

**Table 2:** Thermodynamic Parameters for the Adsorption of  $\text{Cu}^{2+}$  on Mica-K.

$\Delta H^\circ$  values are a measure of the energy barrier that must be overcome by reacting molecules/ions. The value for  $\Delta H^\circ$  ( $24.11 \text{ kJ mol}^{-1}$ ) suggests that sorption of  $\text{Cu}^{2+}$  ions is endothermic, meaning that, it consumes energy (Jardine and Sparks, 1984). Endothermicity of the heat of sorption may be due to the removal of water molecules from the solid/solution interface and from the sorbing cations. The magnitude of these values indicates moderately weak bonding between the metal ions and Mica-K.

The entropy ( $\Delta S^\circ$ ) value was positive (i.e., entropy increases as a result of adsorption). This occurs as a result of redistribution of energy between the adsorbate and the adsorbent. Before adsorption occurs, heavy metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free heavy metal ions to ions interacting with the adsorbent will be higher than in the adsorbed state. As a result, the distribution of rotational and translational energy among a small number of metal ions will increase with increasing adsorption by producing a positive value of  $\Delta S^\circ$  and randomness will increase

at the solid–solution interface during the process of adsorption (Mehmet *et al.*, 2007). Adsorption is thus likely to occur spontaneously at normal and high temperatures because  $\Delta H > 0$  and  $\Delta S > 0$ .

The value of  $\Delta S^\circ$  is also an indication of whether or not a reaction is an associative or dissociative mechanism. The entropy of activation ( $\Delta S^\circ$ ) parameter is often regarded as a measure of the width of the saddle point of the potential energy surface over which reactant molecules must pass as activated complexes (Horsfall *et al.*, 2006). Entropy values  $> -10 \text{ Jmol}^{-1}$  generally imply a dissociative mechanism. In Table 2 however, one sees a large positive value for  $\Delta S^\circ$ , suggesting that  $\text{Cu}^{2+}$  sorption on Mica-K surfaces is an associative mechanism.

Negative values for the Gibbs free energy ( $\Delta G^\circ$ ) in  $\text{Cu}^{2+}$  sorption show that the adsorption process is spontaneous in nature without any induction period and that the degree of spontaneity of the reaction increases with increasing temperature.

With increasing temperature, the magnitude of Gibbs energy decrease comes down in conformity with the exothermic nature of the adsorption process as an increased supply of heat energy would lead to enhanced desorption. The Gibbs energy decrease with temperature in each case was responsible for imparting stability to the metal ion-mica-K adsorption complexes. Similar results have been reported by Manju *et al.* (2002) on adsorption of  $\text{Pb}^{2+}$  on polyacrylamide-grafted hydrous  $\text{Fe}^{3+}$  oxide in the temperature range of 303 to 333K with  $\Delta G$  decreasing from  $-6.38$  to  $-11.13 \text{ kJ mol}^{-1}$ .

It is worthwhile to note here that  $\Delta G^\circ$  values up to  $-20 \text{ kJ mol}^{-1}$  are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption) while  $\Delta G^\circ$  values more negative than  $-40 \text{ kJ mol}^{-1}$  involve charge sharing or transfer from Mica-K surface to the metal ion to form a coordinate bond.

Coefficients of determination,  $R^2$  confirms that the isotherm models are a good fit to the data. The constancy in  $\Delta G^\circ$  with surface coverage is usually attributed to the absence of lateral interactions between sorbed ions (Horsfall *et al.*, 2006).

Thermodynamic data on metal adsorption on naturally occurring minerals are however, limited. The results obtained in this research work, compares well with those achieved in other studies using similar adsorbents (Echeverria *et al.*, 2003; Arivoli *et al.*, 2007)

### 3.3 Modeling of Sorption Isotherms

Equilibrium adsorption isotherms are of fundamental importance in the design of adsorption systems since they indicate how metal ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of metal ion concentration.

Sorption isotherms of Mica-K for  $\text{Cu}^{2+}$ , removal were expressed mathematically in terms of the Langmuir and Freundlich (Mehmet *et al.*, 2007) models. The quality of the isotherm fit to the experimental data is typically assessed based on the magnitude of the correlation coefficient for the regression  $R^2$ .

### 3.3.1 Langmuir and Freundlich Isotherms

The Langmuir model has the following form:

$$\frac{1}{q_e} = \frac{1}{bQ_o C_e} + \frac{1}{Q_o} \quad (6)$$

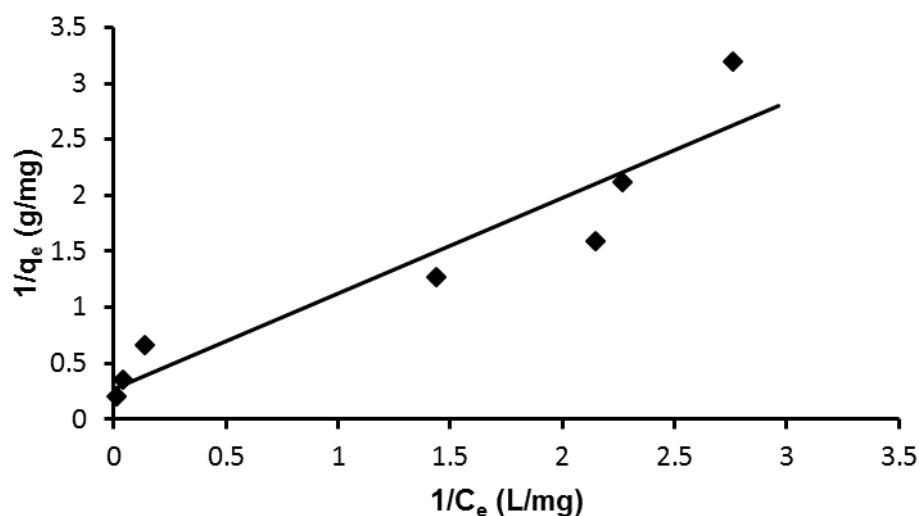
Where  $q_e$  is the amount adsorbed per unit mass of adsorbent at equilibrium ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ),  $Q_o$  and  $b$  are Langmuir constants relating to the maximum adsorption capacity and adsorption energy, respectively. Linear plots of  $1/q_e$  versus  $1/C_e$  shows that the adsorption obeys the Langmuir model and  $Q_o$  and  $b$  can then be determined from the slope and intercept, respectively.

The logarithmic form of the Freundlich model may be expressed by the equation

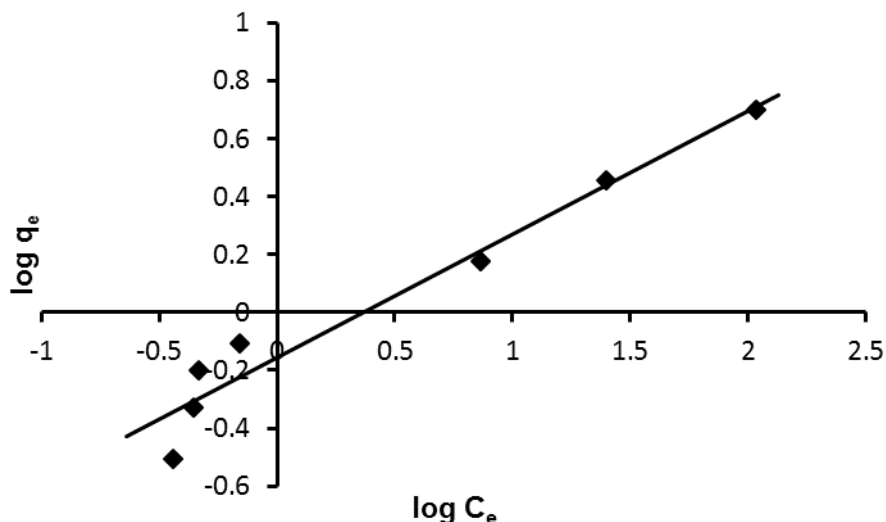
$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

Where:  $q_e$  is the amount adsorbed per unit mass of adsorbent at equilibrium ( $\text{mg g}^{-1}$ ),  $C_e$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ),  $K_f$  and  $n$  are Freundlich constants related to the adsorption capacity and intensity of adsorption, respectively. If the adsorption data obeys the Freundlich equation, then a straight line must be obtained in the system co-ordinates,  $\log q_e$  versus  $\log C_e$  with the slopes and intercepts yielding  $n$  and  $K$ , respectively.

From the linear plots (Figures 8 and 9), the Langmuir and Freundlich adsorption coefficients were obtained and used in computing the adsorption parameters presented in Table 3.



**Figure 8:** Langmuir Isotherm for Sorption of  $\text{Cu}^{2+}$  Ions on Mica-K.



**Figure 9:** Freundlich Isotherm for Sorption of Cu<sup>2+</sup> Ions on Mica-K.

**Table 3:** Isotherm Constants for Single, Binary and Ternary Adsorption of Cu<sup>2+</sup> on Mica-K.

Metal Ion	Langmuir Parameters			Freundlich Parameters		
	<i>Q<sub>o</sub></i> (mg/g)	<i>b</i> (L/mg)	<i>R</i> <sup>2</sup>	<i>K<sub>f</sub></i> (mg/g)	<i>n</i>	<i>R</i> <sup>2</sup>
Cu <sup>2+</sup>	3.717	0.316	0.893	0.701	2.353	0.955

A comparison of the Langmuir constants, *b*, which represent the adsorption capacity of Mica-K for metal ions, show that the mineral had a mass capacity for Cu<sup>2+</sup> ions. Small value of *b* however, shows that the equilibrium, is shifted predominantly to the left, i.e., towards the desorption of heavy metal ions from the surface of the adsorbent after complex formation.

The Langmuir monolayer capacity, *Q<sub>o</sub>*, is appreciable with a value of 3.717 mg g<sup>-1</sup>. The literature is limited with respect to the values of the isotherm coefficients for adsorption of heavy metals on Mica-K. The results obtained by Attahiru *et al.*, (2003) for adsorption of Cu<sup>2+</sup> on some other types of Kenyan micaceous mineral, found the Langmuir adsorption capacity to lie between 0.617 and 0.850g g<sup>-1</sup>.

The empirical Freundlich isotherm yielded a good linear plot (Figure 9). The value obtained in this study for the adsorption intensity, *n* of 2.353, points to the fact that Cu<sup>2+</sup> is favourably adsorbed by Mica-K. The value of *K<sub>f</sub>* however, is less than unity (0.701), indicating that Mica-K adsorbent has low affinity for Cu<sup>2+</sup> ions. This isotherm, however, does not yield any concrete information about the mechanism of adsorption, but is applicable to non-specific adsorption on heterogeneous solid surfaces.

The correlation coefficients, *R*<sup>2</sup> for Freundlich isotherm (0.955) in comparison to the value obtained for the Langmuir isotherm (0.893) indicating that the adsorption process obeyed both the Langmuir and Freundlich adsorption isotherms.

### 3.4 X-ray Photoelectron Spectroscopic (XPS) Analysis

XPS spectra of the raw and metal-adsorbed Mica-K (Figures 10-12) were obtained using a Kratos Axis Nova Spectrometer.

**Figure 10:** X-Ray Photoelectron Spectrum of Raw Mica-K.

**Figure 11:** X-Ray Photoelectron Spectrum of Mica-K with  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  Adsorbed.

In Figure 11, the XPS spectrum of the metal ion-sorbed Mica-K sample shows major peaks from left to right as labeled: Zn 2p<sub>3/2</sub>, Cu 2p<sub>3/2</sub>(935.39eV), Cu 2p<sub>3/2</sub>(933.47eV), Zn LMM Auger Cd 3d<sub>3/2</sub> and Cd 3d<sub>5/2</sub>, respectively. In Figure 10, there is no sign of these peaks before adsorbing  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  on Mica-K. The Zn 2p<sub>3/2</sub> peak at 1022.92 eV, indicates presence of metallic Zn (1022.0eV), oxidation of Zinc

to  $\text{Zn}^{2+}$  { $\text{ZnO}/\text{Zn}(\text{OH})_2$ , 1022.2eV} and most probably formation of  $\text{ZnF}_2$  whose spectral line has a typical value of 1022.8 eV.

(Nesbitt and Banerjee, 1998).

The Cu 2p<sub>3/2</sub> satellite peak is shown at 935.39 eV, which indicates oxidation of copper and most probably formation of Cu hydroxide  $\text{Cu}(\text{OH})_2$  (Xingyu *et al.*, 2006) on the surface of Mica-K particles. A Cu 2p<sub>3/2</sub> peak at 933.47 eV over and above the satellite peak is typical of pure metallic Cu (933.0eV) and CuO (933.5eV).

The formation of metal fluoride, oxide and hydroxide complexes is supported by the fact that there is a reduction of O 1s and F 1s peaks, (Figures 10 and 11) from 59.3 to 58.7 and 0.9 to 0.7%, respectively before and after metal ion adsorption.

#### **Figure 12:** High Resolution XPS Spectra of Organic Species on the Surface of Mica-K.

The presence of O-C=O (289.10eV), C=O (287.48eV), C-OH, C-O-C (286.30eV) and C-C, C-H at 284.80eV (Figure 12) on the surface of Mica-K points to the fact that most metals on the surface of Mica-K exist in the form of carbonates, hydrogen carbonates, oxide and as hydroxide complexes. High and constant concentration of  $\text{HCO}_3^-$  ions is due to the presence of relatively high amount of calcite and dolomite in the mineral samples (Pawel and Robert, 2006).

## **4.0 Conclusions**

The results indicate that low cost Mica-K removes considerable quantities of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions from aqueous solutions. The adsorption of  $\text{Cu}^{2+}$  onto Mica-K was found to be dependent on; contact time, adsorbate concentration, pH, particle size, sorbent dose, presence of other metal ions and temperature.



Thermodynamic parameters reveal that sorption of  $\text{Cu}^{2+}$  ions is endothermic in nature, involves some structural changes at the solid liquid interface and is spontaneous at normal and higher temperatures. Correlation factors and other parameters for Langmuir and Freundlich confirm good agreement between theoretical models and the experimental results.

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