

**KINETICS AND EQUILIBRIUM STUDIES OF SINGLE  
AND MULTI-COMPONENT METAL ION SORPTION  
ON A MICACEOUS MINERAL OF KENYAN ORIGIN.**

**BY:**

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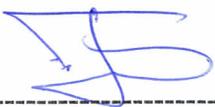
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## Declaration

This is my original work and has not been submitted for examination for a degree in any other university.

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This thesis has been submitted for examination with our approval as the supervisors;

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## Abstract

Water pollution by Chemicals is of great public concern. Improvements in the quality and availability of water are often possible at relatively low costs. The objective of this work was to test the efficacy and applicability of a Micaceous mineral of Kenyan origin (herein referred to as Mica-K or the mineral) in the removal of toxic divalent heavy metal ions from water and wastewater systems.

Mica-K was characterized and utilized in study of single and multi-component removal of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions from aqueous solution over wide range of initial metal ion concentrations (25 mg/L to 500 mg/L), contact duration (0-3hrs), sorbent dose (0.5-10 g/25ml or 20-400g/L), pH (1.5 to 7.5), and temperature (293 to 333 K). The sorption pattern of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions onto the micaceous mineral followed Langmuir, Freundlich, and Dubinin-Kaganer-Radushkevich isotherms.

The dependence of heavy metal adsorption on pH was different for each metal ion. The removal of  $\text{Zn}^{2+}$  was about 0% at pH 2 and it increased to 93% at pH 7.4. For  $\text{Cu}^{2+}$ , 72% was removed at pH 2.5 and it increased to 98% at pH 7.4.  $\text{Cd}^{2+}$ , removal increased with increasing pH from 45% at pH 1.5 to 93% at pH 7.4. In all cases, over 93% of all the three metals were removed at pH 7.4. Metal ion removal was however, considerably affected by the presence of competing metal ions in solution.

Thermodynamic parameters ( $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ ) for  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  sorption onto Mica-K were also determined. Kinetic modeling analysis of the Elovich, pseudo-first order, pseudo-second order, intra-particle diffusion, mass transfer and intra-particle diffusivity equations using the linear coefficient of determination  $R^2$  values showed that the pseudo-second order equation was the most appropriate model for the description of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  transport. Thus the sorption of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions can be said to follow a pseudo-second order model, with chemical sorption as its rate limiting step.

Experiments were also carried out to ascertain the physico-chemical properties of Mica-K. Chemical analysis revealed that the mineral is mainly comprised of  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . Physical parameters such as specific gravity, void ratio, porosity, hydraulic conductivity (at 20°C), unit weight of dry mineral, unit weight of submerged saturated

mineral, unit weight of buoyant mineral, optimum moisture content (OMC), maximum dry density(MDD), and specific surface area have also been determined and reported.

Elemental analyses of Mica-K have shown that; major rock-forming mineral elements comprises of Al, Fe, K, and Mg; major ore-mineral elements present include Ba, Ca, Cr, Ni and Ti; and trace elements, are Co, Mn, Cu, P,S, Si, V, B, Hg, Li, Sr and Zn. The most abundant minerals are; feldspars, chlorites, pyrites and kaolinites with dolomites, calcites and quartz being the least abundant.

X-ray photoelectron spectroscopic (XPS) analysis for  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ion-equilibrated Mica-K, demonstrated that  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ - containing nodules existed on the surface of the mineral. X-Ray diffraction (XRD) studies have pointed to the possibility of formation of metal fluoride, oxide, hydroxide, carbonate and hydrogen carbonate complexes on the surface of Mica-K during metal ion adsorption.

Other studies included comparative batch kinetics whereby the effects of; contact time, initial metal ion concentration, weight of mineral used, solution pH, particle size, agitation speed, temperature and nature of metal ion salt were investigated. Comparative batch equilibrium studies involved determination of the isotherms of sorption, maximum sorption level and modeling.

Fixed bed experiments were performed to determine the breakthrough curves and study the sorption dynamics. The amount of  $\text{Cu}^{2+}$  ions adsorbed in fixed-bed experiment was greater than that of combined alkali and alkaline earth metal cations  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  released. This indicates that ion exchange is not the only mechanism by which  $\text{Cu}^{2+}$  ions are removed from solution.

Regeneration of sorbent for repeated use was carried out using 0.1 M HCl as the desorbing agent. The amount of copper desorbed by the acid was 27.30meq  $\text{g}^{-1}$  (13.65 mg  $\text{g}^{-1}$ ) as compared to 14.26meq  $\text{g}^{-1}$  (7.13mg  $\text{g}^{-1}$ ), copper adsorbed by Mica-K in the column. These shows that Mica-K can be regenerated effectively using weak acids. Excess amounts of acid however, can lead to the degradation of the mineral structure and thus result in the leaching of copper and other ions.

Mica-K adsorbent compared quite well with a commercially available Elgalite ion exchange resin from Elga Company UK, when used to treat real water samples from different sources within Kenya and industrial effluents. It has been proven that Mica-K is a good adsorbent for both metal and non-metal ions with the amount of ion adsorbed being dependant on the type of ion, its concentration and solution pH.

It is hoped that the data obtained from this research work will illustrate the importance of locally available micaceous minerals in their use as economical adsorbents of heavy metals from water and wastewater systems. It is also hoped that the results will convince the public and the decision makers of the urgent need to develop industrial and domestic uses of the locally available materials for water purification.