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Removal of Cr(III) from aqueous solutions using a micaceous poly–mineral from Kenya

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Adsorption of Cr(III) ions from aqueous solutions using a micaceous polymineral (MPM) from Kenya was studied using batch experiments as function of contact time, adsorbent dosage, Cr(III) concentration, pH and temperature. Chromium adsorption was found to be a fast process taking place in less than 20 min to reach equilibrium. Near complete removal of the metal was realized at Cr(III) concentrations of 200 mg/L, using 0.15 g/ml adsorbent doses at pH range of 4 to 6 and 25 to 40°C. Equilibrium and kinetics analysis indicated that Cr(III) adsorption onto MPM progresses through an inner-sphere surface complexation of the hydrolysis products of Cr(III) with surface sites in the adsorbent mineral. The adsorption process could be described by the Lagergren pseudo-second order kinetics model and the adsorption equilibrium was found to conform to H-type according to Giles classification of adsorption isotherms. The adsorption data could therefore be validated by Langmuir model. The adsorption capacity of 7.9 mg/g showed that this low-cost material could be used for the scavenging Cr(III) from aqueous streams.

Key words: Chromium(III) adsorption, Giles classification of isotherms, Lagergren kinetics models, Langmuir isotherm, Micaceous adsorbent mineral.

INTRODUCTION

Uncontrolled discharge of chromium into the environment through industrial wastewater is a problem of serious ecological concern in Kenya because of the toxicity of chromium to humans and other forms of life (Kaluli et al., 2011; Onyancha et al., 2008, Mwinyihija and Killham, 2006). Many industries, especially tanning, wood preservation, metal plating, alloying and those manufacturing pigments release high levels of chromium in wastewaters. Permissible limits, according to guidelines set by Kenya’s National Environmental Management Authority (NEMA), for chromium in wastewaters are 0.05 mg/L or 9.6 mmol/L (Government of Kenya, 2006). The trivalent form of chromium Cr(III) is not as toxic though, and it is an important mineral supplement required for glucose and lipid metabolism in mammals, and its deficiency has been associated with symptoms of diabetes mellitus (Manahan, 2003; Stêpniewska et al., 2007). Hexavalent chromium, Cr(VI), on the other hand, is usually in form of water soluble chromate ions, CrO₄²⁻, and it is readily absorbed into blood stream through epithelial lining through the lungs. It is highly corrosive and possible mutagenic and carcinogenic material associated with lung fibrosis, skin inflammation and nephrotoxicity (kidney damage). The harmful effects of Cr(III) arise from its potential to get oxidized into more stable and toxic Cr(VI) in the environment (Manahan, 2003).

Recovery of chromium from wastewaters is becoming especially important in the developing world as more and more chrome-based industries appear to shift based to developing countries, “where production costs are lower and environmental regulations less stringent” (Mwinyihija and Killham, 2006). Traditional technologies for recovery of chromium from wastewaters include: Chemical precipitation, coagulation and filtration, reverse osmosis, electro dialysis, ion exchange, membrane and nanotechnologies, and adsorption. Both precipitations and coagulation are inefficient and generate high quantities of
metal-laden sludge resulting in sludge disposal problems. From the standpoint of most developing countries, the use of reverse osmosis, electrodialysis, ion exchange, membrane and nanotechnology, and adsorption techniques using conventional adsorbents (carbon, alumina and synthetic resins) is limited by lack of adequate technical skills, high energy requirements and high operation costs. In addition, activated carbons, activated alumina and organic resins as adsorbents require frequent regeneration; they are nonbiodegradable and difficult to dispose off making application of adsorption using these adsorbents more complicated. Increasingly, lots of research work has, therefore, turned towards utilization of abundant natural and low-cost industrial materials as alternatives to conventional adsorbents. The low-cost natural adsorbents are advantageous in that they are readily available in safe and stable forms, they possess attractive natural adsorptive properties and require minimum preparation. They can easily be customized to local conditions and, on proper cleansing, be incorporated back into their natural environment with relative ease after use (Wambu et al., 2011).

During preliminary tests carried out in our laboratories, a naturally occurring micaceous mineral from parts of Kajiado County in Kenya was found to have especially high sorptive properties for a number of aqueous metal ions including Cr(III) ions. Cr(III) is one of the most water-polluting metal ions in Kenya (Mwinyihija and Killham, 2006). The current work was designed to systematically assess Cr(III) removal from aqueous solution using this potent polymineral as an adsorbent. The effect of adsorption parameters including Cr(III) concentration, amount of adsorbent, contact time, pH and adsorption temperature was studied and the chromium adsorption data discussed based on selected kinetics and equilibrium mathematical models to establish the rate, adsorption capacity, and mechanism of Cr(III) immobilization into the adsorbent.

**EXPERIMENTAL**

**Materials**

The adsorbent materials were collected from their natural deposits in Kajiado, Kenya. They were washed with distilled water, dried at 100°C and crushed before they were employed in the adsorption tests. Analar grade reagents (Aldrich Chemical Co.) were employed throughout this work. Stock solutions of Cr(III) were prepared from Cr(NO₃)₃ in deionized H₂O and working solutions were prepared from it by appropriate serial dilutions.

**Instrumentation**

Batch adsorption mixtures were agitated using a Maxmix Type 65800 Thermolyne orbital shaker temperatures being regulated and maintained constant using a Boekel Scientific Model 133730 incubator and a Col Parmer Model 8891 sonicator bath employed in tests on the effect of sonication on MPM uptake of the adsorbate. An SP8-15 Turner spectrophotometer was used in supernatant Cr(III) measurement and a Fischer Scientific Accum combination pH electrode/meter Model 15, for pH measurements.

**Adsorption experiments**

All adsorption tests unless otherwise specified were carried out on batch basis at room temperature (25 ± 0.5°C) as follows: Known amounts of MPM were shaken for a given time of contact with 20 ml of adsorbate solution containing known concentration of Cr(III) ions. The mixture was centrifuged and chromium concentration in the supernatant measured by atomic absorption spectrophotometry (AAS). The amount of Cr(III) adsorbed, qe (mg/g) was calculated from the respective expression as:

\[
\text{Amount of Cr(III) adsorbed, } q_e = (C_o - C_e) \text{ V/m} \quad (1)
\]

\[
\% \text{Cr(III) adsorption} = 100(C_o - C_e)/C_o \quad (2)
\]

Where \(C_o\) and \(C_e\) are the initial and equilibrium aqueous Cr(III) concentrations (mg/L), \(V\) (ml) is the adsorption volume and \(m\) the mass of adsorbent (g).

**RESULTS AND DISCUSSION**

**Effect of time of contact**

The effect of change in time of contact on the Cr(III) uptake by MPM was investigated by varying contact time from 0 to 60 min at constant initial Cr(III) concentration of 37 and 850 mg/L, respectively and the results are presented in Figure 1.

At low concentration (37 mg/L), the adsorption equilibrium was attained rapidly within 10 min to near complete (100%) removal. The uptake was however less rapid at higher Cr(III) concentrations (850 mg/L) reaching equilibrium after 20 min. It can be assumed that as more Cr(III) ions were adsorbed on the surface, the number of available adsorptive sites rapidly decreased. This created electrostatic hindrance to the incoming Cr(III) species from the solution as was also observed by Pandey et al., (2010). This coulombic hindrance then slowed down pore

![Figure 1. Effect of time of contact on Cr(III) adsorption onto MPM at 25°C, 0.15 g/ml adsorbent dosage and adsorbate solution pH of 4.](image-url)
with increasing mass of MPM from about 90% at 1 g/mL and leveled off at 100% when the adsorbent dosage was increased to 3 g. This indicated that as the amount of adsorbent was increased progressively, more adsorbent sites were availed which enabled more uptake of Cr(III) ions resulting in higher percentage Cr(III) adsorption. Similar trends were reported for palygorskite adsorbent by Potgieter et al. (2006). For practical purposes, therefore, minimum adsorbent dosage of 3 g per 20 ml of adsorbate solution was required for complete removal of Cr(III) at 397 mg/L initial Cr(III) concentration. This adsorbent-solution ratio was therefore employed in all subsequent experiments in this work.

Effect of initial chromium concentration

Adsorbate concentration plays an important role in determining the kinetic and equilibrium properties of an adsorption protocol. In many cases, especially involving low-affinity surfaces, it becomes the sole driving force behind the reaction equilibrium. The influence of change in concentration of Cr(III) ion on its equilibrium removal from solution by MPM was studied at constant adsorbent dosage (3 g per 20 ml) and the results are presented in Figure 3.

It was observed that Cr(III) ions were completely removed from solution up to initial concentration of 200 mg/L. The percentage removal then decreased rapidly with increasing initial concentration of Cr(III) ions to about 40% at 800 mg/L initial Cr(III) concentration. Thereafter, it decreased gently to about 16% as the initial Cr(III) concentration approached 4200 mg/L. Thus, a near constant partition of Cr(III) between the solid and the aqueous phase is observed at concentrations above 1000 mg/L and surface saturation is not attained. This shows that at low concentration, Cr(III) adsorption is influenced strongly by the available adsorbent surface. However, as the concentration increase, apparently, more and more surface sites are generated with increasing Cr(III) adsorption resulting in constant partition of Cr(III) between the solid and aqueous phases.

Because of their high tendency to polymerize in solution to form \( \text{Cr}_2(\text{OH})_4^{2+} \), \( \text{Cr}_3(\text{OH})_5^{3+} \) and other polymeric species at high concentrations (Wehrli et al., 1990), it can be assumed that as soon as monomeric Cr(III) ions are adsorbed at MPM surfaces, they formed secondary sites upon which more Cr(III) species from solution adsorbed forming dimer, trimer, etc Cr(III) surface complexes. Accordingly, this created additional adsorptive sites leading to more and more adsorbate ions being adsorbed from solution and elevated concentrations. This means that just a small mass of adsorbent could be utilized to remove large amounts of the adsorbate. Therefore relatively low batch dosage of MPM could be employed eliminating generation of large volumes of metal-laden sludge and its disposal concerns.

**Effect of change in the adsorbent dosage**

Consequently, the effect of change in amount of adsorptive sites in the adsorption mixture on Cr(III) adsorption onto MPM was investigated by varying the mass of MPM between 1 and 10 g while maintaining the concentration (397 mg/L) and volume (20 ml) of Cr(III) solution constant. The results of these tests are presented in Figure 2.

Percentage of Cr(III) uptake by MPM increased rapidly during the first 10 minutes. This was attributed to the rapid diffusion of the ions into the adsorbent at higher surface concentration of Cr(III). Nonetheless, it was clear that at low concentrations, akin to normal Cr(III) contamination levels in wastewater streams, MPM could effectively and rapidly be employed to scavenge Cr(III) from the solutions in just 10 min.

**Effect of change in initial Cr(III) concentration**

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Effect of pH

The pH is an important factor in adsorption chemistry of aqueous metal ions because of its influence on aqueous metal ion speciation and surface characteristics of the adsorbent. The solution pH therefore plays a vital role in influencing the metal adsorption equilibrium. The effect of change in solution pH on Cr(III) adsorption onto MPM was studied for pH range of 2 to 8 using 40 and 190 mg/L initial Cr(III) concentrations at 25°C. Figure 4 shows that the effect of pH on chromium uptake by MPM was concentration dependent.

Percentage of Cr(III) adsorption increased rapidly from about 60% at pH 2 and 100% removal could be achieved at pH 3.5 when using 40 mg/L initial Cr(III) concentration. The rise in Cr(III) uptake with increasing pH was however somewhat less rapid for 190 mg/L initial adsorbate concentration; increasing steadily from 50% adsorption at pH 2, complete Cr(III) removal could not be achieved until pH > 5. Percentage of Cr(III) adsorption remained constant for both initial Cr(III) concentrations there on. This shows that MPM has got such strong affinity for Cr(III) that, at lower concentrations, about 60% Cr(III) adsorption onto MPM could be achieved against strong coulombic repulsions from highly protonated and positively charged MPM surface in strong acidic media (pH = 2). It indicates that chemical interactions involving exchange or sharing of valence electrons between trivalent Cr with MPM adsorptive surfaces could be the underpinning process in Cr(III) uptake by MPM especially at lower aqueous concentrations.

The rapid rise in percentage of Cr(III) adsorption with increasing pH under acidic conditions could be attributed to increase in MPM surface negative charge due to progressive uptake of OH ions by MPM surface and, to hydrolysis and subsequent polymerization of Cr(III) which occur in mid acidic pH values (Fendorf, 1995). Formation of hydrolysis and polymeric products, such as CrOH$^{2+}$, Cr$_2$(OH)$_4^{4+}$, Cr$_3$(OH)$_5^{5+}$ etc, would enhanced Cr(III) adsorption by disrupting the hydration sphere of the hexaqua monomeric ions, [Cr(H$_2$O)$_6$]$^{3+}$ which in turn would open up Cr(III) ions and enhance their ligand exchange activities. This would then result in increased reactivity with surface groups in the adsorbent. The overall lower net positive charge of the hydrolysis products lessens electrostatic repulsions of the ions by positively charged adsorbent surface in acidic media. This means that the ions could then more favorably approach and coordinate with adsorbent surface groups resulting in higher percentage uptake of the ions by the mineral surfaces (Wehrli et al., 1990; Xu et al., 1985).

In general, MPM had wide pH adsorption edge for Cr(III) ions showing that by appropriate manipulation of solution pH, MPM could effectively be used to sorb aqueous chromium at a wide range of adsorbate concentration.

Effect of temperature

The effect of change in adsorption temperature on the adsorption of Cr(III) onto MPM was studied at temperatures between 20 and 60°C using constant initial Cr(III) concentrations of 37 and 190 mg/L. Figure 5 shows that, at the two concentrations of Cr(III), percentage Cr(III) adsorption first increased rapidly with temperature, it flattened off and then increased again indicating heterogeneity in adsorption energies of the adsorbent surfaces. This shows that surface exposed sites which are utilized at lower concentrations require lower activation energy than less exposed sites. Saturation of the material did not take place at the concentrations employed in this section because at 60°C the percentage Cr(III) adsorption was still increasing. Close to 100% Cr(III) uptake could be achieved within 25 to 40°C which are within the normal range of ambient tropical temperatures. This shows the adsorbent could be used to treat Cr(III) contaminated aqueous streams within ambient tropical conditions such as are prevalent in many developing countries, without the need for prior adjustments of solution temperature.
Adsorption isotherm

Adsorption isotherms are employed in evaluation of adsorption equilibriums because they offer useful insight into the adsorption kinetics, capacities of the adsorbents, characteristics of the adsorbate particles and adsorbent surfaces and they are often used to elucidate the reaction mechanisms between the solute particles and adsorbent sites (Giles et al., 1960). To validate the MPM Cr(III) uptake equilibrium, an adsorption isotherm was constructed for Cr(III) adsorption onto MPM by plotting equilibrium adsorption; \( q_e \) (mg/g) against equilibrium concentration of Cr(III), \( c_e \) (mg/L) and the results are presented in Figure 6.

The MPM Cr(III) adsorption isotherm was a typical H-type isotherm according to Giles classification of isotherms. This shows that Cr(III) ions has got such high affinity for the MPM surfaces that at concentrations less than 200 mg/L, the ions were completely adsorbed from solution. This was consistent with earlier postulates under 'effects of change in mass of adsorbent' where it was found that there is complete removal of metal ions even at low adsorbent dosage ratios. MPM adsorbent could completely remove Cr(III) ions from aqueous systems under similar conditions up to 200 mg/L.

To further assess the adsorption process and determine the maximum adsorption capacity of the adsorbent, the adsorption data was fitted to the Langmuir model in the form:

\[
\frac{1}{q_e} = \frac{1}{a b c_e} + \frac{1}{b}
\]

where, \( a \) is maximum adsorption capacity (mg/g) of MPM, and \( b \) is the Langmuir constant related to the energy of adsorption of Cr(III) onto MPM. The isothermal constants were calculated and compared to those of other low cost adsorbents in the literature. The results of this analysis are presented in Figure 7 and Table 1.

The Langmuir isotherm was well correlated to the adsorption data with \( R^2 \) values of 0.9987 showing that MPM Cr(III) adsorption data could be described by this model. The Cr(III) adsorption capacity of the MPM was however lower compared with those of Cement Klin Dust, Sargassum sp. biomass, and activated carbon. However it was higher than those of carbon nanotubes and Montmorillonite clay. Differences in Cr(III) adsorption capacities of the adsorbents result from differences in properties of the adsorbents such as specific surface area, structure, surface characteristics etc and operating conditions of the adsorbent. It should be noted that, the adsorption capacity of MPM was not the highest; its adsorption affinity (\( b \)) for Cr(III) is quite high as compared with that of the other adsorbents. More so, the adsorbent could be obtained cheaply and in large quantities from its natural deposits and safely used with minimal processing for the removal of Cr(III) from aqueous streams.

Adsorption kinetics

In order to clarify the kinetics of the adsorption of Cr(III) ions onto MPM, Lagergren's pseudo-first-order and pseudo-second-order kinetics and the Morris–Weber intraparticle diffusion models were applied to the experimental data. The plot for the second order model and the respective kinetics constants are presented in Figure 8 and Table 2, respectively. The linearized form of the Lagergren pseudo-first-order rate equation was adopted as:

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

where \( q_t \) (mg/g) and \( q_e \) (mg/g) are the amounts of the Cr(III) ions adsorbed at equilibrium and \( t \) (min), respectively, and \( k_1 \) (min\(^{-1}\)) is the rate constant. The plots
Table 1. Comparison of the Langmuir isotherm constants for the adsorption of Cr(III) onto mineral with those of other low-cost adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent and source</th>
<th>Langmuir constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (mg/g)</td>
</tr>
<tr>
<td>Polymineral (this study)</td>
<td>7.9428</td>
</tr>
<tr>
<td>Montmorillonite (Chantawong, 2004)</td>
<td>3.12</td>
</tr>
<tr>
<td>Activated carbon (Tangjuank et al., 2009)</td>
<td>13.93</td>
</tr>
<tr>
<td>Carbon nanotubes (Atieh et al., 2010)</td>
<td>0.3853</td>
</tr>
<tr>
<td>Sargassum sp. biomass (Cossich et al., 2002)</td>
<td>68.94</td>
</tr>
<tr>
<td>Cement kiln dust (Al-Meshragi et al., 2008)</td>
<td>303.149</td>
</tr>
</tbody>
</table>

Figure 8. Lagergren pseudo-second order kinetics plot for Cr(III) adsorption onto MPM for adsorption data obtained at 25°C using 0.15 g/mol MPM dosage.

Table 2. Equilibrium and kinetics constants for the adsorption of Cr(III) on heat regenerated spent bleaching earth.

<table>
<thead>
<tr>
<th>Pseudo-second order kinetics</th>
<th>K_{2ad} \times 10^{-1} (g/mg min)</th>
<th>q_e \times 10^{-1} (mg/g)</th>
<th>h_o \times 10^{-2} (mg/g min)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.97</td>
<td>4.789</td>
<td>6.81</td>
<td>0.9851</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pseudo-first order kinetics</th>
<th>K_{1,ad} \times 10^{-2}</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.86</td>
<td>0.6295</td>
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</table>

<table>
<thead>
<tr>
<th>Intra-particle diffusion model</th>
<th>k_w \times 10^{-2}</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.13</td>
<td>0.7371</td>
</tr>
</tbody>
</table>

of ln (q_e−q_t) versus t from which the rate constant k_1 could be calculated should be linear. The experimental data (the plot not shown) did not fit the Lagergren-first-order model well and the R² value for this model was low (0.6295). The insufficiency of the first-order model to fit metal sorption kinetic data has been reported for similar systems in the literature (Wambu et al., 2011; King et al., 2006).

The pseudo-second order kinetics model (Ho and McKay, 2003) was employed in the form:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{1}{q_e} \frac{1}{t}
\]  

A plot of t/q_t versus t from which the rate constant k_2,
equilibrium adsorption, $q_e$ and the initial rate $h_0$, given by $h_0 = K_d q_e^2$ could be obtained should be linear.

The second order rate model fitted the adsorption data well with $R^2$ value of 0.9851 and the determined equilibrium adsorption (4.789 mg/g) was consistent with observed experimental values indicating that Cr(III) adsorption could be described by this model. Adherence of these data to this model indicate that the rate limiting step was chemical in nature involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate (Taty-Costodes et al., 2003). This was in agreement with earlier postulates mentioned previously in this work which states that Cr(III) adsorption on MPM could be chemical in nature involving strong valence interactions between Cr(III) ions and MPM surfaces. The correlation coefficient was considerably lower for intra-particle diffusion kinetics ($R^2 = 0.737$) indicating that the adsorption process is not diffusion-driven. Therefore intraparticle migratory movements may not play a major role in Cr(III) adsorption onto MPM.

**Conclusion**

The results of this work shows that Cr(III) adsorption onto MPM was strongly influenced by time of contact, MPM dosage, initial Cr(III) concentration, pH and temperature. Highest percentage of 100% Cr(III) adsorption was achieved at initial Cr(III) concentrations up to 200 mg/L, using 0.15 g/ml MPM batch dosage at pH range of 4 to 6 and 25 to 40°C. The adsorption process was found to follow high affinity, H-type isotherm (according to Giles classification of adsorption isotherms) with high correlation to Langmuir isotherm and maximum Langmuir adsorption capacity of 7.9428 mg/g. Equilibrium and kinetics analysis indicated that, the adsorption phenomenon was fast, reaching equilibrium in less than 20 min. The adsorption process was therefore chiefly based on hydrolysis and polymerization enhanced inner sphere surface complexation of Cr(III) ions involving exchange with surface H⁺ ions in the adsorbent. It has been demonstrated that Cr(III) could effectively be removed from aqueous streams using this mineral as a safe low cost adsorbent.

**REFERENCES**

