SYNTHESIS AND CHARACTERIZATION OF KAOLINITE COATED WITH CU-OXIDE AND ITS EFFECT ON THE REMOVAL OF AQUEOUS MERCURY(II) IONS: PART I

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In this paper, a novel copper oxide coated kaolinite was prepared as an adsorbent of Hg(II) ions from aqueous media. The materials used for this study were synthesized, characterised and the product tested for mercury ion removal using standard laboratory procedures. Reactivity and removal kinetic models derived from Freundlich isotherm were used to investigate contact time and pH effects on the coefficient of protonation and rate of mass transfer of Hg(II) ions to the reactive sites. Proton coefficient of 0.89 indicated a decrease in proton consumption function when compared with uncoated kaolinite. At the 12th reaction time, a maximum adsorption capacity of 85% was achieved. Mass transfer rates of 0.9359 h⁻¹ and 0.0748 h⁻¹ for the first and second reaction phases indicated a reduction when compared with uncoated kaolinite. These changes may be ascribed to masking of reaction sites and exposed surface area of the Cu-Oxide coated kaolinite.

Keywords: kaolinite, Cu-Oxide, contact time, pH, reactivity, removal kinetics

INTRODUCTION

Mercury is toxic and remains a threat to environmental and human lives. Mercury bioaccumulates in the environment and creates neurological health impact (Cao et al., 2008: 2555–2559). Its transformation to methyl mercury generates critical problems to humans. This is because it is non-biodegradable in humans causing neurological health concerns (Taman et al., 2015: 1-8.). Mercury remains a sinister poison and can be stored in vital organs of the human body causing several health problems (Bulut and Tez, 2007).

Therefore, the toxic properties of mercury have attracted considerable attention (Kannan and Malar, 2005, Husein, 2013). Kinetic studies have shown that mercury removal involves a fast process, involving intraparticle diffusion (Ding et al 2014: 1115-1121., Dos et al.,2015: 1230-40).

Recent studies revealed that solution dilution and exchange stoichiometry, contact time, pH and initial metal concentration govern mercury removal from aquatic systems (Egirani et al 2013: 73-81.,2014:991-1005).

Most conservative techniques employed in removal of mercury ions from aqueous solution involve chemical precipitation, adsorption by activated carbon, ion exchange resins and electrochemical recovery (Uzum et al., 2009: 172–181). There is high unsuccessful rate of these techniques particularly for low level mercury concentrations of 1-10 mg L⁻¹).

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This is because toxic sludge is costly to dispose of it. In addition, chemical reagents are required for mercury recovery and this comes at a high energy cost (Arshadi et al., 2017: 293–306., Hua et al., 2012: 317–331). Due to these challenges, there is need to source for cheap and readily available modified adsorbents. Here, the use of kaolinite coated with Cu-Oxide is being postulated. Therefore, the aim of this paper is to use Cu-Oxide coated kaolinite in the treatment of mercury aqueous solution.

The objectives include synthesis of the adsorbent, characterisation of the system and the use of experimental parameters to elucidate the removal and reactivity kinetics of the interaction.

**MATERIALS AND METHODS**

All reagents used were of analytical purity. Concentrated stock solutions were used to prepare the synthetic solutions. Richard Baker Harrison Company (United Kingdom) provided the kaolinite used in this study. This was nitrogen flushed and stored in containers that were airtight to avoid surface reaction. Hg(II) ions were sourced from Mercuric chloride (HgCl₂) obtained from Merck (Canada).

Various concentrations of Hg(II) ions in ppm were prepared by dissolving HgCl₂ (Merck) in double distilled water. Sodium Chloride used for potentiometric titration, HCl and NaOH used as pH regulators were obtained from Merck. These reagents were all analytical grade. Double distilled water was used to prepare all the solutions.

**System Characterisation**

The Richard Baker Harrison kaolinite known as RBH- kaolinite was treated with deionized water several times at a 1:10 kaolinite/water ratio. The mixture was continuously agitated for 3 h and set aside for 24 h. This was followed by separation, washing and drying at 60 °C. The percent colloid with less than 1000 nm was estimated from the particle size distribution curves. The particle size range of RBH kaolinite, was determined using Coulter Laser method. pH of RBH kaolinite suspensions and reacting solutions were determined using the Model 3340 Jenway ion meter. The cation exchange capacity (CEC) was determined by Na saturation method. The specific surface area of the RBH kaolinite mineral was measured using the standard volumetric Brunauer, Emmett and Teller (BET) method (Brunauer et al., 1938: 309–319). Here, determination was by measuring the adsorption of N₂ gas on the mineral solid phase at the boiling point of liquid nitrogen (Lowell and Shield, 1991). Spectral analysis was done using Energy Dispersive Spectroscopy (EDS) and Scanning Electron Microscopy (SEM) (Karickhoff and Bailey 1973, Janaki, et al., 2014: 443-446). The uncoated samples were viewed and secondary electron images were acquired at low vacuum control pressure using a JEOL JSM 5900 LVSEM with Oxford INCA EDS.

The point of zero salt effect (PZSE) of the RBH kaolinite was carried out using standard laboratory procedures (Alves and Lavorenti, 2005, Bolan et al., 1986: 379–388). Potentiometric titrations involved the equilibration of 1% (by mass) of RBH kaolinite suspensions. References containing only a 1:1 electrolyte solution were initially adjusted to pH range near the point of zero salt effect.

**Synthesis of Cu-Oxide Coated Kaolinite**

Cu-oxide-coated kaolinite was set by precipitating the copper ions on the surface of the RBH kaolinite. This was done using sodium hydroxide tracked by thermal treatment (Phiwdanga, et al., 2013: 740 – 745., Eren, 2009) 20.0 g of RBH was mixed with 100 ml 1 M Cu(NO₃)₂ solution and 180 ml of 2 M NaOH solution. These were freshly prepared. The mixture of the reaction was maintained at 90 °C for 48 h. The RBH activated with the NaOH solution was dispersed into 150 ml of 0.1 M Cu(NO₃)₂ solution. 0.1 M NaOH aqueous solution amounting to three hundred microliters was added dropwise at the rate of 1 ml/h. To minimize the formation of carbonate salts, the titration was carried out under nitrogen flow condition (Maruthupandy et al., 2017: 167–174., Wang et al., 2016: 328–334). Centrifugation and washing of the precipitate was carried out to free the content from NO₃⁻ ions. Heating the solid for 4 h in air at 700 K led to the formation of Cu-Oxide kaolinite. RBH kaolinite was verified from the X-ray diffraction (XRD) patterns of the product.

**H⁺/M²⁺ Stoichiometry and Proton Exchange Experiments**

For reactivity studies to determine the proton coefficient, the proton exchange isotherm known as change of pH versus LogKd was determined using standard laboratory procedure (Egirani et al., 2013: 73-81, Campos et al., 2007). This empirical model was derived from Freundlich isotherm, suitable for heterogenous surfaces (Egirani et al., 2014:991-1005). A 1% RBH kaolinite coated Cu-Oxide suspension with no added electrolyte made unto 50 ml, were reacted with solution containing 10 ppm of Hg(II) regulated to required pH. Experimental studies were conducted in triplicates. Samples were stored in the dark (23±3 °C). Filtration using a cellulose acetate filter (pore size 0.2 μm) was carried out on the supernatant and analysed for Hg(II) ions, using a Hitachi Atomic Absorption Spectrophotometer (HG-AAS).

The proton consumption function is given (Equations 1-2):

\[ \propto SOH + M^{2+} \leftrightarrow (SOH)_{x} - M + \propto H^{+} \quad \ldots \ldots \quad (1) \]

\[ \log K_{\text{d}} = \log (K_{\text{d}}(SOH))^{n} \propto \propto \text{pH} \quad \ldots \ldots \quad (2) \]

Here, SOH denotes the mineral surface-binding site, M²⁺ denotes the soluble metal species, \((SOH)_{x} - M\) denotes
the surface bound metal, logKf denotes the apparent equilibrium-binding constant and \( \alpha \) denotes the coefficient of protonation. This represents the number of protons displaced when one mole of metal binds to the mineral surface (Egirani et al., 2013: 73-81., Contescu et al., 1993: 1754–1765). Proton coefficients were obtained by graphical analysis using logKd versus pH plots. A regression analysis of the plot gave \( \alpha \) the proton coefficient as its slope.

**Kinetic Experiments**

Kinetic experiments for Hg(II) removal were conducted, using 1% Cu-Oxide coated kaolinite. This system was reacted with solution containing 10ppm of Hg(II) ions regulated to required pH. Amounts of Hg(II) ions remaining in solution after 2nd, 4th, 6th, 8th, 12th, 18th and 24th h reaction was determined using Hitachi Atomic Absorption Spectrophotometer (HG-AAS). Kinetic studies were conducted in 24h because adsorption reactions take place rapidly (Egirani et al., 2013: 73-81).

The amount of metal sorbed (Q) on a mineral at time t, is given by the following mass-balance (Equation.3):

\[
Q(t) = \frac{[C_0 - C_t]}{V/m} \quad \text{mgs} \quad \text{(3)}
\]

Here, \( C_0 \) denotes the initial metal concentration (mg/L) at time t=0; \( C_t \) denotes the concentration (mg/L) at time t; V denotes the total Cu-Oxide coated kaolinite suspension volume and m is the weight of the sorbent (kg) (Egirani et al., 2013: 73-81., Vijayakumar et al., 2012: 157-170). The mass transfer constant \( K_f \) determines the transport of adsorbate from external layers to the mineral surface binding sites. This is obtained from the slopes of the curve derived from plotting \( C_t / C_0 \) vs. time based on equation 4 (Egirani et al., 2005: 319–325):

\[
\frac{d\left(\frac{C_t}{C_0}\right)}{dt} \quad \text{at} \quad t=0 \quad \cong -K_f S_s \quad \text{......... (4)}
\]

Here, \( C_t \) and \( C_0 \) denote the initial concentrations of Hg(II) at time t, Ss denotes the exposed external surface area of the adsorbent, and \( K_f \) denotes the mass transfer coefficient (Tang et al., 2011: 689-697). The Freundlich isotherm was adopted to describe sorption of Hg(II) ions because this is appropriate for heterogeneous surfaces over a wide range of solute concentrations (Vijayakumar et al., 2012: 157-170).

**RESULTS AND DISCUSSION**

**RESULTS**

In this study, RBH kaolinite was characterised by RBH as containing 47% SiO\(_2\) (%), 38% Al\(_2\)O\(_3\) (%), 1.5% moisture content, 2.6 specific gravity, 0.2(%) water soluble salt (%). This paper reported 0.60-20\(\mu\)m particle size range 3% colloid, 6.00 pH, 47.00 surface area (m\(^2\)/g), 170.00 CEC and 7.00 point of zero salt effect. The systems involved in this study have been characterized and summarized (Table 1, Figures. 1-4). The X-ray diffraction indicated kaolinite as the key constituent. The EDS spectrum and SEM morphology indicated the presence of hydrous alumino silicates (Al, Si and K). This agrees with the chemical constituents of the RBH kaolinite and micron range values of the particle sizes. The point zero charge pH\(_{pzc}\) also known as point of zero salt effect and the surface area of adsorbents are important characterization concerning adsorption. Here, the amount of negative charges on the surface of the adsorbent equals the quantity of positive charges. Therefore, it determines the positive and negative charge divide on the mineral surface. The external surface area of the adsorbent controlled the quantity of exposed mineral surface available for reaction. Proton coefficient (\( \alpha \)) was based on a theoretical framework given by equations (1, 2), predicted and derived from the regression value of the plot (Figures 5-6), (Table 2). The value was 0.89, < 1. Mass transfer coefficient (K\( f \)) was based on a theoretical framework given by equation (5), predicted and derived from the regression value of the plot (Figure 8), (Table 3).

**Table 1: Summary of system characterisation**

<table>
<thead>
<tr>
<th>Components of Characterisation</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2) (%)</td>
<td>47.00</td>
</tr>
<tr>
<td>Al(_2)O(_3) (%)</td>
<td>38.00</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>1.50</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.60</td>
</tr>
<tr>
<td>Water soluble salt (%)</td>
<td>0.20</td>
</tr>
<tr>
<td>CEC (mmols/kg)</td>
<td>170.00</td>
</tr>
<tr>
<td>% (&lt;1000 nm) colloid</td>
<td>3.00</td>
</tr>
<tr>
<td>Particle size range ((\mu)m)</td>
<td>0.60-20.01±0.5</td>
</tr>
<tr>
<td>pH ± σ</td>
<td>6.05±0.05</td>
</tr>
<tr>
<td>Surface Area(SSA±σ) (m(^2)/g)</td>
<td>47.01±0.24</td>
</tr>
<tr>
<td>Point of Zero Salt Effect (PZSE)</td>
<td>7.00</td>
</tr>
</tbody>
</table>
SYNTHESIS AND CHARACTERIZATION OF KAOLINITE COATED WITH CU-OXIDE AND ITS EFFECT ON THE REMOVAL OF AQUEOUS MERCURY(II) IONS: PARTI

Figure 1: X-ray diffraction of kaolinite

Figure 2a: EDS for kaolinite showing element peaks

Figure 2b: SEM for kaolinite showing particle sizes.

Figure 2c: X-Ray spectra of synthetic CuO-Kaolinite matrix showing peaks of kaolinite and Cu at a and b respectively

Figure 3: Particle size distribution of kaolinite

Figure 4: Point of Zero Salt Effect of Kaolinite
Table 2: Statistical presentation of proton coefficient

<table>
<thead>
<tr>
<th>Equation</th>
<th>( Y=a+b*x )</th>
</tr>
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<tbody>
<tr>
<td>Proton coefficient ( a )</td>
<td>0.891</td>
</tr>
<tr>
<td>Residual Sum of Squares</td>
<td>0.019</td>
</tr>
<tr>
<td>Pearson’s r</td>
<td>0.939</td>
</tr>
<tr>
<td>Adj. R-Square</td>
<td>0.843</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Log Kd(L/kg)</th>
<th>Intercept 1.946</th>
<th>Standard Error 0.755</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>0.605</td>
<td>0.127</td>
</tr>
</tbody>
</table>

Table 3: Mass transfer rates for Hg(II) sorbed on Cu-Oxide coated kaolinite

<table>
<thead>
<tr>
<th>Slope I(hr(^{-1}))</th>
<th>Slope II(hr(^{-1}))</th>
<th>Exposed Surface Area (cm(^2))</th>
<th>( K_{fI} ) (cm(^{2})hr(^{-1}))</th>
<th>( K_{fII} ) (cm(^{2})hr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.935</td>
<td>0.074</td>
<td>4700</td>
<td>1.990e-4</td>
<td>1.590e-5</td>
</tr>
</tbody>
</table>

Figure 5: Plot of distribution coefficient versus pH for proton coefficient

Figure 6: Plot of logKd versus Final Ph

Figure 7: Plot of Hg adsorption % versus contact time(h)

Figure 8: Plot of Ct/Co versus contact time (h)

The mass transfer coefficient derived from the slope were 0.935h\(^{-1}\) and 0.074h\(^{-1}\). This plot consists of two linear parts. The mass transfer rate predicted from equations (3, 4) and derived from Figure 8 are given (Tables 3). Also, this consist of two linear parts with the first part lower than the second. The second linear part started after the 15\(^{th}\) h. There was increase in capacity of adsorption as pH was increased. Distribution coefficient increased from 215 to 340 mg/kg over the range of pH investigated (Figure 5). The maximum distribution coefficient occurred at pH=8.

DISCUSSION

In previous studies without coated Cu-Oxide on kaolinite, proton coefficient was greater than one (Egirani et al 2013;
73-81). Here, $\alpha$ for Cu-Oxide coated kaolinite was less than one (Table 2). Differences may be ascribed to differences in the availability of strongly acidic sites in the two systems. This suggested that protonation was lowered in the presence of Cu-Oxide coating. Acidic sites present on kaolinite planar surfaces could be masked by the presence of a coated medium.

The dependent on time attitude of Hg(II) removal was assessed at different time intervals ranging from 2 to 24h at 23°C. This was at initial Hg(II) concentration of 10 mgL$^{-1}$ at pH 4. Based on Figure 7, the percent of Hg(II) ions removed increased with increase in contact time. This reaction pattern plateaued after the 12th h at 85% adsorption. The adsorption rate was initially fast and the capacity of adsorption increased over time. The initial speedy adsorption of Hg(II) in the first step may be ascribed to larger numbers of active adsorption sites (Egirani et al., 2013: 73-81., Tuzun et al., 2005).

The mass transfer rate derived from equation 4 is provided (Figure 8 and Table 3). Adsorption kinetics indicated a two-phase process ascribed to outer sphere and inner sphere complexation. Here, intra-particle diffusion was probably minimal. In previous studies (Egirani et al., 2013: 73-81), mass transfer rate for the first ($K_i$) and the second reaction phase($K_{f1}$) were higher when compared with rates observed in the presence of Cu-Oxide coating. Mass transfer rate is a function of exposed surface area. Decrease in mass transfer rate could be ascribed to complex reduction in the exposed surface area of the coated Cu-Oxide RBH kaolinite.

**CONCLUSIONS**

Synthesis, characterisation and application of Cu-Oxide coated kaolinite in Hg(II) removal was investigated. Using empirical models derived from Freundlich isotherm, proton coefficient for mercury sorbed on Cu-Oxide coated RHB kaolinite was less than one. This suggested a lowering of protonation during the adsorption process when compared with uncoated kaolinite. Attenuation of protonation may be ascribed to masking of reaction sites. In addition, mass transfer rates for coated RBH kaolinite were lower when compared with uncoated kaolinite. Here, complex reduction in exposed surface area may account for this decrease. The observed reaction plateau after the 12th h, may account for the limited available reactive sites after the initial fast reaction phase.

**REFERENCES**


