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

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In this paper, the effect of copper oxide coated kaolinite on mercury (II) removal based on initial metal concentration, particle concentration, and prolonged residence time have been investigated. Experimental methods involved batch mode techniques at ambient temperature. The content was analysed for Hg(II) adsorbed, using standard laboratory procedures. Here, using empirical models derived from Freundlich isotherm, adsorption capacity increased from 300 to 400 mg/kg over the range of initial metal concentration investigated. The complex behavior of existing reactive sites and the generation of new active sites accounted for these changes in adsorption capacity. Increase in particle concentration led to decrease in adsorption. This was over the range of 2, 4, 6, 8 and 10 gL⁻¹ solid concentration. Higher Cp reduced the specific surface area for adsorption. Hg(II) ions removal increased with increase in residence time. The most efficient ratio of Cu-Oxide coated kaolinite was at 0.002kgL⁻¹ at 40mgL⁻¹ mercury concentration. Values of between 600 to 900 mg/kg for Cu-Oxide coated kaolinite was higher when compared with the uncoated kaolinite. As ageing was increased, hydroxylation probably increased thus leading to the formation of new reactive sites.

Keywords: kaolinite, Cu-Oxide, initial metal concentration, particle concentration, ageing

INTRODUCTION

Reliable systems of minerals and solution chemistry are required for effective removal of mercury ions at low concentrations. Studies have revealed that mercury(II) ions easily dissolve in solution and a combination of factors regulate its removal from contaminated water (Gaśior and Tic, 2016; Herrero et al., 2005: 3199-3210).

Water bodies as recipient of mercury ions is increasing, thus levels above recommended standards (1μg/L) are found in the aquatic environment (Egirani et al., 2013a: 73-81). Severe chronic diseases are caused by mercury poisoning. In addition, mercury in its elemental form bio-accumulates in the environment and creates neurological health impact (Egirani et al., 2014: 1006-1017). Methyl mercury induced by microbial biomethylation of Hg(II) ions can accumulate in the body and can cause brain damage and other chronic diseases (Egirani et al., 2016: 188-194). Testing the removal of Hg(II) ions using standard laboratory procedures mimics its removal from natural bodies of water. This remains a current and relevant research topic.

The hydrolysis performance of mercury ions and the solubility of its species are controlled by pH. Increase in concentration of particles and particle sizes may attenuate mercury removal from aqueous solution (Deshicar et al., 1990: 1011-1016), (Zhu et al., 2009: 2014-2025).

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The latter depicts outer sphere complexation. In some cases, increase in particle size and particle concentration does not necessarily lead to an increase in mercury uptake (Eze et al., 2013: 852-860). Presence of surface area and surface-active sites control mercury uptake (François et al., 2012: 803-818), (Mishra et al., 2013: 175-184). Increasing the residence time of solid mineral phase in aqueous solution could results in much mineral surface reorganization (Bonnissel-Gissinger et al., 1999: 313-322). Increase in metal concentration led to initial decrease in adsorption capacity (Akpmie et al., 2015: 757-767).

Here, the effect of solution composition and ageing on the removal of mercury (II) ions from solution has received limited attention. Previous studies centered on the use of untreated kaolinite in removing Hg(II) ions from aqueous solution (Egirani et al., 2013b: 49-55; 2016: 188-194). Others have reported the use of modified activated carbon and polyzwitterionic resin in mercury removal (Saleh et al., 2017a: 1079-1088, b: 230-238, Vandervennet et al., 2012: 157-170). The aim of this study was to determine the role of Cu-Oxide coated kaolinite in mercury removal in relation to solution composition and ageing. Batch mode experiments were conducted based on solution composition, initial metal concentration and prolonged residence time.

MATERIALS AND EXPERIMENTAL METHODS

All reagents used were of analytical grade. Kaolinite was provided by Richard Baker Harrison Company of the United Kingdom. This is known as RBH kaolinite. Merck (Canada), provided the mercuric chloride used for the sourcing of Hg(II) ions. Mercuric chloride dissolved in double distilled water was used in the preparation of different concentrations of Hg(II) ions.

Characterization

RBH kaolinite contained 47.00% SiO₂, 38.00% Al₂O₃, 1.50% moisture content as provided by the company. In this study, particle size range was 0.60-20 µm, cation exchange capacity (mmols/kg) was 170, surface area (m²/g) was 47.01 and point of zero salt effect was 7. 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 external surface area of the RBH kaolinite was measured using the standard volumetric Brunauer, Emmett and Teller (BET) method (Brunauer et al., 1938: 309–319). Spectral analysis was done using a JEOL JSM 5900 LVSEM with Oxford INCA EDS (Table 1 and Figure 1).

Synthesis of Cu-Oxide Coated Kaolinite

Setting of Cu-oxide-coated kaolinite was by precipitating the copper ions on the RBH kaolinite surface. Sodium hydroxide addition tracked by thermal treatment was conducted (Eren, 2009).

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 g of RBH was mixed with 100 mL 1M 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 0.10 M Cu(NO₃)₂ solution. 0.10 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.
Table 1: Summary of system characterisation

<table>
<thead>
<tr>
<th>Components of Characterisation</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (%)</td>
<td>47.00</td>
</tr>
<tr>
<td>Al₂O₃ (%)</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 (μm)</td>
<td>0.60-20.0±0.5</td>
</tr>
<tr>
<td>pH ± σ</td>
<td>6.05±0.05</td>
</tr>
<tr>
<td>Surface Area(SSA±σ) (m²/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>

Table 2: Statistical presentation of proton coefficient

<table>
<thead>
<tr>
<th>Equation</th>
<th>Y=a+b*x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton coefficient α</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>
<tr>
<td>Log Kd(L/kg)</td>
<td>Intercept 1.946</td>
</tr>
<tr>
<td></td>
<td>Standard Error 0.755</td>
</tr>
<tr>
<td></td>
<td>Slope 0.605</td>
</tr>
<tr>
<td></td>
<td>Standard Error 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>SlopeII(hr⁻¹)</th>
<th>Exposed Surface Area (cm²)</th>
<th>Kᵢ (cmhr⁻¹)</th>
<th>Kᵢᵢ (cmhr⁻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>

Batch Mode Experiments

To determine the effect of initial metal concentration, 10ppm, 15ppm, 20ppm and 40ppm of Hg(II) solutions were reacted with 1% each of Cu-Oxide coated kaolinite suspension. This was made up to 50mL solution and equilibrated for 24h at pH=4 below the point of zero salt effect. This was used to determine the effect of initial metal concentration.

To determine particle concentration effect (Cp), solid concentrations of Cu-Oxide kaolinite of 2, 4, 6, 8 and 10 gL⁻¹ made unto 50mL were reacted with solutions containing 10ppm, 15ppm, 20ppm and 40ppm of Hg(II) ions and equilibrated for 24h at pH=4.

To determine the effect of ageing, 10ppm, 15ppm, 20ppm and 40ppm mercury concentrations were reacted with 1% Cu-Oxide coated kaolinite at pH=4. In each case the content was equilibrated, made unto 50mL and aged from 24 to 720h. All experiments were conducted at room temperature.

Here, amount of metal adsorbed (Qₜ) on a mineral at time t, is provided in Equation (1):

\[ Q(mg/kg) = [C₀-Cₜ] V/m \] (1)

RESULTS AND DISCUSSION

Results

Cu-Oxide Coated Kaolinite and Initial Metal Concentration

Initial metal concentration affected the proton coefficient and the mass transfer rates. These were based on 10mgL⁻¹ initial metal concentration (Table 2 and Table 3). Adsorption capacity increased from 300 to 400 mg/kg over the range of metal concentration investigated (Figure 2).

Cu-Oxide Coated Kaolinite and Particle Concentration (Cp) Effect

There was a decrease in sorption capacity as particle concentration was increased (Figure 3).
Cu-Oxide Coated Kaolinite and Ageing Effect.

The rate of removal of Hg(II) ions increased from 600 to 900 mg/kg over the range of residence time investigated (Figure 4).

DISCUSSION

The range of increase in adsorption capacity as initial metal concentration was increased, was higher than those of uncoated kaolinite. These reports provided a linear decrease in Hg(II) adsorption as initial metal concentration, over the range of initial metal concentration investigated. Also, uncoated kaolinite provided an increase in Hg(II) adsorption as particle concentration was increased. Furthermore, uncoated kaolinite revealed a decrease in Hg(II) adsorption over the range of ageing investigated (Egirani et al., 2016:188-194; 2013a:73-81; 2014:1006-1017).

Here, the overall adsorption capacity decreased with increase in initial metal concentration. This decrease is ascribed to the fact that Cu-Oxide coated kaolinite possesses a constant number of active and reactive sites. As the metal concentration was increased, the reactive sites became saturated. For particle concentration effect, the values for coated kaolinite were higher when
compared with uncoated kaolinite. Here, the most efficient ratio of Cu-Oxide coated kaolinite was at 0.002kgL⁻¹ at 40mgL⁻¹ mercury concentration. The lower sorption capacity as Cp was increased could be assigned to the fact that higher Cp reduced the specific surface area for adsorption. Increase in Cp reduced accessibility of Hg(II) ions to intra-particle diffusion was probably reduced. For ageing, adsorption capacity for the uncoated kaolinite was lower when compared with the coated kaolinite. This may be ascribed to increased presence of active and reactive sites on the surface of the Cu-Oxide coated kaolinite. As ageing was increased, hydroxylation increased thus leading to the formation of new active and reactive sites.

CONCLUSIONS

Adsorption of Hg(II) ions on Cu-Oxide coated kaolinite was investigated in batch mode systems. Adsorption properties such as initial metal concentration, particle concentration and ageing effect demonstrated complex behavior. Adsorption capacity decreased with increase in metal concentration. Here, as the metal concentration was increased, the reactive and active sites became saturated. Increase in particle concentration led to a decrease in adsorption. In this case, the values for coated kaolinite were higher when compared with uncoated kaolinite. Over the range of residence time investigated, adsorption capacity for the uncoated kaolinite was lower when compared with the coated kaolinite. Increased presence of reactive and active sites may account for this development. Therefore, the highlight of the conclusions are as follows:

1) Adsorption capacity increased from 300 to 400 mg/kg over the range of initial metal concentration investigated.
2) Higher Cp reduced the specific surface area for adsorption. Hg(II) ions
3) As ageing was increased, hydroxylation probably increased thus leading to the formation of new reactive sites.

REFERENCES


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