 Adsorption of As, B, Cr, Mo and Se from coal fly ash leachate by Fe\textsuperscript{3+} modified bentonite clay

Masindi Vhahangwele, Gitari W. Mugera and Tutu Hlanganani

ABSTRACT

Fly ash contains the potentially toxic elements As, B, Cr, Mo and Se which upon contact with water may be leached to contaminate surface and subsurface water bodies. This study aims to evaluate the adsorption of these elements from coal fly ash leachates on Fe\textsuperscript{3+}-modified bentonite (Fe-Bent); such modification improved the physicochemical properties of bentonite clay. For optimization of adsorption of the five elements, the effects of time, adsorbent dosage, adsorbate concentration, and pH were optimized. Adsorption affinity of oxyanions followed in the order B > Se > Mo > Cr = As. Experimental data fitted well to Langmuir and Freundlich adsorption isotherms.

Key words | adsorption, coal fly ash leachates, Fe-Bent, oxyanions

INTRODUCTION

Coal combustion for power generation in power utilities produces large volumes of waste materials such as bottom ash, fly ash, boiler slag, flue gas desulfurization and non-captured particles (Gitari et al. 2008; Pandey et al. 2009; Eze et al. 2013). Coal fly ash constitutes 90\% of the produced waste (Gitari et al. 2008). Coal fly ash is captured from power utilities by means of mechanical devices such as electrostatic precipitators, and scrubbers (Steenari et al. 1999; Yao et al. 2013). After collection, fly ash is hydraulically transported to holding ponds, lagoons, landfills and slag heaps where it can be reacquired for treatment purposes or discarded (Masindi & Gitari 2013). The transportation water is recollected as penstock overflow and recirculated for more ash slurry (Iyer 2002; Gitari et al. 2008; Masindi & Gitari 2013). Thereafter, it is disposed of to a series of ash retention ponds, lagoons, landfills and slag heaps (Bhattacharyya et al. 2009; Akar et al. 2012; Akinyemi et al. 2012; Córdoba et al. 2012).

Disposal of coal fly ash into the environment has raised public concern since it contains toxic chemical species such as As, B, Cr, Mo and Se. Wet slurry disposal and rainfall on the sites may lead to leaching of oxyanions, since in the majority of cases these sites are not lined with impervious material or do not contain geo-synthetic liners (Masindi & Gitari 2013). On contact with an aqueous medium, fly ash leaches out inorganic contaminants of As, B, Cr, Mo and Se to waterbodies (van der Hoek & Comans 1994; Nathan et al. 1999; Pires & Querol 2004; Wang et al. 2008; Izquierdo & Querol 2012; Jones et al. 2012; Tsiridis et al. 2012; Polowczyk et al. 2013). This alters the chemical profile of the surface and underground water resources, hence posing hazardous effects to terrestrial and aquatic organisms on exposure (Steenari et al. 1999; Praharaj et al. 2002; Kashiwakura et al. 2011; Su & Wang 2011; Jones et al. 2012; Tsiridis et al. 2012; Neupane & Donahoe 2013; Seshadri et al. 2013). Gitari et al. (2008) and Alloway (1990) pointed out that chemical species of As, B, Cr, Mo and Se exist as toxic oxyanions circumneutral to basic pH conditions. In light of the above, it is therefore significant to manage, contain and remove chemical species of As, B, Cr, Mo and Se from coal fly ash leachates prior to contamination of surface and underground water.
ecosystems. This will go a long way in minimizing the risk of contamination of surface and underground water resources by ash retention ponds.

To date, very few documented studies have been developed to solve the problem of leaching of potentially toxic chemical species from wet disposal ash retention systems. This signifies a need for stringent regulations that proclaim that no dry or wet fly ash disposal is permitted unless proper treatment technology is in place. Also, it is of the utmost importance to contain and treat coal fly ash leachates prior to pollution of surface and subsurface water contamination. This will be the best way for power utilities to conserve water resources and eliminate probable environmental problems that may arise. The overall purpose of this study is to evaluate the feasibility of modifying bentonite clay by polymeric species of Fe$^{3+}$ and use the modified clay for removal of oxyanionic species of As, B, Cr, Mo and Se from coal fly ash leachates. Modified and mechanochemically activated bentonite clays have been widely used in depollution science. They have been used for the removal of arsenic (Masindi et al. 2014a), boron (Masindi et al. 2015a), fluoride (Gitari et al. 2013; Masindi et al. 2014b), phosphates (Masindi et al. 2015b), toxic metals attenuation (Masindi & Gitari 2015a, 2015b) and removal of organic contaminants (Ochoa-Loza et al. 2007). Considering its wide application in depollution science, Fe-Bent has the potential for attenuation of oxyanionic species.

**EXPERIMENTAL**

**Sampling and preparation of bentonite clay samples**

Bentonite clay was obtained from ECCA Pty (Cape Town, South Africa) and coal fly ash was collected from the Hendrina power utility in Mpumalanga, South Africa. All reagents used in this study were of analytical grade. The raw bentonite clay samples were washed with ultra-pure water (Millipore, USA). The washed bentonite was then dried in an oven for 24 hours at 105 °C. The samples were milled into fine powder using a vibratory disc mill RS 200 miller, Retsch (Haan, The Netherlands).

**Modification of bentonite clay samples**

The optimum conditions for loading Fe$^{3+}$ polycations onto a bentonite clay lattice were observed to be 30 min of contact time, 2 g of adsorbent dosage and 100 mg L$^{-1}$ of adsorbate concentration (Masindi & Gitari 2013). Bentonite clay, 10 g, was transferred into a 1,000 mL high density polyethylene (HDPE) container containing 500 mL of 100 mg L$^{-1}$ Fe$^{3+}$ from FeSO$_4$. The mixture was shaken for 30 min on a table shaker. This was repeated 25 times to make up a total of 250 g of adsorbent (Masindi & Gitari 2013).

**Physiochemical characterization**

Chemical characteristics of clay samples were ascertained using X-ray fluorescence spectroscopy (XRF) in an accredited laboratory (Facility of Geology, University of Pretoria, South Africa). Surface area was determined by Brunauer-Emmett-Teller (BET; A Tristar II 3020, Micrometrics BET from Norcross, GA, USA). pH$_{pzc}$ (the pH at the point of zero charge) was determined using a solid addition method (Masindi et al. 2014c). Cation exchange capacity (CEC) was determined using an ammonium acetate method (Masindi et al. 2014c).

**Preparation of standard working solutions**

One thousand mg L$^{-1}$ standard solutions of As, B, Cr, Mo and Se from Lab Consumables Supply, Johannesburg, South Africa, were used to prepare the combined working solutions. From 1,000 mg L$^{-1}$ stock solution, 10 mg L$^{-1}$ solution was prepared by extracting 10 mL of 1,000 mg L$^{-1}$ oxyanion standard solution and transferring it into a 1,000 mL volumetric flask. The volumetric flask was topped to the mark by adding ultra-pure water.

**Adsorption of As, B, Cr, Mo and Se onto Fe-Bent**

Adsorption of oxyanions onto Fe-Bent was evaluated in a batch experimental procedure. Stock solutions of metal ions were prepared in ultra-pure water using the obtained standard solutions. Several operational and optimization parameters were evaluated and they included effects of time, dosage, concentration and pH. All the experiments
were carried out using 250 mL HDPE containers and mixed at 250 rpm using a Labcon model 3100E table shaker.

**Effects of shaking time**

Effects of time were investigated by varying time from 1 to 180 mins. Other conditions included: 1:100 S L$^{-1}$ ratios, 10 mg L$^{-1}$ adsorbate concentration, pH 7.5 and 26 °C room temperature.

**Effects of adsorbent dosage**

Effects of Fe-Bent dosage on adsorption of oxyanions were evaluated by varying the dosages from 0.5 to 5 g. Other conditions included: 30 min of equilibration, 10 mg L$^{-1}$ adsorbate concentration, pH 7.5 and 26 °C room temperature.

**Effects of chemical species concentration**

Effects of ion concentration on the removal of oxyanions by Fe-Bent were investigated by varying concentration ranges from 0.1 to 15 mg L$^{-1}$. Other conditions included: 30 min of equilibration, 1:100 S L$^{-1}$ ratios, pH 7.5 and 26 °C room temperature.

**Effect of supernatant pH**

Effects of pH were evaluated by adjusting the pH of aqueous media to the required pH using HCl or NaOH at the beginning of batches, and not controlling afterwards. Other conditions were 30 min of equilibration, 1:100 S/L ratios, 15 mg L$^{-1}$ and 26 °C temperatures. Optimum adsorption conditions obtained were used for treatment of coal fly ash leachates.

**Coal fly ash leachate generation and treatment**

**Coal fly ash generation**

Coal fly ash leachates were generated at 10 g:100 mL S L$^{-1}$ ratio using ultra-pure water. Three 10 g samples of coal fly ash were measured and transferred to individual 250 mL HDPE plastic containers with 100 mL of ultra-pure water. The mixtures were equilibrated for 60 min on a reciprocating table shaker. After agitation, the leachates were filtered through a 0.45 μm cellulose filter membrane and acidified with two drops of concentrated HNO$_3$ acid to prevent aging and immediate precipitation of As, B, Cr, Mo and Se ions. The samples were refrigerated at 4 °C until analysis by PerkinElmer 700 series ICP-OES (inductively coupled plasma optical emission spectrometry).

**Coal fly ash treatment**

One hundred mL of coal fly ash leachates was transferred into three 250 mL HDPE containers and 4 g of Fe-Bent was added. The mixtures were equilibrated for 60 min using a reciprocating orbital shaker. After shaking, the mixture was filtered through a 0.45 μm cellulose membrane. The filtrates were acidified with three drops of nitric acid and stored in the refrigerator until analysis for As, B, Cr, Mo and Se using PerkinElmer 700 series ICP-OES.

**Modelling of experimental results**

Determination of % removal and adsorption capacity were carried out using Equations (1) and (2):

\[
\text{Percentage removal} \% = \left( \frac{C_i - C_e}{C_i} \right) \times 100 \quad (1)
\]

\[
\text{Adsorption capacity} (q_e) = \frac{(C_i - C_e)V}{m} \quad (2)
\]

where $C_i$ = initial concentration, $C_e$ = equilibrium ion concentration, $V$ = volume of solution, and $m$ = mass of Fe-Bent.

\[
r = \frac{n \sum xy - (\sum x)(\sum y)}{\sqrt{n(\sum x^2) - (\sum x)^2} - \sqrt{(\sum y^2) - (\sum y)^2}} \quad (3)
\]

Theoretically, the $R^2$ value varies from 0 to 1. The $R^2$ value shows the variation of experimental data as explained by the regression equation (Masindi & Gitari 2015a). In the present study, the regression coefficient ($R^2$) was applied to point out the relationship between the experimental data and modelling results.

**Adsorption mechanisms**

Traditionally, the adsorption of ions has been described by adsorption isotherms. Adsorption isotherms are models...
which are used to describe the relationship between equilibrium concentration of the adsorptive and the quantity of adsorbate on the surface at constant temperature. Mainly, they are employed to describe the mechanisms and intensity of adsorption. The two commonly used isotherms were used to point out the mechanisms of adsorption, and they are the Langmuir and Freundlich adsorption isotherms. These models indicate whether adsorption processes are taking in homogenous or heterogeneous surfaces (Sparks 1995; Selim & Amacher 1996; Selim & Kingery 2003).

RESULTS AND DISCUSSION

Chemical characterization

Variations in chemical composition of raw bentonite clay and Fe-Bent are presented in Table 1.

The experimental results show that that bentonite clay is primarily characterized with Al, Si, and Fe as the predominant elements (Table 1). The elevated amount of SiO₂ and Al₂O₃ verifies that bentonite clay is an aluminosilicate material (Vicente et al. 2013). The high concentrations of MgO, Na₂O, CaO and K₂O indicate that these are the main exchangeable cations in bentonite clay (Sparks 1995). XRF results also revealed that there is an insignificant proportion of Mn and P impurities which might have been incorporated in clay fractions during deposition. After modification, XRF analysis revealed that the content of Fe increased with a decrease in the contents of MgO, Na₂O, CaO and K₂O, hence indicating that those are the cations exchanged for Fe³⁺ in the interlayers. Moreover, after treatment of oxyanions containing water, traces of anionic species were observed to be present in the matrices of secondary residue, hence proving that the modified clay acts as a sink for inorganic contaminants from aqueous media.

CEC, surface area, pHₚₛ𝑪 and water holding capacity

CEC of raw and modified clay at pH 5.4 and 7.4 revealed that Mg²⁺, Ca²⁺, Na⁺ and K⁺ are the main base cations on the clay matrices. This corroborated the XRF results which showed the presence of Ca, Na, Mg and K in clay matrices. The CEC results showed that South African bentonite clay is characterized by a high CEC of 262 meq 100 g⁻¹ at pH 5.4 and 265.5 meq 100 g⁻¹ at pH 7.4, which decreased to 195.5 meq 100 g⁻¹ at pH 5.4 and 188.9 meq 100 g⁻¹ at pH 7.4 on introducing Fe³⁺ onto bentonite clay interlayers. The results showed that CEC is independent of pH. BET results indicated that the loading of Fe³⁺ onto bentonite clay interlayers increased the surface area from 16 to 50 m² g⁻¹, the external surface area from 11.1 to 37.4 m² g⁻¹, and the micro-pore area from 4.9 to 12.5 m² g⁻¹. A high surface area will enable modified clay to encapsulate low density anionic species in aqueous solution. The pHₚₛ𝑪 was observed to increase from 8.0 for raw bentonite clay to 9.0 for Fe³⁺ modified bentonite clay. An increase in pHₚₛ𝑪 shows that modification will favor adsorption of anions from aqueous media.

Adsorption of As, B, Cr, Mo and Se onto Fe-Bent

Batch experiments were carried out to evaluate the effects of contact time, adsorbent dosage, ion concentration and pH on the adsorption of As, B, Cr, Mo and Se onto Fe-Bent surfaces.

Table 1 | Elemental composition of raw bentonite clay and Fe-Bent

<table>
<thead>
<tr>
<th>% Composition</th>
<th>Raw bentonite clay</th>
<th>Fe³⁺ bentonite clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>66.51</td>
<td>67.26</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.14</td>
<td>0.13</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.81</td>
<td>16.99</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.26</td>
<td>3.76</td>
</tr>
<tr>
<td>MnO</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>MgO</td>
<td>3.12</td>
<td>3.12</td>
</tr>
<tr>
<td>CaO</td>
<td>1.43</td>
<td>1.33</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.17</td>
<td>0.43</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.54</td>
<td>0.46</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>LOI</td>
<td>7.19</td>
<td>6.96</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100.35</td>
<td>100.62</td>
</tr>
<tr>
<td>Traces (ppm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>–</td>
<td>6.3</td>
</tr>
<tr>
<td>B</td>
<td>–</td>
<td>7.8</td>
</tr>
<tr>
<td>Cr</td>
<td>–</td>
<td>8.1</td>
</tr>
<tr>
<td>Mo</td>
<td>–</td>
<td>9.1</td>
</tr>
<tr>
<td>Se</td>
<td>–</td>
<td>8.7</td>
</tr>
</tbody>
</table>
Effect of agitation time

The effects of contact time on the adsorption of As, B, Cr, Mo and Se by Fe-Bent were evaluated at an initial concentration of 10 mg L\(^{-1}\), adsorbent dosage of 1 g, 250 rpm, 26 °C and 1 g:100 mL S/L. The uptake of As, B, Cr, Mo and Se onto Fe-Bent was evaluated for 3 hours at intervals of 1, 5, 10, 15, 30, 60, and 180 min. Figure 1 shows the % removal of As, B, Cr, Mo and Se by Fe-Bent.

As shown in Figure 1, it is clear that the sorption of As, B, Cr, Mo and Se increases with contact time until it flattens out. From the first minute of interaction, adsorption of chemical species was very rapid and gradually approached a steady state after 30 min of contact time, thus indicating that the adsorption process had reached equilibrium. The equilibrium process indicates that the adsorbent is saturated with the chemical species. As shown in Figure 1, B exhibits a higher sorption rate than other species. B adsorption occurred in 5 min, reaching a maximum of 99.9% removal. Sorption of chemical species onto Fe-Bent showed a varying rate of adsorption: As and Mo adsorption increased from the first minute of agitation and approached a steady state after 30 min where greater than 50% was removed; Cr uptake showed a gradual increase in adsorption with shaking time, after 15 mins adsorption it had approached a steady state with 75% removed; and Se showed poor adsorption affinity compared to the other chemical species under study. Its sorption increased gradually with agitation time, reaching a steady state after 30 min where approximately 20% was removed. The affinity of Fe-Bent for the oxyanionic chemical species followed the order: B > Cr > Mo = As > Se.

The results show that Fe-Bent is more effective for As, B, Cr, Mo, and Se adsorption. This is attributed to a higher surface area and micro-pore area of modified bentonite clay as compared to raw bentonite clay. After the reaction kinetics, 30 min contact time was selected as the optimum contact time for the subsequent experiments.

Effect of Fe-Bent dosage

Effects of adsorbent dosage on the adsorption of As, B, Cr, Mo and Se by Fe-Bent were evaluated at 10 mg L\(^{-1}\) of adsorbate concentration, 30 min contact time, 250 rpm and 26 °C. The adsorbent dosage was varied from 0.5 to 5 g. The variation of % removal of As, B, Cr, Mo and Se onto Fe-Bent is shown in Figure 2.

An observation from Figure 2 indicates that the adsorption of As, B, Cr, Mo and Se onto Fe-Bent increased with an increase in adsorbent dosage, reaching a maximum at 4 g. As shown in Figure 2, 4 g:100 mL of Fe-Bent was enough for quantitative adsorption of As, B, Cr, Mo and Se. At 4 g, the adsorption affinity of Fe-Bent for tested chemical species varied as follows: B > Cr = Mo > As = Se. An increase in adsorbent dose provides more sites for adsorption of oxyanionic chemical species. As seen from Figure 2, 4 g:100 mL of Fe-Bent was selected as the optimum dosage for quantitative adsorption of As, B, Cr, Mo and Se from aqueous solution.

Effect of ion concentration

The effects of adsorbate concentration on the adsorption of As, B, Cr, Mo and Se by Fe-Bent were evaluated at the contact...
time of 30 mins, adsorbent dosage of 4 g, 250 rpm and 26 °C. The concentrations of As, B, Cr, Mo and Se were varied from 0.1 to 15 mg L\(^{-1}\). The variation of % removal of the selected species with an increase in adsorbate concentration is shown in Figure 3.

As depicted in Figure 3, the adsorption of As, B, Cr, Mo and Se by Fe-Bent were high at low adsorbate concentration and gradually decreased with an increase in adsorbate concentration. Fe-Bent adsorbed greater than 98% of the evaluated chemical species at the concentration range of 0.1–10 mg L\(^{-1}\). At low concentration, the adsorption sites are numerous and adsorption is very high, but as the concentration increases the adsorption sites becomes a limiting factor resulting in lower adsorption capacity (Masindi et al. 2014c). The affinity for chemical species varied as follows: As = B = Cr = Mo = Se. Optimum adsorbate concentration on Fe-Bent was greater than 98% at 10 mg L\(^{-1}\). Therefore, 10 mg L\(^{-1}\) was selected as the optimum adsorbate concentration for subsequent experiments.

**Effect of supernatant pH**

The effects of pH on adsorption of As, B, Cr, Mo and Se onto Fe-Bent were evaluated for 30 min of contact time, 4 g of adsorbent dosage, 10 mg L\(^{-1}\) adsorbate concentration, 250 rpm, 26 °C and 4 g:100 mL S:L ratio. Variation in % removal of selected chemical species with varying pH is presented in Figure 4.

Figure 4 shows the effect of varying the initial pH on the % removal of As, B, Cr, Mo and Se onto Fe-Bent. The percentage removal of the evaluated chemical species increased with increasing pH, except for As and Cr, which initially decreased from pH 2 to 4 for Fe-Bent. The % adsorption increased for all chemical species up to pH 12 except for B, Cr and Mo, which decreased at pH greater than 10. The higher adsorption capacity of Fe-Bent for selected chemical species is attributed to the positively charged surface at pH < pH\(_{pzc}\) (9) and the increased surface area. From the obtained results, it can be deduced that pH 2–10 favors the adsorption of As, B, Cr, Mo and Se onto Fe-Bent. Based on the obtained results, pH 10 was selected as the optimum pH condition for removal of these chemical species from aqueous solutions. The adsorption affinity of oxyanions onto Fe-Bent at pH 10 was Se > B > Mo > As > Cr. Henceforth, pH 10 was selected as the optimum pH for removing oxyanionic chemical species from aqueous solution.

**Adsorption capacities of Fe-Bent**

The variation of adsorption capacities of Fe-Bent for As, B, Cr, Mo and Se at optimized conditions is presented in Table 2.

As shown in Table 2, as the concentration of species in solution increases, the amount adsorbed also increases. At low concentrations, the limiting factor on adsorption is the adsorbate concentration. The overall adsorption capacity of Fe Bent was 1.86 mg g\(^{-1}\).

**Adsorption mechanisms**

As mentioned above, Langmuir and Freundlich adsorption isotherms were employed to describe the mechanisms of
Oxyanion sorption onto Fe-bent. In this study, correlation coefficient ($R^2$) values were used to determine the best fitted model between the two. The Langmuir model is expressed by the equation:

$$\frac{Ce}{Qe} = \frac{1}{Qmb} + \frac{Ce}{Qm}$$

(4)

where $Ce =$ equilibrium concentration (mg L$^{-1}$), $Qe =$ amount adsorbed at equilibrium (mg g$^{-1}$), $Qm =$ Langmuir constants related to adsorption capacity (mg g$^{-1}$) and $b =$ Langmuir constants related to energy of adsorption (L mg$^{-1}$). These parameters are listed in Table 3.

The Langmuir adsorption isotherm can also be expressed in terms of $R_L$, a dimensionless factor known as a separation factor (Equation (5)). It is used to determine whether the reaction was favorable or not.

$$R_L = \frac{1}{1 + bCo}$$

(5)

where $Co =$ initial concentration. If $R_L$ is between 0 and 1, the adsorption is favorable (Sparks & Sparks 2003).

The results of adsorption efficiency ($Qm$) and adsorption energy $b$ of the adsorbent concludes that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface with constant energy. However, a high $Qm$ value confirms that there was enhanced adsorption at a very low temperature. To confirm the favorability of the adsorption process, the separation factor ($R_L$) was computed and is presented in Table 3. The value was found to be in the range of 0–1, indicating that the adsorption process is ongoing and favorable. Moreover, the regression coefficient ($R^2$) is above 0.86 (86%) for As, B, Mo and Se, indicating a positive, very good and strong mathematical fit. For Cr, it showed 60% fit, hence indicating a positive and fairly strong mathematical fit.

The Freundlich adsorption isotherm describes the heterogeneous surface energy by multilayer adsorption and is expressed in linear form (Equation (6)):

$$\log Qe = \frac{1}{n} \log Ce + \log Kf$$

(6)

where $Ce =$ equilibrium concentration (mg L$^{-1}$), $Qe =$ amount adsorbed at equilibrium (mg g$^{-1}$), $Kf =$ partition coefficient (mg g$^{-1}$) and $n =$ intensity of adsorption. The Freundlich adsorption isotherm constants for As, B, Cr, Mo and Se onto Fe$^{3+}$ modified bentonite clay is shown in Table 4.

According to Masindi et al. (2014c), an $n$ value between 1 and 10 represents beneficial adsorption. The $n$ value in the present adsorption experiment is 1.8, 1.6, 2.8, 3.3, and 1.8 respectively, hence confirming that the adsorption process is favorable. Also, the above reason suggests that the present adsorption process occurred on a heterogeneous surface and obeyed the Freundlich isotherm strongly.

| Table 2 | Adsorption capacities (mg g$^{-1}$) of Fe$^{3+}$ modified bentonite clay for oxyanions of As, B, Cr, Mo and Se
<table>
<thead>
<tr>
<th>Concentration (mg L$^{-1}$)</th>
<th>As</th>
<th>B</th>
<th>Cr</th>
<th>Mo</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>0.5</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
</tr>
<tr>
<td>1</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>3</td>
<td>0.074</td>
<td>0.075</td>
<td>0.075</td>
<td>0.074</td>
<td>0.075</td>
</tr>
<tr>
<td>6</td>
<td>0.149</td>
<td>0.149</td>
<td>0.150</td>
<td>0.149</td>
<td>0.149</td>
</tr>
<tr>
<td>10</td>
<td>0.247</td>
<td>0.247</td>
<td>0.249</td>
<td>0.248</td>
<td>0.249</td>
</tr>
<tr>
<td>15</td>
<td>0.370</td>
<td>0.370</td>
<td>0.373</td>
<td>0.373</td>
<td>0.373</td>
</tr>
</tbody>
</table>

| Table 3 | Langmuir adsorption isotherm constants for adsorption of As, B, Cr, Mo and Se onto Fe$^{3+}$ modified bentonite clay
<table>
<thead>
<tr>
<th>As</th>
<th>B</th>
<th>Cr</th>
<th>Mo</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Qm$ (mg g$^{-1}$)</td>
<td>30.10</td>
<td>24.20</td>
<td>89.30</td>
<td>68.50</td>
</tr>
<tr>
<td>$b$ (L mg$^{-1}$)</td>
<td>0.03</td>
<td>0.04</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>$R_L$</td>
<td>0.66</td>
<td>0.61</td>
<td>0.86</td>
<td>0.82</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.85</td>
<td>0.82</td>
<td>0.60</td>
<td>0.88</td>
</tr>
</tbody>
</table>

| Table 4 | Freundlich adsorption isotherm constants for adsorption of As, B, Cr, Mo and Se onto Fe-Bent
<table>
<thead>
<tr>
<th>As</th>
<th>B</th>
<th>Cr</th>
<th>Mo</th>
<th>Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>1.84</td>
<td>1.58</td>
<td>2.77</td>
<td>3.25</td>
</tr>
<tr>
<td>$Kf$ (mg g$^{-1}$)</td>
<td>0.90</td>
<td>0.93</td>
<td>0.89</td>
<td>0.79</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.93</td>
<td>0.92</td>
<td>0.98</td>
<td>0.87</td>
</tr>
</tbody>
</table>
regression coefficients ($R^2$) showed that the adsorption process is positive, very good and strong. Both Langmuir and Freundlich adsorption isotherms showed very good and strong mathematical fits, thus revealing that the adsorption process was taking place on homogenous and heterogeneous surfaces, hence forming inner and outer sphere complexation.

**Treatment of coal fly ash leachates under optimized conditions**

The results of the treatment of coal fly ash leachates with Fe-Bent under optimized conditions are shown in Table 5.

As shown in Table 5, for raw bentonite the adsorption of As, B, Cr, Mo and Se were observed to be very high. Fe-Bent showed good adsorption of these chemical species by reducing their concentration to below the Department of Water Affairs and Forestry (DWAF) water quality guidelines. Based on these results, it can be concluded that Fe-Bent is an effective adsorbent for As, B, Cr, Mo and Se from coal fly ash leachates. This also implies that Fe-Bent can be used as a liner or passive barrier in ash retention ponds for adsorption of these oxyanionic species. This also has positive implications on the application of bentonite clay barriers for remediation of waste effluents used for hydraulic transport of ash on wet disposal systems.

**CONCLUSIONS AND RECOMMENDATIONS**

Modification of raw bentonite clay with polycations of Fe$^{3+}$ revealed that 15 min of contact time, 2 g of adsorbent dosage and 100 mg L$^{-1}$ adsorbate concentration are the feasible optimum conditions for loading polymeric Fe$^{3+}$ ions onto bentonite clay lattice. Modification increased the physicochemical properties of bentonite clay. Elemental composition by XRF and electron dispersion spectrometry (EDS) showed SiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CaO, Na$_2$O, K$_2$O and MgO as the major chemical species. XRF and EDS results also confirmed that bentonite clay is an aluminosilicate material. XRD results showed that bentonite clay is dominated by smectite, quartz, plagioclase, muscovite, calcite and magnetite. Adsorption of As, B, Cr, Mo and Se from coal fly ash leachates revealed that 30 min of contact time, 4 g of adsorbent dosage, 10 mg L$^{-1}$ of adsorbate concentration and pH 10 are the optimum conditions for removing these oxyanionic species from aqueous media. The adsorption affinity of these species obeyed the following order: $B = Se > Mo > Cr = As$. The adsorption capacity of Fe-Bent increased with an increase in adsorbate concentration. The data fitted well to the Langmuir and Freundlich adsorption isotherms, hence showing that the adsorption is energetically favorable. Fe-Bent successfully removed As, B, Cr, Mo and Se from generated coal fly ash leachates to below DWAF water quality guidelines at the optimized conditions. This shows that Fe-Bent is an effective adsorbent for removal of oxyanionic species of As, B, Cr, Mo and Se from coal fly ash leachates and could be applied as a passive barrier or liner in ash retention ponds or soil amendment in contaminated agricultural areas. This study successfully proved that As, B, Cr, Mo and Se can be adsorbed from aqueous media in significant amounts by Fe-Bent.

**ACKNOWLEDGEMENTS**

The authors wish to convey their sincere gratitude to Research and Innovation Directorate, Department of Ecology and Resource management, School of Environmental Sciences, University of Venda, Council of Scientific and Industrial Research (CSIR), ESKOM-TESP, SASOL-INZALO, National Research Foundation (NRF) and Department of Science and Technology (DST) (DST/NRF) for funding this project.

**REFERENCES**

Akar, G., Polat, M., Galecki, G. & Ipekoglu, U. 2012 Leaching behavior of selected trace elements in coal fly ash samples


Masindi, V. & Gitari, W. M. 2015a The potential of ball-milled South African bentonite clay for attenuation of heavy metals from acidic wastewaters: simultaneous sorption of Cu(II), Co(II), Ni(II), Pb(II) and Zn(II) ions. Environ. Chem. Eng. 3 (4), 2416–2425.


Prahara, T., Powell, M. A., Hart, B. R. & Tripathy, S. 2002 Leachability of elements from sub-bituminous coal fly ash from India. Environ. Int. 27 (8), 609–615.


First received 16 July 2015; accepted in revised form 9 November 2015. Available online 7 December 2015.