Simultaneous sorption of As, B, Cr, Mo and Se from coal fly ash leachates by Al^{3+}-pillared bentonite clay: Implication for the construction of activated geo-synthetic clay liner

Vhahangwele Masindi[1,3&4], W. Mugera Gitari [1], Hlanganani Tutu[2]

[1]Department of Ecology and Resources Management, School of Environmental Sciences, University of Venda, P/bag X5050, Thohoyandou, 0950, South Africa. masindivhahangwele@gmail.com
[2]Molecular Science Institute, School of Chemistry, University of Witwatersrand, P/Bag X4, WITS, Johannesburg, 2050, South Africa
[3]CSIR (Council of Scientific and Industrial Research), Built Environment, Hydraulic and Infrastructure Engineering (HIE), P.O Box 395, Pretoria, 0001, South Africa. VMasindi@csir.co.za, Tel: 0128412787
[4]Department of Environmental Sciences, School of Agriculture and Environmental Sciences, University of South Africa (UNISA), P. O. Box 392, Florida, 1710, South Africa

Abstract

The present study reports the optimum conditions for intercalating the Al^{3+} species to bentonite clay matrices and evaluate the potential of using Al^{3+}-modified bentonite clay (Alum-Bent) for removal of oxyanionic species of As, B, Cr, Mo and Se from coal fly ash leachates. Removal of oxyanionic species was done in batch experimental procedures. Parameters optimized were: contact time, adsorbent dosage, concentration and pH. The adsorption affinity of Al^{3+}-bentonite clay for oxyanionic species varied as follows: B ≈ Se > Mo > Cr ≈ As respectively. The adsorption data fitted better to Langmuir adsorption isotherm than Freundlich adsorption isotherm hence confirming mono-site adsorption. The adsorption kinetics fitted well pseudo-second-order kinetic model hence confirming chemisorption. The fact that most of the oxyanion were adsorbed at pH ≥ pHpzc indicated that both electrostatic and chemical interactions occurred with the clay surface and interlayers. The Al^{3+}-modified bentonite clay successfully removed oxyanion species from generated coal fly ash leachates. This study shows that Al^{3+}-modified bentonite clay is an effective adsorbent for oxyanion species in coal fly ash leachates and could be applied as a reactive barrier in coal fly ash retention ponds.

Keywords: bentonite clay; coal fly ash leachates; oxyanions; adsorption; isotherms; kinetics

---

[1] Corresponding Author: Masindi Vhahangwele: VMasindi@csir.co.za; masindivhahangwele@gmail.com

1   Introduction

South Africa relies mainly on coal combustion for power generation (Vadapalli et al., 2010, Somerset et al., 2011, Vadapalli et al., 2012, Gitari et al., 2013c, Muriithi et al., 2014). Low grade bituminous coal mainly used for power generation and it has been documented to generates huge volumes of by-products such as bottom ash, fly ash, boiler slag, flue gas desulfurization sludge and non-captured particles (Adriano et al., 1980, Steenari et al., 1999, Sherly and Kumar, 2011, Seshadri et al., 2013, Wang et al., 2014). Amongst the generated waste, of most concern is fly ash which is mainly collected from flue gases by means of mechanical devices such as electrostatic precipitators, bag house, scrubbers and cyclones (Ahmaruzzaman, 2010).

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 or conveyed to ash heaps in dry disposal systems. The transportation water is collected as penstock overflow and recirculated for more ash slurry uptake in wet disposal systems (Ahmaruzzaman, 2010, Mahlaba et al., 2011, Akar et al., 2012, Akinyemi et al., 2012). Approximately 27 MT of fly ash (FA) is produced annually in South African (RSA) power utilities (Gitari et al., 2008). Of this, only 5% is utilized beneficially for construction (Yao et al., 2015), agricultural purposes (Zevenbergen et al., 2000, Basu et al., 2009, Kishor et al., 2010, Yunusa et al., 2014), treatment of wastewater (Gupta and Torres, 1998, Wang and Viraraghavan, 1998, Ahmaruzzaman, 2011, Wang et al., 2013, Visa and Chelaru, 2014) and beneficiated into new products such as zeolite (Ríos et al., 2008, Vadapalli et al., 2010, Zhang et al., 2011, Xie et al., 2014, Yao et al., 2015).

The remainder is discarded in surface impoundments such as ash retention dams and ponds where it commence with environmental degradation through leaching to underground and surface water resources thus impairing the aquatic and terrestrial ecosystems (Zevenbergen et al., 1999, Zevenbergen et al., 2000, Abbott et al., 2001, Mahlaba et al., 2011, Akinyemi et al., 2012, Muriithi et al., 2013). Coal fly ash is a heterogeneous mixture of inorganic species which were incorporated in coal during the coalification stages. Post ash disposal and on contact with aqueous medium, the toxic inorganic pollutants such as Cl^-, SO_4^{2-}, oxyanion species of As, B,

Cr, Mo, Se and Al, Ba, Ca, Cd, Cu, Fe, K, Mg, Na, Sr and Zn are leached to terrestrial and aquatic ecosystems (Reardon et al., 1995, Steenari et al., 1999, Iyer, 2002, Praharaj et al., 2002a, Vítková et al., 2009, Zheng et al., 2011, Tsiridis et al., 2012, Vítková et al., 2013).

Literature studies have reported that availability of As, B, Cr, Mo and Se in the biosphere are of ecological concern due to possible toxicity that they pose to living organisms. Epidemiological studies have reported that long-term exposure to oxyanions may interfere with metabolic activities of living organisms, failure of multisystem organ by allosteric inhibition of sulfhydryl enzymes that are essential for regulating metabolic activities hence leading to death as an end point of toxicity. Conjunctivitis, hyperkeratosis, hyper pigmentation, cardiovascular diseases, disorder of central nervous system and peripheral vascular system, skin cancer and gangrene of the limbs are some of the toxicity that are triggered by oxyanions (Kashiwa et al., 2000, Hassett et al., 2005, Tajer Mohammad Ghazvini and Ghorbanzadeh Mashkani, 2009, He and Yao, 2010, Puranen et al., 2010). Moreover, coal fly ash leachates can render surface and groundwater unsuitable for numerous defined uses (Iyer, 2002, Praharaj et al., 2002b, Lapa et al., 2007, Prasad and Mondal, 2009, Izquierdo and Querol, 2012, Tsiridis et al., 2012, Neupane and Donahoe, 2013, Reinik et al., 2014).

As such, there is a need to come up with a sustainable and pragmatic technology that will be used to prevent the contamination of underground water resources by coal fly ash leachates. The most prominent technology relies on the use of clay liners and exchange resins beds on the ash retention pond linings (Lange et al., 2005, Mapanda et al., 2007, Lange et al., 2010a, Lange et al., 2010b, Lu et al., 2011, Yang et al., 2012, Fan, 2014b, Fan, 2014a, Musso et al., 2014). Abundancy, high surface area, cation exchange capacity and magnificent swelling capacity of clays made clay and clay minerals to anchor the depollution science (Bhattacharyya and Gupta, 2008, Bhattacharya et al., 2013). Clays are widely utilized for remediation of wastewater as geo-synthetic clay liners, however, they are dependent on pH (Dukić et al., 2015). Due to low density of cations on the clay matrices, clays can be modified with polycations to increase their inorganic contaminants retention abilities (Gitari et al., 2013a, Masindi et al., 2014c). Trivalent species of aluminium has strong

affinity to oxyanionic species (Gitari et al., 2013b, Masindi, 2013, Masindi et al., 2014c). This will reduce the use of virgin material by modifying the clay with species that has high affinity to oxyanionic species. The present study reports the optimum conditions for intercalating the Al^{3+} species to bentonite clay interlayers and evaluate the potential of using Al^{3+}-modified bentonite clay for removal of oxyanionic species of As, B, Cr, Mo and Se from coal fly ash leachates.

2   Materials and methods

2.1   Preparation of bentonite clay samples

Bentonite clay was obtained from ECCA holdings Pty, Ltd and coal fly ash was collected from Hendrina power utility in Mpumalanga, South Africa. All reagents used in this study were of analytical grade.

2.2   Modification of bentonite clay samples

For ion exchange reaction, $Al_2(SO_4)_3.18H_2O$ was used. The optimum conditions for loading Al^{3+} polycations onto bentonite clay lattice were observed to be 60 min of retention time, 1 g of adsorbent dosage and 100 mg/ℓ of adsorbate concentration (Masindi, 2013). Bentonite clay, 10 g, was transferred into a 1000 mL High Density Polyethylene (HDPE) container containing 500 mℓ of 100 mg/ℓ Al^{3+}. The mixture was shaken for 60 min on a table shaker. This was repeated 25 times to make up a total of 250 g of adsorbent (Masindi, 2013).

2.3   Physico-chemical characterization

Elemental composition was ascertained using X-ray fluorescence (XRF). Surface are by Brunauer-Emmett-Teller (BET: A Tristar II 3020, Micrometrics BET from Norcross, GA, USA). pH_{pzc} was determined using solid addition method (Masindi et al., 2014b). Cation exchange capacity (CEC) was determined using ammonium acetate method (Masindi et al., 2014b).

2.4   Characterisation of aqueous samples

pH, Total Dissolved Solids (TDS – mg/ℓ) and Electrical Conductivity (EC - µS/cm) were monitored using CRISON MM 40 portable pH/EC/TDS/Temperature multimeter

probe. Aqueous samples were analysed using ICP-MS (7500ce, Agilent, Alpharetta, GA, USA). The accuracy of the analysis was monitored by analysis of National Institute of Standards and Technology (NIST) water standards. Three replicate measurements were made on each sample and results are reported on average.

2.5   Preparation of standard working solutions

One thousand mg/ℓ 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 1000 mg/ℓ stock solution, 10 mg/ℓ solution was prepared by 100 time dilution of 1000 mg/ℓ oxyanion standard solution and transferred into 1000 mℓ volumetric flask. The volumetric flask was topped to the mark by adding ultra-pure water.

2.6   Optimization of adsorption conditions

Adsorption of oxyanions onto Alum-bent was evaluated in 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 include effects of time, dosage, concentration and pH. All the experiments were carried out using 250 mℓ HDPE containers and mixed at 250 rpm using Labcon model 3100E table shaker.

2.6.1 Effect of residence time

Effects of time were investigated by varying time from 1 – 180 min. Other conditions include: 1:100 S/L ratios, 10 mg/ℓ adsorbate concentration, pH 7.5 and 26⁰C room temperature. After shaking, the mixtures were filtered through a 0.45 μm pore nitrate cellulose filter membrane and refrigerated at 4⁰C prior to analysis by an ELAN 6000 inductively coupled plasma mass spectrometer (ICP-MS). The pH before and after agitation was measured using the CRISON multimeter probe (model MM 40).

2.6.2 Effect of adsorbent dosage

Effects of Alum-Bent dosage on adsorption of oxyanions were evaluated by varying the dosages from 0.5 – 5 g. Other conditions include: 30 min of equilibration, 10 mg/ℓ

adsorbate concentration, pH 7.5 and 26ºC room temperature. The pH and metal content were measured as described in the preceding section.

2.6.3 Effect of adsorbate concentration

Effects of ions concentration on removal of oxyanions by Alum-Bent were investigated by varying concentration ranges from 0.1 – 15 mg/ℓ. Other conditions include: 30 min of equilibration, 1:100 S/L ratios, pH 7.5 and 26ºC room temperature. The pH and metal content were measured as described in the preceding section.

2.6.4 Effect of pH

Effects of pH were evaluated by adjusting the pH of aqueous media to required pH using HCl or NaOH at the beginning of batches and not controlled afterwards. Other conditions were 30 min of equilibration, 1:100 S/L ratios, 15 mg/ℓ and 26ºC temperatures. Optimum adsorption conditions obtained were used for treatment of coal fly ash leachates. The pH and metal content were measured as described in the preceding section.

2.7 Coal fly ash leachates generation and treatment

2.7.1 Coal fly ash leachates generation

Coal fly ash leachates were generated at 10 g: 100 mℓ S/L ratio using ultra-pure water. Three 10 g of coal fly ash was measured and transferred to individual 250 mℓ HDPE plastic 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 pore nitrate 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 4ºC until analysis by ICP-MS.

2.7.2 Coal fly ash leachates treatment

100 mℓ of coal fly ash leachates was transferred into three 250 mℓ HDPE container and 4 g of Alum-Bent added. The mixtures were equilibrated for 60 min using a reciprocating orbital shaker. After shaking, the mixture was filtered through 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 ICP-MS.

2.8 Modelling of analytical results

2.8.1 Percentage removal and adsorption capacity

Computation of % removal and adsorption capacity was done using equations (1) and (2).

$$\text{Percentage removal (\%)} = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \tag{1}$$

$$\text{Adsorption capacity } (q_e) = \frac{(C_i - C_e)V}{m} \tag{2}$$

Where: C_i = initial concentration, C_e = equilibrium ion concentration, V = volume of solution; m = mass of bentonite clay.

2.8.2 Adsorption kinetics

The pseudo-first-order is a kinetic model described by the following equation:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K}{2.303}\right)t \tag{3}$$

Where qe (mg/g) is adsorption capacity at equilibrium, qt (mg/g) is the adsorption capacity at time t, and K (min/1) is the rate constant of pseudo-first-order. The value of K_1 can be obtained from the slope by plotting t vs Log (qe – qt).

Pseudo-second-order mode is applied when the applicability of the first-order kinetics becomes untenable. The equation of pseudo-second-order is given in the following equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \left(\frac{1}{q_e}\right)t \tag{4}$$

This equation is applied to obtain K_2, the second order rate from the plots t vs t/qe.

2.8.3 Adsorption isotherms

The mechanisms and intensity of adsorption was described by use of two common adsorption models: Langmuir and Freundlich adsorption isotherms these models

describe adsorption processes on a homogenous or heterogeneous surface respectively

The Langmuir isotherm is valid for monolayer sorption due to a surface with finite number of identical sites and can be expressed in the following linear form (Masindi et al., 2015a).

$$\frac{Ce}{Qe} = \frac{1}{Qmb} + \frac{Ce}{Qm} \qquad (5)$$

Where, Ce = Equilibrium concentration (mg/L), Qe = Amount adsorbed at equilibrium (mg/g), Qm = Langmuir constants related to adsorption capacity (mg/g) and b = Langmuir constants related to energy of adsorption (L/mg) The essential characteristics of the Langmuir isotherms can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined as:

$$R_L = \frac{1}{1 + bC_o} \qquad (6)$$

A plot of Ce versus Ce/Qe should be linear if the data is described by the Langmuir isotherm. The value of Qm is determined from the slope and the intercept of the plot. It is used to derive the maximum adsorption capacity and b is determined from the original equation and it represents the intensity of adsorption.

The Freundlich adsorption isotherm describes the heterogeneous surface energy by multilayer adsorption and can be expressed in linear form (Masindi et al., 2015b).

$$\log Qe = \frac{1}{n}\log C + \log Kf \qquad (7)$$

Where Ce = Equilibrium concentration (mg/L), Qe = Amount adsorbed at equilibrium (mg/g), K_f = Partition Coefficient (mg/g) and n = Intensity of adsorption

The linear plot of log Ce versus log Qe indicates if the data is described by Freundlich isotherm. The value of K_f implies that the energy of adsorption on a homogeneous surface is independent of surface coverage and n is an adsorption constant which reveals the rate at which adsorption is taking place. These two constants are determined from the slope

3 Results and discussion

3.1 Chemical Characterization

The chemical composition of raw and Al^{3+} modified bentonite clay is shown in Table 1.

Table 1: Chemical composition of raw and Al^{3+} modified bentonite clay

% Composition	Raw bentonite clay	Al^{3+}-bentonite clay
SiO_2	66.51	66.01
TiO_2	0.14	0.14
Al_2O_3	16.81	17.22
Fe_2O_3	3.26	3.28
MnO	0.13	0.12
MgO	3.12	3.03
CaO	1.43	1.30
Na_2O	1.17	0.46
K_2O	0.54	0.51
P_2O_5	0.03	0.03
LOI	7.19	7.55
TOTAL	**97.21**	**98.32**

Results in Table 1 show that bentonite clay is composed largely of SiO_2 and Al_2O_3 indicating that it's an aluminosilicate material. High levels of Fe_2O_3 could indicate presence of iron oxides which might have been adsorbed during deposition processes. There is insignificant proportion of Mn and P impurities which might have been incorporated in clay fractions during deposition. The increased Al content in the bentonite clay indicate successful introduction of Al^{3+} in the bentonite clay interlayers. The contents of MgO, Na_2O, CaO and K_2O were observed to decrease in the modified bentonite indicating that they are exchanged for Al^{3+}.

3.3 CEC, surface area and point of zero charge of raw and modified bentonite clay

The physicochemical properties of raw and Al^{3+} modified bentonite clay are presented in Table 2.

Table 2: Physicochemical properties of Raw and modified bentonite clay

Parameter		Raw bentonite clay	Al^{3+} modified bentonite clay
CEC	**pH 5.4**	262 meq/100g	186.9 meq/100g
	pH 7.4	265.5 meq/100g	183.3 meq/100g
External Surface Area		11.1 m^2/g	33.1 m^2/g
Specific Surface Area		16 m^2/g	44.3 m^2/g
Micro Pore Area		4.9 m^2/g	11.2 m^2/g
pH_{PZC}		8.0	8.2

Determination of exchangeable base cations by the ammonium acetate method at different pHs (pH 5.4 and 7.4) revealed that Mg^{2+}, Ca^{2+}, Na^+ and K^+ are the exchangeable base cations. This collaborates XRF results which showed a decrease of Ca^{2+}, Mg^{2+}, K^+, and Na^+ in Al^{3+}- modified bentonite clay (Table 1). The CEC results show that South African bentonite clay is characterized by high CEC of 262 meq/100g at pH 5.4 and 265.5 meq/100g at pH 7.4. The CEC decreased to 186.9 meq/100g at pH 5.4 and 183.3 meq/100g at pH 7.4 on introducing Al^{3+}. The results show that CEC is independent of pH for the tested pH ranges. Surface area plays a pivotal role in adsorption of chemical species from the solution, the higher the surface area, the higher the adsorption and vice versa (Masindi et al., 2014a). BET results indicated that the loading of Al^{3+} onto bentonite clay interlayers increased the specific surface area from 16 m^2/g to 44.3 m^2/g. pHpzc is the pH at which a surface has a net charge of zero. There was a slight difference in pH_{PZC} of Al^{3+} modified bentonite clay (8.2) as compared to raw bentonite (8.0). A slight increase in pH_{PZC} will also contribute to the enhanced adsorption efficiencies of anions from aqueous media (Gitari et al., 2013b, Gitari et al., 2015, Masindi et al., 2015a, Masindi et al., 2015c).

3.4　Optimization conditions

Batch experiments were carried out to evaluate the effects of contact time, adsorbent dosage, adsorbate concentration and pH on adsorption of As, B, Cr, Mo and Se on Al^{3+}-modified bentonite clay.

3.4.1　Effect of shaking time

The variation of percentage uptake and adsorption capacity of the selected ions as a function of contact time is presented in **Figure 1**.
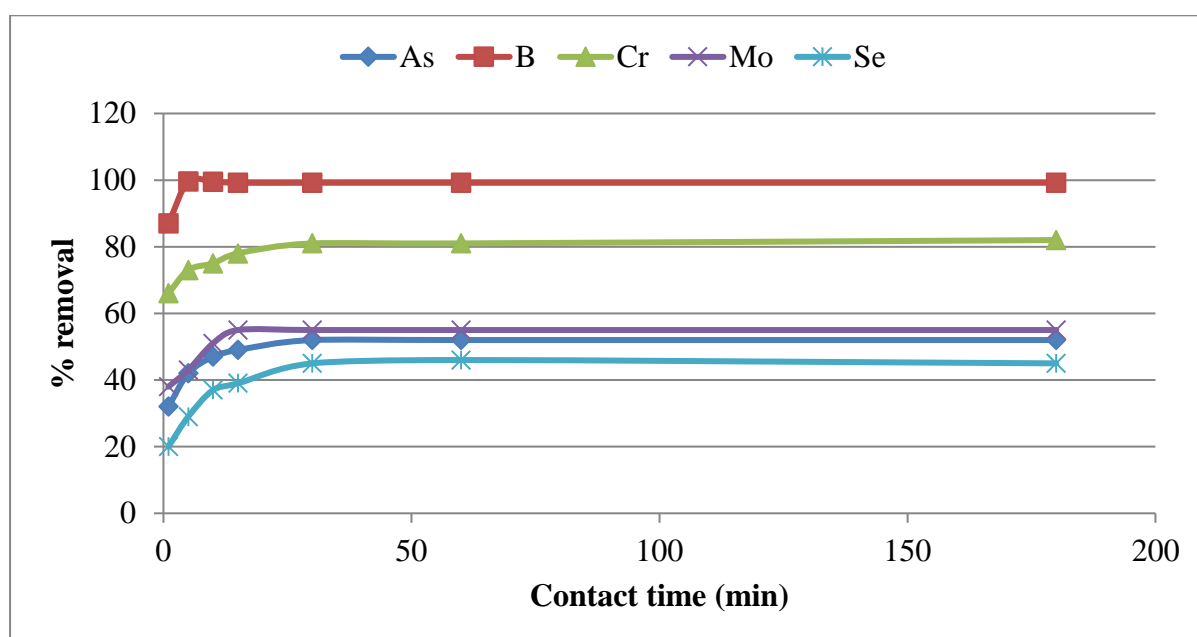

Figure 1: Variation of As, B, Cr, Mo and Se % removal for Al^{3+} modified bentonite clay with contact time (Conditions: 1 g adsorbent dosage, 10 mg/ℓ adsorbate concentration, 250 rpm, 26⁰C room temperature, 1g/100 mℓ S/L ratio and initial pH < 2).

Figure 1 shows sorption of As, B, Cr, Mo and Se onto Al^{3+} bentonite clay increases with an increase in contact time to reach a steady state at 15 min. Within 1st min of contact adsorption of B was very rapid and gradually approached a steady state after 5 minutes. At 30 min the system seems to reach a steady state for all chemical species. Maximum uptake of B was attained in 5 minutes reaching approximately 99.9 % removal (Fig. 1). Adsorption of other chemical species was below 80 % at equilibrium but followed the same adsorption trend as B. This indicates similar adsorption mechanism for all the chemical species. The affinity of the Al^{3+} modified

bentonite clay for the investigated chemical species showed the following order: B > Cr > Mo > As > Se. The adsorption capacity trends were similar to the trends of % removal for all oxyanions investigated. The result shows that modified bentonite clay is more effective and fast for all chemical species. This is attributed to higher surface area, micro-pore volume, and surface charge of modified bentonite clay as compared to raw bentonite clay (Table 2). Other reasons may be an increase in density of sorption sites due to introduction of Al^{3+} which has high charge density. The higher adsorption of most of the species by Al^{3+}-bentonite clay could also be due to increase in interlayer spacing compared to raw bentonite. The maximum adsorption was observed to occur at 30 min hence this was used as the optimum contact time for subsequent experiments

3.4.2 Effect of adsorbent dosage

The variation of percentage uptake of the chemical species as a function of adsorbent dosage is presented in **Figure 2**.
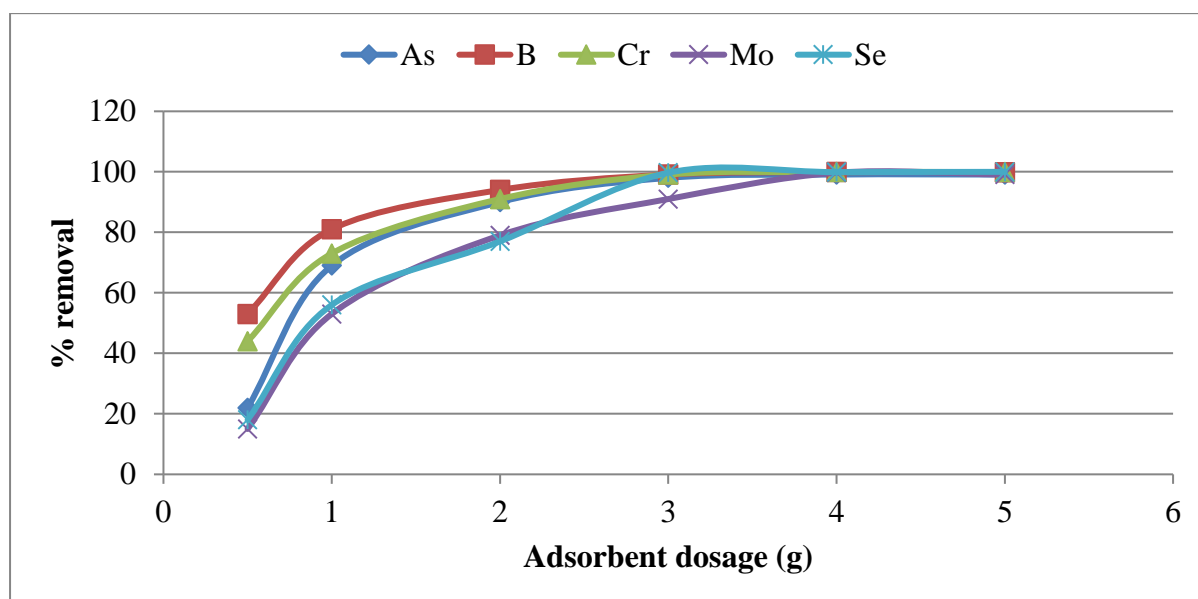

Figure 2: Variation of As, B, Cr, Mo and Se % adsorption for Al^{3+} modified and raw bentonite clay as a function of adsorbent dosage (Conditions: 30 min, 10 mg/ℓ adsorbate concentration, 250 rpm, 26°C room temperature and initial pH < 2).

The % adsorption of As, B, Cr, Mo and Se was observed to increase with adsorbent dosage for both Al^{3+}-modified bentonite clay and raw bentonite clay (Fig. 2). Increase of adsorbent dose provides more sites for adsorption hence increase in %

adsorption. At 3g adsorbent dosage >91% adsorption was observed for all chemicals species for the Al^{3+} modified bentonite clay (Fig. 2). The adsorption affinity for Al^{3+} modified clay for various species varied as follows: B > Cr > As > Se> Mo. pH was observed to increase in final process water for raw bentonite. This could be due to dissolution of alkaline metal oxides (Table 1). High adsorption capacity of the modified clay is attributed to high surface area, micro-pore volume and surface charge of modified bentonite clay (Table 2). Masindi et al. (2014a) observed that Al^{3+}/Fe^{3+} modified bentonite clay had higher adsorption capacity for arsenic species as compared to unmodified bentonite clay. At 4 g adsorbent dosage both systems recorded > 40 % adsorption for all chemical species, consequently, 4 g was taken as the optimum adsorbent dosage and was applied for subsequent experiments.

3.4.3 Effect of adsorbate concentration

The variation of percentage adsorption of the chemical species as a function of adsorbate concentration is presented in **Figure 3**.
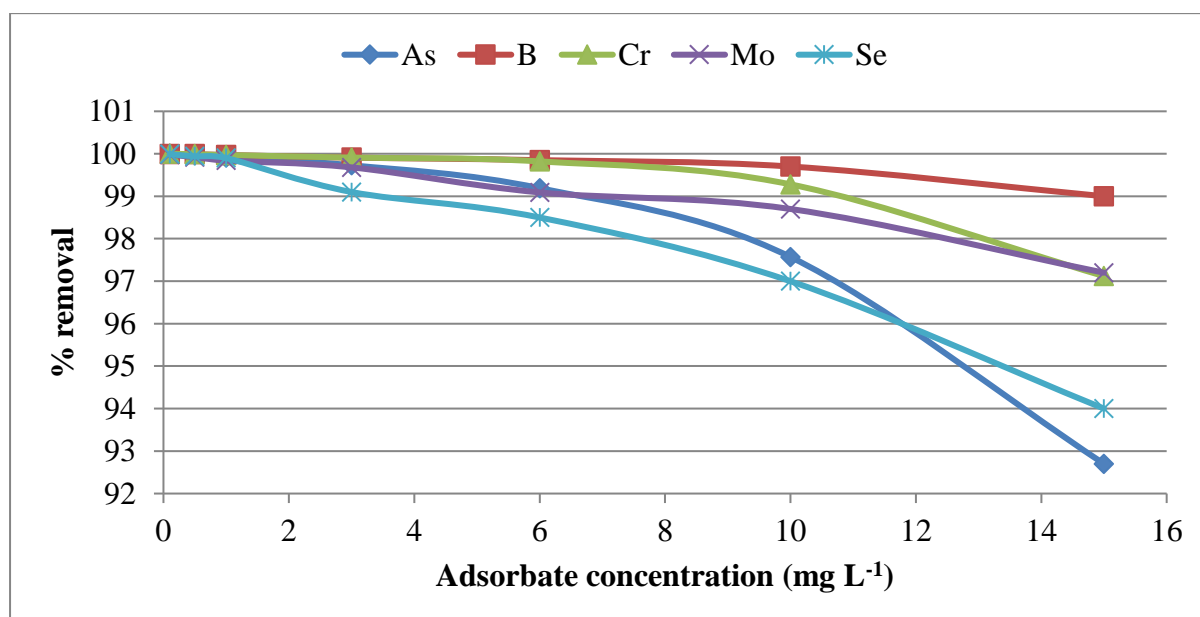

Figure 3: Variation of As, B, Cr, Mo and Se % removal for Al^{3+} modified and raw bentonite clay with adsorbate concentration (Conditions: 30 min of contact time, 4 g adsorbent dosage, 250 rpm, 26ºC room temperature, 4g/100 mℓ S/L ratios, initial pH < 2).

Figure 3 shows that, as the concentration of As, B, Cr, Mo and Se increased the adsorption capacity of the modified bentonite clay decreased. The modified bentonite

clay was observed to adsorb more than 98% of the chemical species over the concentration range of 0.1-10 mg/ℓ (Fig. 3) its adsorption capacity decreased at concentrations greater than 10 mg/ℓ but was still > 80 %. At low concentration, more adsorption sites are available and adsorption is high but as the concentration increases the adsorption sites become the limiting factor hence resulting in lower adsorption. At concentration range 0.1-1 mg/ℓ, raw bentonite clay recorded % adsorption > 98% for all chemical species. As the concentration increased the % adsorption decreased dropping to below 60 % at 6 mg/L for As, Se, Mo, and Cr (Fig. 3). Physicochemical characterization of the modified bentonite clay showed increased surface area and pore volume (Table 2) which could account for the increased adsorption capacity. The final pH of the media in the Al^{3+}-bentonite reactions was observed to be dependent on adsorbate concentration, with 0.1-1 mg/ℓ showing a final pH of 4 - 5 while 3 -15 mg/ℓ solutions having a final pH of 2 - 3. The results show that 10 mg/ℓ would be the optimum adsorbate concentration at which Al^{3+}modified bentonite clay would have optimum adsorption. However 10 mg/ℓ was selected as the optimum adsorbate concentration for the subsequent experiment.

3.4.5 Effect of supernatant pH

The variation of percentage uptake of the chemical species as a function of pH is presented in **Figure 4**.
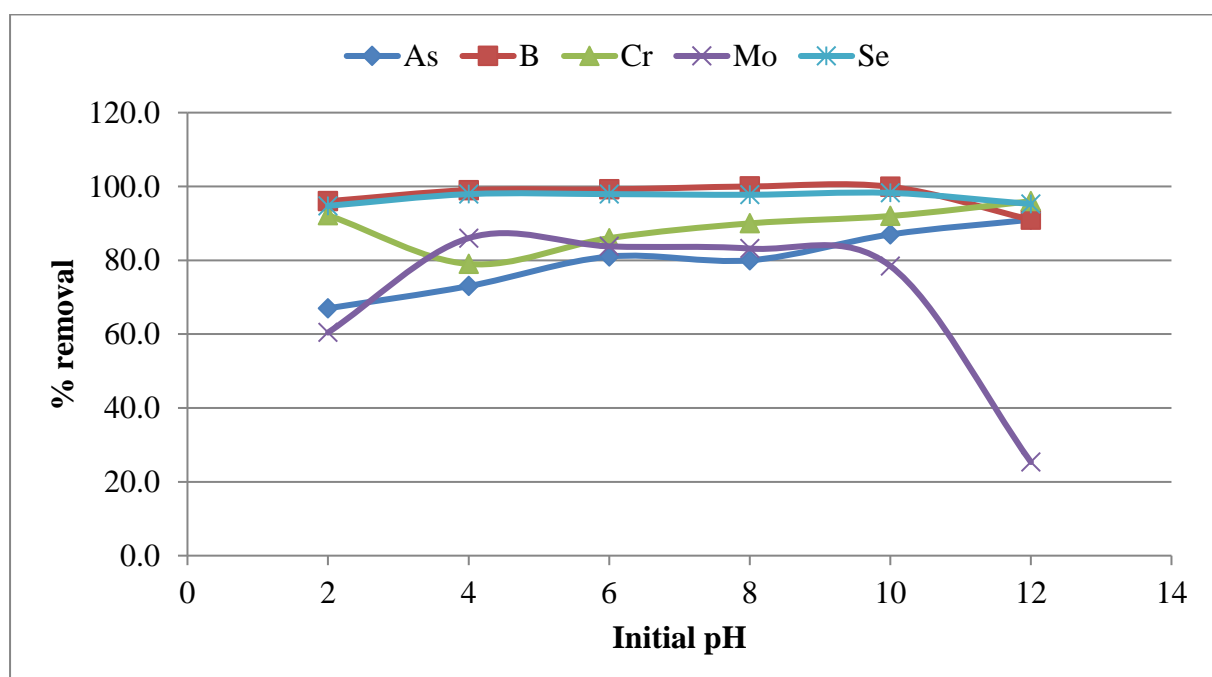
Figure 4: Variation of As, B, Cr, Mo and Se % removal with pH for Al^{3+} modified and raw bentonite clay (Conditions: 30 min of contact time, 4 g adsorbent dosage, 10 mg/ℓ adsorbate concentration, 250 rpm, 26ºC room temperature and 4 g/100 mℓ S/L ratios).

Figure 4 shows the effect of varying the pH on adsorption (% removal) of As, B, Cr, Mo and Se for Al^{3+} bentonite clay. The % adsorption of all the chemical species increases with increasing pH but is maximum at pH 4 -10 except for Se and B (Fig. 4). The % adsorption decreases at pH 12 for B, Se and Mo while an increase is observed for As and Cr (Fig. 4). At pH range of 4-10 the % adsorption for all chemical species was > 70 for the Al^{3+} modified bentonite clay. The Al^{3+} modified bentonite clay recorded > 90 % adsorption for B and Se over the pH range of 2-12. Both raw and Al^{3+} modified bentonite clay exhibit close and high % adsorption capacity and trends for B and Se. This indicates the adsorption mechanism for B and Se is similar for both adsorbents and could involve other surface complexation of the anionic species that does not involve the Al^{3+} in the interlayers (Jain and Jayaram, 2009, Jiang et al., 2009, Mohapatra et al., 2009). At the pH 2, As, Cr, Mo, B and Se will most likely be existing as positively charged ionic species and are likely to be exchanged with the exchangeable alkali metals in the interlayers hence the high adsorption. The decrease in adsorption at pH >10 is mainly due to competition of adsorption sites with OH^- as most of these chemical species will be existing as oxyanions. This is attributed to adsorption of hydroxyl group as the pH increases. Optimum adsorption of As, B, Cr Mo and Se occurred over the acidic, circum-neutral to alkaline pH for both adsorbents. pH 10 was selected as the optimum pH for adsorption of the oxyanionic species and was applied in decontamination experiments of the fly ash leachates.

3.5   Adsorption isotherms

The adsorption isotherms of As, B, Cr, Mo and Se were developed by varying the initial As, B, Cr, Mo and Se concentration over the range 0.1 - 15 mg/ℓ. The adsorption conditions were 30 minutes of contact time, 250 rpm agitation speed, 26ºC and 4g/100 mℓ S/L ratio. Two widely used adsorption isotherms: the Langmuir and Freundlich were used to describe the adsorption data as discussed in previous section.

The Langmuir and Freundlich adsorption isotherm constants for As, B, Cr, Mo and Se are presented in **Table 3**.

Table 3: Langmuir and Freundlich adsorption isotherm constants for adsorption of As, B, Cr, Mo and Se onto Al^{3+} modified bentonite clay

Langmuir adsorption isotherm				
Parameter	Q_m (mg/g)	B (Lmg/g)	R_L	R^2
As	0.5	9	0.4	0.95
B	0.4	9.4	0.7	0.99
Cr	0.4	34.5	0.6	0.98
Mo	2.6	0.6	0.7	0.2
Se	0.7	2.2	0.6	0.9
Freundlich adsorption isotherm				
Parameter	K_f (mg/g)	q (mg/g)	n	R^2
As	1.4	0.024	0.9	0.8
B	2.4	0.025	0.8	0.8
Cr	3.5	0.025	0.9	0.8
Mo	2.5	0.025	1.2	0.9
Se	1.3	0.025	1.1	0.9

The Langmuir model gave a strong fit for As, B, Cr and Se ($R^2 > 0.8$) and Mo ($R^2 = 0.2$) was for Al-bentonite. The Q_m (mg/g) values for most of the species were higher for Al-bentonite. Computed R_L values for both systems were between 0 and 1 showing the adsorption process is favorable. The calculated R^2 values for the Freundlich adsorption isotherms show a strong correlation for most of the species for both systems (Table 4). This would indicate heterogeneity of the adsorbent surface. The higher values of K_f for the Al-modified bentonite indicate that the Al^{3+}-bentonite system offered a much higher adsorption capacity. This could indicate that the adsorption occurred as a multilayer adsorption on the heterogeneous clay surface. The smaller values of 1/n for Al^{3+}-bentonite indicate higher affinity of these species to Al-bentonite.

3.6   Adsorption kinetics

The adsorption of the oxyanions was characterized by an initial fast adsorption followed by a slower equilibration process. This would probably indicate a heterogeneous process. The adsorption kinetics was evaluated under the following reaction conditions: 1 g adsorbent dosage, 10 mg/ℓ adsorbate concentration, 250 rpm, 180 min, 26ºC and 1 g/100 mℓ S/L ratios. The kinetics of the adsorption data were analyzed using Lagergren pseudo-first order and pseudo-second-order model. Only the results of the pseudo-second order model are presented since the data showed poor fit to the pseudo-first order model.
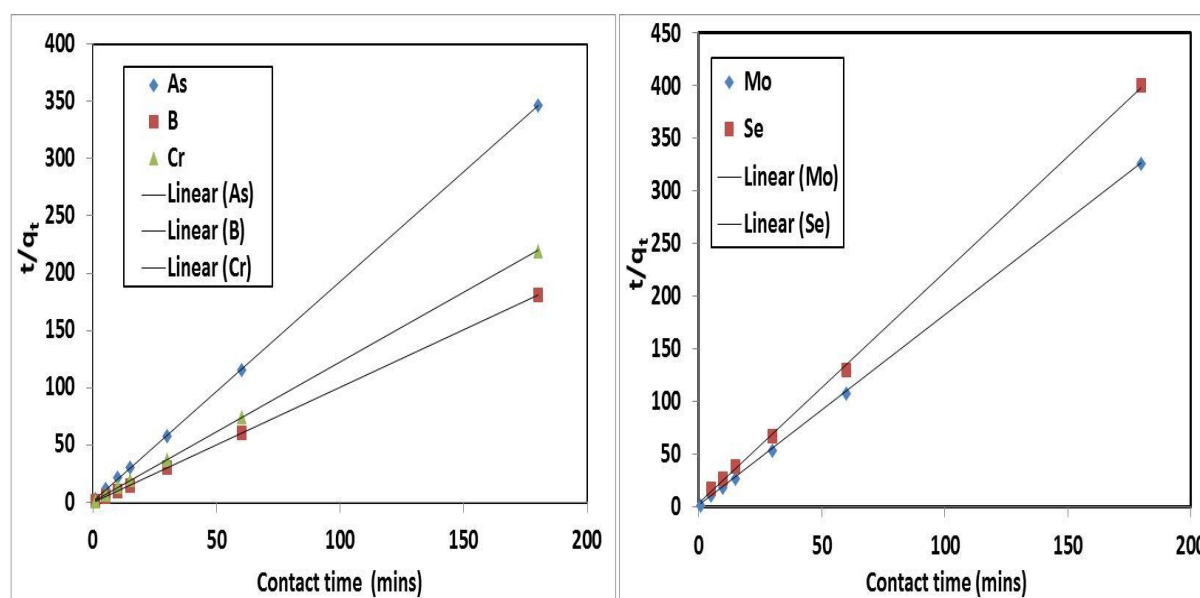

Figure 5: Pseudo-second-order plot of As, Cr, Mo, Se and B adsorption on Al^{3+}-bentonite clay

The correlation coefficients for all the oxyanion species ranged from 0.999-1 indicating a strong fit to the pseudo-second order model. The rate constants k_2 (g/mg/min) were as follows: As=0.035, Mo=0.061, Cr=3.03, Se=0.016 and B=0.076. The fact that the adsorption kinetics of the Al^{3+}-modified bentonite can be described by the pseudo second order indicates the adsorption is chemisorption.

3.7   Treatment of coal fly ash leachates under optimized conditions

Results of treatment of coal fly ash leachates using Al^{3+} modified bentonite clay at optimized conditions are presented in **Table 4**.

Table 4: Adsorption of As, B, Cr, Mo and Se from coal fly ash leachates using Al^{3+} modified bentonite clay at optimized conditions

Elements	CFA Leachates	Optimized conditions
As(µg/L)	55	8
B(µg/L)	1730	730
Cr(µg/L)	270	100
Mo(µg/L)	165	75
Se(µg/L)	170	100
Final pH	11	12

Table 4 shows the adsorption of As, B, Cr, Mo and Se from coal fly ash leachates onto Al^{3+} modified bentonite clay at optimized conditions. Al^{3+} modified bentonite clay exhibited superior adsorption of oxyanionic species from aqueous solution at optimized conditions. This was proved by the reduction in the concentration of oxyanions in the product water quality. The high pH value for CFA leachates may be attributed to high content of Ca in coal fly ash as reported in literature (Ahmaruzzaman, 2010, Gitari et al., 2013c, Masindi, 2013). Based on these results, it can be concluded that Al^{3+} modified bentonite clay is an effective adsorbent for As, B, Cr, Mo and Se from coal fly ash leachates. Similar results were obtained by Masindi et al. (2016) using Fe^{3+} modified bentonite clay. This implies that Al^{3+} modified bentonite clay can be used as a reactive barrier in ash retention ponds for removal of oxyanionic species.

3.8   Mechanisms of oxyanions removal

The initial rapid removal of the oxyanion species (Fig. 1) indicates surface bound adsorption and second slow phase due to the long range diffusion of the species onto the interior pores of the adsorbent. The fitting of the adsorption data could further point to chemical adsorption probably due to interaction with the [Al(H$_2$O)$_6$]$^{3+}$ in the interlayers and hydroxyl groups on the clay surfaces. For example selenite could interact with [Al(H$_2$O)$_3$(OH)$_3$] as follows [equation (9)]

$$Al(H_2O)_3(OH)_3 + SeO_3^{2-} \rightarrow Al(H_2O)_3(OH)(SeO_3) + 2OH^- \qquad (9)$$
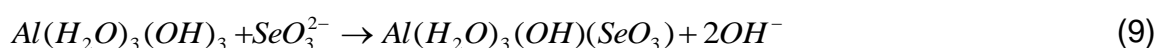
Adsorption of most of the oxyanions was observed at pH ≥ pHpzc which indicates that both electrostatic and chemical interaction occurred with the clay surface and interlayers. Chemical interaction could have occurred through monodentate or multidentate ligands with the surface hydroxyl groups. The interlayer $Al(H_2O)_6^{3+}$ could also chemically interact with the oxyanions through the OH- groups on hydrolysis [equation (9)]. Increase in the adsorption dosage was observed to increase the pH for raw bentonite clay mixtures. This was attributed to dissolution of alkaline oxides from bentonite which is a natural geological material. Increase in adsorption with adsorbent dosage (Fig. 2) pointed to similar adsorption mechanisms of the oxyanionic species in both materials. Introduction of Al^{3+} into bentonite clay interlayers was observed to increase adsorption capacity for the oxyanion species. High charge density Al^{3+} has high affinity for negatively charged species. At low pH and very low concentrations of the oxyanion species (0.1-1 mg/ℓ) both adsorbents exhibited high adsorption capacity, it is postulated that ion exchange process for bentonite clay contributed to this high capacity. At low pH the oxyanion species would be positively charged and hence can exchange with positively charged alkali metals in the interlayers. Different selectivity of the oxyanion species was observed for the two adsorbents as the pH was varied from 2-12 (Fig. 4). Al^{3+}-bentonite showed low adsorption for Mo while raw bentonite showed low adsorption for As, Mo and Cr. This indicates that apart from interaction with Al^{3+} species in the interlayers and ion exchange, another factor could have contributed to the adsorption patterns observed for both adsorbents such as the size of the oxyanions. Bhattacharyya and Gupta, (2008) and Dukic et al. (2015) reported that introduction of mono, di and tri-alkyl surfactants into Na-montmorillonite increased the interlayer spacing. Subsequently it's postulated that the introduction of hydrated Al^{3+} ions increased the interlayer spacing of the bentonite clay which allowed more of the oxyanion species to access the interlayer space of Al^{3+}-bentonite.

4   Conclusion

Bentonite clay was successfully modified by introduction of Al^{3+} in the interlayers through ion exchange. Introduction of Al^{3+} led to decrease in CEC from 262 - 265.5 meq/100 g to 186.9-183.3 meq/100 g at pH 5.4-7.4. CEC was observed to be independent of pH and that Ca^{2+}, Na^+, Mg^{2+} and K^+ were the main exchangeable cations. Modification with Al^{3+} increased the total surface area and micro-pore area.

A slight increase in pH_{PZC} of Al^{3+} modified bentonite clay (8.2) compared to raw bentonite (8.0) was observed, this would enhance adsorption of anions from aqueous media over a wider pH range. XRF showed SiO_2, Al_2O_3, Fe_2O_3 as the major chemical constituents confirming that bentonite clay is an aluminosilicate material. The adsorption affinity of the modified bentonite clay for the oxyanionic species exhibited the following order: B = Se > Mo = Cr > As. Modified bentonite clay showed greater total adsorption capacity as compared to raw bentonite. Modification of the bentonite clay with Al^{3+} increased the adsorptive sites for the oxyanionic species. The adsorption data fitted well to Freundlich adsorption isotherm than Langmuir adsorption isotherm suggestion heterogeneous surface coverage by the adsorbate species. The kinetic data fitted well to Lagergren pseudo-second order kinetic model suggesting chemisorption as the main mechanism of adsorption. The Al^{3+} modified bentonite clay successfully removed As, B, Cr, Mo and Se from generated coal fly ash leachates. The results show that Al^{3+} modified bentonite clay is a potentially effective adsorbent for removal of oxyanionic species from coal fly ash leachates and could be applied as a reactive barrier in ash retention ponds.

Acknowledgements

References

Abbott, D. E., Essington, M. E., Mullen, M. D. & Ammons, J. T. 2001. Fly ash and lime-stabilized biosolid mixtures in mine spoil reclamation: Simulated weathering. *Journal of Environmental Quality,* 30**,** 608-616.

Adriano, D. C., Page, A. L., Elseewi, A. A., Chang, A. C. & Straughan, I. 1980. Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: a review. *Journal of Environmental Quality,* 9**,** 333-344.

Ahmaruzzaman, M. 2010. A review on the utilization of fly ash. *Progress in Energy and Combustion Science,* 36**,** 327-363.

Ahmaruzzaman, M. 2011. Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Advances in Colloid and Interface Science,* 166**,** 36-59.

Akar, G., Polat, M., Galecki, G. & Ipekoglu, U. 2012. Leaching behavior of selected trace elements in coal fly ash samples from Yenikoy coal-fired power plants. *Fuel Processing Technology,* 104**,** 50-56.

Akinyemi, S. A., Akinlua, A., Gitari, W. M., Khuse, N., Eze, P., Akinyeye, R. O. & Petrik, L. F. 2012. Natural weathering in dry disposed ash dump: Insight from chemical, mineralogical and geochemical analysis of fresh and unsaturated drilled cores. *Journal of Environmental Management,* 102**,** 96-107.

Basu, M., Pande, M., Bhadoria, P. B. S. & Mahapatra, S. C. 2009. Potential fly-ash utilization in agriculture: A global review. *Progress in Natural Science,* 19**,** 1173-1186.

Bhattacharya, P., Ghosh, S. & Mukhopadhyay, A. 2013. Efficiency of combined ceramic microfiltration and biosorbent based treatment of high organic loading composite wastewater: An approach for agricultural reuse. *Journal of Environmental Chemical Engineering,* 1**,** 38-49.

Bhattacharyya, K. G. & Gupta, S. S. 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. *Advances in Colloid and Interface Science,* 140**,** 114-131.

Dukić, A. B., Kumrić, K. R., Vukelić, N. S., Dimitrijević, M. S., Baščarević, Z. D., Kurko, S. V. & Matović, L. L. 2015. Simultaneous removal of Pb2+, Cu2+, Zn2+ and Cd2+ from highly acidic solutions using mechanochemically synthesized montmorillonite-kaolinite/TiO2 composite. *Applied Clay Science,* 103**,** 20-27.

Fan, J. J. 2014a. Behavior of geosynthetic clay liners due to the migration of heavy metal. *Advanced Materials Research.*

Fan, J. J. 2014b. Effects of geomembrance on the contaminant transport in compacted clay liner system. *Advanced Materials Research.*

Gitari, W. M., Ngulube, T., Masindi, V. & Gumbo, J. R. 2013a. Defluoridation of groundwater using Fe3+-modified bentonite clay: optimization of adsorption conditions. *Desalination and Water Treatment,* 1-13.

Gitari, W. M., Ngulube, T., Masindi, V. & Gumbo, J. R. Natural clay based adsorbent for defluoridation of groundwater: Optimization of adsorption conditions. 36th

WEDC International Conference: Delivering Water, Sanitation and Hygiene Services in an Uncertain Environment, 2013b.

Gitari, W. M., Ngulube, T., Masindi, V. & Gumbo, J. R. 2015. Defluoridation of groundwater using Fe3+-modified bentonite clay: optimization of adsorption conditions. *Desalination and Water Treatment,* 53**,** 1578-1590.

Gitari, W. M., Petrik, L. F., Etchebers, O., Key, D. L. & Okujeni, C. 2008. Utilization of fly ash for treatment of coal mines wastewater: Solubility controls on major inorganic contaminants. *Fuel,* 87**,** 2450-2462.

Gitari, W. M., Petrik, L. F., Key, D. L. & Okujeni, C. 2013c. Inorganic contaminants attenuation in acid mine drainage by fly ash and its derivatives: Column experiments. *International Journal of Environment and Pollution,* 51**,** 32-56.

Gupta, G. & Torres, N. 1998. Use of fly ash in reducing toxicity of and heavy metals in wastewater effluent. *Journal of Hazardous Materials,* 57**,** 243-248.

Hassett, D. J., Pflughoeft-Hassett, D. F. & Heebink, L. V. 2005. Leaching of CCBs: observations from over 25 years of research. *Fuel,* 84**,** 1378-1383.

He, Q. & Yao, K. 2010. Microbial reduction of selenium oxyanions by Anaeromyxobacter dehalogenans. *Bioresource Technology,* 101**,** 3760-3764.

Iyer, R. 2002. The surface chemistry of leaching coal fly ash. *Journal of Hazardous Materials,* 93**,** 321-329.

Izquierdo, M. & Querol, X. 2012. Leaching behaviour of elements from coal combustion fly ash: An overview. *International Journal of Coal Geology,* 94**,** 54-66.

Jain, S. & Jayaram, R. V. 2009. Removal of fluoride from contaminated drinking water using unmodified and aluminium hydroxide impregnated blue lime stone waste. *Separation Science and Technology,* 44**,** 1436-1451.

Jiang, M.-Q., Wang, Q.-P., Jin, X.-Y. & Chen, Z.-L. 2009. Removal of Pb(II) from aqueous solution using modified and unmodified kaolinite clay. *Journal of Hazardous Materials,* 170**,** 332-339.

Kashiwa, M., Nishimoto, S., Takahashi, K., Ike, M. & Fujita, M. 2000. Factors affecting soluble selenium removal by a selenate-reducing bacterium Bacillus sp. SF-1. *Journal of Bioscience and Bioengineering,* 89**,** 528-533.

Kishor, P., Ghosh, A. K. & Kumar, D. 2010. Use of fly ash in agriculture: A way to improve soil fertility and its productivity. *Asian Journal of Agricultural Research,* 4**,** 1-14.

Lange, K., Rowe, R. K. & Jamieson, H. Attenuation of heavy metals by geosynthetic clay liners. Geosynthetics Research and Development in Progress, 2005.

Lange, K., Rowe, R. K. & Jamieson, H. 2010a. The potential role of geosynthetic clay liners in mine water treatment systems. *Geotextiles and Geomembranes,* 28**,** 199-205.

Lange, K., Rowe, R. K., Jamieson, H., Flemming, R. L. & Lanzirotti, A. 2010b. Characterization of geosynthetic clay liner bentonite using micro-analytical methods. *Applied Geochemistry,* 25**,** 1056-1069.

Lapa, N., Barbosa, R., Lopes, M. H., Mendes, B., Abelha, P., Gulyurtlu, I. & Santos Oliveira, J. 2007. Chemical and ecotoxicological characterization of ashes obtained from sewage sludge combustion in a fluidised-bed reactor. *Journal of Hazardous Materials,* 147**,** 175-183.

Lu, H. J., Luan, M. T. & Zhang, J. L. 2011. Feasibility study using improved clay as landfill liner-soil materials. *Dalian Ligong Daxue Xuebao/Journal of Dalian University of Technology,* 51**,** 719-724.

Mahlaba, J. S., Kearsley, E. P. & Kruger, R. A. 2011. Physical, chemical and mineralogical characterisation of hydraulically disposed fine coal ash from SASOL Synfuels. *Fuel,* 90**,** 2491-2500.

Mapanda, F., Nyamadzawo, G., Nyamangara, J. & Wuta, M. 2007. Effects of discharging acid-mine drainage into evaporation ponds lined with clay on chemical quality of the surrounding soil and water. *Physics and Chemistry of the Earth, Parts A/B/C,* 32**,** 1366-1375.

Masindi, V. 2013. *Adsorption of Oxyanions of As, B, Cr, Mo and Se from Coal Fly Ash Leachates Using Al3+/Fe3+ Modified Benonite Clay,* South Africa, University of Venda.

Masindi, V., Gitari, M. W., Tutu, H. & De Beer, M. 2014a. Application of magnesite-bentonite clay composite as an alternative technology for removal of arsenic from industrial effluents. *Toxicological and Environmental Chemistry,* 96**,** 1435-1451.

Masindi, V., Gitari, M. W., Tutu, H. & De Beer, M. 2014b. Application of magnesite–bentonite clay composite as an alternative technology for removal of arsenic from industrial effluents. *Toxicological & Environmental Chemistry***,** 1-17.

Masindi, V., Gitari, M. W., Tutu, H. & Debeer, M. 2015a. Efficiency of ball milled South African bentonite clay for remediation of acid mine drainage. *Journal of Water Process Engineering,* 8**,** 227-240.

Masindi, V., Gitari, M. W., Tutu, H. & Debeer, M. 2015b. Removal of boron from aqueous solution using magnesite and bentonite clay composite. *Desalination and Water Treatment,* 57**,** 8754-8764.

Masindi, V., Gitari, M. W., Tutu, H. & Debeer, M. 2015c. Synthesis of cryptocrystalline magnesite-bentonite clay composite and its application for neutralization and attenuation of inorganic contaminants in acidic and metalliferous mine drainage. *Journal of Water Process Engineering.*

Masindi, V., Gitari, W. M. & Ngulube, T. 2014c. Defluoridation of drinking water using Al3+-modified bentonite clay: optimization of fluoride adsorption conditions. *Toxicological & Environmental Chemistry***,** 1-16.

Masindi, V., Gitari, W. M. & Tutu, H. 2016. Adsorption of As, B, Cr, Mo and Se from coal fly ash leachate by Fe3+ modified bentonite clay. *Journal of Water Reuse and Desalination***,** 382 - 391.

Mohapatra, M., Anand, S., Mishra, B. K., Giles, D. E. & Singh, P. 2009. Review of fluoride removal from drinking water. *Journal of Environmental Management,* 91**,** 67-77.

Muriithi, G. N., Petrik, L. F. & Doucet, F. J. 2014. Remediation of industrial brine using coal-combustion fly ash and Co2. *Desalination,* 353**,** 30-38.

Muriithi, G. N., Petrik, L. F., Fatoba, O., Gitari, W. M., Doucet, F. J., Nel, J., Nyale, S. M. & Chuks, P. E. 2013. Comparison of CO2 capture by ex-situ accelerated carbonation and in in-situ naturally weathered coal fly ash. *Journal of Environmental Management,* 127**,** 212-220.

Musso, T. B., Parolo, M. E., Pettinari, G. & Francisca, F. M. 2014. Cu(II) and Zn(II) adsorption capacity of three different clay liner materials. *Journal of Environmental Management,* 146**,** 50-58.

Neupane, G. & Donahoe, R. J. 2013. Leachability of elements in alkaline and acidic coal fly ash samples during batch and column leaching tests. *Fuel,* 104**,** 758-770.

Praharaj, T., Powell, M. A., Hart, B. R. & Tripathy, S. 2002a. Leachability of elements from sub-bituminous coal fly ash from India. *Environment International,* 27**,** 609-615.

Praharaj, T., Swain, S. P., Powell, M. A., Hart, B. R. & Tripathy, S. 2002b. Delineation of groundwater contamination around an ash pond: Geochemical and GIS approach. *Environment International,* 27**,** 631-638.

Prasad, B. & Mondal, K. K. R. 2009. Environmental impact of manganese due to its leaching from coal fly ash. *Journal of Environmental Science and Engineering,* 51**,** 27-32.

Puranen, A., Jansson, M. & Jonsson, M. 2010. A study on the immobilization of selenium oxyanions by H2/Pd(s) in aqueous solution: Confirmation of the one-electron reduction barrier of selenate. *Journal of Contaminant Hydrology,* 116**,** 16-23.

Reardon, E. J., Czank, C. A., Warren, C. J., Dayal, R. & Johnston, H. M. 1995. Determining controls on element concentrations in fly ash leachate. *Waste Management & Research,* 13**,** 435-450.

Reinik, J., Irha, N., Steinnes, E., Urb, G., Jefimova, J. & Piirisalu, E. 2014. Release of 22 elements from bottom and fly ash samples of oil shale fueled PF and CFB boilers by a two-cycle standard leaching test. *Fuel Processing Technology,* 124**,** 147-154.

Ríos, C. A., Williams, C. D. & Roberts, C. L. 2008. Removal of heavy metals from acid mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites. *Journal of Hazardous Materials,* 156**,** 23-35.

Seshadri, B., Bolan, N. S., Naidu, R., Wang, H. & Sajwan, K. 2013. Chapter Six - Clean Coal Technology Combustion Products: Properties, Agricultural and Environmental Applications, and Risk Management. *In:* DONALD, L. S. (ed.) *Advances in Agronomy.* Academic Press**,** 309-370.

Sherly, R. & Kumar, S. 2011. Valuable products from fly ash - A review. *Journal of Industrial Pollution Control,* 27**,** 113-120.

Somerset, V., Klink, M., Petrik, L. & Iwuoha, E. 2011. Neutralisation of acid mine drainage with fly ash in South Africa. *Mine Drainage and Related Problems.* 211-226.

Steenari, B. M., Schelander, S. & Lindqvist, O. 1999. Chemical and leaching characteristics of ash from combustion of coal, peat and wood in a 12 MW CFB – a comparative study. *Fuel,* 78**,** 249-258.

Tajer Mohammad Ghazvini, P. & Ghorbanzadeh Mashkani, S. 2009. Screening of bacterial cells for biosorption of oxyanions: Application of micro-PIXE for measurement of biosorption. *Hydrometallurgy,* 96**,** 246-252.

Tsiridis, V., Petala, M., Samaras, P., Kungolos, A. & Sakellaropoulos, G. P. 2012. Environmental hazard assessment of coal fly ashes using leaching and ecotoxicity tests. *Ecotoxicology and Environmental Safety,* 84**,** 212-220.

Vadapalli, V. R. K., Gitari, M. W., Petrik, L. F., Etchebers, O. & Ellendt, A. 2012. Integrated acid mine drainage management using fly ash. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering,* 47**,** 60-69.

Vadapalli, V. R. K., Gitari, W. M., Ellendt, A., Petrik, L. F. & Balfour, G. 2010. Synthesis of Zeolite-P from coal fly ash derivative and its utilisation in mine-water remediation. *South African Journal of Science,* 106.

Visa, M. & Chelaru, A.-M. 2014. Hydrothermally modified fly ash for heavy metals and dyes removal in advanced wastewater treatment. *Applied Surface Science,* 303**,** 14-22.

Vítková, M., Ettler, V., Šebek, O., Mihaljevič, M., Grygar, T. & Rohovec, J. 2009. The pH-dependent leaching of inorganic contaminants from secondary lead smelter fly ash. *Journal of Hazardous Materials,* 167**,** 427-433.

Vítková, M., Hyks, J., Ettler, V. & Astrup, T. 2013. Stability and leaching of cobalt smelter fly ash. *Applied Geochemistry,* 29**,** 117-125.

Wang, S. & Viraraghavan, T. 1998. Wastewater sludge conditioning by fly ash. *Waste Management,* 17**,** 443-450.

Wang, S., Zhang, C. & Chen, J. 2014. Utilization of Coal Fly Ash for the Production of Glass-ceramics With Unique Performances: A Brief Review. *Journal of Materials Science and Technology,* 30**,** 1208-1212.

Wang, Y. R., Tsang, D. C. W., Olds, W. E. & Weber, P. A. 2013. Utilizing acid mine drainage sludge and coal fly ash for phosphate removal from dairy wastewater. *Environmental Technology (United Kingdom),* 34**,** 3177-3182.

Xie, J., Wang, Z., Wu, D. & Kong, H. 2014. Synthesis and properties of zeolite/hydrated iron oxide composite from coal fly ash as efficient adsorbent to simultaneously retain cationic and anionic pollutants from water. *Fuel,* 116**,** 71-76.

Yang, Q., Zhang, J., Yang, Q., Yu, Y. & Yang, G. 2012. Behavior and mechanism of Cd(II) adsorption on loess-modified clay liner. *Desalination and Water Treatment,* 39**,** 10-20.

Yao, Z. T., Ji, X. S., Sarker, P. K., Tang, J. H., Ge, L. Q., Xia, M. S. & Xi, Y. Q. 2015. A comprehensive review on the applications of coal fly ash. *Earth-Science Reviews,* 141**,** 105-121.

Yunusa, I. a. M., Loganathan, P., Nissanka, S. P., Manoharan, V., Burchett, M. D., Skilbeck, C. G. & Eamus, D. 2014. Application of coal fly ash in agriculture: A strategic perspective. *Critical Reviews in Environmental Science and Technology,* 42**,** 559-600.

Zevenbergen, C., Bradley, J. P., Shyam, A. K., Jenner, H. A. & Platenburg, R. J. P. M. 2000. Sustainable ash pond development in India -a resource for forestry and agriculture. *In:* G.R. WOOLLEY, J. J. J. M. G. & WAINWRIGHT, P. J. (eds.) *Waste Management Series.* Elsevier**,** 533-540.

Zevenbergen, C., Bradley, J. P., Van Reeuwijk, L. P., Shyam, A. K., Hjelmar, O. & Comans, R. N. J. 1999. Clay formation and metal fixation during weathering of coal fly ash. *Environmental Science and Technology,* 33**,** 3405-3409.

Zhang, M., Zhang, H., Xu, D., Han, L., Zhang, J., Zhang, L., Wu, W. & Tian, B. 2011. Removal of phosphate from aqueous solution using zeolite synthesized from fly ash by alkaline fusion followed by hydrothermal treatment. *Separation Science and Technology,* 46**,** 2260-2274.

Zheng, L., Wang, C., Wang, W., Shi, Y. & Gao, X. 2011. Immobilization of MSWI fly ash through geopolymerization: Effects of water-wash. *Waste Management,* 31**,** 311-317.