

UNIVERSITY OF VENDA



Adsorption of oxyanions of As, B, Cr, Mo and Se from coal fly ash leachates using Al^{3+}/Fe^{3+} modified bentonite clay

A Masters research submitted to the University of Venda, School of Environmental Sciences, Department of Ecology and Resource Management

By

Masindi Vhahangwele

Student No: 11572071

Signature

Masindi Vhahangwele Date *05/08/2013*

Supervisor

: Dr Wilson Mugerá Gitari (University of Venda)

Signature

Wilson Mugerá Gitari Date *05/08/2013*

Co-supervisor

: Dr Hlanganani Tutu (University of Witwatersrand)

Signature

Hlanganani Tutu Date *05/08/2013*

ABSTRACT

South African coal-fired power stations rely on the use of low grade bituminous coal for electricity generation. During coal combustion processes, this type of coal generates large volumes of waste materials which include Fly ash, bottom ash, boilers slag, flue gas desulphurization and un-captured particles. From the array of generated residues, coal fly ash constitute 90% and of this only 5% is beneficially used with the rest being disposed-off to land as ash dumps or slurried to ash retention ponds. On disposal, coal fly ash leaches out toxic chemical species on contact with the aqueous media hence posing hazardous effects to the aquatic and terrestrial environment. Of prime concern are Oxyanionic species such as As, B, Cr, Mo and Se. This study aims to investigate the adsorption of As, B, Cr, Mo and Se from coal fly ash leachates on Al^{3+}/Fe^{3+} modified bentonite clay.

Coal fly ash samples used in this study were collected from Tutuka, ESKOM power plant in Mpumalanga and Bentonite clay samples were collected from ECCA (pty) Ltd. pH, Electrical Conductivity (EC) and Total Dissolved Solids (TDS) of the samples were determined using a CRISON multimeter probe. Modifications of bentonite clay with Al^{3+} and Fe^{3+} cations were done in batch procedures and the parameters optimized included contact time, adsorbent dose and adsorbate concentration. Cation Exchange Capacity (CEC), Point of Zero Charge (pH_{pzc}) and Water Holding Capacity (WHC) of raw and modified bentonite clay were determined using standard methods. Surface areas of raw and modified bentonite clays were determined by BET. Elemental composition of raw and modified bentonite clay was determined by XRF and Mineralogical composition of raw and modified bentonite clay was determined by XRD. AAS and GFAAS were used to monitor Al^{3+} and Fe^{3+} concentration in the reaction mixture during and after modification while As, B, Cr, Mo, and Se were monitored using GFAAS, ICP- OES and ICP- MS. Adsorption of oxyanions of As, B, Cr, Mo and Se was carried out in batch experiments using synthetic solutions of the species. Effects of contact time, adsorbent dosage, adsorbate concentration and pH on the adsorption of As, B, Cr, Mo and Se were evaluated and optimized.

The modification experiments revealed that loading of Al^{3+} onto bentonite clay interlayers is optimum at 60 minutes of contact time, 3 grams of adsorbent and 100 mg/L of adsorbate concentration and loading of Fe^{3+} onto bentonite clay matrices is optimum at 15 minutes of contact time, 2 grams of adsorbent and 100 mg/L of adsorbate. The CEC results showed 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 which decreased to 186.9 meq/100g at pH 5.4 and 183.3 meq/100g at pH 7.4 on introducing Al^{3+} onto bentonite clay interlayers and 195.5 meq/100g at pH 5.4 and 188.9 meq/100g at pH 7.4 on introducing Fe^{3+} onto bentonite clay interlayers. The results show that CEC is independent of pH. BET results indicated that the loading of Al^{3+} onto bentonite clay interlayers increased the surface area from 16 m^2/g to 44.3 m^2/g and 50 m^2/g for Fe^{3+} , external surface area from 11.1 m^2/g to 33.1 m^2/g for Al^{3+} and 37.4 m^2/g for Fe^{3+} , micro-pore area from 4.9 m^2/g to 11.2 m^2/g for Al^{3+} and 12.5 m^2/g for Fe^{3+} . There was a slight difference in pH_{PZC} of Al^{3+} modified bentonite clay (8.2) as compared to raw bentonite (8.0). For Fe^{3+} modified bentonite clay, the pH_{PZC} was observed to increase from 8.0 for raw bentonite clay to 9.0. An increase in pH_{PZC} shows that modification will favour adsorption of anions from aqueous media. WHC of bentonite clay was determined to be 42.7%. Elemental composition by XRF showed SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , Na_2O , K_2O and MgO as the major chemical species. XRF results also confirmed that bentonite clay is an aluminosilicate material. XRD disclosed that bentonite clay is dominated by montmorillonite as the major mineral phase. Characterization of fly ash leachates revealed that coal fly ash leachates contains 53 $\mu\text{g}/\text{L}$ of As, 1730 $\mu\text{g}/\text{L}$ of B, 271 $\mu\text{g}/\text{L}$ of Cr, 165 $\mu\text{g}/\text{L}$ of Mo and 170 $\mu\text{g}/\text{L}$ of Se. Adsorption of As, B, Cr, Mo and Se onto Al^{3+} modified bentonite clay revealed that 30 minutes of contact time, 4 grams of adsorbent dosage, 10 mg/L of adsorbate concentration and pH 10 are the optimum conditions for removing those species from aqueous media. The adsorption affinity of those species obeyed the following order: $\text{B} = \text{Se} > \text{Mo} = \text{Cr} > \text{As}$. Adsorption of As, B, Cr, Mo and Se onto Fe^{3+} modified bentonite clay revealed that 30 minutes of contact time, 4 grams of adsorbent dosage, 10 mg/L of adsorbate concentration and pH 10 are the optimum conditions for removing those species from aqueous media. The adsorption affinity of those species obeyed the following order: $\text{B} = \text{Se} > \text{Mo} > \text{Cr} = \text{As}$. The adsorption capacities of modified bentonite clays were greater than the adsorption capacities of raw bentonite clay. The data fitted well to both Langmuir and Freundlich adsorption isotherm hence showing that the adsorption is energetically favourable. The unmodified clay

showed poor adsorption for these chemical species. Both Al^{3+} and Fe^{3+} modified bentonite clay 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 Al^{3+} or Fe^{3+} modified bentonite clay 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 reactive barrier or liner in ash retention ponds.

Keywords: *Bentonite Clay, Coal Fly Ash Leachates, Batch Procedures, Adsorption, Oxyanions, Langmuir and Freundlich Isotherms*