OPTIMISATION OF COPPER AND ZINC IONS REMOVAL FROM AQUEOUS SOLUTION BY COAL FLY ASH AS AN ADSORBENT

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Abstract

Rapid urbanization and industrialization of our world has led to accumulation of enormous number of contaminants in our environment. Heavy metal ions hold a superlative position in that list and are responsible for contaminating soil, air and water in many parts of the world. Adsorption technology is emerging as a sustainable effective solution. The possibility of using Coal fly ash as an alternative adsorbent for divalent metal ions (Zn^{2+}, Cu^{2+}) removal from simulated solutions was studied. The coal fly ash was characterised by Brunauer Emmet Teller (BET), X-ray diffraction (XRD), X-ray Fluorescence Spectroscopy (XRF) and Fourier transform infrared (FT-IR). Optimum adsorption conditions were determined as a function of pH, adsorbent dosage and contact time for Zn^{2+} and Cu^{2+} removal. The adsorption of metal ions was found to be pH dependant. Equilibrium data fitted well to the Freundlich model with R^2 values as 0.9932, 0.9971 for Cu^{2+}, Zn^{2+}, respectively. The study showed that disposed coal fly ash could be used as an efficient adsorbent material for the removal of metal ions from aqueous solution.

Keywords: Biosorption, Coal fly ash, equilibrium isotherms, FT-IR, XRD, XRF

1. Introduction

In recent years, extensive attention has been paid on the management of environment pollution caused by hazardous material, such as heavy metal ions. Presence of heavy metal ions even in trace levels is toxic and detrimental to both flora and fauna. Aqueous industrial effluents containing large amounts of heavy metal ions are being discharged into the environment, by either indirectly or directly, from operations such as mining operations, municipal solid waste, waste oil, metal plating facilities and tanneries[1- 4]. As a result, various studies have been conducted for the removal of heavy metal ions before being discharged to receiving sink.
The treatment of this type of wastewater involves recuperative techniques such as solvent extraction, adsorption, filtration, precipitation, ion exchange, biological treatment and destructive techniques such as ozonation and oxidation [5- 9]. Adsorption technology using activated carbon is currently being used extensively for the removal of hazardous pollutants from gaseous and liquid phases. The main disadvantages associated with this adsorbent are the high regeneration cost, intraparticle resistance in adsorption process and poor mechanical strength [10]. Recently, adsorption has attracted considerable interest especially from low-cost materials such as moss [11] modified corn cobs [12], rice husk [13], crabs shell particles [14] and maize tassel [15].
Coal fly ash, is obtained from the combustion of powdered coal as waste product. In this regard coal fly ash is a very attractive alternative because it is cheap, widely available and has been reported to have good mechanical stability [16]. South African coal fly ash [4, 17] and Turkish fly ash [18] have been used for the removal of

phosphates from wastewater, for treatment of acid mine drainage and removal of heavy metal ions. This material requires little processing to increase its sorption capacity. Potgieter et al [16] reported that the nature of fly ash is influenced by amongst others, the origin of the coal and burning condition under which it is was formed.

In this study, we report the investigation on the feasibility of Zimbabwean coal fly ash to remove heavy metal ions (Zn^{2+}, Cu^{2+}) from water, modelling the adsorption process of heavy metal ions and investigation of the interactive effects of process parameters such as adsorbent dose, contact time, solution pH, and initial concentration on the adsorption capacity of coal fly ash towards the metal ions. In addition, the effectiveness of this fly ash is compared with results obtained with commercial activated carbon and coal fly ash from other countries.

2.0 MATERIALS AND METHODS:

2.1 Preparation of adsorbent

The coal fly ash was collected from dumping sites of a local coal power company. The fly ash samples were dried at 105 °C for 2 h before tests. The fly ash samples were ground and sieved to a particle size of between 50-150 µm and used without any pre-treatment.

2.2 Characterisation of adsorbent

The pH value of coal fly ash was determined according to a reported procedure [3]. The loss on ignition (LOI) was determined by heating a pre-weighed sample (left at 105°C in an oven and then cooled in desiccators) for 600°C over a period of 2 hours [18]. The specific surface area of the coal fly ash was determined by the Brunauer Emmet Teller (BET) method. The surface charge was determined by electrophoretic measurements using a zeta-meter (ZM-77 manufactured by Zeta-Meter, USA). X-ray diffraction (XRD) studies were carried out using an X-ray diffractometer (D8 Bruker) with Cu K_{α} radiation at 40 kV and 40 mA. The X-ray pattern was recorded from 10°-70°. Major element concentration within the coal fly ash was determined by X-ray Fluorescence Spectroscopy (XRF). Fourier transform infrared (FT-IR) spectrum to determine the type of functional groups on the coal fly ash before and after absorption was recorded on a PerkinElmer GX2000 FT-IR spectrometer (JEOL, Tokyo, Japan). Samples for FT-IR were prepared by diluting the adsorbent to 5% in KBr and cast in disks for analysis.

2.3 Sorption experiments:

(i) Effect of pH:
The effect of pH on the amount of heavy metal ions removal was analysed over the pH range from 2 to 8. In this study, 100 ml of heavy metal ion solutions with concentration 100 mg L^{-1} were transferred into stopper conical flasks and agitated for 2 hrs at 250 rpm with 0.4 g of coal fly ash using an incubator with a shaking platform at room temperature (27 ± 2^{0}C). The samples were centrifuged and the left out concentration in the supernatant solution after filtration were analysed using a Varian 140 Atomic Absorption Spectrometer (Varian Techtron Pty Ltd., Springvale, Australia).

(ii) Effect of adsorbent dosage:
The effect of coal fly ash mass on the amount of heavy metal ions removed in solution was obtained by contacting 100 ml of heavy metal ions in solution of initial concentration of 100 mg L^{-1} with different masses of coal fly ash ranging from 0.2 g to 2.5 g. Each sample was then agitated for 2 hours at 250 rpm. The samples were then centrifuged and the concentrations were then analysed as before.

(iii) Effect of contact time:
For optimisation of contact time required for the sorptive separation of heavy metals ions on the coal fly ash surface from aqueous solutions, 0.5 g of the adsorbent was equilibrated with 100 ml test solutions containing metal ions at the concentration of 100 mg L^{-1} for contact time in the range from 0-200 minutes.

(iv) Adsorption Equilibrium:
Equilibrium studies were carried out by contacting 0.5 g of coal fly ash powder with 100 ml of heavy metal ions solution of different initial concentrations in the range of 10 to 160 mg L^{-1} in 250 ml stopper conical flasks. The samples were then shaken at 250 rpm for 5 hours. The sorption capacity of the coal fly ash was determined from the concentration difference of the solution, at the beginning and at equilibrium:

$$q_e = \frac{V(C_o - C_e)}{W}$$

(1)

where C_o and C_e are the initial and the equilibrium solution concentrations (mg dm^{-3}), V is the volume of solution (cm^3), and W is the mass of coal fly ash used (g).

Percent removal was also evaluated using the formula:

$$Removal\ (\%) = \frac{C_o - C_e}{C_o} X100$$

(2)

3.0 RESULTS AND DISCUSSION:

3.1 Characterization of the biosorbent:

(i) Physicochemical properties:

Physicochemical characterisation of the coal fly ash was done (Table 1). The N_2 adsorption gave the specific surface area (S_{BET}) of 1.24 m^2/g. The value obtained for the Zimbabwean coal fly ash was lower than the South African fly ash values, 2.5-19.0 m^2/g [20], 1.73 m^2/g [4] and was higher than the Turkish fly ashes values of 0.342 and 0.115 m^2/g [18]. The carbon concentration determination by loss on ignition was found to be less than 5% for the fly ash.

Table 1 Physical characteristics of coal fly ash

Property	Values
pH	8.20
LOI (%)	4.50
pH$_{zpc}$	6.0
Specific surface area (m^2/g)	1.24
Bulk density(g/cm^3)	1.75
Specific gravity(g/cm^3)	2.10

zpc: zero point charge

(ii) Chemical composition:

The chemical composition of the Zimbabwean coal fly ash was determined using an X-ray fluorescence spectrometer. Table 2 shows the results of the chemical analysis of the test sample. More than half of the coal fly ash's composition is made up of Al_2O_3, SiO_2, and Fe_2O_3.

Table 2 Chemical analysis of the sample (XRF)

Compound	Composition, wt %
Al_2O_3	24.67
BaO	0.14
CaO	1.19
Cr_2O_3	0.03
Fe_2O_3	4.84
K_2O	0.74
MgO	0.22
Na_2O	0.11
B_2O_5	0.05
SiO_2	37.81
TiO_2	1.80

The identification of the mineralogical constituents and phase properties of coal fly ash was conducted by X-Ray diffractometer (XRD) and is illustrated in Figure 1 below. It can be observed from Figure 1 that the fly ash consists mostly of mullite ($Al_6Si_2O_{13}$), quartz (SiO_2), a small amount of haematite (Fe_2O_3) and calcium oxide (CaO) with large characteristic peaks of quartz. The coal fly is therefore alkaline and can neutralise wastewater and adsorb heavy metals.

(iii) FT-IR analysis:

The FT-IR technique is an important tool to identify the characteristic functional groups on the adsorbent surface. The FT-IR spectra of the coal fly ash before and after adsorption of the heavy metal ions from simulated solutions are shown in Figures 2 to 4. The FT-IR spectrum of coal fly ash before adsorption show small absorption peaks at 3400 and3580 cm^{-1} and indicates the presence of the hydroxyl groups on the fly ash [20]. A small sharp medium peak at 1610 cm^{-1} could be associated with C=O or –CH$_3$. A broad peak at 1100 cm^{-1} corresponds to X-O (X= Si, Al). A small peak at 875cm^{-1} could be associated to the presence of Al atoms in the tetrahedral forms of silica framework [21]. The peaks at 780-790 cm^{-1} are indicative of quartz and bands at 694 and 515 cm^{-1} could be assigned to quartz as crystal phase in the coal fly ash. The small absorption peaks at 3400 and 3580 cm^{-1} disappeared forming one broad band for both metals with a lower intensity (Figures 3 and 4).

Mohan and Gandhimathi [3] attributed this to solubility calcium content and (SiO_2 and Al_2O_3 +Fe_2O_3) content of fly ash and hence the percentage transmittance of the possible hydroxyl groups was decreased. The disappearance of some peaks at 3400 cm^{-1},3580 cm^{-1}, 1600cm^{-1}and 11390cm^{-1} indicates that functional groups were involved in adsorption process.
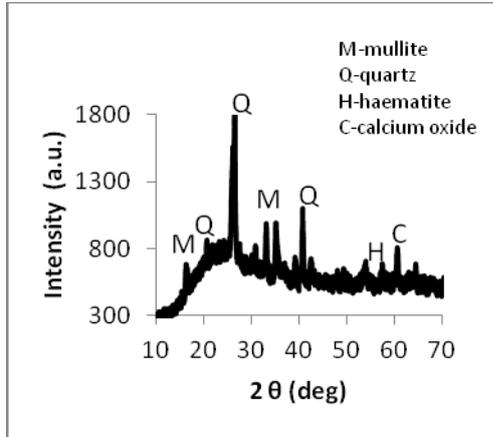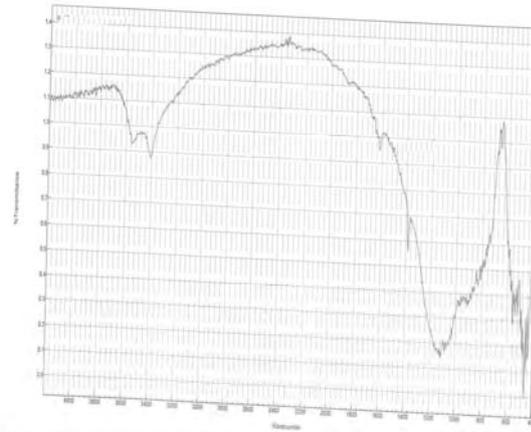

Fig. 1 XRD spectrum of unused coal fly ash
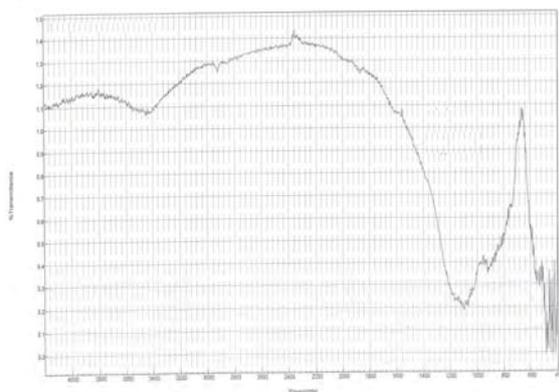

Fig 2 FT-IR spectrum of unused coal fly ash.

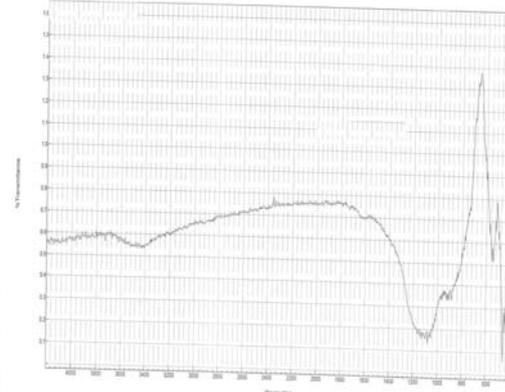Fig. 3. FT-IR spectrum of coal fly ash after biosorption of copper.

Fig. 4. FT-IR spectrum of coal fly ash after biosorption of zinc.

## 3.2 Sorption studies:

(i) Effect of pH:

The biosorption capacity is influenced most by the pH of the solution. The pH of the solution affects the surface charge of the adsorbent, degree of ionisation and speciation of the adsorbate species, which may lead to change in kinetics and equilibrium characteristics of the adsorption process [4]. Figure 5 shows the effect of pH on the adsorption of coal fly ash within the range 2-8 and the maximum pH of 8 was chosen to avoid precipitation of metal ions [18].
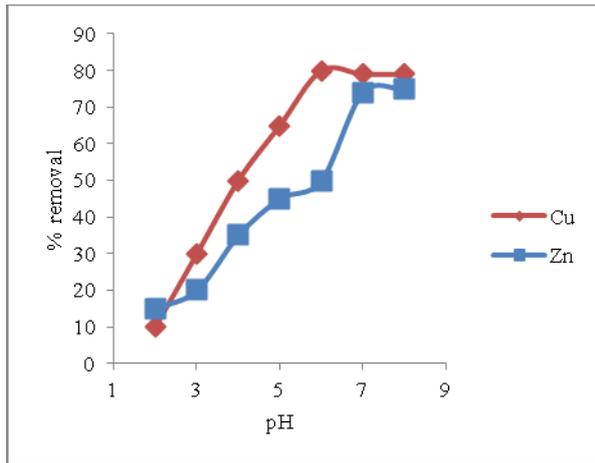
Fig.5. Effect of pH on Cu^{2+} and Zn^{2+}.

Generally, below pH 2 a positive counter ion layer on the surface of coal fly ash develops and the complexes $[Zn(OH)_4]^{2-}$ and $[Cu(OH)_4]^{2-}$, are formed which will be adsorbed on the surface[22]. Hydroxyl-metal complexes have higher affinity for adsorption than hydrated metal ions because the formation of the hydroxyl group of the metal ion reduces the free energy required for adsorption. The amount of Cu^{2+} and Zn^{2+} ions absorbed increased as pH is increased from pH 2. The total number of negative groups available for binding of metal ions increased and therefore competition between proton and metal ion becomes less pronounced [23]. Coal fly ash possessed optimum sorption capacity for both copper and zinc ions at pH 6 and 8 respectively. The functional oxidised groups as revealed by XRF on surface of coal fly ash exists as SiO_2, Al_2O_3 and Fe_2O_3 and thus the synergistic effect of these oxidised groups may affect the adsorption of copper and zinc ions. Mohan and Gandhimathi [3] reported that the oxygen atoms on the surface of silica are free to react with water which will eventually lead to the formation of surface silanol (SiOH) groups. As a result the surface of silica is positively charged at low pH and negatively at high pH.

(ii) Effect of adsorbent dosage:

This parameter determines the capacity of adsorbent for a given heavy metal ion concentration and adsorbate-adsorbent equilibrium of the system. As shown in Figure 6, the percentage removal of both metals increases when the adsorbent dose is increased from 0.2 to 2.5 g. The critical value of dosage of coal fly ash obtained from the graph was 0.4 g and 0.6 g for zinc and copper respectively. Increasing the amount of coal fly ash increases the availability of active sites of the adsorbent, hence adsorption percentage and efficiency also increased.
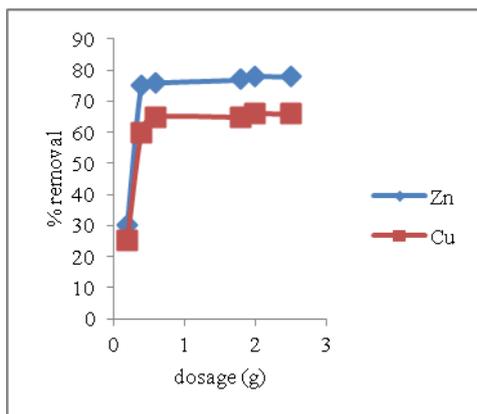
Fig.6. Effect of adsorbent dosage on Cu^{2+} and Zn^{2+}.
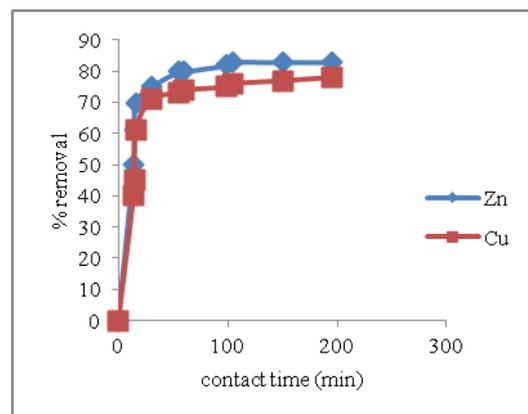
Fig. 7. Effect of contact time on Cu^{2+} and Zn^{2+}.

(iii) Effect of contact time:

The effect of agitation time is one of the important factors when considering batch sorption systems. This is important since it gives insight into a sorption process, provides information on the minimum time required for considerable adsorption to take place and the possible diffusion control mechanism between the metal ion as it moves from the bulk solution towards the adsorbent surface [24]. As shown in Figure 7 above, the optimum contact time was for copper and zinc removal were determined at 60 minutes and 55 minutes respectively.

(iv) Adsorption isotherms:

There are several models that have been reported in literature to show equilibrium relationships between sorbent and sorbate. The Langmuir and Freundlich models are the most frequently employed models. The linear form of the Langmuir isotherm model can be represented by the relation:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ} \cdot \frac{1}{C_e} \qquad (3)$$

where, q_e is the amount adsorbed at equilibrium (mg g^{-1}), Q (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants related to the maximum adsorption and energy of adsorption respectively. The linear form of the Freundlich isotherm is given by the relation:

$$Log(q_e) = Log(k) + \frac{1}{n} Log(C_e) \qquad (4)$$

where, q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg l^{-1}), k and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity respectively of the adsorbent.

The equilibrium studies carried out in the metal ion concentration range of 10mg to 160mg/L (Figure 8) for both metal ions (Zn^{2+}, Cu^{2+}) were tested to fit Langmuir and Freundlich isotherms. The obtained experimental data could not fit the Langmuir isotherm well (data not shown). Freundlich isotherm constants (Zn^{2+}, Cu^{2+}) were determined from the plot of log q_e versus log C_e (Figure 9).and are summarized in Table 3. Figure 9 shows Freundlich isotherm fit well for Zn^{2+}and Cu^{2+}. The n values of both metals were observed to be very close to the value of 1, thus indicating that the adsorption is favourable.
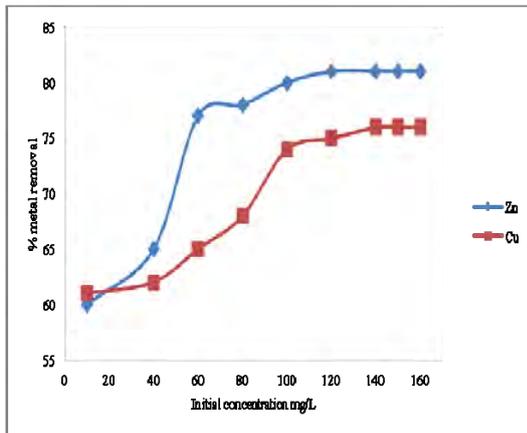

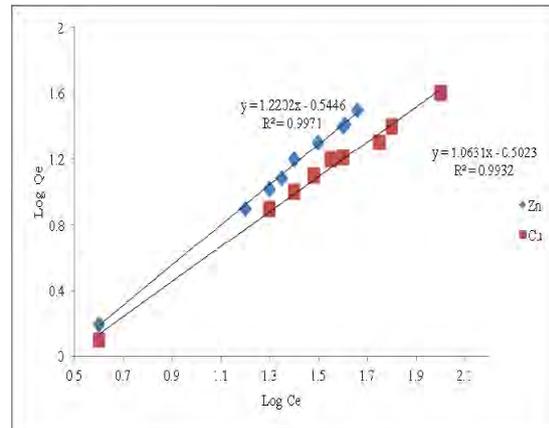Fig. 8. Effect of initial concentration of Cu^{2+} and Zn^{2+} Fig 9 Freundlich isotherm for copper and zinc

Table 3 Isotherm Equilibrium Summarization

Metal	Freundlich constants		
	n	k	R^2
Cu^{2+}	0.9407	0.3581	0.9932
Zn^{2+}	0.8195	0.3146	0.9971

(v) Application of coal fly ash to industrial wastewater treatment:

The application of coal fly ash as an adsorbent was assessed by its application in treatment of mining waste water. The mining waste water was collected from mine dumps and results (not shown here) revealed that the removal efficiency of metal ions in mining waste water was not significantly different from results of simulated solutions. Thus the present study shows that Zimbabwean coal fly ash can be used in the removal of Cu^{2+} and Zn^{2+}ions from mining waste water.

4. CONCLUSION:

Batch studies show that coal fly ash can be a promising low cost biosorbent in removal of Cu^{2+} and Zn^{2+}ions from aqueous solutions. Characterisation of the coal fly ash was done by BET, XRF, XRD and FTIR. The adsorption of Cu^{2+}and Zn^{2+} ions by coal fly ash is a function of contact time, adsorbent dosage and pH. The adsorption isotherm studies showed that the Freundlich isotherm model fits well with R^2 values as 0.9932, 0.9971 for Cu^{2+}, Zn^{2+}, respectively. The study recommends that Zimbabwean coal fly ash can be exploited as an alternative adsorbent for chosen metal ions from waste water.

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REFERENCES

[1] R.J. Slacka, J.R. Gronowb and N. Voulvoulisa, Household hazardous waste in municipal landfills: contaminants in leachate, Science of the Total Environment, 2005, 337, 119-137.
[2] B.M.P.K. Amarasinghe and R.A.Williams, Tea waste as a low adsorbent for the removal of Cu and Pb from wastewater, Chem. Eng., 2007, 132, 299-309.
[3] S. Mohan and R. Gandhimaki, Removal of heavy metal ions from municipal solid waste leachate using coal fly ash as an adsorbent, Journal of Harzadous Materials, 2009, 169, 351-359.
[4] E.T. Musapatika, M.S. Onyango, and O. Aoyi, Cobalt (II) removal from synthetic wastewater by adsorption on South African coal fly ash, South African Journal of Science, 2010, 106, 9-10.
[5] K.C. Sekhar, S. Subramanian, J.M. Modak and K.A. Natarajan, Removal of metal ions using an industrial biomass with reference to environmental control, International Journal of Mineral Processing, 1998, 53, 107-120.
[6] H. Kim, K. Baek, J. Lee, J. Iqbal and J. Yang, Comparison of separation methods of heavy metal from surfactant micellar solutions for the recovery of surfactant, Desalination, 2006, 191, 186-192.
[7] V. Mavrov, S. Stamenov, E. Todorova, H. Chmiel, and T. Erwe, Removal of nickel ions from wastewater by Mg (OH)2/MgO nanostructures embedded in Al2O3 membranes, Alloys Compd., 2006, 426, 281-285.
[8] A.S. Murathan and M. Butun, Removal of lead ions from dilute aqueous solution in packed columns by using natural fruit shells through adsorption, Fres.Environ. Bull., 2006, 15(12a), 1491-1498.
[9] S.A. Covaco, S. Fernandes, M.M. Quina and L.M. Ferreira, Removal of chromium from electroplating industry by ion exchange resins, Journal of Hazardous Materials, 2007, 144, 634-638.
[10] R. Aravindhan, J.R. Rao, and B.U. Nair, Application of a chemically modified green macro alga as a biosorbent for phenol removal, Environ. Manag., 2006, 90(5), 1877-83.
[11] K.S. Low and C.K. Lee, Cadmium uptake by moss Calymperes delessertii, Bioresource Technology, 1991, 38, 1-6.
[12] T. Vaughan, C.W. Seo and W.E. Marshall, Removal of selected metal ions from aqueous solution using modified corncobs, Bioresource Technology, 2001, 133-139.
[13] K.K. Wong, C.K. Lee, K.S. Low and M.J. Haron, Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions, Chemospheres, 2003, 50, 23-28.
[14] K. Vijayaraghavan, K. Palanivelu and M. Velan, Biosorption of Cu (II) and Cobalt (II) from aqueous solution by crabs shell particles, Bioresource Technology, 2006, 97, 1411-1419.
[15] C.M. Zvinowanda, O.J. Okonkwo, M.M. Sekhula, N.M. Agyei, and R. Sadiku, Application of maize tassel for the removal of Pb, Se, Sr, U and V from borehole water contaminated with mine wastewater in the presence of alkaline metals, Journal of Harzadous Materials, 2009, 164, 884-891.
[16] J.H. Potgiester, S.O. Bada and S.S. Potgiester-Vermaak, Adsorptive removal of various phenols from water by South African coal fly ash, Water South Africa, 2009, 35, 89-96.
[17] J.H. Potgiester and S.S. Potgiester-Vermaak, A comparison of the adsorption of heavy metal ions from multicomponent solutions onto industrial clay and fly ash, Proc. Int. Conf. Coal Ash 2-4 October 2006, Pretoria, South Africa
[18] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes 1.The case of Nickel (II), Copper (II) and Zinc (II), Journal of Hazardous Materials, 2002, 144, 251-273.
[19] N.M. Agyei, J.H. Potgieter and C.A. Strydon, The removal of phosphate ions from aqueous solution by coal fly ash, slag, ordinary cement and related blends, Cem. Concr. Res., 2000, 32, 1189-1897.
[20] V. Boonamnuayvitaya, C. Chaiya, W. Tanthapanichakoon, and S. Jarndilokkul, Removal of heavy metals by adsorbent prepared from pyrolysed coffee residues and clay, Separation and Purification Technology, 2004, 35, 3511-22.
[21] A.F. Jimenez and A. Palomo, Mid-infrared spectroscopy studies of alkali-activated fly ash structure, Microporous and Mesoporus Materials, 2005, 80, 207-214.
[22] I.J. Alinnor, Adsorption of heavy metal ions from aqueous solution by flash ash, Fuel, 2007, 86, 853-857.
[23] S.S. Zamil, S. Ahmad, M.H. Choi, J.Y. Park and S.C. Yoon, Correlating metal ionic characteristics with biosorption capacity at Staphylococcus Saprophyticus BMSZ 711 using QICAR model, Bioresource Technology, 2009, 100, 1895-1902.
[24] A.A. Augustine, B.D. Orike and A.D. Edidiong, Adsorption kinetics and modeling of Cu (II) ion sorption from aqueous solution by mercaptoacetic acid modified cassava (manihot sculenta cranz) wastes, Journal of Environmental, Agricultural and Food Chemistry, 2007, 6 (9), 309-312