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Effects of Adsorbent Activation on Bioremediation of Hg (II) and Cd (II) Ions from Aqueous Solution using Boiler Fly Ash

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ABSTRACT

Heavy metal (HM) removal from wastewater has attracted much attention in the past few decades. The search for low cost sorbents became the focus recently as a result of the expensive nature of conventional adsorbents. The use of unactivated and nitric acid activated boiler fly ash an agricultural by-product in the bioremediation of mercury (Hg) (II) and cadmium (Cd) (II) ions from aqueous solution was investigated in this work. The amount adsorbed increased as the initial metal ion concentration was increased. For unactivated boiler fly ash (BFA), the amount of Hg (II) ion adsorbed was higher than the amount of Cd (II) ion that was adsorbed. The acid-activated BFA adsorbed more than the unactivated BFA, with the influence of activation much more on the amount of Cd (II) ion adsorbed. The sorption process was modeled using two kinetic models: pseudo-first order and the pseudo-second order equations; and also six isotherm models namely Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin, Harkins-Jura (H-J) and Smith equations. For the kinetic models, the pseudo second-order equation gave a better fit to the sorption process. The differences in fitness of the isotherm models to the sorption process were not significant by two-way ANOVA. Also, analysis of the equilibrium sorption data in accordance with the six isotherm models and applying a normalized standard deviation Δq revealed that the Harkins-Jura isotherm model gave a better fit to experimental data. The apparent energy of sorption E (KJ mol^{-1}) from the D-R equation gave values of 26.72, (unactivated), 223.61 (activated) for Cd (II) ion and 50.00 (unactivated), 158.11 (activated) for Hg (II) ion, all in KJ mol^{-1}. Hence, activation increased the sorption capacity of the adsorbent and the values of apparent energy of sorption. Also, from the values of E, the sorption process could be said to follow a chemisorption mechanism.

Keywords: adsorption, agricultural by-products, environment, heavy metal ions, isotherms, surface chemistry
Keywords: BFA, boiler fly ash; **HM**, heavy metal

INTRODUCTION

The treatment of effluent water from industries and other sources have been achieved through adsorption principles. In recent times the use of agricultural residues or waste materials in the removal of HM ions has revealed good potential in wastewater treatment (Brandley and Duong 1988; Sun and Shi 1998; Igwe and Abia 2003; Okoronkwo 2008). This recent research and development of agricultural waste materials as adsorbents are based on a need to increase utility and for better adaptation of renewable materials to specific ends in order to make better use of limited resources available and to meet with consumers' needs and wishes compared to the use of ion exchanged resin, precipitation and other conventional methods which are also effective methods of removing metals from effluent water, but which are costly (Brandley and Duong 1988; Lin and Liu 2000).

Heavy metals (HMs) are poisonous metallic elements in the environment. The toxicity of HMs to marine life and consequently to man has for many years been established. Cadmium (Cd), a naturally occurring HM can be found in food, water and cigarette smoke. It is a known human carcinogen. Exposure of people to Cd may not only be through foods but also through drinking contaminated water (Sun and Shi 1998). Mercury (Hg) is one of the most problematic of all toxic HMs because despite its dangerous and known roles as a neurotoxin, many people have it implanted in their mouth, injected into their blood stream or are consuming it daily in fish. The removal of these HMs from solution by unmodified and modified cellulosic materials such as maize cob has been reported (Okeimen and Oriaki 1987; Okeimen and Okundaye 1989; Igwe and Abia 2003; Abia *et al*. 2005).

Similar works have been carried out by researchers which include the removal of lead from aqueous solution by palm kernel fiber (Ofomaja *et al*. 2005), the use of polyaminated highly porous chitosan (Takatsuji and Yoshida 1998), the use of chemically modified and unmodified waste (Abia and Igwe 2005). Furthermore the role of pH, temperature and particle size effect of some of these biosorbents has been investigated (Ho 2003; Igwe *et al*. 2005). Also sorption kinetics and intraparticulate diffusivities of Cd, Pb, and Zn ions on maize cob have been reported (Abia *et al*. 2005). The modeling of some of these biosorbents with an adsorption isotherm has been shown to follow some well known isotherms.

Boiler fly ash (BFA), which is a porous substance, results from the burning of mainly fruit bunch and kernels for boiler fuel. It is known that every tonne of fresh fruit bunch (FFB) produces about 4 to 6 kg of BFA (Majid *et al* 1999). BFA has also been reported to be made up of phosphorus (0.28-1.33%), potassium (1.02-4.31%), calcium (0.39-3.24%) and magnesium (0.29-2.60%) (Rusnani and Ma 1999). BFA has been applied as a soil conditioner because of these mineral contents. It has also been used as a landfill because its generation has been enormous from the numerous palm oil mills that exist. BFA have also been used in various other ways such as an adsorbent for removal of HMs from aqueous solution (Pandy *et al.* 1985; Mathur and Rupainwar 1988; Weng and Huang 1994; Hashim *et al*. 1996) and in the reduction of BOD, TSS and colour from palm oil mill effluent (POME) (Majid *et al*. 1999).

Therefore, this work aimed to investigate the effect of concentration of these HMs on the adsorption capacity of

Received: 27 December, 2009. Accepted: 4 September, 2010.

Original Research Paper

unactivated and activated BFA waste and the effect of contact time on the equilibrium sorption processes of both adsorbents. A second objective was to find the influence of activating the adsorbent on the sorption capacity.

MATERIALS AND METHODS

Materials

The BFA used for this research was obtained from Ukelu Palm oil mill, Umulolo Okigwe in Imo State, Nigeria. BFA is a waste ash from the combustion of palm kernel shell (PKS), palm fiber (PF) empty fruit bunch (EFB), etc used as fuel for the boiler. It was collected using black polyethylene bags and the big lumps were sorted out and ground to a powdered form. The ground powder was sieved using a 425 μm mesh. Some of the BFA was then activated by soaking in 2% (v/v) nitric acid for 24 hrs while the remainder was left unactivated. A standard solution of 1000 mg/L of each HM ion was prepared from its salts from where serial dilutions of 50,100, 150 and 200 mg/L were made using deionized water.

Determination of equilibrium sorption of metal ion on BFA

100 mL of each of the various concentrations prepared from a standard solution was transferred into reagent bottles containing 2 g of unactivated BFA. The reagent bottle was corked and shaken in a constant temperature rotary shaker at 30°C and 100 rpm. Different samples were left for 20, 40, 60, 80 and 100 min, which were later filtered at the end of each time interval and the filtrate concentration, were determined by a UNICAM 919 model atomic absorption spectrophotometer (AAS). The same procedure was repeated for the activated BFA. All experiments were performed in triplicate and average values were used for result analysis.

Statistical analysis

Statistical tools used include descriptive statistics such as mean, normalized standard deviation and least square regression and correlation analysis using Microsoft excel package 2003. Also, a two-way analysis of variance (ANOVA) for statistical significance of models at $P < 0.05$ was used.

RESULTS AND DISCUSSION

The reason for soaking BFA in 2% (v/v) nitric acid was to wash off any soluble biomaterials and also to activate it. Activation helps to open up the pores of BFA prior to sorption. The amount of the HM ions adsorbed (q_e) was calculated from experimental data using a simplified mass balance equation as follows (Chu and Hashin 2001; Ho and Wang 2004):

$$q_e = V(C_o - C_e)/m \qquad (1)$$

where V is the volume (mL) of the HM ion solution; C_o is initial HM ion concentration (mg/L); C_e is the equilibrium liquid phase concentration (mg/L) and m is the mass of adsorbent (g).

Sorption capacity and effect of activation

The amount adsorbed (mg/g) as time increased at various initial HM ions concentrations for activated and unactivated BFA is shown in **Fig. 1** for Cd (II) ion and **Fig. 2** for Hg (II). As time increased from 0 to 20 min, the amount adsorbed increased rapidly. For Cd (II) (**Fig. 1**), after 20 min the amount adsorbed appeared to decrease. For the Hg (II) ion, after 20 min, the amount adsorbed remained fairly constant as time increased. Also it could be observed that as initial concentration of HM ion increased, the amount adsorbed increased. This could be seen by an upward shift in the adsorption line on the plots in **Figs. 1** and **2**.

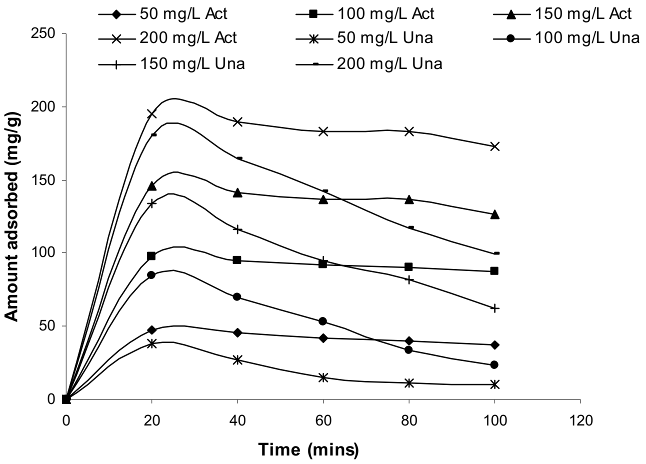

Fig. 1 Amount adsorbed (mg/g) against time (mins) at various initial concentrations for Cd (II) ion using activated (Act) and unactivated (Una) boiler fly ash.

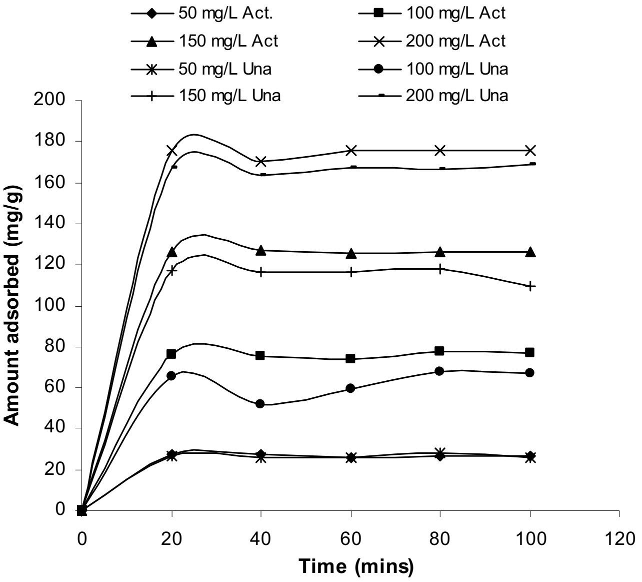

Fig. 2 Amount adsorbed (mg/g) against time (mins) at various initial concentrations for Hg (II) ion using activated and unactivated boiler fly ash.

The effect of BFA activation could be seen by comparing a particular initial HM ion concentration or particular time for each of the HM ions. By varying the initial HM ion concentration at a particular time (1 hr), the effect of activation on change in initial HM ion concentration is shown in **Fig. 3**. For the variation of time at a particular initial HM ion concentration (150 mg/L), the effect of activation is shown in **Fig. 4**. The activated adsorbent had a higher sorption capacity than the unactivated BFA for the two HM ions.

Generally, for unactivated BFA Hg (II) ion was adsorbed more than Cd (II) ion and for activated BFA, Cd (II) ion was adsorbed more than Hg (II) ion. Sorption capacities have always been linked with values of ionic radii of HM ions. The smaller the ionic size, the greater its affinity to reaction sites (Horsfall *et al.* 2003; Abia and Asuquo 2006; Akpohonor and Egwaikhide 2007). The ionic radii of Cd (II) and Hg (II) are 109 and 116, respectively. This means that for the activated BFA, the smaller the ionic radius, the higher the amount adsorbed. This is why Cd (II) was adsorbed more than Hg (II) ion. For the unactivated BFA, the sorption trend could be explained by the hydrolysis constant values of the HM ions. The hydrolysis constant (pK_h) of the HM ions is given as 3.4 for Hg (II) and 10.1 for Cd (II) (Burgess 1978). The hydrolysis constant could be taken as the rate or strength at which the HM ions attract water molecules in solution. Thus, HM ions with higher hydrolysis constant will attract more water molecules and hence

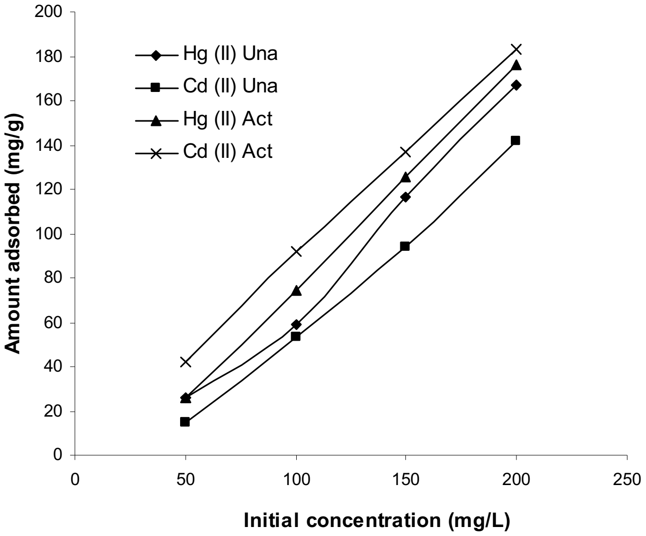

Fig. 3 Amount adsorbed (mg/g) against initial concentration (mg/L) at initial concentration of 150 mg/L for Cd (II) and Hg (II) ions using activated and unactivated boiler fly ash.

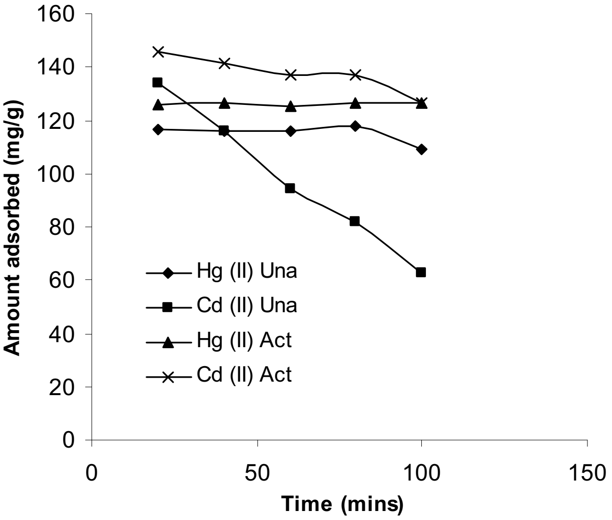

Fig. 4 Amount adsorbed (mg/g) against time (mins) at initial concentration of 150 mg/L for Cd (II) and Hg (II) ions using activated and unactivated boiler fly ash.

have a lower sorption capacity. These effects have also been reported, for the adsorption of Mn (II), Fe (II), Ni (II) and Cu (II) ions on activated carbon (Uzun and Guzel 2000); for the effect of pH and concentration on the adsorption of Cd (II) and Hg (II) on BFA (Okoronkwo *et al.* 2010). The values of the charge-size function (Z^2/r ratio) of the cation also support this sorption trend with the Z^2/r ratio = 0.034 for the Hg (II) ion and 0.037 for the Cd (II) ion (Burgess 1978). The higher the charge-size function, the greater the tendency for the HM cation to hydrolyse and this results to lower sorption capacity. The increase in the tendency to hydrolyze also increases the hydrodynamic radius of the HM ion. That is, the effective radius of the cation and the water molecules surrounding it in the hydration sphere, hence, decreasing sorption capacity.

Activation of the adsorbent with 2% (v/v) nitric acid helped to open the micropores. This will probably change the surface characteristics of the adsorbent. Horsfall and Spiff (2004) reported the activation of *Caladium bicolor* with nitric acid, sodium hydroxide and deionized water. Their report showed that both acid and base treatment increased the cation exchange capacity (CEC) and the surface charge density (SCD). The SCD gives an overall intensity of charges on the solid matrix surface. Therefore, activation of BFA is an indication of improvement of the biomass surface towards the sorption of cationic and anionic species in solution and also an enhancement of sorption sites as a result of greater surface charges. This probably indicates ion exchange process between the adsorbent and the HM ions. Therefore, this is why the activated BFA gave a better sorption capacity than the unactivated BFA. Other groups have reported that ion exchange mechanism prevails in high SCD materials and during acid treatment of biomaterials (Bernal and Lopez-Real 1993; Horsfall and Abia 2003).

Sorption kinetics

The study of sorption kinetics in wastewater treatment is understandably very significant as it provides valuable insight into the reaction pathways and into the mechanism of sorption reactions. Also, kinetics describes the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid-solution interface (Ho and McKay 1999). This means that the appropriate design of sorption treatment plants could depend on the accurate prediction of the rate at which a pollutant is removed from an aqueous solution. To develop sorption kinetics, knowledge of the rate law describing the sorption system is required. The rate law is determined by experiment and cannot be inferred by mere examination of the stoichiometry of the overall chemical reaction equation (Ho and McKay 1999). The rate law has been reported to have three primary requirements (Sparks 1986):

- Knowledge of all the molecular details of the reaction including the energetics and stereochemistry;
- Inter-atomic distances and angles throughout the course of the reaction;
- The individual molecular steps involved in the mechanism.

Some theories or explanations have been put forward for treatment of sorption kinetic data. Ho and McKay (1998) reported that diffusion mass transport models are extremely important, particularly in processes where ion exchange and ionic bonding are not as prevalent as in chemisorption processes. Diffusion models have been reported to be based on one or more of the following mechanistic steps such as: bulk diffusion, external diffusion and surface or pore diffusion (Findon *et al.* 1993; Weber and Digiano 1996). Then the proper HM ion sorption would take place by physicochemical sorption, ion exchange, precipitation or complexation. The type of sorption that predominates depends on prevalent sorption conditions. Abia and Didi (2007) viewed the sorption process as a transfer zone behaviour of the HM ions on the adsorbent. They considered the adsorbent surface and overlying interface as a mass transfer zone. Here the adsorbent stationary phase and the liquid mobile phase presents a picture of partial electric double layer, where the adsorbent active sites are considered negatively charged and the HM ions in solution, notwithstanding the covalent orientation of some of their moieties have a positively charged core. Thus, the predominant type of mechanism here is either metal ion core strive or dipole induced interactions and these depends on the penetrant K_{id} or n values.

One thing that is certain is that it is often incorrect to apply simple kinetic models such as first or second-order rate equations to a sorption with solid surface which are rarely homogenous and because the effects of transport phenomena and chemical reactions are often experimentally inseparable (Ho and McKay 1999). Two kinetic models, the pseudo-first order and the pseudo-second order, were used to model the sorption kinetic data. The pseudo first order equation is given by (Özacar 2003; Özacar and Sengil 2004);

$$\log (q_e - q_t) = \log q_e - K_1 t/2.303 \qquad (2)$$

where q_t and q_e are the amounts of HM ion adsorbed at time t and at equilibrium respectively (mg/g), and K_1 is the rate constant of pseudo-first order adsorption process (min^{-1}). The slopes and the intercepts of the plots of $\log (q_e - q_t)$ versus t (**Fig. 5**) were used to determine the first order rate

Table 1 Kinetic constants for adsorption of Cd (II) and Hg (II) ions onto activated and unactivated boiler fly ash.

S/N	**Kinetic Equation (constants)**	**Cd (II)**		**Hg (II)**	
		Unactivated	**Activated**	**Unactivated**	**Activated**
1	**Pseudo-first order**				
	K_1 (min^{-1})	0.0244	0.0037	0.0018	4.61×10^{-5}
	qe (mg L^{-1})	181.97	154.03	89.27	102.02
	R^2	0.7871	0.8728	0.4119	0.0136
2	**Pseudo-second order**				
	K_2	-9.81×10^{-4}	-2.33×10^{-3}	-3.91×10^{-3}	6.24×10^{-2}
	h_o	13.133	-35.59	-47.17	1000.00
	qe	56.50	123.46	109.89	126.58
	R^2	0.9522	0.9922	0.9953	0.9999

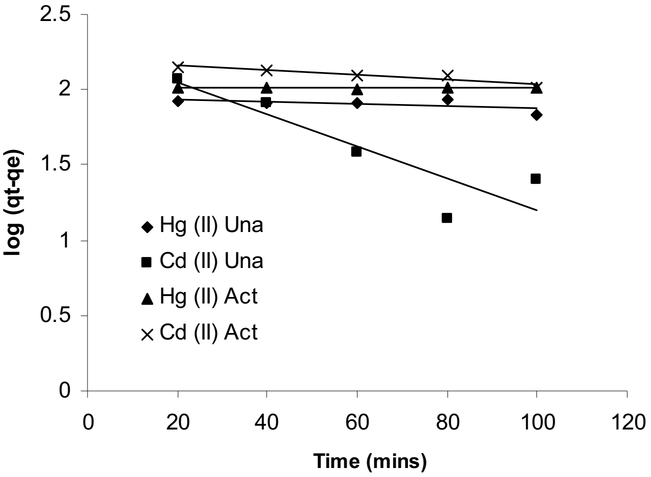

Fig. 5 Pseudo-first order plot at initial concentration of 150 mg/L for Cd (II) and Hg (II) ions using activated and unactivated boiler fly ash.

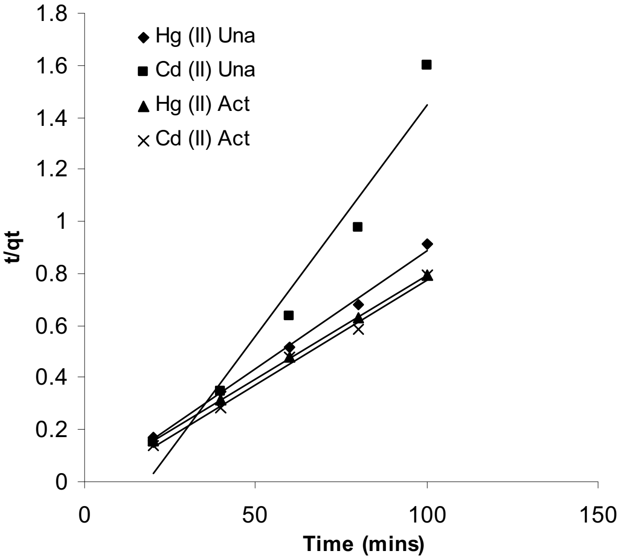

Fig. 6 Pseudo-second order plot at initial concentration of 150 mg/L for Cd (II) and Hg (II) ions using activated and unactivated boiler fly ash.

constant K_1, and equilibrium adsorption density q_e. A comparison of the results with correlation coefficients is shown in **Table 1**. The correlation coefficients for the two HM ions were very low both for activated and non-activated adsorbents. In the present work q_e values computed from the Largergren plots deviated considerably from the experimental q_e values. This indicates that the pseudo first order equation is not sufficient to describe the mechanism of the metal ion-adsorbent interactions (Bhattacharyya and Sharma 2004).

The second kinetics equation used is the pseudo second order which is given by Ho and McKay (1998, 1999):

$$dq_t / dt = K_2 (q_e - q_t)^2 \tag{3}$$

where K_2 is the pseudo second order rate constant (g mg^{-1} min^{-1}) is applicable for the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, the integrated form of equation is given as:

$$1/ (q_e - q_t) = 1/q_e + K_2 t \tag{4}$$

This can also be rearranged to obtain a linear form as:

$$t/qt = 1/K_2 q_e^2 + t/q_e \tag{5}$$

where the initial sorption rate h_o is given by:

$$h_o = K_2 q_e^2 \tag{6}$$

If the pseudo-second order equation is applicable, the plot of t/qt versus t gives a linear relationship which allows for the computation of K_2 and q_e without having to know any parameter beforehand. These plots are shown in **Fig. 6**. The constants for the pseudo-second order equation as calculated from the slopes and intercepts of these plots are shown in **Table 1**. The plots yielded very good straight lines and the correlation coefficients are high. Thus, the pseudo-second order model based on Eq. (5), which considers the rate limiting steps as the formation of chemisorption bond involving sharing or exchange of electrons between adsorbate and the adsorbent was applied. Therefore, this indicates that the adsorptive system studied belongs to the second order kinetic model.

Many researchers have reported the use of kinetic models in the treatment of sorption experimental data for sorption of HMs on low cost agricultural by-products. The pseudo-second order model have always been reported to give a better fit to sorption experimental data more than other kinetic models (Ho and McKay 2000; Igwe *et al.* 2008; Babatunde *et al.* 2009; Urik *et al.* 2009; Vinodhini and Das 2010). This holds when the calculated or theoretical q_e values approximates well with the experimental q_e values; and the regression coefficient values (R^2) are high. When pseudo-second order model gives the best fit, it means that the rate limiting step may be chemical sorption or chemisorption. This is because pseudo-second order model was based on chemisorption assumption (Ho and McKay 1999). Similar research have reported chemisorption mechanism such as adsorption of Cr (VI) onto used tyres and sawdust (Hamadi *et al.* 2000); adsorption of Cr (VI) onto activated carbons derived from agricultural waste materials (Mohan *et al.* 2005); adsorption of Hg (II), As (III) and Pb (II) onto unmodified and thiolated coconut fiber (Igwe *et al.* 2008); adsorption of Cr (VI) onto waste acorn of *Quercus ithaburensis* (Malkoc and Nuhoghu 2007); adsorption of Pb (II) and Ni (II) onto lichen biomass (Sari *et al.* 2007).

Also, Babatunde *et al.* (2009) reported a chemisorption mechanism as well as, that the sorption process was rapid which can be attributed to the presence of high affinity ligands on the surface of the biomass providing fast HM ion binding. Sari *et al* (2007), reported that the pseudo-first and pseudo-second order rate constants decreased as temperature was increased and Vinodhini and Das (2010), found out that the pseudo-first order rate constant increased with increase in adsorbent dosage. Also, it has been reported that a rapid kinetics will facilitate smaller reactors (lower retention time for effective metal uptake) whereas a slow rate of uptake will necessitate long column or series of columns to utilize maximum potential of the adsorbent (Vinodhini and Das 2010). Generally, the rate of sorption onto a sorbent surface depends upon a number of parameters such as structural properties of the sorbent, initial concentration of the solute and the interaction between the solute and the active sites of the sorbent (Vinodhini and Das 2010).

Sorption isotherm

The applicability of sorption process as a unit operation can be evaluated using isotherm models. The equilibrium distribution of HM ions between the sorbent and the solution is important in determining the maximum sorption capacity. Therefore, the successful representation of this dynamic adsorptive separation of solute from solution unto an adsorbent depends upon a good description of the equilibrium separation between the two phases (Akkaya and Ozer 2005). An adsorption isotherm is characterized by certain constant values, which expresses the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants (Dursun *et al.* 2005). Several sorption isotherms have been applied to sorption processes. The sorption experimental data obtained from this work were applied to six adsorption isotherm equations namely: Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin, Harkins-Jura and Smith.

The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. It is based on the assumption that all adsorption sites are equivalent and adsorption in an active site is independent of whether the adjacent sites are occupied or not. The Langmuir equation is given by (Langmuir 1918);

$$q_e = q_m K_L C_e / (1 + K_L C_e) \quad (7)$$

where q_e is the equilibrium HM ion solid phase concentration (mg/g); C_e is the equilibrium HM ion concentration in solution (mg/L); q_m is the monolayer biosorption capacity of the adsorbent (mg/g) and K_L is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption. The linearized form of the equation is given as;

$$C_e/q_e = 1/q_m K_L + C_e/q_m \quad (8)$$

The plot of C_e/q_e versus C_e is shown in **Fig. 7**.

The Freundlich model was chosen to estimate the adsorption intensity of the sorbate towards the biomass. It can be applied to non-ideal sorption on heterogeneous surface and multilayer sorption. The Freundlich model is given as (Freundlich 1906):

$$q_e = K_F\, C_e^{\,1/n} \quad (9)$$

where K_F is a constant relating the biosorption capacity and 1/n is an empirical parameter relating the biosorption intensity, which varies with the heterogeneity of the material. The linear form of Eq. (9) is given as:

$$\log q_e = \log K_F + 1/n \log C_e \quad (10)$$

The Freundlich plot of log q_e versus log C_e is given in **Fig. 8**.

The Dubinin-Radushkevich (D-R) isotherm was chosen to estimate the characteristic porosity of the biomass to the HM ions and also to estimate the apparent energy of adsorption. The D-R isotherm is more general than the Langmuir isotherm, because it does not assume a homogenous surface or constant sorption potential (Akcay 2006). The D-R equation is given by (Dubinin and Radushkevich 1947):

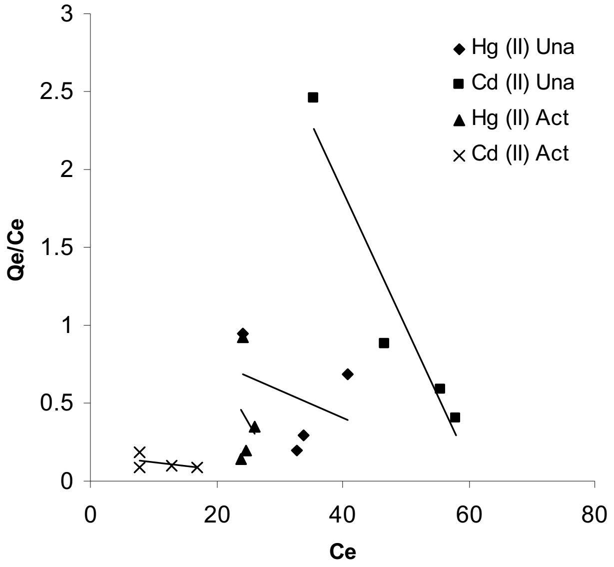

Fig. 7 Langmuir isotherm plot at initial concentration of 150 mg/L for Cd (II) and Hg (II) ions using activated and unactivated boiler fly ash.

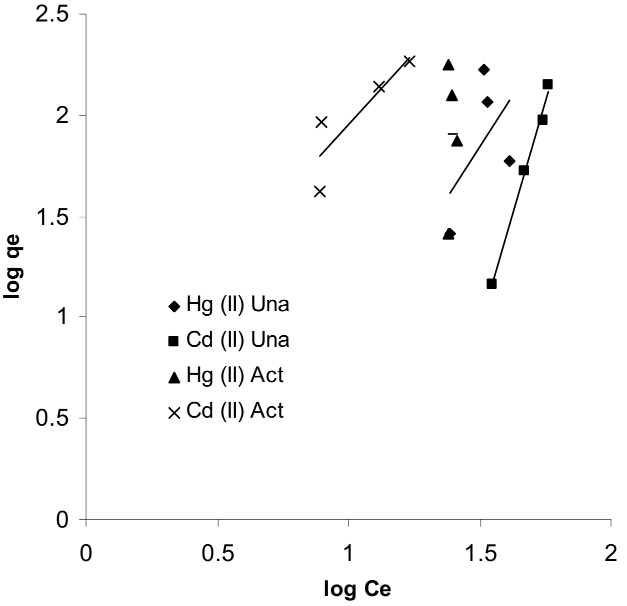

Fig. 8 Freundlich isotherm plot at initial concentration of 150 mg/L for Cd (II) and Hg (II) ions using activated and unactivated boiler fly ash.

$$q_e = q_m \exp(-\beta\varepsilon^2) \quad (11)$$

The linear form of the equation is given as:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (12)$$

where q_e is the equilibrium solid phase concentration, q_m is the theoretical saturation capacity, ε is the Polanyi potential given as:

$$\varepsilon = RT \ln(1+1/C_e) \quad (13)$$

and β is a constant related to the adsorption energy by Eq. (14)

$$E = (2\beta)^{-1/2} \quad (14)$$

The sorption mean free energy is the energy required to

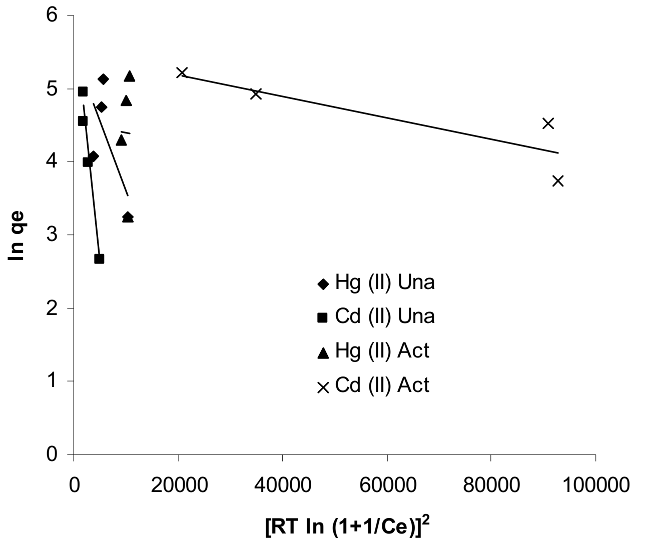

Fig. 9 Dubinin-Radushkevich isotherm plot at initial concentration of 150 mg/L for Cd (II) and Hg (II) ions using activated and unactivated boiler fly ash.

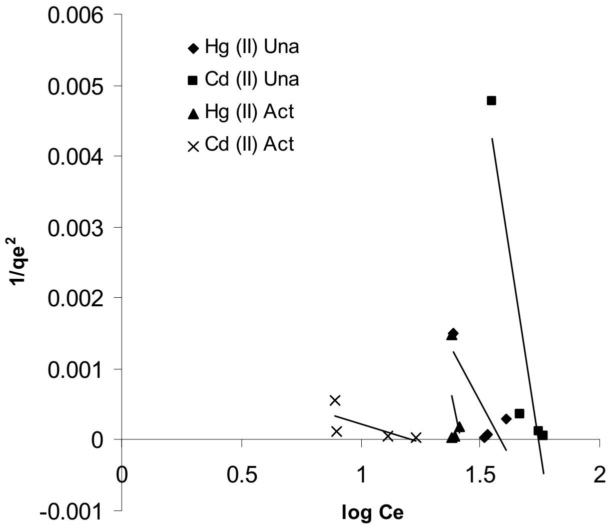

Fig. 11 Harkins-Jura isotherm plot at initial concentration of 150 mg/L for Cd (II) and Hg (II) ions using activated and unactivated boiler fly ash.

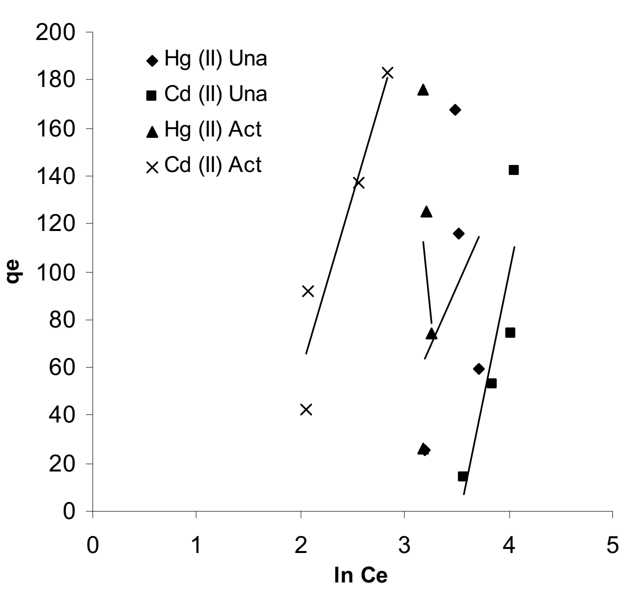

Fig. 10 Temkin isotherm plot at initial concentration of 150 mg/L for Cd (II) and Hg (II) ions using activated and unactivated boiler fly ash.

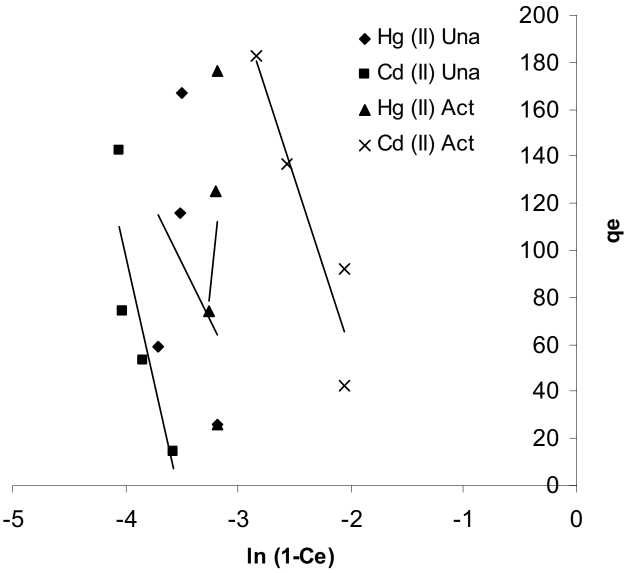

Fig. 12 Smith isotherm plot at initial concentration of 150 mg/L for Cd (II) and Hg (II) ions using activated and unactivated boiler fly ash.

transfer one mole of the sorbate from infinity in solution to the surface of solid. The magnitude of the sorption mean free energy E is widely used for estimating the type of adsorption (Saeed *et al.* 1999; Abusafa and Yücel 2002; Mahramanlioglu *et al.* 2002; Erdem *et al.* 2004). The plot of D-R isotherm is shown in **Fig. 9**.

The Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic as implied by the Freundlich equation. Temkin equation is given by Malkoc and Nuhoglu (2007):

$$q_e = RT/b\ (\ln (AC_e) \qquad (15)$$

$$q_e = B \ln A + B \ln C_e \qquad (16)$$

where $B = (RT/b)$; q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount adsorbed at equilibrium and the equilibrium concentration respectively. Also T is the absolute temperature (K) and R is the universal gas constant. The constant b is related to the heat of adsorption (Pearce *et al* 2003; Akkaya and Ozer 2005). The plot of q_e versus ln C_e for the Temkin isotherm is shown in **Fig. 10**.

Another isotherm that was used in analysis of the experimental results is the Harkins-Jura isotherm. The Harkins-Jura isotherm accounts for multilayer adsorption and can be explained based on the existence of a heterogeneous pore distribution (Basar 2006). The equation is given as:

$$1/q_e^2 = (B/A) - (1/A \log C_e) \qquad (17)$$

The plot of $1/q_e^2$ versus log C_e for the Harkins-Jura isotherm is shown in **Fig. 11**.

The last but not least isotherm equation used is the Smith equation (Karaca *et al.* 2006). This is given by:

$$q_e = W_b - W \ln (1-C_e) \qquad (18)$$

where W and W_b are the constant parameters for the isotherm equation (Karaca *et al.* 2006). The plot of q_e versus ln $(1-C_e)$ is shown in **Fig. 12** for the Smith isotherm.

From all the plots, the isotherm constants were calculated from the slopes and intercepts of linear regression lines of the plots. The values of the various isotherm constants and the coefficient of determination (R^2) are shown in **Table 2**. High values of R^2 show good correlation of experimental data whereas low values show poor correlation. From **Table 2**, it can be seen that all the coefficient of deter-

Table 2 Isotherm constants for adsorption of Cd (II) and Hg (II) ions onto activated and unactivated boiler fly ash.

S/N	**Isotherm equation (constants)**	**Cd (II)**		**Hg (II)**	
		Unactivated	**Activated**	**Unactivated**	**Activated**
1	**Langmuir**				
	q_m (mg g^{-1})	-11.35	-192.31	-55.56	-12.32
	K_L (L g^{-1})	-1.63×10^{-2}	-3.00×10^{-2}	-1.60×10^{-2}	-3.37×10^{-2}
	R^2	0.9173	0.2411	0.1235	0.0404
	Δq (%)	28.95	31.38	66.16	79.27
2	**Freundlich**				
	n	2.24	6.99	4.92	14.79
	K_F (L g^{-1})	1.76×10^{-6}	3.31	6.24×10^{-2}	64.95
	R^2	0.9897	0.7559	0.2832	8.0×10^{-6}
	Δq (%)	115.47	109.31	115.22	127.42
3	**D-R**				
	q_m (mg g^{-1})	440.80	242.02	242.14	102.19
	β (mg^2 KJ^{-2})	7.0×10^{-4}	1.0×10^{-5}	2.9×10^{-4}	2.0×10^{-5}
	E (KJ mol^{-1})	26.72	223.61	50.00	158.11
	R^2	0.9798	0.7649	0.4276	0.0004
	Δq (%)	14.28	74.83	65.83	132.13
4	**Temkin**				
	A (L g^{-1})	2.91×10^{-2}	2.0×10^{-1}	7.96×10^{-2}	3.22×10^{-2}
	B	211.04	147.46	97.33	-433.12
	R^2	0.7712	0.8910	0.1129	0.0575
	Δq (%)	35.25	35.31	105.01	189.17
5	**H-J**				
	A	44.84	1000.0	163.93	64.53
	B	1.74	1.20	1.57	1.42
	R^2	0.8662	0.4622	0.6577	0.1184
	Δq (%)	50.18	32.11	47.83	70.35
6	**Smith**				
	W	211.04	147.46	97.852	-433.12
	W_b	-746.35	-237.11	-248.18	1488.60
	R^2	0.7712	0.891	0.1141	0.0575
	Δq (%)	35.05	35.52	104.63	6876.62

Note: D.R = Dubinin-Radushkevich; H-J = Harkins-Jura

mination (R^2) are below 97%. The highest R^2 value obtained was 0.9897 from the Freundlich isotherm and for Cd (II) on unactivated BFA. Thus, based on the coefficient of determination, it could be stated that all the isotherms gave slightly high values for sorption of Cd (II) on unactivated BFA.

The Freundlich and the Langmuir models have been the most frequently used isotherms for modeling of equilibrium sorption data. Many research have reported the use of these isotherms such as; the removal of hexavalent chromium from drinking water by granular ferric hydroxide (Asgari *et al.* 2008); pollution removal using agricultural fibers (Mahvi 2008); cadmium biosorption from wastewater by Ulmus leaves and their ash (Mahvi *et al.* 2008); chromium adsorption from waste water by *Platanus orientalis* leaves (Mahvi *et al.* 2007); bioremediation of Cd (II), Pb (II) and Zn (II) using unmodified and EDTA-modified maize cob (Igwe and Abia 2007); removal of Cr (VI) from aqueous solutions using Lewatit FO36 nano ion-exchange resin (Rafati *et al.* 2010); and so on. The Langmiur model has been successfully applied to a wide range of system that exhibit limiting or maximum sorption capacity (Rafati *et al.* 2010). It assumes uniform energies of ion exchange onto the adsorbate in the plane of the surface (Yu *et al.* 2001). The Langmiur maxi-mum sorption capacity (q_{max} mg/g) obtained in this work are very low (-11.35 mg/g for Cd (II) on unactivated; -192.31 mg/g for Cd (II) on activated; -55.56 mg/g for Hg (II) on unactivated and -12.32 mg/g for Hg (II) on activated), compared to other q_{max} values that have been reported such as; 0.85 mg/g for Cr (III) on tyre rubber (Entezzari *et al* 2005); 0.949 mg/g for toxic HMs on coconut husk (Hasnany and Ahmed 2006); 2.52 mg/g for HMs on cocoa shells (Meunier *et al.* 2003); 29.30 mg/g for HMs on sunflower stalks (Sun and Shi 1998); 91.64 mg/g for Cr (VI) on Bengal gram husk (Ahalya *et al.* 2005); 51.0 mg/g for HMs on *sargassum fluitans* (Davies *et al.* 2000); 201.81 mg/g for Cr (VI) on cone biomass of *Pinus syvestris* (Ucun *et al.* 2002); 9.259 mg/g for As (V) on chemically modified sawdust of spruce (Urik *et al.* 2009); and so on.

The Freundlich constant K_F gives a measure of the adsorption intensity and the exponent n gives the shape of the isotherm (Akgerman and Zardkoohi 1996). According to Kadirvelu and Namasivayam (2000), n values between 1 and 10 shows easy separation beneficial adsorption. The value of n, which is related to the distribution of bonded ions on the sorbent surface (Ahalya *et al.* 2005), were all found to be greater than unity. The values obtained for Cd (II) on unactivated and activated and Hg (II) unactivated BFA were between 1 and 10, that is 2.24, 6.99 and 4.92, respectively while that obtained for Hg (II) on activated BFA (14.79) was greater than 10. Several authors have reported different values of n for different adsorbates on various adsorbents such as; 2.1659 and 2.5967 for Cr (VI) biosorption on neem and mango sawdust respectively (Vinodhini and Das 2010); 1.03 and 1.10 for Cu (II) and Cd (II) adsorption on cassava waste, respectively (Horsfall *et al.* 2004); 7.93 for Cr (VI) adsorption on waste acorn of *Quercus ithaburensis* (Malkoc and Nuhoglu 2007); 2.0 and 3.33 for Pb (II) and Ni (II) adsorption on lichen (*Cladonia furcata*) biomass respectively (Sari *et al.* 2007); 0.336 for adsorption of As (V) on chemically modified sawdust of spruce (*Picea abies*) (Urik *et al.* 2009); 0.625 for vanadium removal onto *Pinus sylvestris* sawdust (Kaczala *et al.* 2009); and so on.

From the D-R isotherm, the apparent energy (E/KJmol^{-1}) of adsorption was 26.72 for Cd (II) unactivated BFA; 223.61 for Cd (II) activated BFA; 50.0 for Hg (II) unactivated BFA and 158.11 for Hg (II) activated BFA. The apparent energy of adsorption shows if the sorption process follows physiosorption, chemisorption, ion-exchange mechanism, etc. It has been reported that physiosorption processes usually have adsorption energies less than 40 KJ/mol and above this value sorption is of chemisorption mechanism (Horsfall *et al.* 2004). If the mean biosorption energy (E) value is between 8.0 and 16.0 KJmol^{-1}, the biosorption

Table 3 Two-way analysis of variance (ANOVA) without replication at α = 0.05.

Source of variation	*df*	*ss*	*ms*	F_{cal}	F_{tab}
Unactivated					
Models	5	0.1858360	0.0371672	0.839	5.05
Metal ions	1	1.0658860	1.0658860	24.070	6.61
Error	5	0.2214101	0.044282002		
Total	11	1.47313206			
Activated					
Models	5	0.1596105	0.0319221	0.650	5.05
Metal ions	1	1.1605848	1.1605848	23.639	6.61
Error	5	0.2454856	60.04909712		
Total	11	1.5656809			

process follows chemical ion-exchange and if E < 8.0 KJ mol^{-1}, the biosorption process is of a physical nature (Lodeiro *et al.* 2006; Sari *et al.* 2007). Therefore, from the results of this work shown above, it could be seen that the sorption process was of chemisorption mechanism except for Cd (II) on unactivated BFA. Also, it could be seen that activation increased the value of the apparent energy of sorption. Several other authors have reported on the mean sorption energy being less than 8 KJ/mol depicting physical sorption (Horsfall *et al.* 2004); between 8-16 KJ/mol showing chemical ion-exchange (Sari *et al.* 2007; Shah *et al.* 2009) and above 40 KJ/mol showing chemisorption mechanism (Özacar *et al.* 2008).

The Temkin, Harkins-Jura and Smith isotherms are suitable for multilayer adsorption. Especially, the fitting of these equations can be seen in heteroporous solids (Karaca *et al* 2004). These isotherms have been used to model sorption experimental data (Malkoc and Nuhoglu 2007; Özacar *et al.* 2008). The values of A the sorption capacity obtained from the Harkins-Jura isotherm were higher than those obtained from the Temkin isotherm whereas the value of B were higher for the Temkin isotherm than the Harkins-Jura isotherm.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L that is used to predict if an adsorption system is favourable or unfavourable. The separation factor is given by (Ho *et al.* 2002; Horsfall *et al.* 2004):

$$R_L = 1 / (1 + K_L C_o) \qquad (19)$$

where C_o is the initial concentration (mg L^{-1}) and K_L is the Langmuir adsorption equilibrium constant (L g^{-1}). The isotherm is unfavourable when $R_L > 1$, linear when $R_L = 1$, favourable when $0 < R_L < 1$ and irreversible when $R_L = 0$. The value of R_L obtained were all negative. These values did not fall into any category of the classification hence, could be taken as being very unfavourable. Thus based on the essential features of the Langmuir isotherm, the sorption process is very unfavourable. Many authors have used this dimensionless separation factor (R_L or S_F) to indicate the favourability of the sorption system based on the Langmuir isotherm (Ho *et al.* 2002; Horsfall *et al.* 2004; Malkoc and Nuhoglu 2007).

Furthermore, to investigate the significance of the various isotherms used in the sorption studies, the HMs were taken as objects or blocks and R^2 values for the isotherms as variables or treatments (Horsfall *et al* 2004). A two-way analysis of variance (ANOVA) without replication at the 5% level of significance was used to describe the relationships, (1) between the six isotherms in describing the adsorption of the two divalent HMs on the biomass and (2) between the two divalent HM ions for binding sites on the biomass; for both unactivated and activated BFA. The results are shown in **Table 3**. The data from **Table 3** shows that for unactivated BFA, the difference in the models was not significant. This is also the same for the models on activated BFA. For the HM ions the differences in the sorption capacity were significant.

Again, in order to compare the validity of each model more efficiently, a normalized standard deviation, Δq was calculated using the following equation (Abd El-Rahman *et al* 2006);

$$\Delta q\ (\%) = 100 \times \sqrt{\left(\Sigma\left[(qe^{\exp} - qe^{cal}) / qe^{\exp}\right]^2 / n-1\right)} \qquad (20)$$

where the superscripts ‘exp’ and ‘cal’ mean the experimental and calculated values respectively and n is the number of measurements. The values of Δq are given in **Table 2**. It could be seen that the lowest value obtained was for Cd (II) ion on unactivated for the Dubinin-Radushkevich isotherm (Δq = 14.28%), and the highest value of 6876.62% was obtained for Hg (II) ion on activated BFA for Smith isotherm. Going by Δq values generally, it could be seen that relatively lower values were obtained for Harkin-Jura isotherm and higher values for Freundlich isotherm. Hence, Harkins-Jura isotherm could be said to give a better isotherm model for the sorption process.

CONCLUDING REMARKS

In this study, the effect of activation using 2% (v/v) nitric acid on BFA for sorption of Cd (II) and Hg (II) ions were investigated and the following conclusions could be made.

1. The recovery of the metal ions increased as the initial concentration increased and the amount uptake of Hg (II) ion was higher than Cd (II) ion for unactivated. For activated, the reverse was the case.
2. Activating the BFA increased the sorption capacity of the adsorbent towards the metal ions.
3. Pseudo-second order kinetic equation gave a better fit to the sorption experimental data more than pseudo-first order equation.
4. Analysis of the respective equilibrium sorption data in accordance with six isotherm models, applying a two way ANOVA and a normalized standard deviation Δq revealed that there was no significant difference in the applicability of the models to the sorption data, although Harkins-Jura isotherm could be said to give a better fit.
5. Hence, activating the adsorbent helps to improve the amount of uptake of sorbate, thus improving the economics of the sorption process by reducing cost.

ACKNOWLEDGEMENTS

We would like to express our gratitude to Dr. Johnson Ohakwe of Department of Statistics, Abia State University Uturu Nigeria for helping out with the statistical analysis.

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