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Detoxification of Hg^{2+}, Cd^{2+} and Fe^{2+} from Aqueous Solution using Waste Boiler Fly Ash

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ABSTRACT

Heavy metal pollution is one of the main problems for the ecosystem due to technological development. The pollution and toxicity problems posed by heavy metals in the environment have long been established. Efforts to minimize production of hazardous waste and to remediate existing accumulated waste have become one of the most important environmental challenges that the world faces today. The detoxification of Hg (II), Cd (II) and Fe (II) from aqueous solution using boiler fly ash was studied. The amount of the metal ions adsorbed increased as the initial concentration of the metal was increased. The sorption process was very rapid reaching equilibrium at about 20 minutes for the three metal ions. The trend of the sorption is Cd (II) > Fe (II) > Hg (II). The sorption process was modeled using the pseudo-first and pseudo-second order equations with the later giving a better fit with R^2 values of Hg (II) (0.9967), Cd (II) (0.9947) and Fe (II) (0.9837). The pseudo-second order rate constants for the metal ions were 13.46 for Cd (II), and 7.22 for Fe (II) and 7.78×10^{-4} for Hg (II), all in mg g^{-1} min^{-1}, which confirms the trend of the sorption. Therefore, boiler fly ash which is a waste from palm oil mills could be used as an effective adsorbent for the removal of heavy metals from waste water.

Keywords: adsorption, environment, heavy metal, removal

INTRODUCTION

The use of agricultural residues and related materials such as sunflower stalks, maize cob and husk and cassava waste, in the removal of heavy metal ions has revealed good potential in waste water treatment (Sun and Shi 1998; Igwe and Abia 2003; Abia *et al*. 2003). Heavy metals constitute a major category of toxics that pose a significant threat to health through occupational as well as environmental exposure (Theodore 2003). These metals are not friendly to life in our environment and have been the theme of numerous studies and innovative researches by many modern scientists (Asiendu 1990; Okoronkwo *et al*. 2005; Obasohan *et al*. 2006; Okoronkwo *et al*. 2007). The environmental interaction of heavy metals such as Hg, Fe, Cd, etc. calls for more studies and to extend their removal (Asiendu 1990; Howard 2003). The adsorptive removal of heavy metals from waste water is usually achieved by using activated carbon or activated alumina. But there are limitations in the use of activated carbon or alumina and even other established adsorbents. These include the cost of getting these materials, their regeneration and complex formations with the metal ions (Furst and Aly 1987; Volesky 1990a). It has also been reported that the use of these conventional adsorbents in heavy metal removal may be ineffective especially when the heavy metal ions are in solutions containing in the order of 1-100 mg dissolved heavy metal ions/L (Volesky 1990b; Volesky and Holan 1995). Also, it has been reported that activated carbon is only able to remove around 30-40 mg/g of Cd, Zn and Cr in water and it is non-regenerable, which makes it quite costly to wastewater treatment (Sun and Shi 1998). Also the regeneration of the exhausted adsorbents on the site is not very easy to perform for custommers. Thus the need for an economic and effective adsorbent for the removal of toxic ions from waste water (Lu *et al*. 2000).

Similar work has been carried out by many researchers, including Abia and Igwe (2005) who reported on the feasibility of utilizing maize cob and husk as adsorbents for the removal of cadmium, lead and zinc ions from aqueous solution. The utilization of other agricultural by-products for adsorption of heavy metals has been reported elsewhere (Gardea-Torresday *et al*. 1998; Igwe *et al*. 2008), which include the removal of lead ions from aqueous solution by palm kernel fibre (Ofomaja *et al*. 2005), shear butter seed husks (Eromosele and Otitolaye 1994) and the use of chemically modified and unmodified cassava waste (Abia *et al*. 2005).

Boiler fly ash is abundant in Nigeria and it constitutes a waste problem. The fibre and shell are by-products used as boiler fuel to produce heat for mills and for domestic consumption within the mill. Boiler fly ash is produced in palm oil mills from the burning of fibre and shell. The porous ash contains about 0.28-1.133% K, 1.02-4.31% P, 0.39-3.24% Ca and 0.29-2.60% Mg (Rusnani and Ma 1999). Boiler fly ash, an agricultural waste, also constitutes waste problems. This material can be easily processed and acquired. Most of the reported works on the use of fly ash products for the removal of heavy metals have to do with the capability of such materials in adsorbing heavy metals. There are few reports on the specific mode of action of the adsorbents and the extent of that adsorption (Takatsuji and Yoshida 1998).

Boiler fly ash is a renewable agricultural waste available at no or low cost (El Geundi 1991). The adsorptive capacities of natural products such as maize cob, sugar cane, sunflower stalks, cocoa pods to cationic dyes were significantly higher compared to the anionic compounds (Sun 1997). Therefore, it is necessary to explore the adsorption capacity of boiler fly ash to inorganic cations such as heavy metal ions. This study examined the effect of initial concentration of the Hg (II), Cd (II) and Fe (II) and also at varying concentrations over time on the adsorption of the metals from aqueous solution by boiler fly ash. These metals amongst other heavy metals constitute much environmental problems to the ecosystem. The accumulation of these heavy metals, if not controlled or treated from the source of effluent discharge may be accumulated in the concentrations

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in the water, soil and air. This can then further be transferred into food chain and cause metal poisoning in animals and humans (Ajayi and Osibanjo 1981; Binay *et al.* 1994; Okoronkwo *et al.* 2005) A pseudo-first and-second order model was applied to describe the adsorption process and to determine the variation in kinetic parameters produced by the change in initial concentration.

MATERIALS AND METHODS

Waste boiler fly ash was collected from Ukelu Oil Mill in Umulolo Okigwe Local Government Area of Imo State, Nigeria. The boiler fly ash was crushed and sieved through a 425 µm mesh. It was then activated by soaking overnight in 2% (v/v) of nitric acid, rinsed with deionized water. Thereafter, it was air dried and kept for experimental use.

Stock solutions of 1000 mg/l of each of Hg (II), Cd(II) and Fe(II) metal ions were prepared with deionised water using mercuric chloride powder, cadmium sulphate crystals and ferrous sulphate. All working solutions were prepared by diluting the stock solution with deionized water.

To determine the effect of contact time, 2 g of the waste boiler fly ash was put into a 100 ml solution of the metal ions of different initial concentrations: 50, 100, 150 and 200 mg/L. Different samples were left to stand for 20, 40, 60, 80 and 100min. The samples were filtered rapidly and the filtrate was analyzed by a UNICAM 919 atomic absorption spectrophotometer (AAS). The amounts of the metal ions adsorbed were obtained by difference that is, subtracting the final concentration of filtrate from the initial concentration of metal ions used, given by the equation:

$$qe = Co - Ce \qquad (1)$$

where qe is the amount of metal ions adsorbed (mg g^{-1}), Co is the initial metal ion concentration and Ce is the amount of metal ion remaining in solution. All experimental readings were performed in triplicates and the average values of each reading were used in the calculations. The standard deviations are shown as error bars in **Figs. 1** to **3**. Also, a two way analysis of variance (ANOVA) was used to analyze the results.

RESULTS AND DISCUSSION

The effect of contact time on adsorption of Hg (II), Cd(II) and Fe(II) for varying initial concentrations are shown in **Fig. 1** for Hg (II), **Fig. 2** for Cd(II) and **Fig. 3** for Fe(II) ions. The amount of the metal ions adsorbed increased with time. The sorption process was very rapid reaching equilibrium at about 20 min for the three metal ions. The trend of the sorption is Cd (II) > Fe (II) > Hg (II). For all the initial concentrations used, there was an initial rapid uptake of Cd (II) from solution.

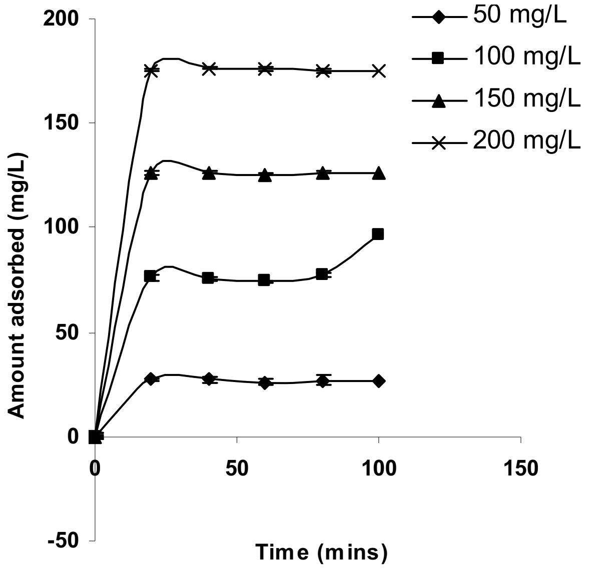

Fig. 1 Amount adsorbed (mg/g) against Time (mins) for adsorption of Hg (II) using boiler fly ash.

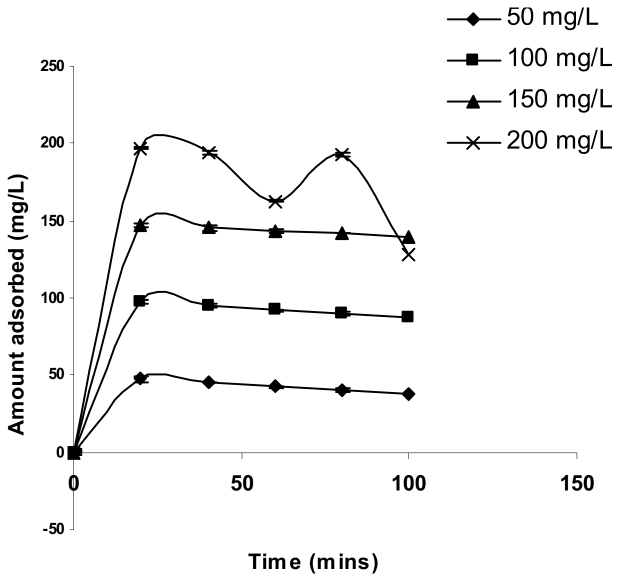

Fig. 2 Amount adsorbed (mg/g) against Time (mins) for adsorption of Cd (II) using boiler fly ash.

It can also be seen from these figures that as the initial concentration of the metal ions increased, the amount adsorbed also increased. This increase in the amount adsorbed as the initial concentration is increased has been reported by several workers (Horsfall *et al.* 2004; Babarinde-Adesola *et al.* 2007; Malkoc and Nuhoglu 2007). Again, looking at any particular initial concentration, for example 50 mg/L, as time was varied, the amount of Cd (II) ion adsorbed was higher followed by Fe (II) ion and then Hg (II) ion. This gives the trend of sorption as Cd (II) > Fe (II) > Hg (II).

The mode and trend of sorption of these metal ions on boiler fly ash could be explained based on the hydrolysis constants of the metal ions. The hydrolysis constants of the three metal ions are 10.1 for Cd (II), 9.5 for Fe (II) and 3.4 for Hg (II) (Burgess 1978). The hydrolysis reaction equilib-

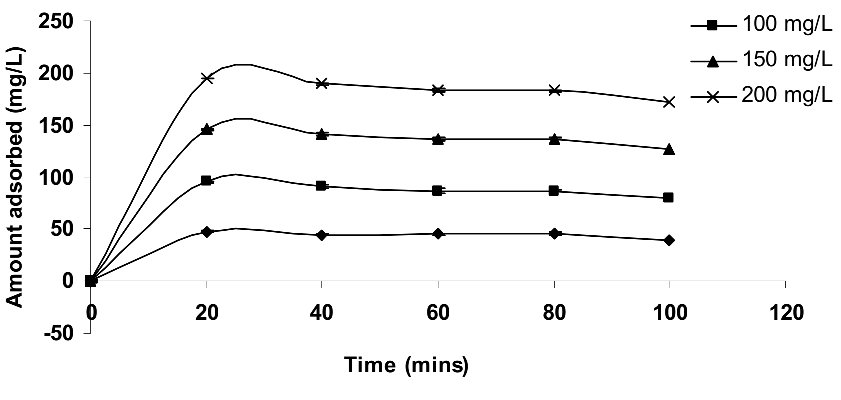

Fig. 3 Amount adsorbed (mg/g) against Time (mins) for adsorption of Fe (II) using boiler fly ash.

rium (using Cd (II) as an example) is in two stages:

$$Cd^{2+} + H_2O \leftrightarrows Cd\,OH^{+} + H^{+} \quad (2)$$

$$Cd\,OH^{+} + H_2O \leftrightarrows Cd\,(OH)_2 + H^{+} \quad (3)$$

In the first step, MOH+ is formed (M represents the metal ions, Cd in this case) and the adsorption event is completed through prompt interaction of heavy metal ions with negative groups on boiler fly ash. The overall reaction equilibrium is given as:

$$Cd^{2+} + 2H_2O \leftrightarrows Cd\,(OH)_2 + 2H^{+} \quad (4)$$

This means that from our experimental results, the metal ion that was adsorbed more is that which is more hydrolyzed. These observations of adsorption trend based on hydrolysis constant have also been reported (Uzun and Guzel 2000). Again, the sorption trend is in agreement with the enthalpy change of hydration for the metal ions.

A two way analysis of variance (ANOVA) without replication at 0.05 level of significance was used to describe the relationships (1) between the variation of time and initial concentration of the metal ions and (2) between the three divalent metal ions for binding sites on the adsorbent surface. The results are presented in **Table 1**. The data (**Table 1**) shows that for concentration effect, the variations reported are significant for the three metal ions. This means that the changes in the amount adsorbed as initial concentration was changed are significant. For the effect of time, only the changes in the amount adsorbed as time changed for Hg (II) ion was significant. For the other metal ions these changes were found to be insignificant. Therefore, these results indicate the potential of boiler fly ash to recover the metal ions from aqueous solutions. Similar results have also been reported (Horsfall and Abia 2003).

The sorption process was modeled using the pseudo-first and pseudo-second order equations. **Table 2** shows the rate constant, K, the equilibrium sorption $q_{e,}$ and initial sorption rate h_o, for the sorption of the three metal ions. These parameters were calculated from the intercept and slopes of the plot of log (q_e-q_t) versus time for the pseudo-first order and t/q_t versus time for pseudo-second order. Then the parameters were calculated from the intercepts and the slope of the plots using the following equations:

$$\log (q_e - q_t) = \log q_e - K_{ad}\, t/2.303 \quad (5)$$

for the pseudo-first order and

$$t/q_t = 1/h_o + 1/q_e(t) \quad (6)$$

for the pseudo-second order.
where
q_t = amount adsorbed at time (t)
q_e = equilibrium amount ($q_o - q_t$)
q_o = initial concentration
k_{ad} = rate constant for pseudo-first order

Table 1 Two way Analysis of Variance (ANOVA) without replication for the sorption process.

Sources of Variation	df	SS	MS	F_{cal}	F_{tab}
Cd^{2+}					
Concentration	3	50764.696	16921.565	95.356	3.49
Time	4	1524.0127	381.003	2.147	3.26
Error	12	2129.4809	177.457		
Total	19	54418.1896			
Fe^{2+}					
Concentration	3	55509.80	18369.933	132.0786	3.49
Time	4	556.333	139.083	15.4336	3.26
Error	12	108.141	9.01175		
Total	19				
Hg^{2+}					
Concentration	3	60774.2273	20258.076	931.9740	3.49
Time	4	89.422	22.355	1.0285	3.26
Error	12	260.841	21.7367		
Total	19				

Table 2 Shows the parameters for the pseudo-first and pseudo-second order equations.

Heavy metal	Pseudo-first order			Pseudo-second order			R^2
	k_{ad}	q_e	R^2	K_2	h_o	q_e	
Hg	2.303×10^{-3}	3.95	0.0382	2.78×10^{-4}	26.6667	-185.185	0.9987
Cd	7.369×10^{-3}	53.47	0.9884	13.46	312.5000	-4.8193	0.9947
Fe	4.376×10^{-3}	50.64	0.6459	7.22	39.2156	-2.3310	0.9837

Table 3 Comparison of pseudo kinetic constants for various sorption processes.

Contaminant	Adsorbent	Pseudo-first order	Pseudo-second order	Reference
Pb (II)	Valonia tannin resin	0.026	11.9	Ozacar *et al.* 2008
Cr (VI)	Waste acorn of *Quercus ithaburensis*	0.027	0.012	Malkoc and Nuhoglu 2007
Cr (VI)	Cornelian cherry	0.218	0.0081	Demirbas *et al.* 2004
Cr (VI)	Apricot stone	0.112	0.021	Demirbas *et al.* 2004
Cr (VI)	Almond shells	0.084	0.0018	Demirbas *et al.* 2004
Phenol	*Pseudomonas pictorium*	0.0487	7.723	Annadurai *et al.* 2007
As (III)	Coconut fiber	0.076	0.00116	Igwe and Abia 2006
Co(II)	Maize cob	0.0751	0.0167	Igwe and Abia 2007
Fe (II)	Maize cob	0.0113	0.0676	Igwe and Abia 2007
Cu (II)	Maize cob	0.0217	0.00054	Igwe and Abia 2007
Hg (II)	Coconut fiber	0.018	0.002	Igwe *et al.* 2008
As	Coconut fiber	0.018	0.002	Igwe *et al.* 2008
Pb (II)	Coconut fiber	0.022	0.0009	Igwe *et al.* 2008
Hg (II)	Boiler fly ash	0.023	0.00028	This study
Cd (II)	Boiler fly ash	0.074	13.34	This study
Fe (II)	Boiler fly ash	0.044	7.22	This study

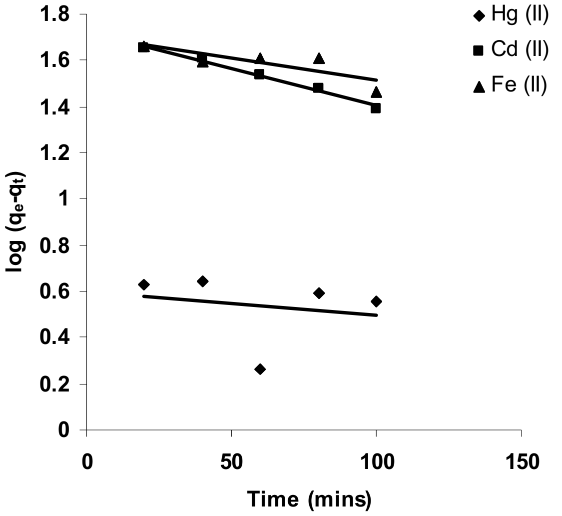

Fig. 4 Pseudo-first order plot for adsorption of Cd (II), Fe (II) and Hg (II) ions using boiler fly ash.

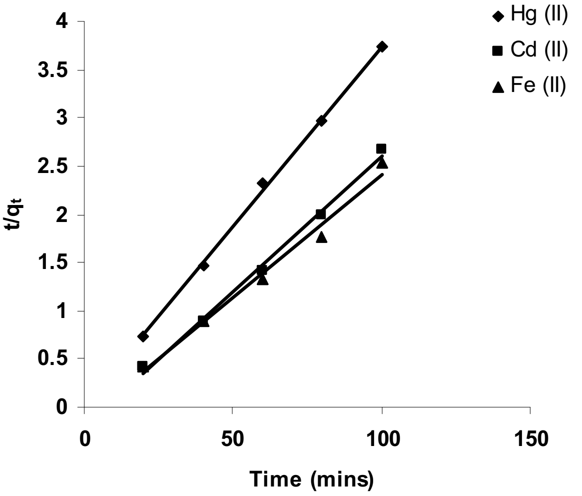

Fig. 5 Pseudo-second order plot for adsorption of Cd (II), Fe (II) and Hg (II) ions using boiler fly ash.

$k_2 = h_o/q_e^2$ for pseudo-second order (rate constant)
h_o = initial sorption rate
t = time (mins)

The pseudo-first order and pseudo-second order plots at initial concentration of 50 mg/L are shown in **Fig. 4** and **Fig. 5** for the various metal ions, respectively. The pseudo-second order gives a better fit with R^2 values of 0.9987, 0.9947 and 0.9837 for Hg(II), Cd(II) and Fe(II) respectively. The pseudo-second order rate constant for the metal ions were 13.46 for Cd(II), 7.22 for Fe(II) and 7.7 x 10^{-4} for Hg (II) all in mg $g^{-1}min^{-1}$. This confirms the trend of the sorption as Cd (II) > Fe (II) > Hg (II), which was proposed above because the rate constant was higher for Cd (II) ion followed by Fe (II) ion and then Hg (II) ion. The higher the rate constant, the higher the reaction rate, hence the sorption rate. Also, the use of pseudo first and pseudo second order kinetic equations for the analysis of sorption data has been reported by several authors. A comparison of the results by these authors and the result of this study is shown in **Table 3**. From this table, it could be seen that the results of this present study is similar to those results reported in literature. Most authors also reported that the pseudo second order equation gave a better fit to the sorption process (Ho and Mckay 1999; Malkoc and Nuhoglu 2007; Ozacar *et al.* 2008).

CONCLUSION

The detoxification of Hg (II), Cd (II) and Fe(II) from aqueous solution using boiler fly ash an agricultural waste was studied as effect of contact time on the metal ions for varying initial concentration. The trend of the sorption was found to be Cd (II) > Fe (II) > Hg (II). This trend in the sorption capacity was found to be dependent on the hydrolysis constant of these metal ions. The pseudo–second order kinetic model gave a better fit for the uptake of the metal ions. Therefore, boiler fly ash could be used as an effective adsorbent for the removal of the heavy metals from aqueous solutions.

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