Behavior of *Crastrotrea Gaser* Biomas And The Rate Controlling Mechanism Of Adsorption Process

OSU CHARLES I.* and S.A. ODOEMELAM[2]

*Department of Pure and industrial chemistry, University of Port Harcourt, PMB, 5323, Port Harcourt, Rivers State. Nigeria.

[2]Department of Chemistry, Michael Okpara University of Agriculture, Umudike, Nigeria.

*Corresponding Author: Phone: +2348037783246; Email: Charles.osu@uniport.edu.ng; charsike@yahoo.com

Abstract

The potentials of modified and unmodified shells of *Crastrotrea Gaser* to remove Hg(II), Pb(II), Cd(II) and Cr(III) from aqueous solutions have been investigated in this project. The amount of metal ion adsorbed from solution by these materials at equilibrium is found to depend on agitation time, Results obtained showed that chemical modification blocked some of the adsorption sites therefore, does not improve absorptivity. The percentage of the metal ions removed increases faster as agitation time increases from 1 – 20 minutes until equilibrium was attained at 20 – 40 minutes and decreased to a lower value at 45 – 60 minutes for all the metal ions studied. The level of metal ion uptake from solution follows the trend Hg(II) > Pb(II) Cd(II) > Cr(III) at equilibrium sorption. Different kinetics models were used to characterize the metal ion transport mechanism. The Pseudo-second order was found to best correlate the experimental data, best fit with R^2 values ranging from 0.9998 to 1.000 and average value of 0.9999.

Keywords: pollution, heavy metals, chemical kinetics, adsorbent, adsorption.

Introduction

Heavy metals are metallic elements, which have their atomic density greater than 6 g/cm^3. Considerable amount of most heavy metal ions are toxic and hence pose a threat to human health and the environment when they are discharged in the environment (Ghaffar, 2006). Environmental pollution by toxic metals occurs through industrial, military and agricultural process (Umesh and Dhiraji, 2005); smelling, petroleum refining, glass and ceramic manufacturing industries (Reed et al, 1994; Tsai et al, 2007). Other sources of heavy metals also exist and these have increased as a result of increase in urbanization and industrialization.

Recently, great deals of interest in the research for the removal of heavy metals from aqueous solutions have focused on the use of agricultural by-products in adsorption of heavy metals ions, which is known as bio-sorption.

Due to toxicity and bioaccumulation of these metals, the present study investigates the potential of waste sea animal shells such as *crasstrotrea Gaser* highly available environment friendly commercial adsorbents in removing lead, cadmium, mercury and chromium from aqueous solution. The effect of agitation time on the removal of the metals ions from aqueous solution and kinetic studies of the behavior of the adsorbents on the removal of the metals were also studied.

MATERIALS AND METHODS

Collection and preparation of samples.

The marine animal shells were collected from Okirika village of River state of Nigeria. They were washed thoroughly, clean of adhering dirt, rinsed thoroughly with de-ionized water and dried in the oven at 150 ^{o}C for two days. The process helped to remove moisture present in the material which was different from the chemisorbed water normally released during carbonization reactions of elevated temperature. Higher temperature of 170 ^{o}C was used to ensure complete dehydration. The purpose of dehydration was to effect de-sorption of physically absorbed water which may catalyze the decomposition of the char carbon thereby producing a very low carbon.

$H_2O + C$ ------------ $H_2 + CO$

After oven drying, the samples were macerated into powdered form. The powdered form of the samples obtained were sieved through a 500 µm mesh.

Chemical activation of the adsorbents.

The sieved samples were soaked in 0.3 M/L HNO_3 for 24 hours at room temperature. The adsorbents were then filtered through What man no. 41 filter paper and rinsed thoroughly with de- ionized water to maintain a pH of 7.4. The rinsed adsorbents were kept in an oven at 100^{o}C for 12 hours for the moisture and finally stored in an tight plastic container.

The treatment of the absorbent with 0.3 M/L $HN0_3$ aids to oxidize the adhering organic material, removal of any debris or soluble bio-molecules that might interact with the metal ions during the sorption. This process is called chemical activation of the sea animal shells.

Chemical modification of the absorbent.

The oven dried chemical activated samples were weighed and divided into two parts. 400g of first part were left untreated was labeled the unmodified sea animal shell A (USASA), where A is *Crasstrotrea Gaser.* 600g of second part were treated with 10 dm^3 of 3 M Oxalic acid solution for 24 hours at 28^{o} C in a well ventilation place according to the method of Okieimen and Okieimen,(2001). The biosorbents was then esterified (Drake et al., 1996) by suspending the adsorbent in 2.6 L of ethanol and 240 Ml of concentrated hydrochloric acid. The mixture was shaken for 5 hours at 150 rpm, filtered and the residue were washed thoroughly with distilled water to maintain pH of 6.9 and finally oven dried at 100^{o} C, stored and were labeled modified sea animal shell A,B and C (MSASA) respectively. Surface functional group can be introduced via chemical modification (Okieimen et al., 1991; Drake et al., 1996; Krishnakuma et al., 2007).

All reagents used were analytical grades, purchased and used without further purification.

Effect of contact time.

To determine the effect of contact time, a 1 g of the absorbent both modified and unmodified of particle sizes 500 µm were put into 50 Ml solution of the various metal ions solution 4 Mg/L initial concentration in a conical flask. Different samples were left to stand for 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 minutes in a rotary shaker at a constant speed of 150 rpm at a temperature of 29^{o} C and pH of 7.4. At the end of each time, the sample was filtered. The various metal ions of the filtrates were determined by an air acetylene flame atomic absorption spectrophotometer (UNICAM SOLAAR 32).

Adsorption kinetics and dynamics.

Pseudo- first order kinetic. This was given by

dqt/dt = Ki (qe- qt) - - - - -1.0

Taking the integrated form we have, log (qe-qt) = logqe – Ki t/2.303 - - - -1.1

A plot of log (qe-qt) against t gives a straight line with Ki and qe as the slope and intercept.

Pseudo-second order kinetics, expressed as (Ho et al., 2000)

dqt/dt = K_2 (qe – qt)^2 - - -2.0

Where, k_2 is the rate constant of pseudo – second order adsorption (g/Mg/Min). For the boundary conditions t = 0 to t = t and qt = qt, the integrated form of equation 2.0 becomes

1/ (qe –qt) = 1/ qt + Kt - - - - - -2.1, which is the integrated rate law for a pseudo- second order reaction. Equation 2.1 can be rearranged to obtain equation which has a linear form: t /qt = 1/ (K_2qe^2) + (1/qt)t - - - -2.2

The plot of t/qt against t gives a straight line from which qe band K_2 can be determined from the slop and intercept of the plot.

Elovich kinetic model

This equation is expressed as (Chien and Clayton, 1980; Sparks, 1986):

dqt/dt = αexp(-βdt) - - - 3.0

where α is the initial adsorption rate (Mg/g/min); β is the desorption constant (g/mg). Chien and Clayton (1980) simpilified equation 3.8 to equation 3.9 below

$qt = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t$ - - - - -3.1

Thus, a plot of qt against ln (t), gives a straight line.

Intra-particle diffusion model

Mckay and Poots (1980) proposed one model for intra-particle diffusion given by

$qt = xi + K^1 t^{1/2}$ - - - - 4.0

Plot of qt against $t^{1/2}$ gives a straight line graph. The extrapolation of xi gives the intercept which is proportional to boundary layer thickness.

Intra- particle diffusion model can also be expressed as (Weber and Morris, 1963; Srivastava et al., 1989).

$R = Kid\ (t)^{a}$ - - - 3.1

A linearized form of the equation is log R = log Kid + a log (t). A plot of log R against log t gives a straight line with intercept not passing through the origin.This indicates that the pore diffusion is not only the rate limiting step for the biosorption of Hg (II), Pb(II), Cd(II) and Cr(III) ions on *Crastrotrea Gaser*. Where R is the percent metal adsorbed; t is the contact time (min); a is the gradient of linear plots; Kid is the intra particle diffusion rate constant (min^{-1}).

Results and Discussion

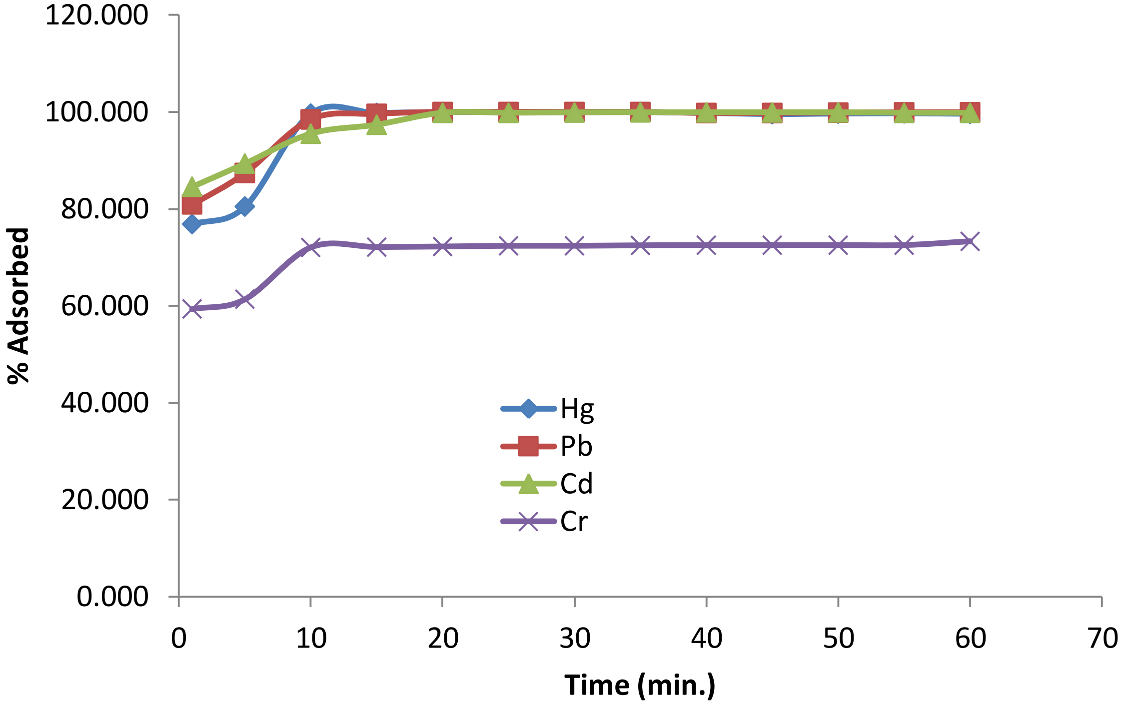

Figure 1. Effect of agitation time for the removal of Hg(II), Pb(II), Cd(II) and Cr(II) ions on USASA

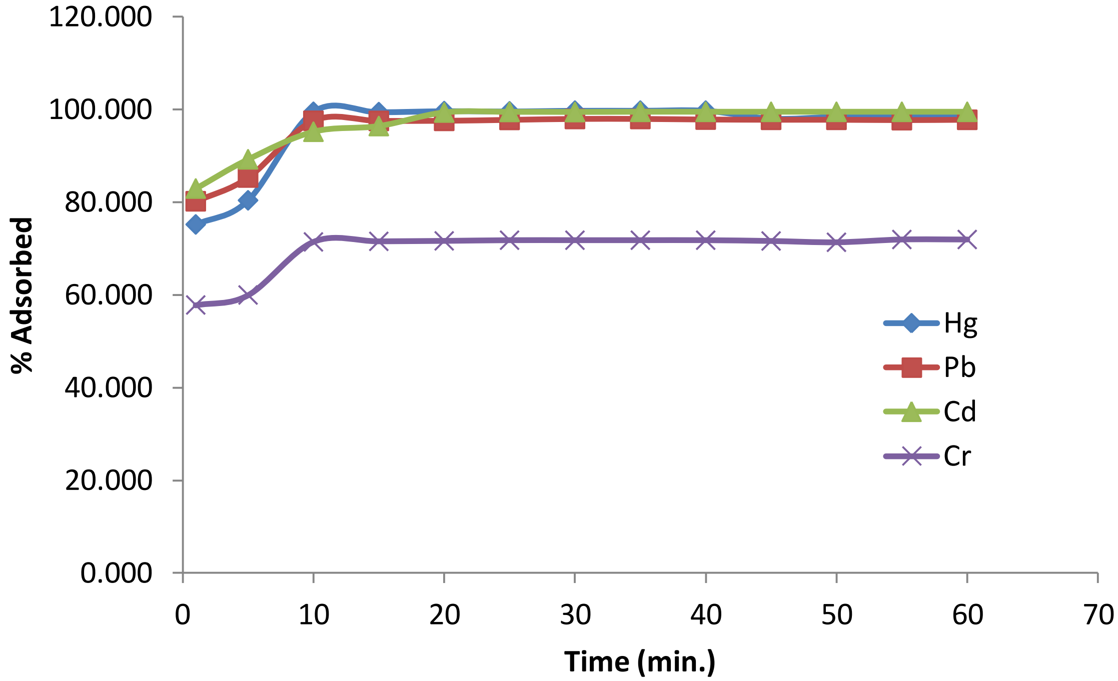

Figure 2. Effect of agitation time for the removal of Hg(II), Pb(II), Cd(II) and Cr(III) ions on MSASA

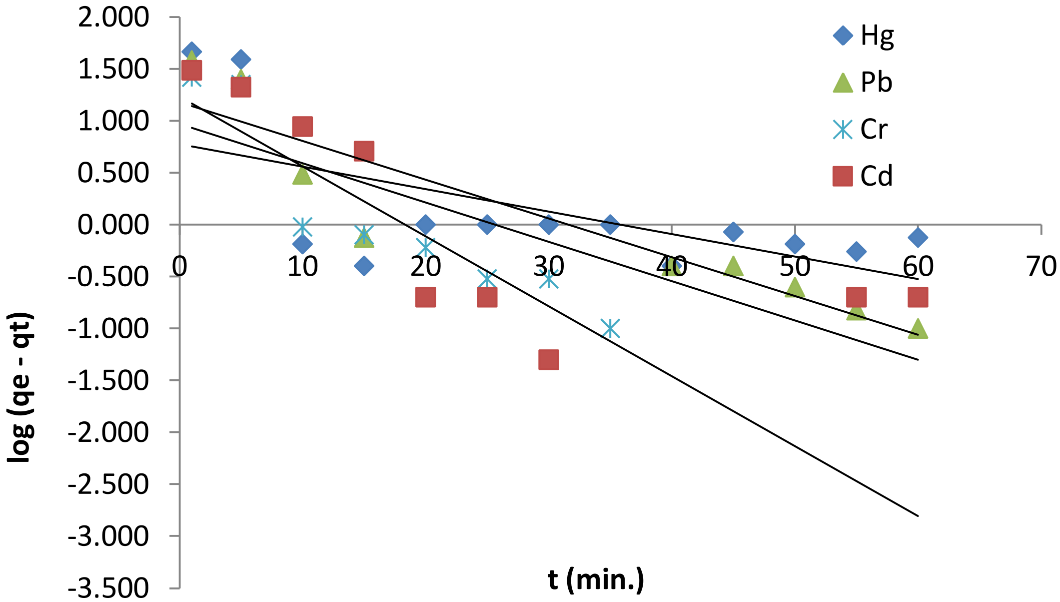

Fig. 3. Pseudo-first order kinetics of Hg(II), Pb(II), Cd(II) and Cr(III) ions USASA

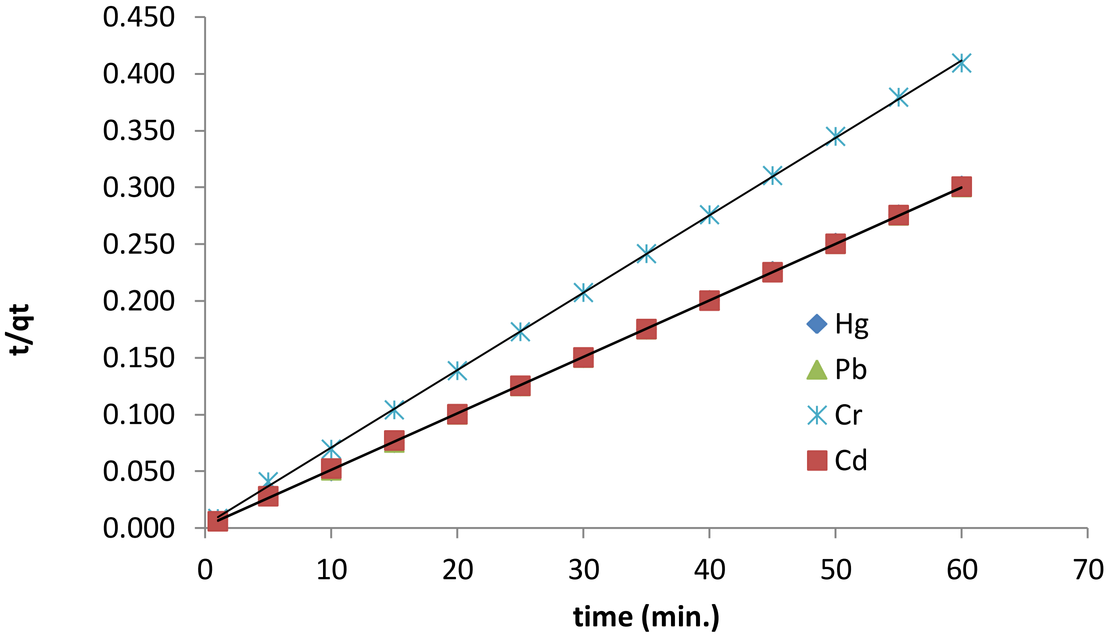

Figure 4. Pseudo-second order kinetics of Pb(II), Hg(II), Cr(III) and Cd(II) ions on USASA

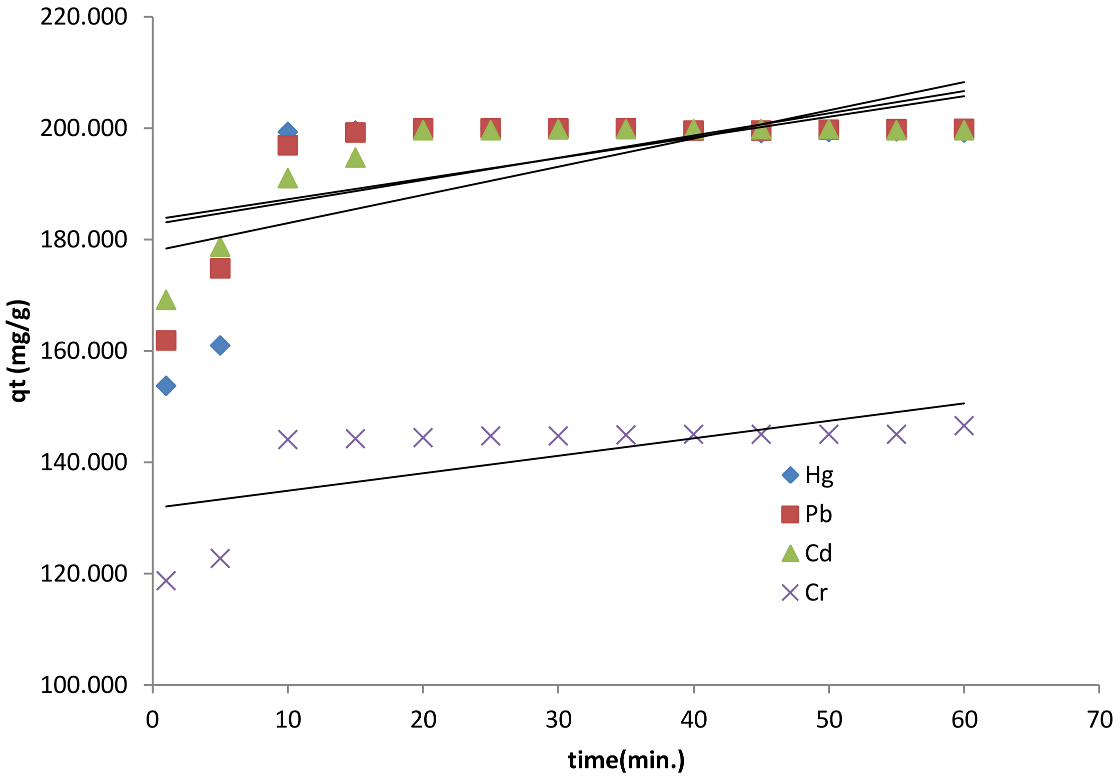

Figure 5.Elovich sorption kinetics for Hg(II), Pb(II), Cr(III) and Cd(II) ions on USASA

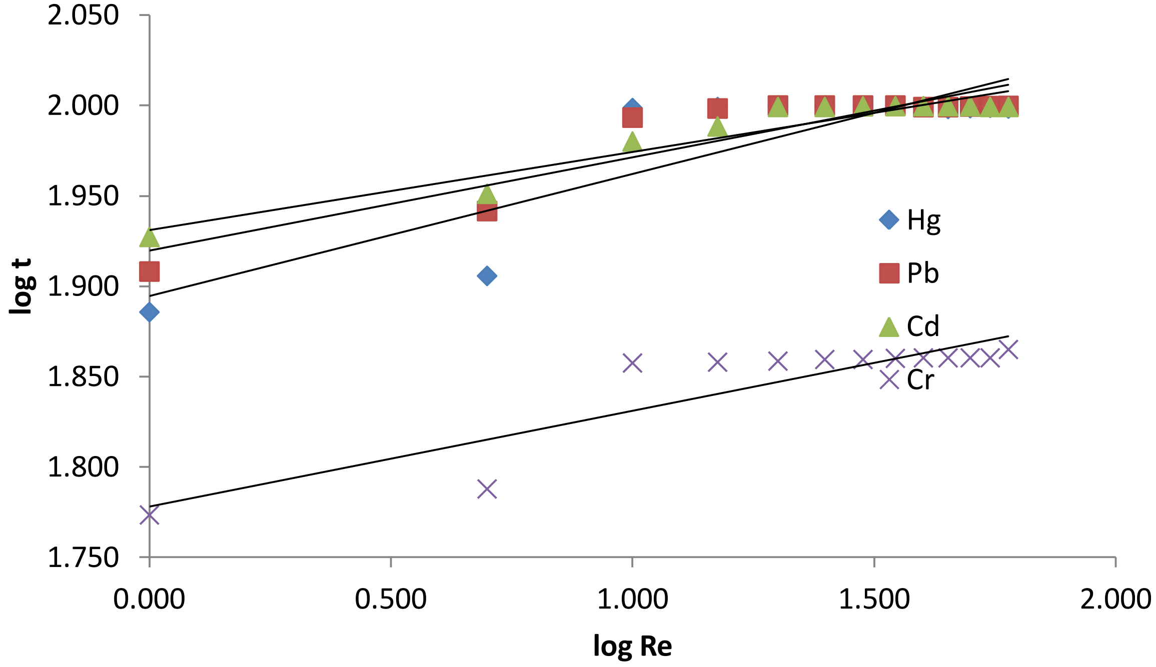

Figure 6. Intra-particle diffussion model for Hg(II), Pb(II),Cd(II) and Cr(III) ions on USASA

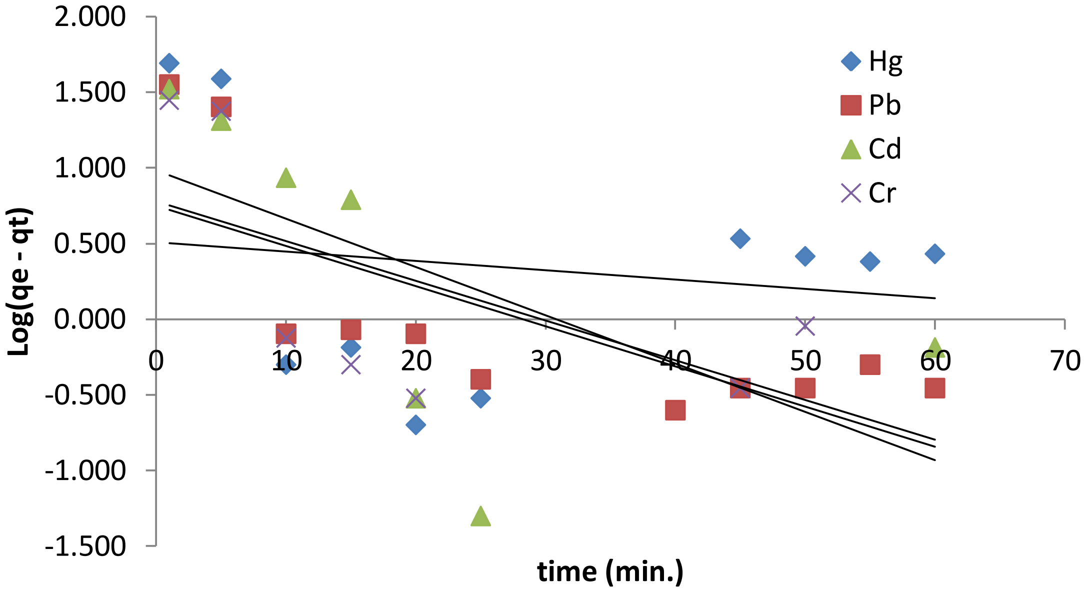

Figure 7. Pseudo-first order kinetics of Hg(II), Pb(II), Cd(II) and Cr(III) ions on MSASA

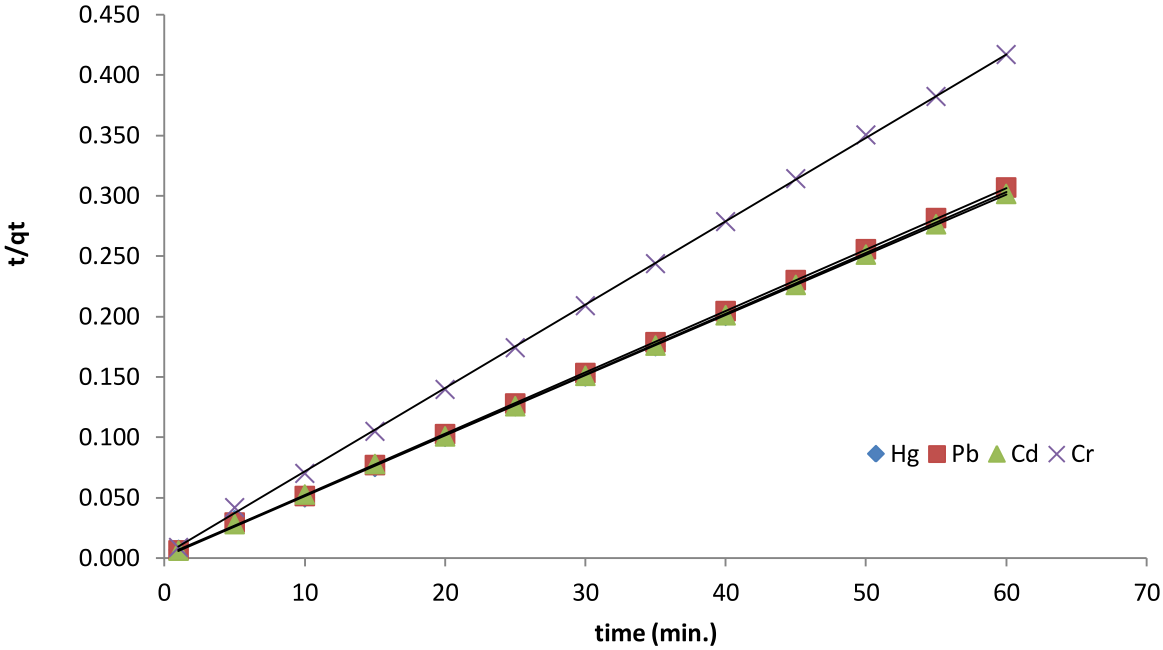

Figure 8. Pseudo-second order kinetics of Pb(II), Hg(II), Cr(III) and Cd(II) ions on MSASA

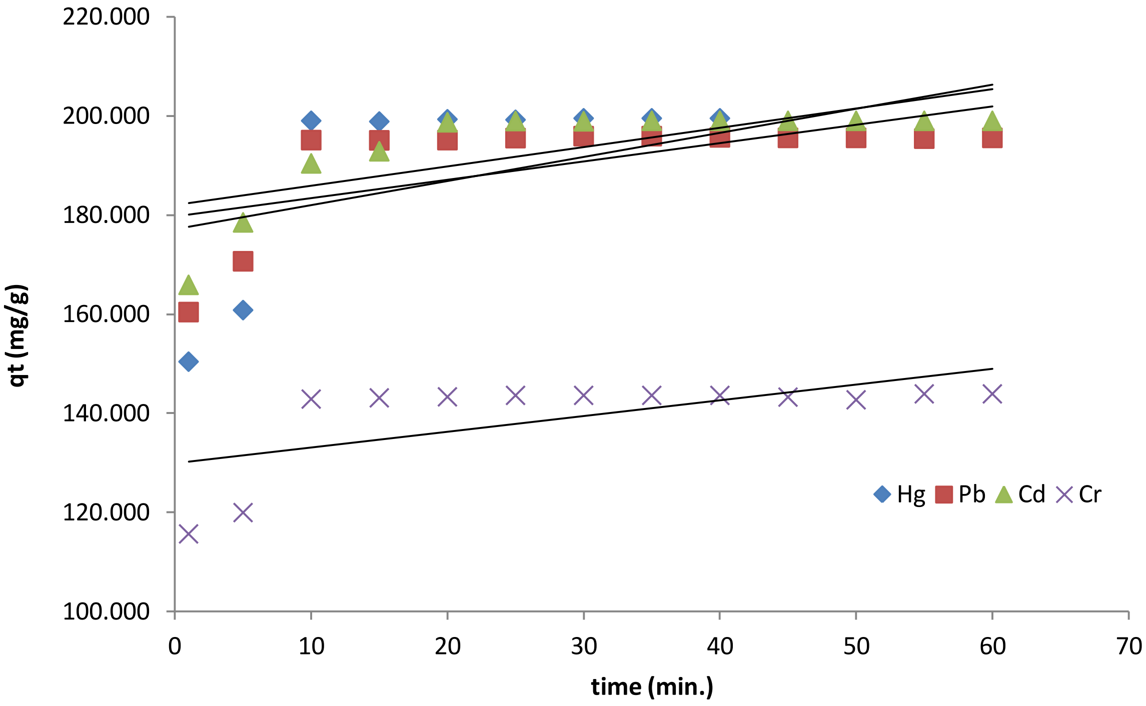

Figure 9.Elovich sorption kinetics for Hg(II), Pb(II), Cr(III) and Cd(II) ions on MSASA

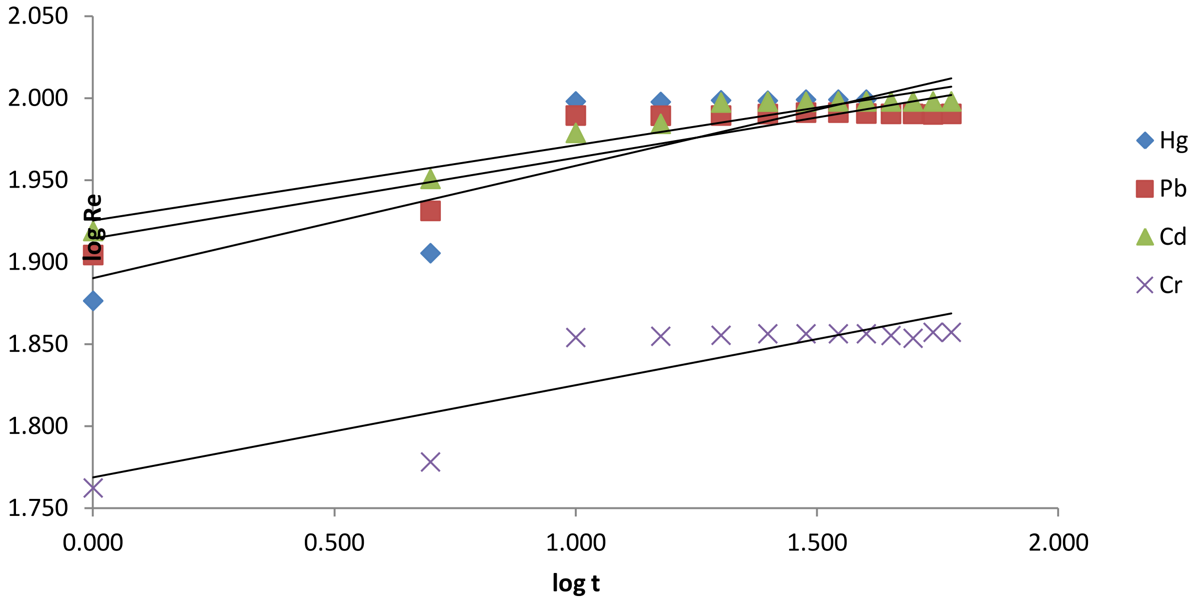

Figure 10. Intra-particle diffussion model for Hg(II), Pb(II),Cd(II) and Cr(III) ions on MSASA

Table 1. Kinetic parameter for pseudo-second order equation for the metal ions on USASA and MSASA

	USASA			MSASA		
Metal ions	h(mg/g/min)	q_e(mg/g)	r^2	h(mg/g/min)	q_e(mg/g)	r^2
Hg(II)	1111.11	200.00	0.9996	588.24	200.00	0.9997
Pb(II)	714.29	200.00	0.9999	1111.11	200.00	0.9996
Cd(II)	555.56	200.00	0.9999	526.32	200.00	0.9999
Cr(III)	344.83	147.03	0.9999	416.17	144.93	0.9998

Table 2. Kinetic parameter for pseudo-first order equation for Hg(II) ion on USASA and MSASA

	USASA			MSASA		
Metal ions	K_1(L/min)	q_e(mg/g)	r^2	K_1(L/min)	q_e(mg/g)	r^2
Hg(II)	0.05	6.01	0.3797	0.014	3.235	0.0285
Pb(II)	0.086	15.06	0.8518	0.061	6.026	0.5469
Cd(II)	0.087	9.36	0.5553	0.073	9.607	0.359
Cr(III)	0.155	17.18	0.8502	0.061	5.622	0.3662

Table 3. Kinetic parameter for Elovich equation for the metal ions on USASA and MSASA

	USASA			MSASA		
Metal ions	α(mg/g/min)	β(mg/g/min	r^2	α(mg/g/min)	β(mg/g/min)	r^2
Hg(II)	11.906	157.07	0.753	11.951	155.64	0.7308
Pb(II)	9.398	166.28	0.824	8.785	164.31	0.7948
Cd(II)	8.03	170.41	0.909	8.473	168.09	0.9196
Cr(III)	1.001	119.96	0.795	7.302	117.39	0.7705

The effect of agitation time for the removal of Hg(II), Pb(II), Cd(II) and Cr(III) ion on unmodified and modified sorbents used in this study were presented in figures 1 to 2. It was observed that the percentage of the metal ions removed increases faster as agitation time increases from 1 – 20 minutes until equilibrium was attained at 20 – 40 minutes and decreased to a lower value at 45 – 60 minutes for all the metal ions studied. A short contact time necessary to reach equilibrium indicates that the predominant mechanism is chemisorption (Poots, 1978).

The initial faster rate of removal of the metal ions at the commencement of sorption may due to the availability of the uncovered surface area of the adsorbent, this trend is due to the phenomenon that adsorption kinetics depend on the surface area of the adsorbents. The enhanced sorption of the metal ions by the adsorbents with increase in agitation time may be due to the decrease in boundary layer resistance to mass transfer in the bulk and an increase in the kinetics of hydrated metal ions (Horsfall and Abia, 2003). Also, the rapd uptake of metal ions from the solution suggests that the binding sites are cell wall functional groups and that diffusion of metal ions through the cell wall is relatively small (Gardea- Torresdey et al., 1998d).

Kinetics of metal sorption governs the rate, which determines the residence time, and it is one of the important characteristics defining the efficiency of an adsorbent (Krishnan and Anirudhan, 2003). Sorption kinetics can be controlled by several independent processes that could act in series or in parallel, such as bulk diffusion, external mass transfer (film diffusion), chemical reaction (chemisorption) and intra-particle diffusion (Ho et al., 2000).

Examination of literature reveals the existence of different opinions concerning the diffusion, giving place to various models for the prediction and the description of the process. However, these approaches coverage at an identical total sight concerning the adsorption mechanisms. These mechanisms are grouped into four phases; transfer of matter of the solution towards the boundary layer surrounding the particle, transfer of the boundary layer towards adsorbent surface (external diffusion), transfer of surface towards the adsorbent sites or intra-particular diffusion (in the solid and the various pores), adsorption complexation and precipitation of metal species and chemical reaction (chemisorption).

However, it is quite common that more than one process can contribute to the system performance at the same time. Hence, the kinetic models that were used in this study were; Pseudo-first order, Pseudo-second order, Elovich and intra-particle diffusion equations.

The Pseudo-first order kinetics of the metal ions on the adsorbents is illustrated in figure 3 and 7. From the graphs the kinetic parameters for the Pseudo – first order equation were presented in table 2. From the tables, it was seen that sorption capacity q_e decrease with chemical modification, while Pseudo- first order rate constant, K_i decreased with chemical modification. Figures 4 and 8 indicates the Pseudo – second order kinetics of the metal ions on the adsorbents. The kinetic constants h and q_e were presented in tables 1. From the tables, the values of h decreases with chemical modification, while q_e are fairly the same for all the metal ion except for Cr(III) ion which ranges from 147.06 -151.52. Figures 5 and 9 illustrates the Elovich equation model, where the constants were presented in table 3. From the tables, it was observed that α increases with chemical modification for the metal ions except Pb(II) ion and β decreases with chemical modification in all metal ion.

However, to determine the most appropriate kinetic model that describes the mechanism of transport of the metal ions onto the adsorbents used, a model selection criterion was used to determine their level of suitability and consistency. In this study, the coefficient of determination, r^2 was used to test the best-fitting of the kinetic models to the experimental data. Comparing the r^2 values of the three models in table 1. shows that the coefficient of determination values for the Pseudo-second order kinetic equation were highest (0.9999) and ranges from 0.9996 to 0.9999. Since the values were closet to unity or unity, the model best described the mechanism of sorption of the metal ions onto the adsorbents.The pseudo- second order model is based on the assumption that sorption follows a second order mechanism. So the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites and has the rate limiting step as a chemical sorption (Chemisorption step)

Furthermore, the agreement between the values of the adsorption capacity, q_e from the pseudo-second order model and the experimental observed values of the sorption capacity also confirmed the assumption that the pseudo-second order equation is the best fitting model for the description of the metal ions sorption onto the adsorbents. This view was also observed for sorption of some heavy metals using various adsorbents (Abia et al., 2007; Krishnan and Anirudhan, 2003; Ho and Mckay, 1999).

Conclusion

The biomass of *Grasstrotrea Gaser* demonstrateda good capacity for Hg(II), Pb(II), Cd(II) ions bio sorption except for Cr(III) ion which is less than 80 %. The incorporation of the ester groups onto the adsorbent surface affected the adsorption. The modification alters the surface characteristics of the adsorbents, hence affects the amount of metal ions adsorbed. Unmodified adsorbents which are environmentally friendly had a higher efficiency than the modified adsorbents which is not environmentally friendly.

Different kinetics models were used to characterize the metal ion transport mechanism. The Pseudo-second order was found to best correlate the experimental data. This is based on the adsorption is that the rate limiting step may be chemical sorption or chemisorptions involving valance forces through sharing or exchange of electrons between sorbent and sorbate.The parameter which has the influence on the kinetics of the sorption reaction was the sorption equilibrium capacity, $q_{e,}$ which is a function of initial metal ion concentration and the nature of the adsorbents.

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