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Comparative sorption studies of some metal ions with animal shells

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ABSTRACT

Comparative study of the adsorption capacities of four calcareous shells for Pb(II), Cr(VI) and Fe(II) was investigated. The study was conducted at room temperature as a function of pH, initial concentration of the metals and contact time. Optimum sorption at pH of 2.0, 5.0 and 6.0 was observed for Fe (II), Cr (VI) and Pb (II) respectively. Adsorption removal efficiency increased proportionally to contact time and decreased as the initial concentration was increased. Langmuir and Freundlich isotherms were applied to model the process and good fitness was found for Langmuir $R^2 > 9.5$ with values of $R_L<1$. Pseudo second-order kinetic provided the best fit for the experimental data with calculated values of q_e almost equal to the experimental values. Chemical reaction was determined to be the primary mechanism of adsorption. Results indicated that animal shells could be employed as excellent adsorbents for the removal of heavy metals from wastewater pollutants.

Introduction

Natural phenomena such as weathering, biological activity and volcanic activity together with anthropogenic inputs are responsible for the presence of heavy metals in the environment. In Nigeria, increase in infrastructural development fueled by economic growth has created opportunities in solid mineral mining, petroleum processing, metal processing, battery production, petrochemicals and allied products manufacturing. These activities have contributed to the release of heavy metals into the environment. Their presence in the environment has become a serious threat to the lives of fauna and flora as well as human beings. They are drained into surface waters or leached into the underground aquifers from the anthropogenic activities mentioned.

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Srivastava & Majumder, 2008). Heavy metals are extremely toxic, non-biodegradable and tend to bioaccumulate as organo-metallic complex in living organisms (Bailey *et al.*, 1999; Fu & Wang, 2011; Udosen *et al.*, 2001), and many heavy metals ions are known to be toxic or carcinogenic especially in some oxidation states (Fu & Wang, 2011; Xue *et al.*, 2000). Metals such as Fe (II), Fe (III), Mn (II), Mn (VII) and Cr (III) are essential micronutrients for organisms and plants. However, they can become toxic at higher concentrations. Exposure to flue gases or the ingestion of compounds of lead and chromium can cause permanent system dysfunctions in both animals and human beings. Lead is highly hepatotoxic causing damage to the central nervous system, kidney, liver and reproductive system, basic cellular processes and brain functions (Mudipalli, 2007; Inam *et al.*, 2010). The symptoms include anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages (Naseem & Tahir, 2001; Udoessien, 2003). Chromium exits in the aquatic environment mainly in two states: Cr (III) and Cr (VI). In general, Cr (VI) is more toxic than Cr (III). Cr (VI) affects human physiology, accumulates in the food chain and causes severe health problems ranging from simple skin irritation to lung carcinoma (Khezami & Capart, 2005). Iron is the fourth most abundant element in the earth's crust; it is present in a variety of rock and soil minerals both as Fe (II) and Fe (III). Fe (II) is required for proper transport and storage of oxygen by means of hemoglobin and myoglobin while its oxidized forms, methemoglobin and metmyoglobin, which contain Fe (III), will not bind oxygen (Safavi & Abdollahi, 1999). Iron plays an essential role in photosynthesis and is the limiting growth nutrient for phytoplanktons in some parts of the ocean (Kieber *et al.*, 2001). Both Fe (II) and Fe (III) are important in the biosphere, serving as an active center of a wide range of proteins such as oxidases, reductases and dehydrases. Waste effluents from steel tempering, coal coking and mining industries, for example, contain significant quantities of iron as well as other metals, (Aksu *et al.*, 1999). Therefore, the presence of ions of these metals in wastewaters, even at very low concentrations, is hazardous to the aquatic ecosystem and raises many health risks for human beings.

Many conventional techniques such as chemical precipitation, membrane filtration, electrolysis, ion exchange, co-precipitation and adsorption are used for the removal of heavy metals in wastewater treatment, but they are suitable for high concentrations of metals (Shukla & Sakhardande, 1991; Phalman & Khalafalla, 1998; Bailey *et al.*, 1999; Lee & Rowell, 2004; Min *et al.*, 2004; Kamel *et al.*, 2004; Park *et al.*, 2006; Hashem *et al.*, 2007). At low metal concentrations, using these techniques becomes very challenging. The removal of heavy metals via sorption over solid adsorbents has become more convenient and is now recognized as an effective and economic method for removal of heavy metals in wastewater treatment systems (Yeddou & Bensmaili, 2007; Fu & Wang, 2011; Adeogun *et al.*, 2012). The adsorption process offers flexibility in design and operation and in many cases produces high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process. Therefore, the present work is aimed at testing the

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ability of calcareous shells of animal origin (chicken egg shell, snail shell (*Achatina fulica*), periwinkle shell (*Littorina littorea*) and clam shell (*Arctica islandica*)) as adsorbent for the removal of Pb (II), Cr (VI) and Fe (II) from water contaminated with these metals.

Materials and methods

Stock solutions

Stock solutions of Pb (II), Cr (VI) and Fe (II) (0.5M) were prepared by dissolving analytical grade salts of the metals ($Pb(NO_3)_2$, $FeSO_4.7H_2O$ and $K_2Cr_2O_7$) obtained from May and Baker Ltd, Dagenham, England in 1 dm^{-3} of water. Working solutions were prepared from the stock by serial dilution to desired concentrations.

Other reagents used including concentrated Hydrochloic acid (HCl), Sodium Hydroxide (NaOH) and Orthophosphoric acid (H_3PO_4) were obtained from Sigma-Aldrich chemicals. UV-visible spectrophotometer (Jenway 6100 Model) was employed to measure the absorbance of the metals.

Preparation of adsorbent and adsorbate

The empty shells were obtained from waste bins in Uyo Metropolis, Akwa Ibom State, Nigeria. They were washed with tap water to remove adhered impurities, rinsed with deionized water and allowed sun dried. They were then crushed and dried in an oven at 100°C for 12 hours, ground to powdery form and screened with 80-mesh to obtain particles of this size. Each sample was weighed and carbonized in a muffle furnace (model GLM 3) at a temperature of 600°C for 2 hours. The samples were labeled ES, SS, PS and LS for chicken egg shell, snail shell; periwinkle shell and clam shell respectively, and allowed to cool to room temperature. These were leached with 0.1MHCl and washed with distilled water.

Activation of the samples was carried out in a with orthophosphoric acid (H_3PO_4). Each of the samples was placed in a crucible; 0.5MH_3PO_4 was added, mixed and heated until a paste was formed. It was then subjected to a temperature of 700°C for 3 hrs and then cooled to room temperature. Activated samples were washed with distilled water to removed excess acid and oven-dried at 100°C for 12 hrs. Samples were stored in an air-tight container.

Sorption experiments

The adsorption experiments were carried out in 250ml volumetric flask at room temperature. 50ml of 0.05M solutions of Pb (II), Cr (VI) or Fe (II) was measured into four flasks for the respective animal shells. For pH adjustments additions of small volumes of concentrated hydrochloric acid or sodium hydroxide solutions were used. For Fe (II) the pH was set at 2.0, Pb (II) 6.0 and 5.0 for Cr (VI). 0.4g of the each activated shell sample was added to the different flasks. The flasks were sealed and shaken at 200 rpm in a magnetic shaker for 3 hrs. After equilibration, the mixtures were filtered using Whatman No. 42 and analyzed for free metal concentrations using UV-visible spectrophotometry at λ_{max} 217nm for Fe (II), 248nm for Pb (II) and 357nm for Cr (VI) respectively. All experiments were performed in triplicates and average values were used in all calculations. For kinetic experiments, the initial concentration of the metals was set at 0.05 M and 100 mL solution was collected at different time intervals. The free metal concentration is the difference between the initial concentration and final concentration at time, t in solution. The percentage of the metals absorbed at equilibrium, % M is given in the equation below:

$$\% M = \frac{Co - Ce}{Co} \times 100 \qquad (1)$$

The adsorption capacity of the animal shells, q_e is given as:

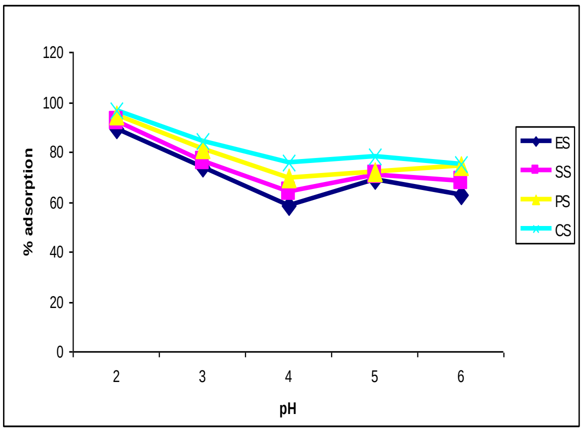
$$q_e = \frac{V}{m}(Ce - Co) \qquad (2)$$

where C_o is the initial concentration of the metal ions (mol), C_e is the concentration of the metal ions at equilibrium (mol), V is the volume of the metal ions in contact with the adsorbent (ml) and m is the mass of the adsorbent in (g).

Results and discussion

Effect of pH on Pb (II), Fe (II) and Cr (VI) sorption on calcareous shells

The sorption of Pb (II), Fe (II) and Cr (VI) (0.05 mol dm^{-3}) on calcareous shells (0.4g in 100 ml) was plotted against the final pH of solution (Figure 1a, b, c) at room temperature (27±0.5ºC). The removal efficiency decreased with increasing pH and almost reaches a steady value at about the pH of 5.0 and 6.0 for Fe (II) (Figure 1a); though a slight decrease was observed for ES. The removal efficiency of Cr (VI) by the shells increased as the pH increased and reached a peak at pH 5.0 and then decreases with increasing pH (Figure 1b). Similarly Pb (II) showed an enhanced removal by the shells at pH of 6.0 (Figure 1c). The results are considerably consistent with eggshells and chitin adsorbents studied by Yeddou & Bensmaili, (2007). In literature the optimal pH for the adsorption of Fe (II) is between 3 and 5 (Ngah *et al*., 2005; Dai *et al*., 2012), Cr (VI) is 5-8 (Wu *et al*., 2010; Wankasi and Tarawou, 2008) as well as Pb (II) around 5-6 (Kabbashi *et al*., 2009; Du *et al*., 2011). At pH lower than 5 and 6 for Chromium and lead respectively, competition between hydrogen and metal ions for the sorption sites exist, which restricts the approach of metal cations as a consequence of repulsive forces, and the removal is strongly inhibited (Hanif *et al*., 2007).



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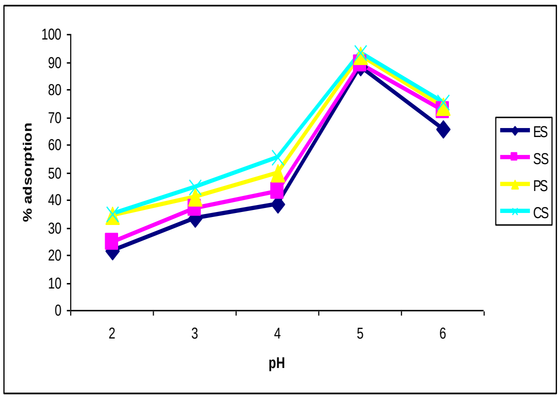

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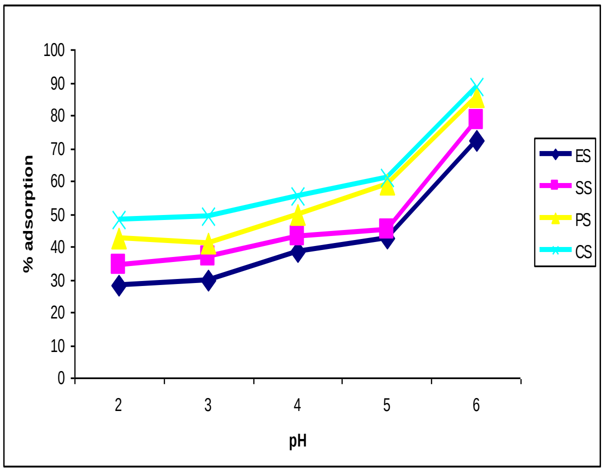

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Figure 1 Effect of pH on the removal of (a) Fe (II); pH= 2, adsorbent dose=0.4g, @ 120min (b) Cr (VI); pH= 5, adsorbent dose=0.4g, @ 120min and (c) Pb (II); pH= 6, adsorbent dose =0.4g, @ 120min onto animal shells at room temperature.

At higher pH values, the sorption decreases significantly. The decrease in sorption at pH higher than these values is due to the formation of soluble hydroxylated complexes of the metal ions and their competition for the active sites (Sari *et al.*, 2007). In the case of Fe (II), as pH increases from 2.0 to 5.0, (Figure 1a) the removal efficiency decreases. It is assumed from the results that the metal adsorption mechanism might probably due to the ion exchange. At low pH, the existence of relatively large number of hydrogen ions may change the direction of reversible ion exchange equilibrium back to starting materials. In a higher pH range, existing of counter ions might result in lower efficiency of adsorption (Yu *et al.*, 2001). Basically, the major component of animal shells is $CaCO_3$ which impart alkalinity to the system. It is expected that any aqueous solution equilibrated with calcareous shells become more basic that could be confirmed by the following mechanism (Brown & Lemay, 1985).

$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$

$CO_3^{2-} + H_2O \rightarrow HCO_3^{-} + OH^{-}$

The hydrolysis of $CaCO_3$ produces basic solution due to Ca^{2+} and OH^{-} ions, responsible for increasing pH of the solution, adjusting the solution pH is paramount in obtaining greater removal efficiency for the metal ions.

Effect of contact time

Adsorption of the metals ion on calcareous shells was investigated as a function of contact time at initial metal concentration of 0.02 mol dm^{-3} and results presented (Figure 2a-b). The graphs show that the sorption process has a fast kinetics, with the rate of ions removal higher at start of experiment. This is due to available surface at beginning for the adsorption for metal ions. As the sorption sites become unavailable, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. For the entire metals ion studied similar pattern was observed for variation in time. Between 5 min and 120 min, an average of 28%, 30.55% and 38.2% of Pb (II), Cr (VI) and Fe (II) respectively were removed. Maximum removal was obtained after about 120 min of equilibration time. However, allowing contact for 180 min did not produce any significant change in removal percentage.

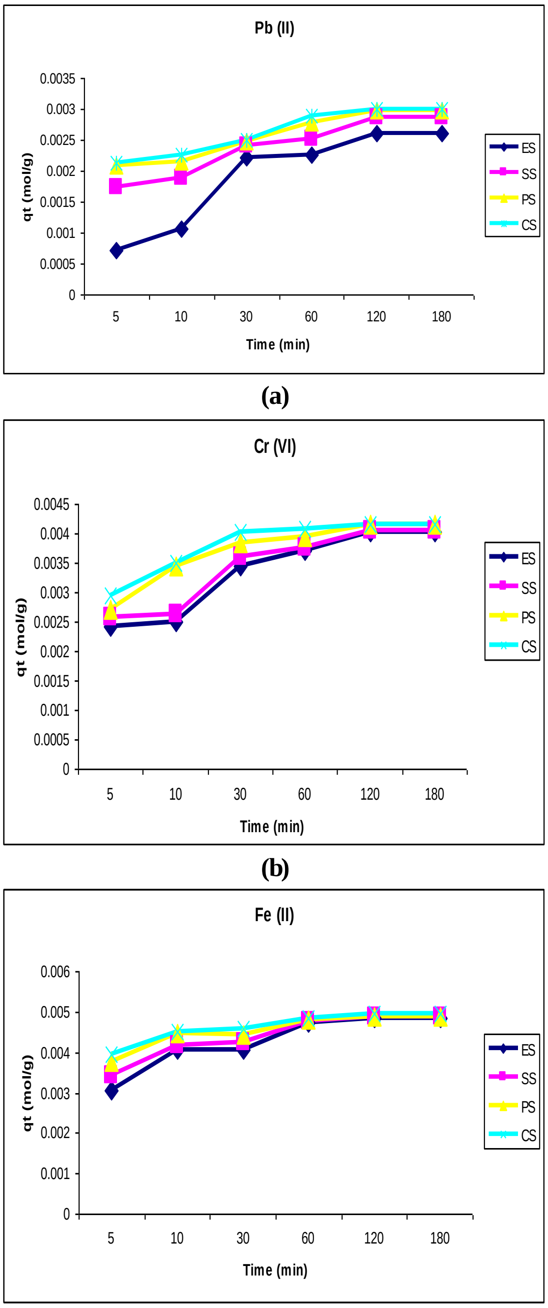

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Figure 2 Effect of contact time for the removal of metals ion onto calacreous shells at room temperature (Pb (II): pH=6, adsorbent dose=0.4g, @ 120min; Cr (VI): pH=6, adsorbent dose=0.4g, @ 120min; Fe (II): pH=6, adsorbent dose =0.4g, @ 120min.

Effect of initial concentration of metals ion

The effect of variation in metal concentration (0.01mol dm^{-3} to 0.05mol dm^{-3}) on sorption of metal ions to calcareous shells was studied. The results are presented in Figure 3a-c. It is evident that the adsorption capacities of the metals increased with increase in concentration of the metals ion. Generally, initial metals concentration provides the necessary driving force to overcome the resistances to the mass transfer of adsorbates between the aqueous phase and the solid phase (Yeddou & Bensmaili, 2007). The increase in initial concentration also enhances the interaction between adsorbate and adsorbent. An increase in initial concentration enhances the uptake of metals ion due to increase in the driving force of the concentration gradient. The adsorption capacity of the calcareous shells increases from 0.00248mol/g in 0.01M Fe (II) to 0.0120 mol/g in 0.05M Fe (II) solution, 0.0037mol/g in 0.01M Pb (II) to 0.0234mol/g in 0.05M Pb (II) solution as well as from 0.00218mol/g in 0.01M Cr (VI) to 0.00998mol/g in 0.05M Cr (VI) solution. It is therefore of note that enhanced adsorption was recorded at low initial concentrations of the metals ion

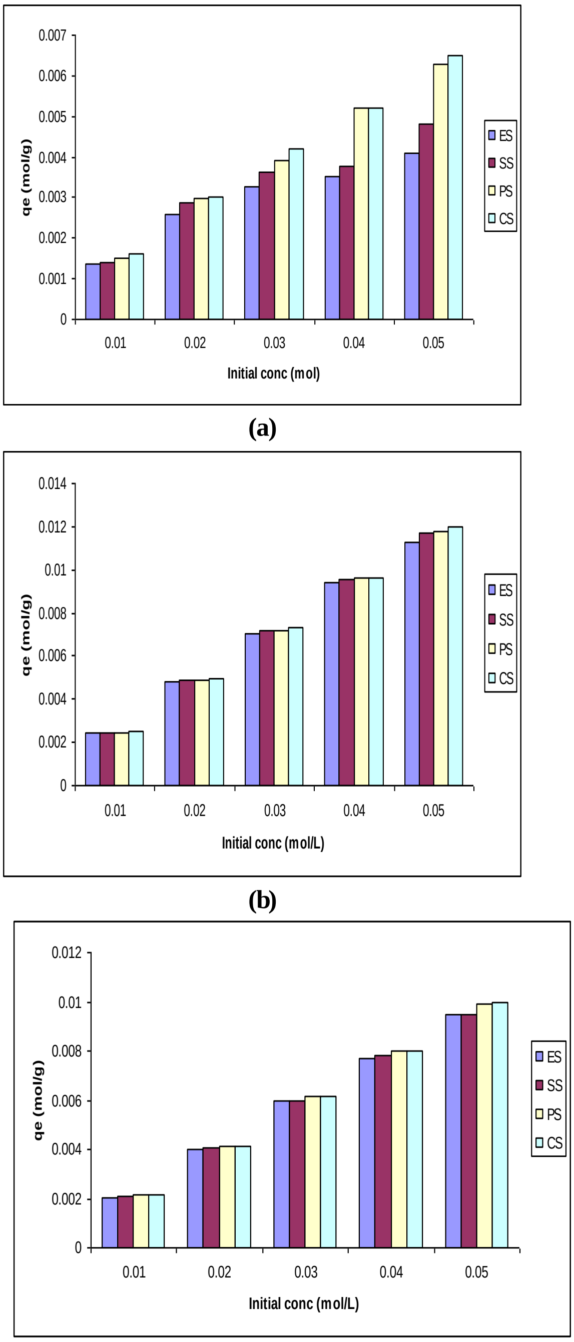

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Figure 3 Initial concentration effect on adsorption capacity of calcareous shells for (a) Pb (II), pH= 6, adsorbent dose =0.4g; (b) Cr (VI), pH= 5, adsorbent dose =0.4g and (c) Fe (II), pH= 2, adsorbent dose =0.4g at room temperature

Comparison of the adsorption performance of the animal shells

The sorption of the metals ions onto the different adsorbents shows parity. These differences on the adsorption capacity are due to chemical properties such as valences and atomic weight and due to the sorbent functional groups and physical characteristics (Sari *et al.*, 2007). Again, the affinity of a sorbent of a metal may be explained by its cationic/anionic state and the electronegativity of the metal ions. For instance, iron, chromium and lead have electrnegativity of 1.83, 1.66 and 2.33 respectively (Lameiras *et al.*, 2008; Pradhan *et al.*, 2007; Shawabkeh *et al.*, 2004). Figure 4 shows adsorption performance of the metals ions onto the shells. From the figure it is obvious that CS has the highest adsorption capacity for the metals. However, affinity of the metal to the adsorbents has a trend in the order Fe (II) > Cr (II) > Pb (II). The high uptake of iron (II) by the all the shells might be due the fact that iron is an essential micronutrient in living organisms and its strength attached to the charge on the adsorbent surfaces compared with other metals in the present study.

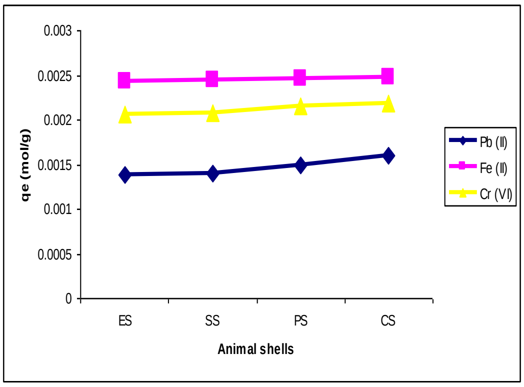
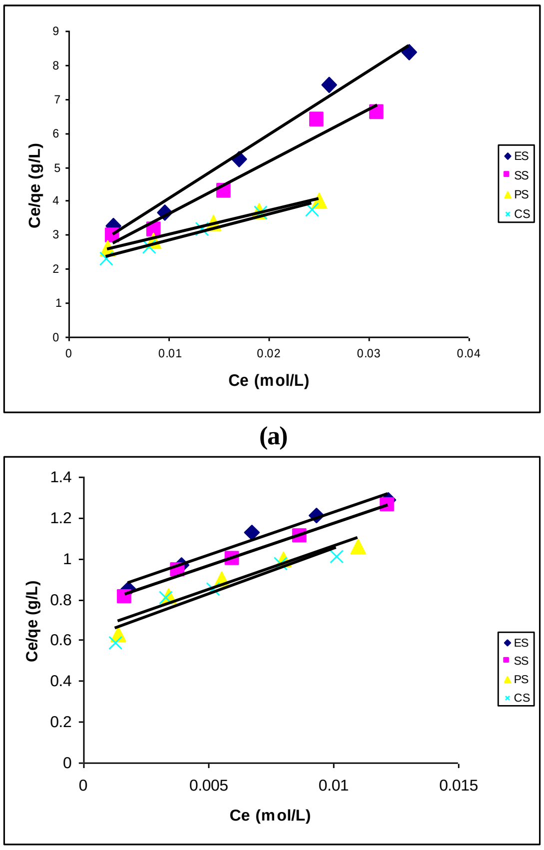


Figure 4 Performance of the shells for metals ion removal

Adsorption Isotherms

Adsorption isotherms are commonly used to describe the interaction of the sorbate with the sorbent. It also furnishes information for the understanding of the nature of reaction which is fundamental to optimizing the design of a sorption system. Several isotherm models have been developed and utilize for the analysis of equilibrium data. For this work, two basic isotherms, Langmuir and Freundlich, are applied for evaluation of data.



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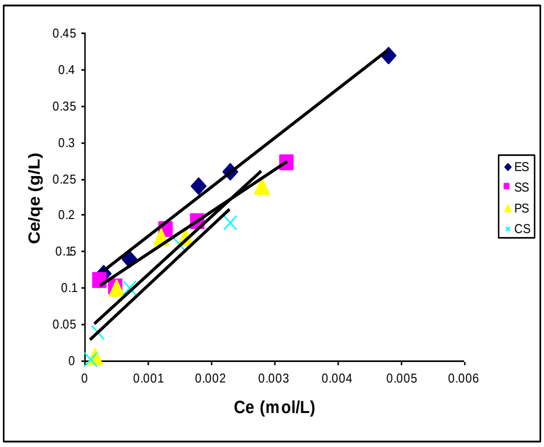


(c)

Figure 5 Langmuir isotherm plots for the adsorption of metals ion onto animal shells at 30°C

The Langmuir isotherm describes adsorbate-adsorbent system in which the extent of adsorbate coverage is limited to one monolayer of adsorbent (Langmuir, 1918). This model usually explains chemisorption when ionic or covalent chemical bond is formed between adsorbent and adsorbate. It has a linear form of equation given as:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \qquad (3)$$

where C_e is the equilibrium concentration (mol/L), q_e is the amount of adsorbate adsorbed per unit mol of adsorbent at equilibrium (mol/g). q_{max} is the theoretical maximum adsorption capacity (mol/g), K_L is the Langmuir isotherm constant related to the energy of adsorption (L/mol). The values of K_L and q_{max} can be calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e (Figure 5).

The Freundlich isotherm unlike the Langmuir does not indicate an adsorption limit when coverage is sufficient to fill a monolayer (Freundlich, 1907). It assumes a heterogeneous adsorption surface with sites that have different energies of adsorption and are not equally available (Freundlich, 1907). The Freundlich equation is given as:

$$q_e = K_F C_e^{1/n} \qquad (4)$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mol/g), C_e is the equilibrium concentration of the adsorbate (mol/L), K_F is the Freundlich adsorption constant related to adsorption capacity of the adsorbent.
((mol/g) $(L/mol)^{1/n}$) and 1/n is the adsorption intensity. A linear form of the Freundlich equation is expressed as follows:

$$Log\, q_e = Log\, K_F + \frac{1}{n} Log\, C_e \qquad (5)$$

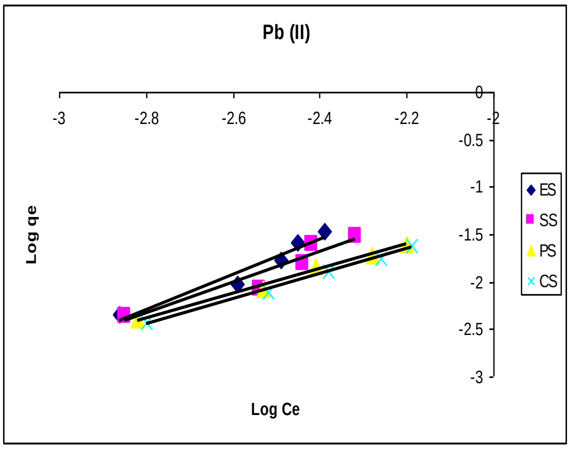
The calculated results of the Langmuir and Freundlich isotherm constants are presented in Table 1. It is found that the adsorptions of the metal ions; Pb (II), Cr (VI) and Fe (II) on the shells correlated well with the Langmuir under the concentration studied. The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant known as separation factor or equilibrium parameter, R_L which is used to predict if an adsorption system is ''favourable'' or ''unfavourable''. The separation factor or equilibrium parameter is defined by:

$$R_L = \frac{1}{1 + K_L C_O} \qquad (6)$$

where C_o is initial concentration. The parameter suggests the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$). As can be seen from Table 2, at the temperature of study the value of R_L is less 1 which suggest that adsorption is favourable. Similarly, Freundlich isotherm can be characterized by 1/n values obtained from the slope of the plots of $\log q_e$ against $\log C_e$ (Figure 6). The constant 1/n indicates the type of isotherm to be irreversible (1/n=0), favourable (0<1/n<1), unfavourable (1/n>1) (Alley, 2000). It has been shown in Table 1 that for the metals ion, 1/n>1 which suggest non applicability of this isotherm model in describing the adsorption process. In other words adsorption occurs on a monolayer surface.

Table 1: Isotherm parameters for the adsorption of metals by calcareous shells at 30°C

Isotherm models		Langmuir Isotherm			Freundlich Isotherm		
		q_{max} (mol/g)	K_L	R^2	K_F	1/n	R^2
Pb(II)	ES	0.0053	85.66	0.9850	800.00	1.86	0.9476
	SS	0.0065	75.08	0.9665	167.20	1.63	0.9025
	PS	0.0140	30.14	0.9874	18.21	1.30	0.9905
	CS	0.0130	35.77	0.9666	18.52	1.33	0.9949
Cr(VI)	ES	0.0240	52.77	0.9712	4.47	1.27	0.9989
	SS	0.0240	54.44	0.9912	4.23	1.27	0.9972
	PS	0.0230	67.36	0.9208	6.04	1.37	0.9993
	CS	0.0220	75.31	0.8995	5.91	1.37	0.9984
Fe(II)	ES	0.0150	653.4	0.9929	9.90	1.75	0.9710
	SS	0.0170	651.9	0.9668	3.61	1.61	0.9670
	PS	0.0130	2089.3	0.8655	9.21	1.84	0.9948
	CS	0.0120	3819.2	0.9308	13.2	1.95	0.9782



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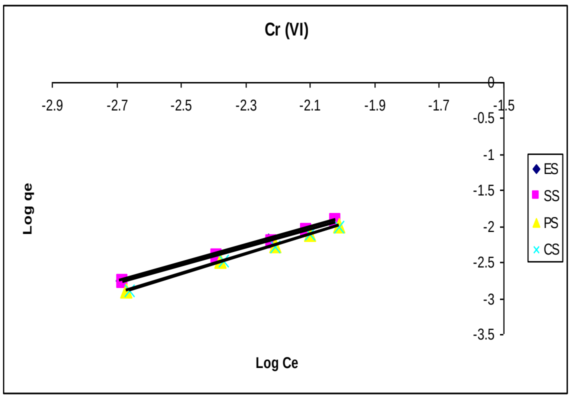

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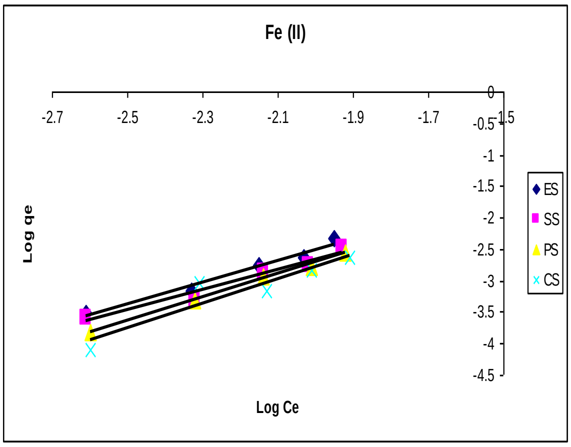

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Figure 6 Freundlich isotherm plots for the adsorption of metals ion onto animal shells at 30°C

Table 2: R_L values calculated from the Langmuir equation

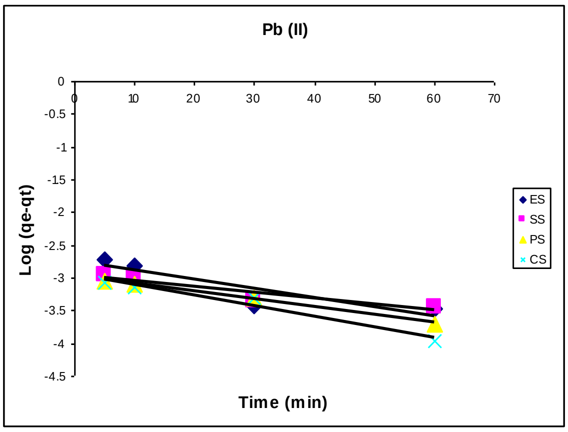
Adsorbates	Initial concentration mol/L	Adsorbents	R_L values
Pb (II)	0.05	ES	0.19
		SS	0.21
		PS	0.40
		CS	0.56
Cr (VI)	0.05	ES	0.28
		SS	0.27
		PS	0.23
		CS	0.21
Fe (II)	0.05	ES	0.03
		SS	0.03
		PS	0.01
		CS	0.01

Adsorption Kinetics

The pseudo-first order kinetic model can be represented by Lagergren rate equation (Lagergren, 1898),

$$Log(q_e - q_t) = Log\, q_e - \frac{K_1}{2.303}t \qquad (7)$$

where qe and qt are the amounts of metal ions adsorbed (mol/L) at equilibrium and at time t (min), respectively and K_1 the rate constant of adsorption (min^{-1}). Values of K_1 were calculated from the plots of Log (qe-qt) versus t (Figure 7) for 0.02mol/L metals ion. The experimental q_e values disagree largely with the calculated ones, obtained from the linear plots (Table 3). Again correlation coefficient (R^2) values are less than 0.90 at some points these show that the whole sorption process could not be account for with first-order kinetics.



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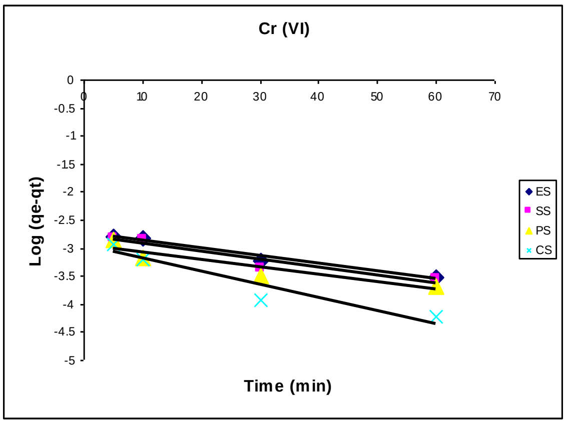

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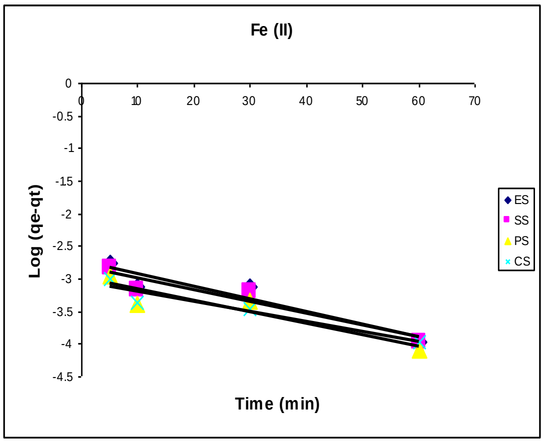

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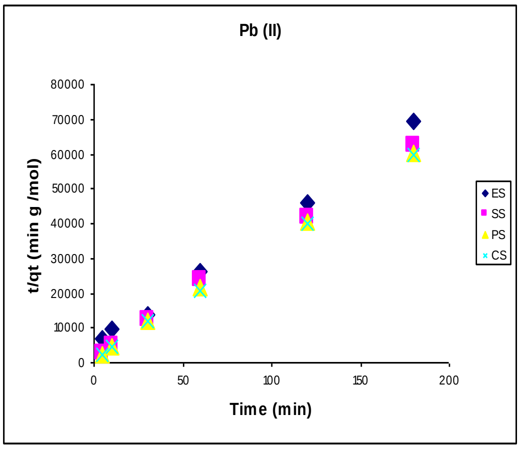
Figure 7 Pseudo-first-order kinetic plots for the adsorption on metals ion onto calcareous shells



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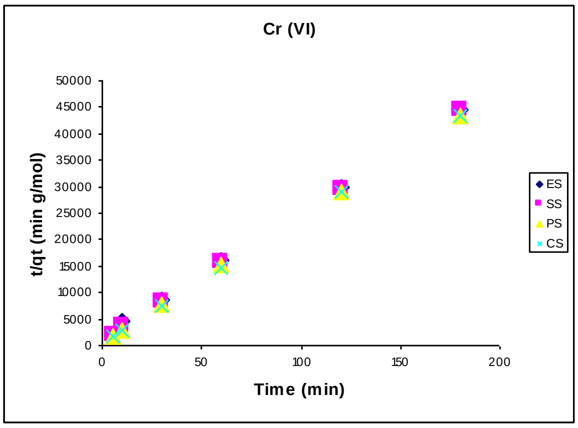

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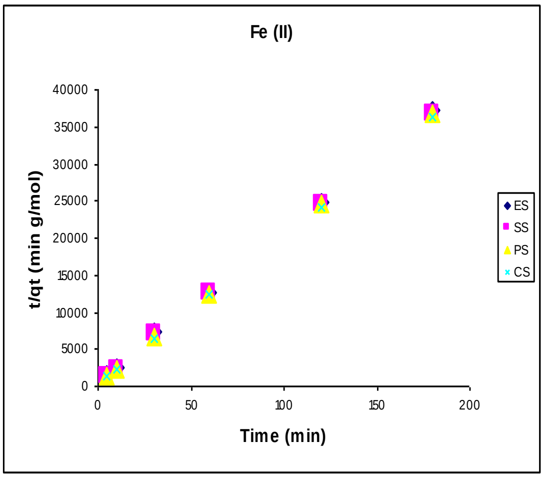

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Figure 8 Pseudo-second-order kinetic plots for the adsorption of metal ions on calcareous shell

On the other hand, the pseudo second-order equation based on equilibrium adsorption (Malik, 2004; Ho, 2002; 2006) is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad , \qquad (8)$$

where K_2 is the rate constant of pseudo-second order adsorption (molg^{-1}min^{-1}). Figure 8 shows pseudo-second order plots for the adsorption process for 0.02mol/L of the metal ions. K_2 and q_e values were determined from the intercepts and slopes of the linear plots of t/qt versus t respectively (Figure 8). Calculated values of the adsorption capacity $q_{e,\ cal}$ (mol/L) gave a better agreement with that of the experimental values $q_{e,exp,}$ (mol/L) and correlation coefficient ($R^2 > 0.99$) (Table 3).

Thus, adsorption process could be said to follow pseudo-second order kinetic model. The applicability of the pseudo-second order model suggested that chemical reaction might be one of the mechanisms being responsible for adsorption of metallic ions onto the calcareous shells.

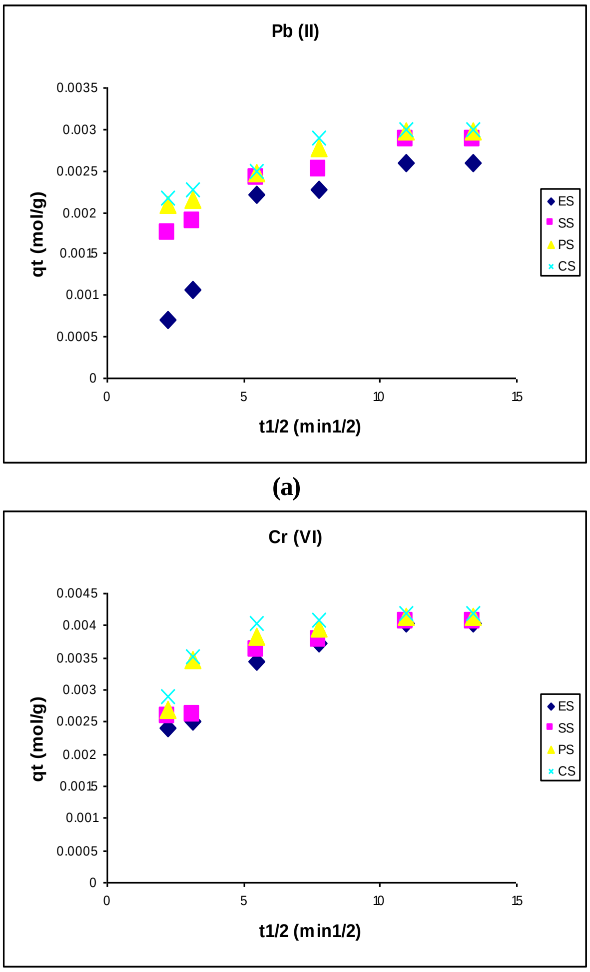
The kinetics of adsorption of metals ion onto various materials has earlier been reported to conform to pseudo-second order kinetic model (Adeogun *et al.*, 2012; Ehrampoush *et al.*, 2011).

Adsorption mechanism

The intraparticle diffusion model which is used to elucidate the mechanism of adsorption is generally expressed as:

$$q_t = K_{id} t^{\frac{1}{2}} + C \qquad (9)$$

where q_t is adsorption capacity at a time, t (mol/g), K_{id} is the rate constant for the intraparticle diffusion (mol/gmin$^{-1/2}$) and C is a constant (mol/g). For intraparticle diffusion to be the rate limiting step for the adsorption process the plots of qt versus $t^{1/2}$ should be a straight line passing through the origin with a slope K_{id} and intercept C (Bekci *et al.*, 2008). Figure 9 shows the intraparticle diffusion plots for the adsorption process. In this case it is proper to predict that mechanism of adsorption is far from diffusion through the pores of the adsorbents particle but likely other forces such as chemical reaction as proposed by pseudo-second order model. Nevertheless, ion-exchange and precipitation reaction are important reactions which might aid adsorption due to the exchange of the ions of the metal ions with those on the surface of the adsorbent and precipitation of ions in solution at basic pH values.

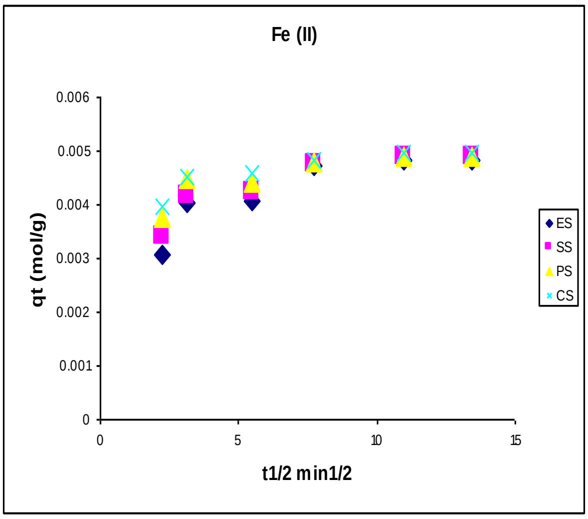


(a)

(b)

Table 3: Kinetic parameters for the adsorption of 0.02M metals by calcareous shells

Kinetics		Pseudo-first order parameters			Pseudo-second order parameters		
		$q_{e\ (mol/g)}$	K_1	R^2	$q_{e(mol/g)}$	K_2	R^2
Pb(II)	ES	1.86×10^{-3}	0.033	0.8098	2.83×10^{-3}	1.68×10^{-9}	0.9978
	SS	1.13×10^{-3}	0.021	0.8868	2.98×10^{-3}	4.29×10^{-9}	0.9986
	PS	1.06×10^{-3}	0.027	0.9648	3.06×10^{-3}	6.30×10^{-9}	0.9994
	CS	1.13×10^{-3}	0.037	0.9559	3.06×10^{-3}	6.30×10^{-9}	0.9993
Cr(VI)	ES	1.84×10^{-3}	0.031	0.9665	4.19×10^{-3}	1.11×10^{-8}	0.9991
	SS	1.67×10^{-3}	0.032	0.9100	4.16×10^{-3}	1.52×10^{-8}	0.9996
	PS	1.16×10^{-3}	0.031	0.8389	4.22×10^{-3}	2.62×10^{-8}	0.9999
	CS	1.11×10^{-3}	0.053	0.8999	4.20×10^{-3}	4.23×10^{-8}	1.0000
Fe(II)	ES	1.90×10^{-3}	0.045	0.8921	4.94×10^{-3}	3.43×10^{-8}	0.9995
	SS	1.54×10^{-3}	0.042	0.9073	4.96×10^{-3}	4.32×10^{-8}	0.9997
	PS	1.04×10^{-3}	0.041	0.8578	4.94×10^{-3}	6.42×10^{-8}	0.9990
	CS	8.97×10^{-4}	0.035	0.9089	5.00×10^{-3}	7.57×10^{-8}	0.9999



(c)

Figure 9 Intra-particle diffusion model plots for the adsorption of metals ion onto calcareous shells

Conclusions

The results of this investigation show that activated carbons derived from calcareous shells are an excellent adsorbents for the removal of metals from wastewater especially for Fe(II) and Cr(VI) where maximum percentage adsorption at optimum conditions stood at 99.2 and 87.1% respectively. Adsorption capacities of the shells were observed to be affected by initial concentration, pH and contact time. The shell with the highest adsorption capacity was the clam shell which showed highest percentage removal for all the metals studied. Adsorption equilibrium data could only be explained by the Langmiur isotherm with favourable isotherm parameters indicating that adsorption was on a monolayer surface. Kinetic of the process was best described by pseudo-second order model with q_e values agreeing well with that of experimental data. It was also pointed out that adsorption was possible through chemical reactions and ion-exchange at the surface of the adsorbents.

Additional information:

Ubong M. Eduok had been involved in several researches and projects in University of Uyo, Nigeria before leaving for KFUPM, Saudi Arabia.

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