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Studies on the Use of Oyster, Snail and Periwinkle Shells as Adsorbents for the Removal of Pb^{2+} from Aqueous Solution

STEVENS A. ODOEMELAM* and NNABUK OKON EDDY§

*Department of Chemistry, Michael Okpara University of Agriculture, Umudike, P. M. B. 7267, Umuahia, Abia state, Nigeria.
§Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.
saodoemelam@yahoo.com

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Abstract: In view of increasing rate of lead pollution resulting from discharge of lead containing effluents by industries into the environment, this study was carried out to investigate the removal of Pb^{2+} from aqueous solutions by oyster, snail and periwinkle shells. The effects of contact time and concentration on adsorption, thermodynamics of sorption and distribution coefficients of the adsorbents were examined to optimize the conditions to be utilized for decontamination of effluents containing Pb^{2+}. The study revealed that these materials are good adsorbents that can be used for the removal of Pb^{2+} from aqueous solution. Adsorption of Pb^{2+} by oyster, snail and periwinkle shells were found to conform to the classical models of Langmuir, Freundlich and Temkin adsorption isotherms. Thermodynamic consideration revealed that adsorption of Pb^{2+} by these materials was spontaneous and proceeded via chemical adsorption. The use of these materials for the removal of lead ion from aqueous solution is therefore advocated.

Keyword: Lead ions, Adsorption, Pollution, Aqueous effluents, Animal shells.

Introduction

Lead is one of the most toxic heavy metals known to man[1]. The risk posed by indiscriminate discharge of lead-containing wastes into the environment is enormous because lead is acutely toxic and can bioaccumulate from one trophic level to the other through the food chain. Thus lead poisoning through ingestion of lead-contaminated food can occur between successive organisms within the ecosystem[2-3].

Several methods have been used to remove of heavy metals from industrial effluents. However, one of the best methods is the use of adsorbent. In the light of this, waste biomass has been successfully used for the removal of heavy metals from industrial effluents[4-14] Results from most of these studies revealed that materials that can significantly remove lead ion from aqueous solution are uncommon. Besides most of these studies are centered on quantitative determination of the amount of heavy metal ion(s) received without reference to the effect of concentration, contact time and adsorption characteristics of the adsorbent. The present study seeks to investigate adsorptive properties of oyster, periwinkle and snail shells for the removal of Pb^{2+} from aqueous solution.

Experimental

Samples of periwinkle, oyster and snail shells were respectively dried in the open air. The dried samples were introduced into a furnace whose temperature was successively maintained at 200, 300 and 400°C. The furnace dried samples were ground to powdered form and exposed to free air for four hours (in order to increase it surface area). All reagents used were Analar grade. Double distilled water was used for the preparation of all solutions.

Adsorption study was conducted by adding 100 mL of different concentrations (0.000302-0.001208 M) of $Pb(NO_3)_2$ to a column containing 100 g of each adsorbent. The contact times between the adsorbent and the adsorbate were 10, 20, 30 and 40 min, respectively. After each set of experiment, 10 mL of the effluent was eluted and preserved for analysis.

Concentration of Pb^{2+} was determined using Pye Unicam model of atomic absorption spectrophotometer. From the measured concentration of Pb^{2+}, percentage of Pb^{2+} adsorbed and the amount of sorption per unit mass of adsorbent (x/m) was calculated using equations 1 and 2, respectively[1-2].

$$\%\text{sorption} = (C_i - C)/C_i \times 100 \quad (1)$$

$$x/m = (C_i - C)/C_i \times V/m \quad (2)$$

where C_i and C are initial and final (outlet or effluent) concentrations of Pb^{2+}, m is the mass of the adsorbate (in g) and V (in cm^3) is the volume of solution added.

Results and Discussion

Values of % sorption of Pb^{2+} by snail, oyster and periwinkle shells calculated through Equation 1 have been used to plot Figures 1- 3.

Effect of concentration and contact time

Figures 1-3 show plots of % sorption *versus* contact time for adsorption of different concentrations of Pb^{2+} by snail, oyster and periwinkle shells, respectively. From the Figures, it can be seen that the amount of Pb^{2+} adsorbed increased with contact time and decreased with concentration of Pb^{2+} in the solution. This implies that the rate of adsorption of Pb^{2+} (given by the slopes of respective lines on the plots) by the adsorbents decreased with concentration. According to Ekop and Eddy[15], adsorption of metal ions by animal materials depends on the charge of the ion, the surface area of contact, pH of the solution, duration of contact, the ionic radius of the metal, the organic content of the biomass and the concentration of heavy metals. However, in this study the major factors are duration of contact, organic content and the concentration of Pb^{2+} ion since other factors were constant. The implication is that the rate of adsorption of Pb^{2+} by oyster, snail and periwinkle shells should vary with these three factors. At constant contact time and concentration of Pb^{2+}, adsorption capacity of snail shell was highest followed by that of oyster while that of periwinkle shell was the least. The observed trend is due to the difference in organic matter content of the respective adsorbents.

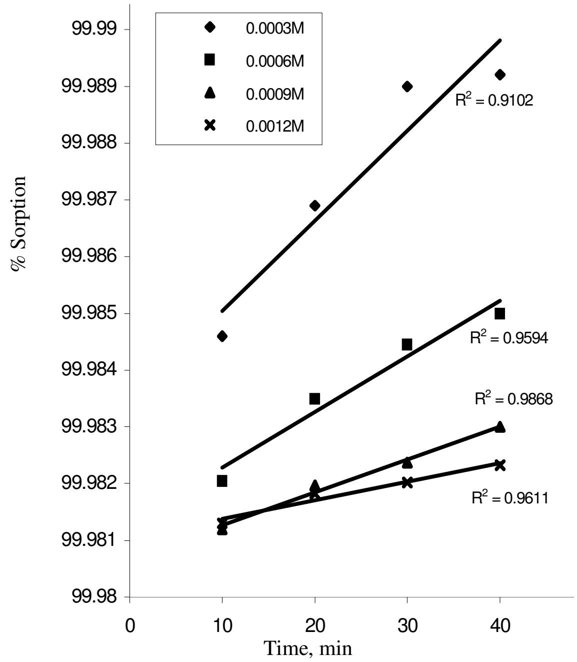

Figure 1. Variation of % of Pb adsorbed by snail shell with time.

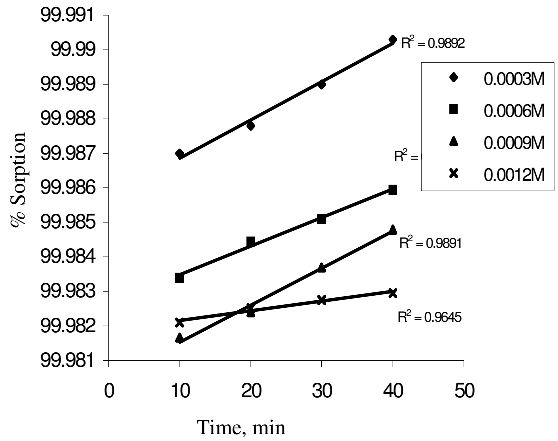

Figure 2. Variation of % of Pb ion adsorbed by oyster shell with time.

The effect of concentration of Pb^{2+} on the percentage of Pb^{2+} adsorbed was investigated. In all cases, it was seen that % sorption decreased as the concentration of Pb^{2+} increased. The decrease may be due to desorption of Pb^{2+} as its concentration increased[16-17]. It was also observed that above certain concentration, adsorption of Pb^{2+} tends to stabilize. At this stage, it is expected that the common ion effect must have set in[18].

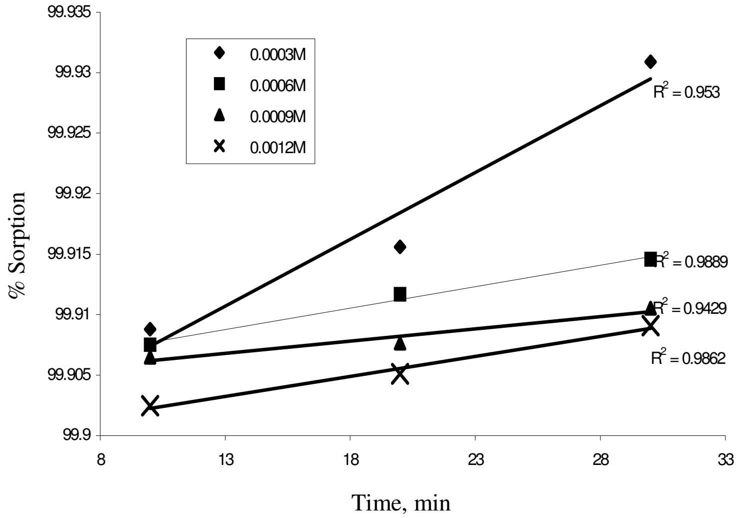

Figure 3. Variation of % Pb ion adsorbed by periwinkle shell with time

Adsorption considerations

Adsorption isotherm is informative in providing knowledge about the nature and mechanism of adsorption. The most commonly used isotherms are those of Langmuir, Freundlich, Temkin and Florry-Huggins. The general formula for adsorption isotherms is expressed[19] by Eq 3.

$$f(0, x) \exp(-2a\theta) = KC \quad (3)$$

Where, $f(0, x)$ is configurational factor, θ is the degree of surface coverage, C is the concentration of the adsorbate in the bulk solution, K is the adsorption constant and a is the interaction parameter.

In order to investigate the adsorption models for the used adsorbents, values of degree of surface coverage and concentrations were used to fit curves for different adsorption models. The results revealed that all the adsorbents obeyed Langmuir and Temkin adsorption isotherms. In addition, adsorption of Pb^{2+} by oyster shell also obeyed Florry-Huggins adsorption isotherm.

Assumptions of Langmuir adsorption isotherm relates the amount of adsorbate per unit mass of adsorbent to the equilibrium concentration (C) of the adsorbate in solution according[4-5] to Eq. 4.

$$(C/x/m) = (1/KV_m)+(C/V_m) \quad (4)$$

Where, V_m is the monolayer capacity or surface area of the solid and K is the binding constant. The implication of Eq. 4 is that a plot of (C/x/m) *versus* C should give a straight line with slope equal to $1/V_m$ and intercept equal to $1/KV_m$. Figure 4 shows Langmuir plot for the adsorption of Pb^{2+} on oyster, snail and periwinkle shells, respectively.

Values of Langmuir parameters (K and V_m) calculated through slopes and intercepts of Langmuir plots are recorded in Table 1. From the results, it was found that the surface areas of oyster, snail and periwinkle shells were equal to 0.9998, 0.9998 and 0.9900, respectively. This indicates that the surface areas of oyster and snail shells were similar while that of periwinkle was slightly lower. This also explains why the adsorption capacities of oyster and snail adsorbents were comparable and higher than that of periwinkle. Values of the binding constant (K) for oyster, snail and periwinkle were found to range from $1.1x10^7$-$3.33x10^7$, $1.67x10^7$-$3.33x10^7$ and $1.28x10^7$-$33.4x10^7$, respectively. Although there was no significant difference between values of K for oyster and snail shells (P = 0.05), the slight differences in values of their respective binding constants explain why values of % sorption of Pb^{2+} by snail shell was slightly higher than that of oyster shell. It is also interesting to note that contact time did not affect the monolayer capacity but values of the binding constant varied slightly with time. Thus since x/m depends on K and V_m, it is remarkable to note at this point that period of contact does not significantly affect the adsorption of Pb^{2+} ion by the adsorbents used. According to Freundlich adsorption isotherm, the fraction of surface coverage (x/m) is related to equilibrium concentration of the adsorbate according[6-7] to Eq. 5.

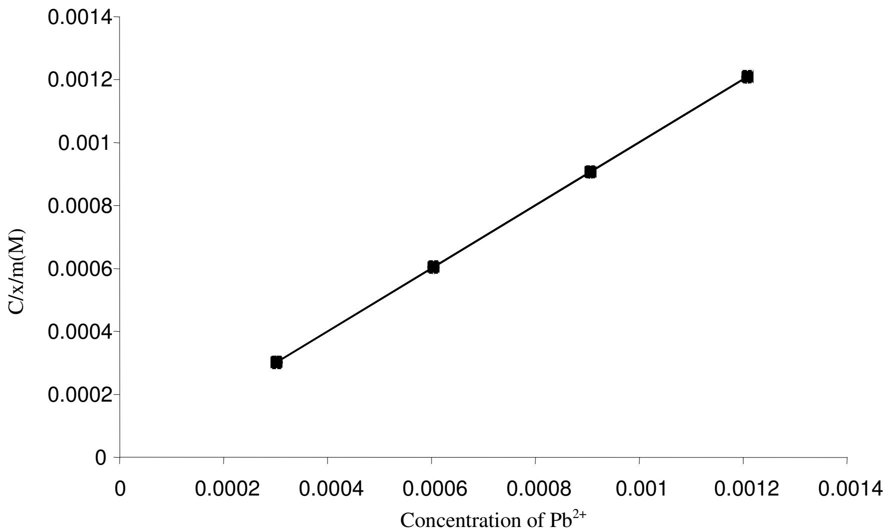

Figure 4. Curve fitting for adsorption of lead ion by snail, oyster(oyst) and pererwinkle (perew) shell according to Lagmuir adsorption isotherm

Table 1. Values of Langmuir parameters for adsorption of Pb^{2+} on oyster, snail and periwinkle shells.

Contact time, min	Binding constant, K			Monolayer capacity, V_m		
	Oyster	Snail	Periwinkle	Oyster	Snail	Periwinkle
10	11×10^7	1.67×10^7	3.37×10^7	0.9998	0.9998	0.9900
20	5.0×10^7	1.67×10^7	33.4×10^7	0.9998	0.9998	0.9900
30	1.67×10^7	1.67×10^7	1.28×10^7	0.9998	0.9998	0.9900
40	3.33×10^7	3.33×10^7	-	0.9998	0.9998	-

$$X/m = KC^{1/n} \quad (5)$$

Taking logarithm on both sides of Eq 5, we get the following Eq. (6)

$$\log(x/m) = \log K + 1/n \log C \quad (6)$$

Where, K and 1/n are Freundlich constants. Figure 5 show Freundlich adsorption isotherm for the adsorption of Pb^{2+} by oyster, snail and periwinkle shells. Values of Freundlich constant.are recorded in Table 2.

From Table 2, it can seen that values of n for oyster, snail and periwinkle ranged from 2.0 x 10^4 - 2.25 x 10^4, 2.0 x 10^5 - 3.33 x 10^5 and 1.25 x 10^4 - 5.0 x 10^5, respectively. The number of adsorption sites that is available for adsorption is defined by n. This parameter alone does not determine the concentration of adsorbate that can be adsorbed at a given time. Other factors such as pH, contact time, physicochemical composition and ionic radius of the adsorbate must be taken into consideration; hence values of n obtained from this work indicate that the number of adsorption site varied with time. Values of K calculated from Freundlich isotherms with respect to oyster and snail shells were constant within the contact time of 10 and 40 min but for periwinkle shell, K value tend to increase with time.

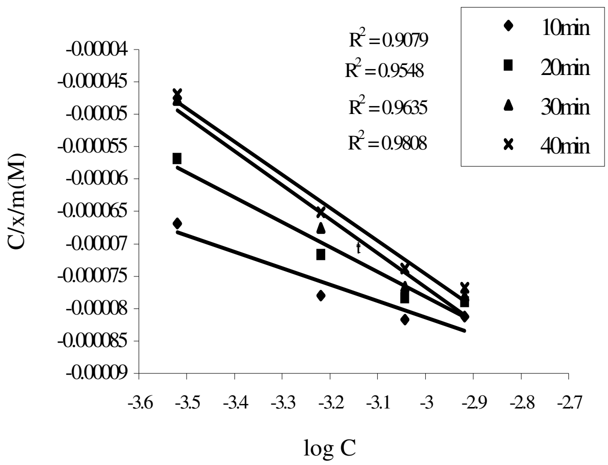

Figure 5. Curve fitting for adsorption of Pb ion on snail shell according to Freundlich isotherm.

Table 2. Values of Freundlich parameters for adsorption of Pb^{2+} on oyster, snail and periwinkle shells.

Contact time, min	n			Equilibrium constant of adsorption, K		
	Oyster	Snail	Periwinkle	Oyster	Snail	Periwinkle
10	2.25 x 10^4	3.33 x 10^5	2.25 x 10^4	1.0005	1.0005	1.0012
20	2.25 x 10^4	2.50 x 10^5	1.25 x 10^4	1.0005	1.0005	1.0013
30	2.00 x 10^4	2.00 x 10^5	50.0 x 10^4	1.0005	1.0005	1.0021
40	2.00 x 10^4	2.00 x 10^5	-	1.0005	1.0005	-

The linear form of Temkin adsorption isotherm can be written as:

$$\text{Exp}(-2ax/m) = KC \tag{7}$$

Rearranging and taking logarithm on both sides of Equation 7, we get the following Eq.,

$$X/m = -2.303/2\ \alpha\ \log K - 2.303/2\ \alpha\ \log C \tag{8}$$

Where, K is the equilibrium constant of adsorption and α is the interaction parameter. Temkin plot for the adsorption of Pb^{2+} by oyster shell is shown by Figure 6. Temkin adsorption isotherm was also applicable to adsorption of Pb^{2+} by snail and periwinkle shells (plots not shown). Values of Temkin constants are recorded in Table 3.

From Table 3, it can seen that values of the interaction parameter (α) for oyster, snail and periwinkle ranged from 1.0 x 10^4 – 9.0 x 10^5, 1.0 x 10^4 – 9.0 x 10^5 and 2.0 x 10^4 – 9.0 x 10^5 respectively. Values of *α* were also found to vary with contact time indicating that the attractive behaviour of α depends on contact time. Values of K calculated from slopes of lines on Temkin plots ranged from 9.9885 - 9.9908, 9.8855 - 9.9908 and 9.9541 - 9.9724 for oyster, snail and periwinkle shells, respectively. For periwinkle shell, values of K were found to decrease with contact time. For snail shell, K values were constant between 10 and 20 min of contact, but decreased after 20 min and increased marginally after 30 min of contact. However, for oyster, K was highest within 10 min of contact but reduced to a constant value between 20 and 40 min of contact. This indicates that the value of the equilibrium constant of adsorption varied with time.

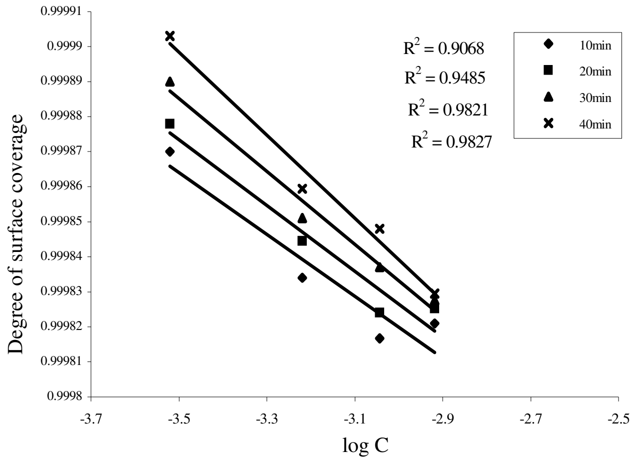

Figure 6. Curve fitting for adsorption of Pb ion on oyster shell according to Temkin isotherm.

Table 3. Values of Temkin parameters for adsorption of Pb^{2+} on oyster, snail and periwinkle shells**.**

Contact time, min	Interaction parameter, a			K		
	Oyster	Snail	Periwinkle	Oyster	Snail	Periwinkle
10	6.0×10^5	9.0×10^5	9.0×10^5	9.9908	9.9908	9.9724
20	9.0×10^5	9.0×10^5	2.0×10^4	9.9885	9.9908	9.9655
30	1.0×10^4	1.0×10^4	4.0×10^4	9.9885	9.8855	9.9541
40	1.0×10^4	1.0×10^4	-	9.9885	9.9885	-

Thermodynamic considerations

The direction of any chemical reaction can be predicted by considering the free energy of the reaction[20-22]. The free energy of adsorption (ΔG_{ads}) of Pb^{2+} by oyster, snail and periwinkle shells is related to the binding constant of adsorption according[8] to Eq. 9

$$\Delta G_{ads} = -2.303RT\log K \qquad (9)$$

Where, R is the universal gas constant and T is the temperature. Using values of K calculated from intercept of lines on Langmuir plots, values of ΔG_{ads} for adsorption of Pb^{2+} by oyster, snail and periwinkle shells were calculated. These values were recorded in Table 4. Calculated values of ΔG_{ads} ranged from 40.9512 - 44.6662 kJ/mol, 41.9032 - 43.6421 kJ/mol and 41.2332 - 49.4512 kJ/mol for oyster, snail and periwinkle shells, respectively. These values are negative indicating that adsorption of Pb^{2+} on the adsorbents were spontaneous. The values are also greater than 40.00 kJ/mol indicating the mechanism of chemical adsorption is applicable to the adsorption of Pb^{2+} by the adsorbents.

Table 4. Values of ΔG_{ads} for adsorption of Pb^{2+} by oyster, snail and periwinkle shells.

Contact time, min	$-\Delta G_{ads}$, kJ/mol		
	Oyster	Snail	Periwinkle
10	40.8512	41.9032	43.6722
20	44.6662	41.9032	49.4512
30	41.9032	41.9032	41.2331
40	43.6421	43.6421	-

Distribution coefficient

According to Eddy and Ukpong,[23] the distribution of a solute between two phases is governed by a chemical law and the ratio of the concentration of the solute in one phase to the concentration of the solute in the second phase bears a constant value called distribution ratio or distribution coefficient (D). Ogunsuye *et al.*,[24] also stated that D is another measure of adsorption efficiency. It follows from the above that expression of the D can be written as Eq. 10.

$$D = \frac{[Pb^{2+}]_{ads}}{[Pb^{2+}]_{aq}} \tag{10}$$

Where, $[Pb^{2+}]_{ads}$ and $[Pb^{2+}]_{aq}$ are the concentrations of Pb^{2+} in the adsorbent and in the aqueous phase, respectively. Rearranging Eq. 10, we get the following equation.

$$[Pb^{2+}]_{ads} = D \times [Pb^{2+}]_{aq} \tag{11}$$

The mathematical implication of Eq. 11 is that a plot of $[Pb^{2+}]_{ads}$ *versus* $[Pb^{2+}]_{aq}$ should give a straight line if the assumptions establishing Eq.10 are valid. Distribution plot with respect to adsorption of Pb^{2+} by snail shell is shown by Figure 7, (Distribution plots for oyster and periwinkle shells not shown). From slopes of lines on the plots, values of D were obtained and are recorded in Table 5. On the average, D values were higher for oyster and snail shells and least for periwinkle shell, thus confirming their relative adsorption efficiencies. Also values of D varied slightly with contact time indicating that time is of essence in determining the adsorption capacity of the adsorbents used.

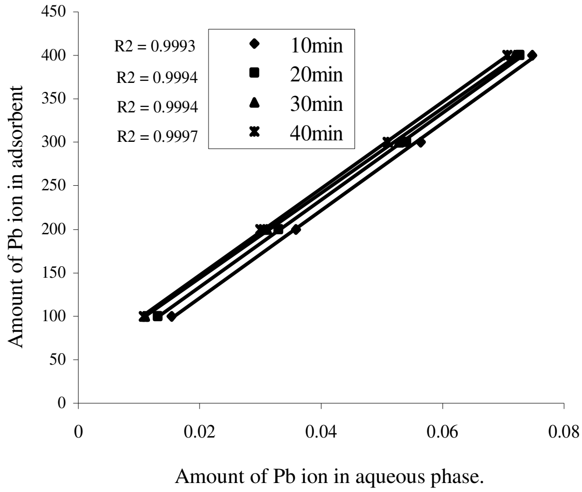

Figure 7. Distribution plot for adsorption of Pb ion by snail shell.

Table 5. Distribution coefficient for adsorption of Pb^{2+} by oyster, snail and periwinkle shells.

Contact time, min	D		
	Oyster	Snail	Periwinkle
10	5028.30	5045.40	1005.40
20	4998.70	5122.90	1012.50
30	4885.90	5176.40	1017.70
40	4980.20	5163.10	-

Conclusion

From the study, it has been found that shells of snail, oyster and periwinkle are good adsorbents for the removal of Pb^{2+} from aqueous solution. This confirms results obtained from previous studies. In addition, from the present study, the following conclusions are made:

(i) Based on their relative values of adsorption capacity, available surface area, distribution ratio and percentage sorption, adsorption efficiencies of these shells vary according to the trend: snail > oyster > periwinkle.

(ii) Adsorption capacities of snail, oyster and periwinkle shells are affected by contact time and by the initial concentration of Pb^{2+} in the solution.

(iii) Adsorption characteristics of snail, periwinkle and oyster shells are consistent with classical adsorption models of Temkin, Freundlich and Langmuir adsorption isotherms.

(iv) Within the limit of the studied concentrations, snail, oyster and periwinkle shells are confirmed to be good adsrbents for Pb^{2+} from aqueous solution.

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References

1. Eddy N O and Udoh C L, Fundamentals of Environmental Chemistry; Pattom Communication, Nigeria., 2006, Chapter 2-5.
2. Ansari R and Raofile F, *E J Chem.,* 2006**, 3**, 35.
3. Ansari R and Raofile F, *E J Chem*., 2006**, 3**, 49.
4. Lori J A, Umoniyi I K and Ekanem E J, In Adsorption characteristics of mucin on Ca-hydroxyapalite*,* Akiniyi J A, Ed., Conference Proceedings, Chemical Society of Nigeria, Maidugri, Nigeria, 2005, pp 60 –64.
5.. Gimba C E and Musa I A, In Adsorption of phenols and some toxic metals from textile effluents*,* Akiniyi J A, Ed., Conference Proceedings, Chemical Society of Nigeria, Maidugri, Nigeria, 2005, pp 55 –59.
6. Oviawe A P and Ademoroti C M A, In Adsorption of heavy metal ions from aqueous solution by some keratinous substances (cow horns). Akiniyi J A, Ed., Conference Proceeding, Chemical Society of Nigeria, Maidugri, Nigeria, 2005, pp 47 –50.
7. Rahman M A. Asadullah M, Hague M M, Motin N A, Siltan M B and Azad M A K, *J Surf Sci Technol.,* 2006**, 22**, 133.
8. Ufuah M O E, Ikhuaria E U and Okiemen F E, In Removal of select metal ions from aqueous solution with groundnut husk modifield with thioglycolic acid. Ahonkhai S I, Ed., Conference Proceeding, Chemical Society of Nigeria: Lagos, Nigeria, 2004, pp 235-236.

9. Katsumata H, Kaneco S, Susuki T, Ohta K and Yobiko Y, *Photo/Electrochem Photobiol, Environ Energy Fuel.*, 2004, **2**, 165.
10. Blais J F, Shen S, Meunier N and Tyagi R D, *Environ Technol.,* 2003, **24**, 205.
11. Okuo J M, *Global J Pure Appl Sci.,* 200**6**, **12**, 355.
12. Okuo J M and Ozioko Anthony C, *J Chem Soc Nigeria.,* 2001, **26**, 60.
13. Badmus M A O, Audu, T O K and Anyata B U, *Turk J Eng Environ Sci.,* 2007, **31**, 251.
14. Tudor H, Gryte C and Harris C, *Water Air Soil Pollut.*, 2006, **173**, 209.
15. Ekop A S and Eddy N O, *Afri J Environ Pollut Health.*, 2005, **4**, 33.
16. Horsefall M and Spiff A I, *Electronic J Biotech.,*. 2004, **8**, 162.
17. Horsfall M and Spiff A I, *Afri, J Biotech*., **2005**, 4, 191.
18. Yurt A, Bereket G, Rivrak A, Balaban A and Erk B, *J Appl Electrochem.,* 2005, **35**, 1025.
19. Ofomaga A E, Okieimen F O and Omonmhenle S E, In Adsorption of Cd^{2+} and Zn^{2+} from aqueous solution by modifield koalanite, Ahonkhai S I, Ed., Conference Proceeding, Chemical Society of Nigeria: Lagos, Nigeria., 2004, pp 265 –272.
20. Sharma K K, Sharma L K, A textbook of physical chemistry, 4th revised Ed., Vikas India, 2004, Chapter 7-8.
21. Khan R A, Tahir H, Uddin F and Hameed U, *J Appl Sci Environ Manag*., 2005 , **9**, 29.
22. Ogboinghale F, Ugbesia O S, In Adsorption of Pb^{2+} and Ni^{2+} on orange peels. Akiniyi J A, Ed, Conference Proceeding, Chemical Society of Nigeria, Maidugri, Nigeria, 2005, pp 45- 46.
23. Eddy N O and Ukpong I J, *J Appl Sci*., 2006, **8**, 60.
24. Ogunsuyi H O, Ipinmorpti K O, Amoda I A and Ajayi O, In Adsorption of Cu^{2+} aqueous solution using agricultural waste and oyster shell, Akiniyi J A, Ed, Conference Proceeding, Chemical Society of Nigeria, Maidugri, Nigeria, 2005, pp 43-46.