

REMOVAL OF HEAVY METAL IONS BY BLENDED PERIWINKLE SHELLS

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ABSTRACT

Samples of periwinkle shells, palm kernel fiber and coco nut husk were obtained from New Benin market, Benin City, Nigeria. These were milled, sieved with a 300 μ m mesh sieve, blended in seven different ratios: - 1:1:1, 1:1:4, 1:4:1, 4:1:1, 1:3:2, 2:1:3, 3:2:1 and characterized. They were all thiolated and the best blend having the highest surface area was used to remove heavy metal ions - Co²⁺, Ni²⁺ and Cd²⁺ ions from solutions. The effect of time, temperature and concentration on the removal of heavy metal ions were studied. The optimum time for the removal of Co²⁺, Ni²⁺ and Cd²⁺ ions were 65 min, 90min and 65min respectively. The blended sample was more effective in the removal of heavy metal ions from their solutions when compared with periwinkle shells. The blended periwinkle shells were found to adsorb twenty six times as much as the periwinkle shells alone.

KEYWORDS: Heavy metals, adsorption, biomaterials, characterization, husk

INTRODUCTION

Heavy metals are of great ecological significance today due to their toxic and accumulative nature. Warren (1981), noted that various activities of man in recent years have increase the quantity and distribution of heavy metals in the atmosphere, land and water bodies. The extent of this wide-spread heavy metal pollutant has caused concern about its possible hazard on plants, animals and human beings. Mining, dumping of dangerous military wastes on sites and dumping of old damaged vehicles are some of the sources of heavy metal pollution. Pollution of streams and rivers flowing through agricultural areas where fungicides and pesticides may have been used and even pollutants from industrial effluents contribute most of these heavy metals at the reception sites.

In Nigeria, the Federal Environmental Protection Agency (FEPA) is the body saddled with the responsibility for the protection of the environment. This agency has put in place laws and regulations guiding wastes management and disposal, emphasizing the treatment of wastes before disposal by the concerned industries.

Adsorption processes have been known over the years as the primary method of metal ions removal from polluted environment. Other methods used for the removal of heavy metals from wastes water effluents include the use of chemical precipitation, evaporation, electrochemical treatment and the use of ion exchange resins. These methods have been found to be expensive and sometimes inefficient especially when the toxic heavy metals are present in low concentration (Yang and Lins, 1998, Ouki and Kavannagh, 1997).

In recent years, the use of biomaterials in the sorption process as adsorbent for the removal of heavy metal ions from polluted waste water has been an emerging field of interest for many researchers. These biomaterials have gained importance due to their efficiency, low cost and ready availability. The unique ability of these materials of plant origin to bind metals has been attributed to be due to the presence of some functional groups on the surface of the adsorbent, which can attract or sequester these metal ions. Gardea, et al (1990), demonstrate that the carboxyl groups found on the cell wall of dead algal biomass are potentially responsible for copper binding.

Effluents from industries all over the world contained some of these hazardous heavy metal ions. Most industries in

Nigeria discharge their untreated effluents into the environment, particularly nearby rivers. The major reason of indulging in such unlawful act is to reduce cost and maximize profit and thereby endangering the life of the populace.

What come to mind in the use of agricultural materials for metal removal is availability and low cost sorbents for adsorption. In this study, the adsorbents used are usually disposed off indiscriminately into the environment and constitute environmental hazard to the public, particularly in the southern part of the country where they are widely available. These sorbents can gainfully be employ to treat effluents from industries before being discharge into the environment.

Several workers have reported the use of agricultural biomass of both plant and animal origin for the sorption of heavy metals from solutions (Okolo and Okuo, 2004, Ricordel et al, 2001, Volesky, 1987, Blanco et al, 1990, Eguakhide et al, 2004, Azzi et al, 2003). Okuo and Ozioko, (2001), reported the use of chemically treated periwinkle shells to remove lead and mercury from aqueous medium. Periwinkle shells are known to contain polar functional groups such as primary amines groups, hydroxyl groups, carboxylic acid groups, amide and phenolic groups. Similarly coco nut husk and palm kernel fiber also contained these functional groups. Most of these functional groups can donate electron to metal ions thereby enhancing adsorption by chemisorptions and consequently their removal from aqueous medium. These functional groups are responsible for the adsorption capacity of the blended periwinkle shells.

In this paper, coconut husk and palm kernel fiber were characterized, blended with periwinkle shells, thiolated and used to remove heavy metal ions - Co²⁺, Ni²⁺ and Cd²⁺ ions from aqueous solution.

MATERIALS AND METHODS

Preparation of the Blend

Periwinkle shells, coconut husk and palm kernel fiber were obtained from New Benin market, Benin City, Nigeria. The palm kernel fiber was treated with warm water and petroleum ether until the oil was completely removed. The coconut husk was pulled off from the pericarp of the coconuts. Periwinkle shells were thoroughly washed with distilled water to remove the remnant of periwinkle. They were then air dried. The oil-free palm kernel fiber, coconut husk and periwinkle

shells were oven dried at 400°C. All the materials were milled individually using grinding mill and thoroughly washed with distilled water. The milled materials were blended to some chosen ratios. The blend with a ratio of 1:1:1 was used for the adsorption experiment since it has been established by Okuo and Ozioko, (2001) and Okolo and Okuo, (2004), that samples with larger surface areas are more effective in metal ions removal.

Chemical Compositions

Metals such as Fe and alkaline earth metals – Ca, alkali metals – Na, K, and non-metals - C and N were determined. The chosen ratio sample was dissolved in a 70:30 HF/HCl acid mixture for the determination of Ca, Na, K and Fe. The resulting solution was filtered and then subjected to atomic absorption spectroscopy using Buck Scientific model 200/210A atomic absorption spectrophotometer with an acetylene flame for the analysis of Fe, alkali metals and alkaline earth metals. Estimation of each ion was performed using their principal wavelengths. A calibration curve was prepared recording absorbance of standard concentration solutions of each ion. The absorbance of a sample was measured and the concentration determined from the calibration curve. The non-metals C and N were determined according to standard methods (APHA, AWWA and WPCF, 1985).

Infra red (IR) Spectra

In order to obtain information about the maximum absorption spectra, the sorbents were milled into a fine powder. This was followed by dilution and homogenization to 0.05% (w/w) with KBr and additional grinding. Disc (25mm diameter and approximately 1mm thick) were pressed in a vacuum KBr press. The transmission FTIR spectra were measured using spectrophotometer Buck Scientific model M500 and recorded with varying number of scans and resolutions. The absorption spectra (4000-1000cm⁻¹) were then collected and analyzed.

Chemicals and Reagents

The metal ion solutions – Co²⁺, Ni²⁺ and Cd²⁺ were prepared from analar grade CoCl₂ · 6H₂O, NiCl₂ · 6H₂O and Cd(NO₃)₂ · 4H₂O respectively. Sodium thiosulphate, thioglycolic acid, hydrochloric acid, sulphuric acid, potassium iodide, potassium iodate, sodium carbonate, ethanol and ether were of BDH grade. Starch indicator was freshly prepared.

Measurement of Surface Area and Standardization of Iodine Solution

The iodine number method was used to calculate the surface area of the blend sorbent (Vogel, 1989). The determination of the concentration of the iodine involves the titration of aliquots with sodium thiosulphate solution already standardized against pure potassium iodate (KIO₃) solution using freshly prepared starch solution as indicator (Vogel, 1989 and Okuo and Ozioko, 2001). The stoichiometry of the equation is thus



The iodine value (I.V.) was calculated using the formula:

$$\text{I.V. (mg iodine/g sample)} = \frac{(Q - P) \cdot V \cdot N \cdot 126.91}{Q \cdot W}$$

Where P = volume of thiosulphate used for sample treatment,
Q = volume of thiosulphate used for the blank solution (6.3ml),
V = volume of iodine solution used for titration (10ml),
N = normality of iodine solution used for titration,

W = weight of the blend sample used (0.5g),
The extent of thiolation (EOT) = P/Q · 100
The inverse of iodine value gives the surface area.

Thiolation Method

15g of the blend sample ratio 1:1:1 was hydrolyzed with 7% v/v sulphuric acid for about 2hr, filtered and air dried. The dried residue was treated with 0.1M thioglycolic acid solution for about 27hr, in a well ventilated laboratory to ensure complete dissolution of the blend. Thereafter, the thiolated blend sample was filtered and the entire residue washed with distilled water and ethanol to aid the deacidification process. The residue was then air dried.

The extent of thiolation was determined by reacting 0.5g of the thiolated blend sample with 5ml of iodine solution and then back – titrated with standard sodium thiosulphate solution (0.1M). Blank solution of the same volume of iodine solution was also titrated with standard sodium thiosulphate solution.

Adsorption Experiment

1g of the thiolated blend sample was shaken with different concentrations of heavy metal ions – Co²⁺, Ni²⁺ and Cd²⁺ ions and the solution allowed to settle. Filtration was done at time interval of 10mins. The equilibrium concentration of heavy metal ions in the solutions were determined using atomic absorption spectrophotometer (AAS). Triplicate readings were taken and the average recorded. The effect of time, temperature and concentration were monitored.

RESULTS AND DISCUSSION.

Tables (I) and (II) showed ratios, the iodine value, surface area and the extent of thiolation of the different blends. The iodine value and the surface area of the best blend ratio 1:1:1 are 10.62 · 10⁻² g/mg iodine and 92.06% respectively. It was reported by Okuo and Ozioko and, (2001) and Okolo and Okuo, (2004) that samples with larger surface areas provide more active sites for the adsorption of metal ions from aqueous medium.

Table (I): Blend Ratios of Milled Materials Used for Blending (Wt in g)

Periwinkle shell	Coconut husk	Oil-free palm kernel fiber
1	1	1
1	1	4
1	4	1
4	1	1
1	3	2
2	1	3
3	2	1

The effects of concentration, temperature and time on the sorption of metal ions – Co²⁺, Ni²⁺ and Cd²⁺ ions are shown in tables (III), (IV) and (V). Thiolation with glycolic acid effectively created the acidic –SH groups on the surface area of the adsorbent in addition to the functional groups already present in the substrate. The adsorption mechanism can be explained using the surface complex formation model. This model visualizes the attachment of metal ion species onto activated carbon samples by the formation of multidentate metal complexes with the incorporated –SH groups (Atkins, 1998; Glastone and Lewis, 1987 and Okieimen, 1992). This will effectively enhance the removal of Co²⁺, Ni²⁺ and Cd²⁺ ions from the solution. It is evident from table (III) that cobalt ion is

Table II: Effect of Thiolation on The Surface Area (S.A.), Iodine Value (I.V.) and The Extent of Thiolation (EOT) of The Different Blends.

Blends	I.V. (mg iodine/g sample)	S.A. (g/mg of iodine)	Extent of Thiolation (EOT) %
1:1:1	9.37	$10.67 \cdot 10^{-4}$	92.02
1:1:4	27.16	$3.68 \cdot 10^{-2}$	76.98
1:3:2	17.80	$5.62 \cdot 10^{-2}$	84.92
1:4:1	12.18	$8.21 \cdot 10^{-2}$	89.68
2:1:3	40.28	$2.48 \cdot 10^{-2}$	65.87
3:2:1	10.87	$9.20 \cdot 10^{-2}$	90.79
4:1:1	39.72	$2.52 \cdot 10^{-2}$	66.35

Table III: Effect of Concentration on Co^{2+} , Ni^{2+} and Cd^{2+} Ions Removal

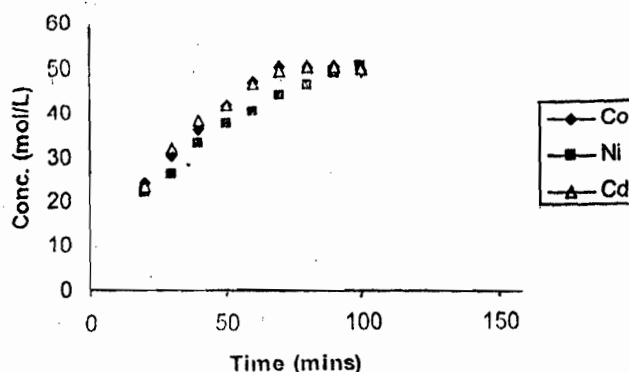
Initial concentration (mg/L)	Equilibrium concentration (mg/L)			Amount removed (mg/g)		
	Co^{2+}	Ni^{2+}	Cd^{2+}	Co^{2+}	Ni^{2+}	Cd^{2+}
30	0.065	1.387	0.9691	29.935	28.613	29.031
50	0.130	5.905	2.903	48.870	44.095	47.097
70	0.065	13.812	5.186	69.935	56.188	64.814

Table (IV): Effect of Temperature on Co^{2+} , Ni^{2+} and Cd^{2+} Ions Removal

Temperature ($^{\circ}\text{C}$)	Initial concentration (mg/L)	Equilibrium concentration (mg/L)			Amount removed (mg/g)		
		Co^{2+}	Ni^{2+}	Cd^{2+}	Co^{2+}	Ni^{2+}	Cd^{2+}
27	50	0.065	0.029	1.348	49.935	49.971	48.632
50	50	0.065	3.531	2.429	49.935	46.469	47.571
70	50	0.065	6.715	3.231	49.935	43.285	46.769

Table (V): Effect of Time on Co^{2+} , Ni^{2+} and Cd^{2+} Ions Removal

Time (min)	Initial concentration (mg/L)	Equilibrium concentration (mg/L)			Amount Removed (mg/g)		
		Co^{2+}	Ni^{2+}	Cd^{2+}	Co^{2+}	Ni^{2+}	Cd^{2+}
20	50	26.068	27.977	26.600	23.932	22.023	23.400
30	50	19.875	23.892	18.218	30.125	26.108	31.782
40	50	14.074	17.072	11.901	35.926	32.929	38.019
50	50	8.711	12.919	8.594	41.279	37.081	41.406
60	50	2.987	9.978	3.679	47.013	40.022	46.321
70	50	0.170	6.219	0.960	49.830	43.781	49.040
80	50	0.000	4.999	0.000	50.000	46.001	50.000
90	50	0.000	1.100	0.000	50.000	48.900	50.000
100	50	0.000	0.000	0.289	49.880	50.000	49.711

**Fig. II: Effect of time on Co^{2+} , Ni^{2+} and Cd^{2+} ion adsorption**

more adsorbed when compared with nickel and cadmium ions. It was also observed that adsorption increases with increasing concentration. The variation in the adsorption of these metal ions might be due to differences in the chemical properties of the adsorbate, particularly hydration energies and ionic sizes of the three ions. The effect of the external solution temperature was observed to play a significant role on the sorption of Ni^{2+} and Cd^{2+} ions. At all initial concentrations, maximum adsorption was observed at the lowest temperature of 27°C . For these two metal ions, adsorption decreases with increasing temperature. Increase in entropy increases the random molecular motion of these ions. This might affect the stability of the metal ions adsorbed and hence an increase in temperature decreases the amount of metal ions removed from solution. Conversely temperature has no effect on the adsorption of Co^{2+} ion as seen from table (IV). Co^{2+} and Ni^{2+} ions are among the best complexing agents. Because of the small size and high ionic charge of Co^{2+} ion, it is more hydrated and consequently a large ionic size and radius that is far greater than that of Ni^{2+} and Cd^{2+} ions result. Hence its adsorption behaviour is not likely to be effected by temperature in aqueous medium.

The effect of time on the adsorption of these metal ions is presented in table (V) and fig (I). The optimum time for the adsorption of Co^{2+} , Ni^{2+} and Cd^{2+} ions are 65min, 90min and 65min respectively.

Distribution Coefficient (D) and Chemical Compositions.

The distribution coefficient and chemical composition results are shown in tables (VI) and (VII). The distribution coefficient of Co^{2+} , Ni^{2+} and Cd^{2+} ions ranged between -1.91 to 1.24mg/L, 1.54 to 10.43mg/L and -1.46 to 3.63mg/L respectively. There is a large variation of D with concentration of metal ions. The value of D is of practical importance in the treatment of heavy metal laden waste waters. Primarily, it allows the number of cycles of equilibrium sorption processes required to reduce the levels of metal ions in solution to be deduced. For example Co^{2+} ion with a negative value of D

would be more easily removed from water containing Co^{2+} , Ni^{2+} and Cd^{2+} contaminants.

From table (VI), a plot of $\log a_e$ against $\log c_e$, i.e. plot of Freundlich isotherm has an approximate straight line which suggests that adsorption process followed the isotherm. The Freundlich isotherm equation is given by:

$$a = kc^n$$

Where 'a' is the equilibrium sorption, 'c' is the equilibrium concentration of the metal ions. n and k are the exponent and coefficient of the isotherm equation respectively. The equation can also be rendered into logarithm terms as:

$$\log a = \log k + n \log c$$

A plot of $\log a$ against $\log c$ gives a linear plot with slope equals $1/n$ and intercepts on the $\log a$ axis allows for the estimation of k. Thus the values of 'n' and 'k' determined for the blend sorbent were approximately 0.32 and 24 respectively. However, the intercept 'k' shows that the blended periwinkle shells adsorbed twenty six (26) times that obtained by Okuo and Ozioko, (2001), when chemically treated periwinkle shells were used alone.

The values of the chemical compositions are expressed in percent (w/w). As can be seen the blend (sorbent) is a complex material that is made up of mainly carbon (48.86%), potassium (2.21%) and sodium (2.14%). The levels of N, Ca and Fe are very low. The total percentage is below 100, suggesting that the sorbent contained more chemical species not accounted for.

Functional Groups.

It is important to have an idea of the structure of the sorbent used. This will enable us to understand the adsorption mechanism of the substrate. Adsorption is a surface phenomenon and the structure of the sorbent surface will determine its adsorption capacity. The functional groups known to be effective in the removal of heavy metal ions from solution are the carboxyl, phenolic, hydroxyl, amine and amide groups. The functional groups identified are shown in table (VIII) and fig (I).

Table (VI): The Distribution Coefficient (D) of Metal Ions Adsorbed from Aqueous Solution

Initial Conc. (mg/L)	Co^{2+}			Ni^{2+}			Cd^{2+}		
	$\log a_e$	$\log c_e$	$D=a_e/c_e$	$\log a_e$	$\log c_e$	$D=a_e/c_e$	$\log a_e$	$\log c_e$	$D=a_e/c_e$
30	1.48	-1.19	-1.24	1.46	0.14	10.43	1.46	-0.01	-1.46
50	1.70	-0.89	-1.91	1.64	0.77	2.13	1.67	0.46	3.63
70	1.81	-1.19	-1.55	1.75	1.14	1.54	1.81	0.72	2.51

Where a_e = amount adsorbed per unit mass of adsorbate,
 c_e = equilibrium concentration,
 D = distribution coefficient.

Table (VII): Chemical Compositions of The Blend Sorbent

Element	C	K	Na	Ca	N	Fe
%	48.56	2.21	2.14	1.11	0.43	1.15

Table (VIII): Functional Groups Identified.

Wave number (cm ⁻¹)	Assigned functional groups
3737.6	Phenols (Ar-OH)
3450.4	Alcohols (-OH)
2930.1	Carboxylic acids (COOH)
1699.4	Unsaturated ketones (-C = CH -CO)
1650.0	Alkenes (C = C)
1422.2	Alkyl groups (-C _x H _{x-1})
1081.6	Ethers (R-O-R)

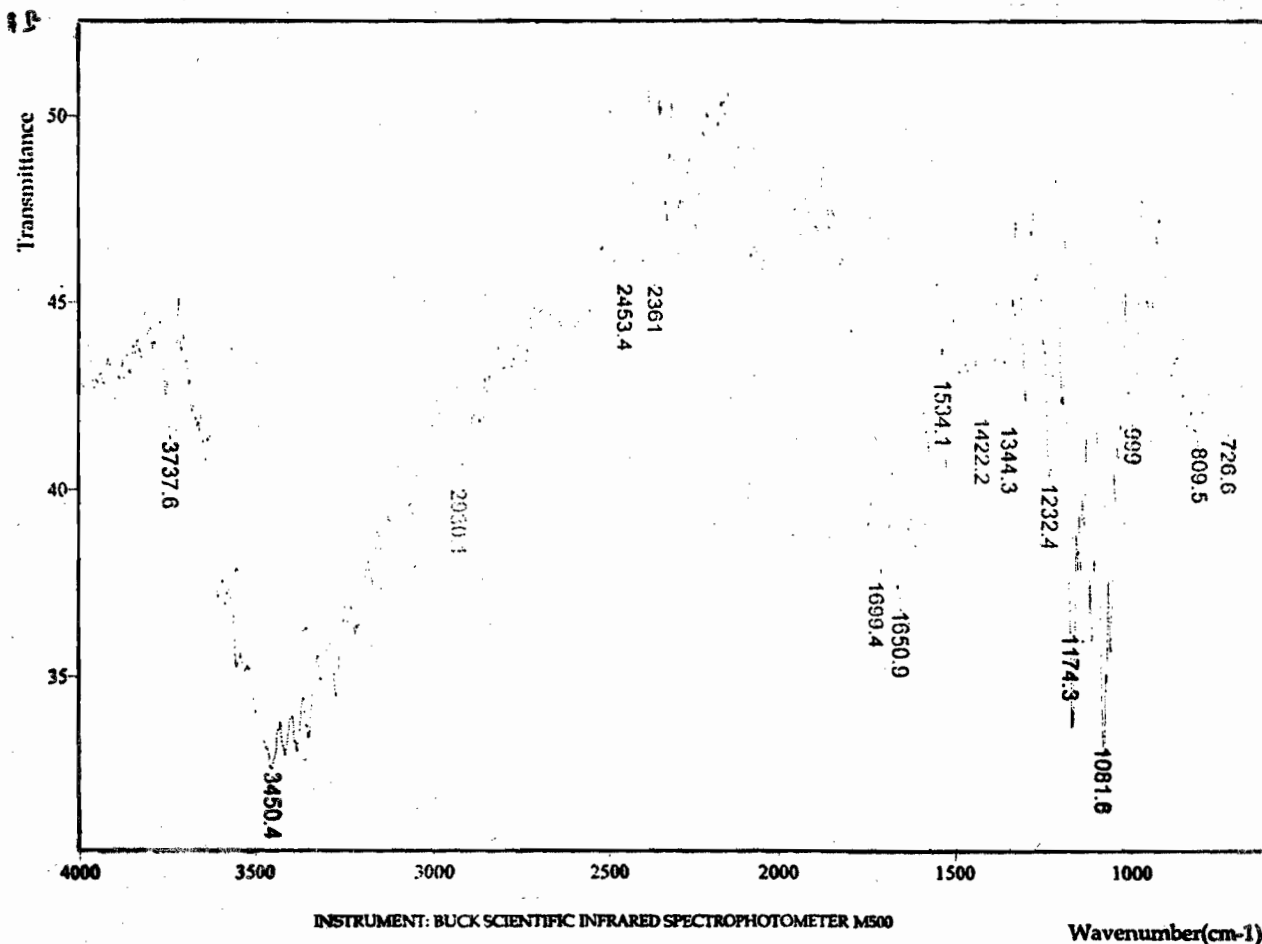


FIG. 1.

CONCLUSION

This work has shown that thiolated keratinous and plant materials can be used to remove heavy metal ions from aqueous solution. The use of low temperature of sorption and blending of biomass materials are thus recommended for effective application of adsorption for the removal and recovery of toxic metal ions from waste water and effluent from industries. Since biomass adsorbents are biodegradable they are thus said to be environmental friendly and the problem of non-biodegradable biomass waste products is completely eliminated. Chemical treatment and blending may thus be applied to commercial activated carbon to improve its adsorption capacities in its various fields of application.

REFERENCES

- Apha. Awwa. Wpcf., 1985. Standard Methods for the Examination of Water and Waste Water. Publish by American Health Association, 16th Edition pg 39-411.
- Atkins, P. W., 1998. Physical Chemistry, 6th Ed. Oxford University Press, Oxford Melbourne, Tokyo, 857-862.
- Azzi, R R., Denio, E.A., Itza, D., Silvio, F.V.B., Claudio; L.D. and Rochel, M.L., 2003. Tailoring Activated Carbon by Surface Chemical Modification with O, S, and N containing Molecule. J. Material Research 6 (2): 1439-1516.
- Blanco, A.B., Sanz, B., Liama, M.J. and Serra, J.L., 1990. Biosorption of Heavy Metals to Immobilized Phormidium Lamosum Biomass. J. Biotechnology, 69 227-240.
- Eguakhide, P.A., Jegede, S.I., and Esekigbe, A. 2004. Biosorption of Zinc Nickel and Cadmium from Aqueous Solution with Carbonized Palm Kernel Shell. J. Advances in Natural and Applied Sciences Research, 1 (1): 191-197.

- Gardea Torresday, J.L., Hapak, M.K., Hosea, J.M. and Darnall D.W., 1990. Effect of Chemical Modification of Algal Carboxylic Groups on Metal Ion Binding. *J. Environmental Science Technology*, 24: 1372-1378.
- Glastone, S. and Lewis., 1987. *Element of Physical Chemistry*, 2nd Ed. London, pg 559.
- Joyclvn, P.C., 1972. *Biochemistry of SH Group*. Academic Press Inc. London Ltd. 120.
- Okieimen, F. E., 1992., *Adsorption Foundation Kinetics*. Basic University Series, Ambic Press, Nigeria.
- Okolo, P.O. and Okuo, J.M., 2004. Heavy Metal Ions Adsorption by Chemically Treated Coconut Husk, Shells and Palm Kernel Fiber. *International Journal of Chemistry, India*. 14 (4):185-194.
- Okuo, J.M. and Ozioko, A.C., 2001. Adsorption of Lead and Mercury Ions on Chemically Treated Periwinkle Shells. *J. Chem. Soc. Nigeria*, 26 (1): 60-65.
- Ouki, S.K. and Kavannagh, M., 1997. Performance of Natural Zeolite for The Treatment of Mixed Metal Contaminated Effluent. *J. Waste Management Research*, 15: 383-394.
- Ricordel, S., Taha, S. Cisse, I. and Dorange, G., 2001. Heavy Metal Removal by Adsorption onto Peanut Husks Carbon:Characterization, Kinetic Study and Modeling. *Separation and Purification Technology*, 24, 389-401.
- Vogel, A.I., 1989. *Text Book of Inorganic Analysis*, 5th Ed. London, Longman.
- Volesky, B., 1987. Biosorbent for Metal Recovery. *Tibtech*, 5: 96-101.
- Warren, J., 1981. Contamination of Sediment by Lead, Cadmium and Zinc. A Review. *Environmental Pollution Series B*, 2: 401-436.
- Yang, C.C., and Lins, S., 1998. Removal of Lead from Silt Loam Soil by Electrokinetic's Remediation. *J. Hazardous Materials* 58: 285-299.