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Sorption of Heavy Metals from Electroplating Effluents by Low-Cost Adsorbents II: Use of Waste Tea, Coconut Shell and Coconut Husk

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Abstract: Present research focuses on the use of waste tea, coconut shell and coconut husk as potential low-cost adsorbents for removal of heavy metals chromium (Cr), zinc (Zn) and nickel (Ni) from three different electroplating plant effluents. The traditional activated carbon was also compared for objective assessment of the efficiency of the low cost adsorbents. The adsorbents were used in batch tests with electroplating effluents, its metal binding capacity, pH dependence of metal uptake and kinetics of metal adsorption were investigated. The study showed most of the metal uptake was within the first 60 min of exposure for all the adsorbents. Cr (VI) was optimally bound to the adsorbents at pH 3-4 and Zn(II) and Ni(II) at pH 7-9. The metal binding capacity differed for the adsorbents. Coconut shell was more effective for Ni (97.36% removal). All the three showed high rate of adsorption Zn (coconut shell, 99.74%, coconut husk 99.76% and waste tea 90.74% removal). All three satisfied the Freundlich Adsorption Isotherm.

Key words: Adsorption, coconut husk, coconut shell, electroplating effluent, heavy metals

INTRODUCTION

According to public health surveys, large number of people have been exposed to the health hazards caused by heavy metals presence in drinking water, surface water, ground water and animal tissue. The toxic effects of heavy metals have remained a major source of concern globally and such effects have been well documented. The toxic effect of heavy metals is made more serious because of their non-biodegradable nature which makes heavy metals pollution a serious environmental problem. Some of these heavy metals are also known to attack the active sites of enzymes in the body therefore inhibiting the enzymes.

Heavy metals can be found in water, air and soil. The major sources of heavy metals in water and soil are wastewater streams of many industrial processes. Effluents from industrial processes such as electroplating, mining, nuclear power operation, battery manufacturing, dye and pigment have been identified to contain high level of heavy metals. Such metals include Cr (III), Cr (VI), Zn, Cd, Cu, Ni, Hg and Pb (Blais *et al.*, 2000). The indiscriminate disposal of untreated effluents is a major source of concern in this part of the world. Some of the methods of treatment of effluents laden with heavy metals are chemical precipitation, ion exchange, reverse osmosis, electrodialysis and adsorption with activated carbon (Forster and Wittman, 1983; Olayinka *et al.*, 2005). These

methods have been found to be expensive and may not be suitable for developing countries like Nigeria. This concern necessitated the use of agricultural waste as low-cost materials for possible metal removal from wastewater. The potency of this method had been highlighted in some of our earlier study (Olayinka *et al.*, 2005). Agricultural by-products and biological materials have been found to be useful for metal sorption. These occur through accumulation processes involving functional groups. Carrilho and Gilbert (2000) studied biomaterials from marine algae in removing Al, Cd, Co, Cr, Fe, Ni and Zn. The material showed high affinity for the metals at pH 5.5. The feasibility of using chitosan coated oil palm shell charcoal to remove heavy metals has been described (Nomanbhay and Palanisamy, 2005). However, the ability of the materials varies depending on metal binding complexes they possess. Coconut shell, coconut husk are abundant agricultural waste materials in South Western Nigeria.

The main objectives of this study were to determine the effectiveness and feasibility of some low-cost agricultural waste materials (waste tea, coconut husk and coconut shell) in the removal of heavy metals, (namely chromium, nickel and zinc) from selected electroplating effluents. The study included investigation of the effect of adsorbent loading, hydrogen ion concentration (pH), contact time and determination of Adsorption Isotherm

coefficients. Traditional activated carbon was also used in the removal of heavy metals and comparison were made with the potential adsorbents.

MATERIALS AND METHODS

Preparation of adsorbents: As received waste tea bags (Lipton tea) were obtained from the restaurant in the University of Lagos. The contents of the bags were emptied, sieved to a particle size of 2 mm, soaked in distilled water overnight and washed several times. The washed was oven dried at 60°C to constant weight. Coconut shell and husks were obtained as coconut waste from the Lagoon area of the University of Lagos, Nigeria. The husks were obtained by dehusking the coconut pods after removing the white flesh. The shells were pounded using a pestle and mortar and further ground to a powder in a mill. The husk and shell were each sieved to a 2 mm particle size. The shell and husk were washed separately with distilled water to remove impurities and dried at 60°C to a constant weight. Activated charcoal was obtained from a chemical shop in Lagos. It was sieved to a particle size of 2 mm.

Apparatus: A Perkin Elmer model 3110 Atomic Absorption Spectrophotometer was used for the determination of the metals. All centrifugation steps were performed with a centrifuge model operating at 2000 rpm. A Gallenkamp flask shaker was used for agitating the mixture of effluent and adsorbent.

Preparation of adsorbent for batch procedure: In the batch procedure, a known amount of the adsorbent was suspended in effluent solution containing the metal(s) of interest. The mixture was agitated and then transferred to the centrifuge tube for centrifugation. The supernatant was carefully decanted. The amount retained by the adsorbent was calculated by the difference between the amount of metal in the original effluent and that found in the supernatant.

Adsorbent loading experiment: Varying weights of adsorbent (1.0-5.0 g) were suspended in 50 mL each of the effluents. The mixtures were agitated and then centrifuged. The supernatant were separated and analysed for metal determination by flame atomic absorption spectrophotometer. Blank samples were prepared by replacing the effluents with distilled water.

pH dependence: Preliminary studies were performed in order to choose the optimum pH for strong binding of the metals to the adsorbent. Five one gram adsorbent were

each suspended in a 50 mL aliquot of the effluent. Each aliquot corresponds to a pH value and blanks were also prepared at the various pH's. The suspensions were agitated and the pH was adjusted by addition dropwise of 0.1 M NaOH or 0.1 M HCl to the required pH. The final suspension were further agitated and then centrifuged. The pH's of the mixture were varied between 3.0-12.0.

Variation of contact time: The kinetics of Cr(VI), Ni(II) and Zn(II) sorption were assessed to investigate the effect of time on the metal retention of the adsorbents. Dried and sieved adsorbent samples (3.0 g each) were suspended in five 50 mL aliquot effluent samples. The flasks were each shaken in a Gallenkamp shaker for 30, 60, 90, 150 and 180 min, respectively. The aliquots were centrifuged and analysed for the three metals using the FAAS.

Physicochemical analysis of effluents: The analysis of the effluents samples were performed according to the official method of wastewater analysis (APHA, 2001).

RESULTS AND DISCUSSION

The physicochemical parameters of the effluents samples were shown in Table 1 and 2. These results revealed the levels of pollution of these effluents. The concentrations of heavy metals (Cr, Zn and Ni) were significantly higher than the recommended limit of discharge stipulated by the Federal Ministry of Environment. The pH of the effluents; GAL, 4.67 and GRI, 3.61 did not fall within the limit for discharge into surface water. However, the pH of PRI effluent, 6.72 fell within the limit (6-9). The values of Chemical Oxygen Demand (COD) for all the effluents were very high as shown in Table 2. It was also observed that the level of solids in the effluents were considerably low, therefore the metals were in soluble phase. All these suggest a significant level of pollution and if discharge untreated into waterways would constitute serious environmental hazards. The need for a thorough remediation of the effluents is therefore imperative. However, other parameters such as dissolved oxygen fell within the limit.

Table 1: Key to samples

Samples	Key
Effluent A	GAL
Effluent B	GRI
Effluent C	PRI
Waste tea	WT
Coconut shell	CS
Coconut husk	CH
Activated carbon	AC

Table 2: Physicochemical analysis of the effluent samples

Parameters	GAL	GRI	PRI	Fed Min. Env. Limit. of Dis. charge
pH	4.67	3.61	6.72	6-9
Conductivity (µS)	183.00	183.60	189.00	
Dissolved solid (mg L ⁻¹)	0.36	0.41	7.28	2000
Suspended solid (mg L ⁻¹)	0.21	0.26	0.74	30
Total solid (mg L ⁻¹)	0.57	0.07	8.02	2030
Alkalinity (mg CaCO ₃ L ⁻¹)	6.90	ND	1587.00	60-300
Acidity (mg CaCO ₃ L ⁻¹)	88.00	99.31	ND	
Dissolved oxygen (DO), (mg L ⁻¹)	4.61	8.83	33.64	Not less than 0.21
Chemical oxygen demand (mg O ₂ L ⁻¹)	1338.40	6309.60	8795.20	160
Chromium (mg L ⁻¹)	3.28	16.20	582.15	<1.0
Zinc (mg L ⁻¹)	14.64		69.86	<1.0
Nickel (mg L ⁻¹)		20.42		<1.0

Table 3: Freundlich isotherm for the adsorbents on zinc, nickel and chromium adsorptions

Adsorbent/Metal	K _F	n	1/n	R
Waste tea/Zn	0.40	0.68	1.47	0.93
Coconut shell/Zn	2.84	4.52	0.22	0.74
Coconut husk/Zn	3.33	0.90	1.11	0.59
Activated carbon/Zn	1.09	0.83	1.20	0.58
Waste tea/Ni	-0.15	1.76	0.57	0.68
Coconut shell/Ni	4.07	1.10	0.91	0.91
Coconut husk/Ni	2.57	1.23	0.81	0.74
Activated carbon/Ni	0.41	0.74	1.35	0.98
Waste tea/Cr	-0.09	0.42	2.38	0.92
Coconut shell/Cr	1.70	4.65	0.21	-0.28
Coconut husk/Cr	2.57	25.64	0.04	0.11
Activated carbon/Cr	-1.07	0.61	1.61	0.77

The Freundlich Adsorption Isotherm Coefficients were calculated and the results are as shown on Table 3 and in Fig. 10 and 11. Using Freundlich Isotherm Equation (Blais *et al.*, 2000):

$$Ne = K_f Ce^{1/n}$$

Where:

Ne = is X/m (amount of metal ions adsorbed per unit mass of adsorbent)

To simplify the equation, linearize thus:

$$\ln Ne = \ln K_f + 1/n \ln Ce$$

The Freundlich Isotherm coefficients were determined plotting LnNe against LnCe (Fig 10 and 11):

Where:

1/n = Slope of the graph and

K_f = Intercept

The Freundlich equation is an empirical equation based on adsorption on a heterogenous surface. The constants indicate the adsorption capacity and the adsorption intensity, respectively. Linear plots of LnNe vs LnCe

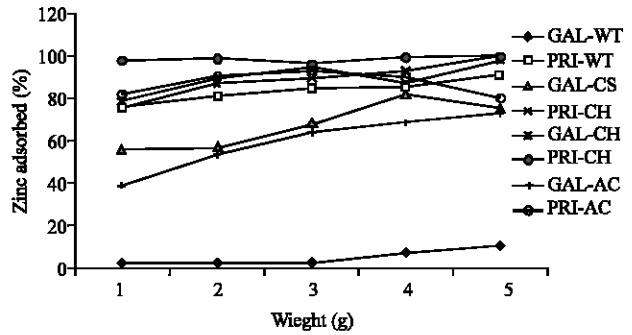


Fig. 1: Effect of adsorbent on adsorption of zinc

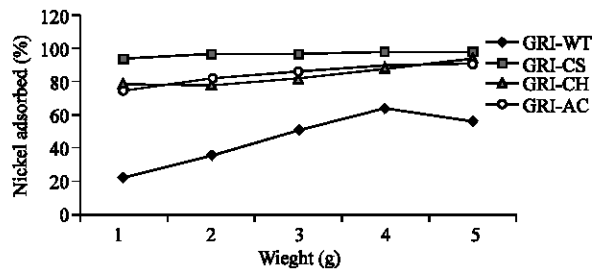


Fig. 2: Effect of adsorbent loading on adsorption of nickel

showed the Freundlich isotherm was representative for the heavy metal adsorption for the adsorbents tested. The correlation regression coefficient showed that heavy metal sorption for the adsorbents were favorable. Comparison of Freundlich Isotherm constants obtained from other studies using other adsorbents showed that apart from waste tea (for chromium and nickel), the values obtained in this study are comparable (Nomanbhay *et al.*, 2005).

Effect of adsorbent loading: Adsorption of heavy metals on the adsorbents i.e., Waste Tea (WT), Coconut Shell (CS) and Activated Carbon are represented in Fig. 1-3.

Zinc: The percentage adsorption of zinc as presented in Fig. 1, increased from 2.32-11.20% as waste

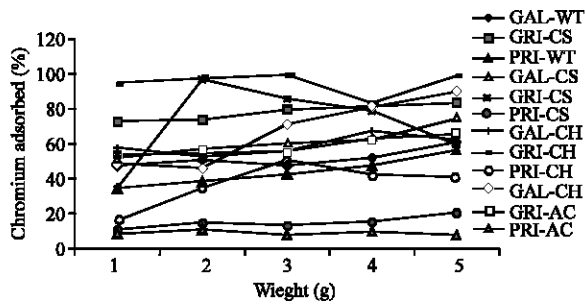


Fig. 3: Effect of adsorbent loading on adsorption of chromium

tea dosage was increased (1-5 g) for GAV effluent, while percentage adsorption increased from 75.72-90.74% for PRI effluents. For coconut shell, the percentage adsorption increased from 75.24-99.74% as CS loading was increased for PRI effluent and from 55.81 to 75.27% for GAL effluent. The percentage adsorption increased from 97.75 to 99.76% as Coconut Husk (CH) dose was increased for PRI, while percentage adsorption for GAL effluent increased from 78.21-97.54%. Also Activated carbon adsorbed 81.88-93.01% of zinc from PRI effluent as the adsorbent loading increased from 1-5 g. While in case of GAL effluent, adsorption with Activated carbon increased from 32.73-72.81%. It is seen that the rate of removal of metal ions increased with the increase in the dose of adsorbent. This could be because of the increase in sorption sites. It was observed that Coconut husk seemed to be the best adsorbent for zinc removal, followed by coconut shell. These could be because of the high lignin content in coconut compared to waste tea. The level of removal also compare closely with that of activated carbon showing that coconut husk could be a better alternative to the high cost activated carbon.

Nickel: Figure 2 represent the percentage adsorption of Nickel with adsorbents. As Waste tea dosage was increased against a fixed volume of GRI effluent, adsorption increased from 21.84-55.78%. In case of Coconut shell, the percentage adsorption increased from 93.54-97.94% while Nickel adsorption with Coconut husk increased from 78.45-93.49% as the dose was increased for the same effluent. Also adsorption of Activated carbon increased from 74.39-90.55% as the dose was increased.

Coconut shell was the best of the adsorbents for removal of Nickel from GRI effluent followed by coconut husk. These results also show the efficiency of using low cost coconut shell instead of activated carbon. The result for coconut shell and husk are comparable and this shows that active sites for adsorption of heavy metals are more in coconut husk than waste tea.

Chromium: Figure 3 showed the adsorption of chromium by all the adsorbents using the three effluents under consideration. As Waste tea dosage increased against a fixed volume of GRI effluent, the level of adsorption increased from 73.26-83.84%, while (GAL) and (PRI) gave an average percentage adsorption from 47.26-61.28 and 34.36-57.00%, respectively. Adsorptive capacity of Coconut shell increased from 34.59-59.82% for GRI effluents. While percentage adsorption for PRI and GAL were 14.61-20.86 and 54.27-65.24%, respectively. Coconut husk also adsorbed chromium from the effluents GRI, GAL and PRI with increase in percentage adsorption from 95.02-99.09, 57.62-62.20 and 15.98-40.85%, respectively.

The percentage of chromium adsorbed from GRI, GAL and PRI were 52.27-74.92, 48.78-90.24 and 8.60-10.09%, respectively as the dosage of Activated carbon was increased. Coconut husk was the best of all the adsorbents for removal of chromium, followed by activated carbon.

The percentages of chromium adsorbed by all the adsorbents from PRI effluent were low compared to other effluents. This may not be unconnected with the high initial concentration of chromium in the effluents. Also, the initial pH of 6.72 is not so favourable for chromium adsorption. The chromium in the study is Chromium VI, an anion.

It has been suggested that the mechanism for metal adsorption is due to the acidic functional groups (C = O) on the adsorbents. The presence of oxygen functional groups make the adsorbent surface negatively charged and there is therefore a repulsive electrostatic interaction between the adsorbent and the anion, whereas for cations, the negatively charged groups enhance the electrostatic interaction i.e., the positively charged cations bind by way of electrostatic interaction with the negatively charged surface of the adsorbents mainly through the carboxylic ligands. The lower results obtained for Chromium compared to the other two cations is similar to the finding of others (Rao *et al.*, 2002).

General increase in adsorption with increase in adsorbent dose was observed for all the adsorbents. This is expected due to the fact that the higher the dose of adsorbents in the solution, the greater the availability of exchangeable sites for the ions. After a certain amount of adsorbents, there was no further increase in adsorption. This suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remain constant even with further addition of adsorbent. This trend was also observed by other authors (Patrick *et al.*, 1992). It is interesting to note that the maximum removal of heavy metals differ for the four adsorbents. This could be due the different amounts of

lignin present in the adsorbents (which is responsible for the acidic functional groups). The adsorbents also fulfilled the Freundlich Adsorption Isotherm equation, as adsorption varied proportionally with the amount of adsorbent in solution. This study showed that coconut husk and shell gave better results in some cases than activated charcoal. It therefore confirms the usefulness of these agricultural waste materials in heavy metal removal.

Effect of pH: The adsorption capacity of adsorbents as function of adsorbate's pH (hydrogen ion concentration) was determined as shown in Fig. 4-6. This was examined over a pH range of 3-12. The experiment was conducted at initial concentrations of the effluents as shown in Table 2. Adsorbent particle size was 2 mm with adsorbent loading of 1 g at an equilibrium time of 2 h. It was apparent that zinc was strongly adsorbed at high pH's for all the adsorbents under consideration. At higher pH values, Zn(II) is less soluble and there is an increasing negative charge density on the adsorbent, hence more Zn(II) would easily be adsorbed as the pH increases. Optimum pH for Nickel removal was found to be pH 7-9 in all the experiments. Chromium was adsorbed most at low pH and adsorption declined as the pH was increased.

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions and the concentration of the ions on the functional groups of the adsorbent. It is apparent that Cr (VI) was strongly adsorbed at low pH. The reason for better adsorption at low pH could be attributed to the large number of H⁺ ions present at low pH values which in turn neutralize the negatively charged adsorbent thereby reducing hindrance to the diffusion of chromate ions. The decrease at high pH may be due to abundant of OH⁻ causing increased hindrance to diffusion of dichromate ions. Similar observations have been reported by other investigators by Rao *et al.* (2002).

For nickel and zinc, it was apparent they were strongly adsorbed at higher pH. The optimum pH of Ni was found to be pH 7-9. An increase in adsorption of Zn and Ni at high pH could be ascribed to an increasing negative charge density on the adsorbent surface. It has however been suggested that at pH greater than 8, the Zn(II) and Ni(II) removal was mostly due to precipitation and not by sorption. Hence pH 8.0 was considered as optimum pH in the case of Ni and Zn. Maximum nickel removal at this pH was found to be 70-90%.

This study is in agreement with other investigators who observed that adsorption of anionic species are favoured at lower pH and vice versa for cationic species.

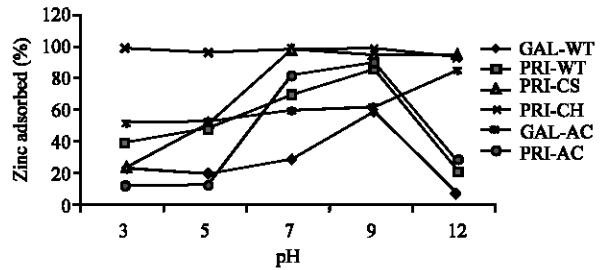


Fig. 4: Effect of pH variation on adsorbent of chromium

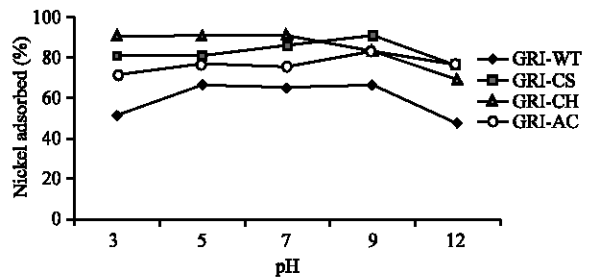


Fig. 5: Effect of pH variation on nickel adsorption

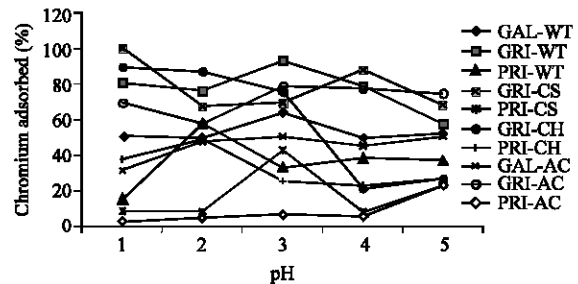


Fig. 6: Effect of pH variation on chromium adsorption

At higher pH the presence of oxygen containing functional groups make the adsorbent surface negatively charged and hence there is a repulsive electrostatic interaction between the adsorbent and the anions (Nomanbhay *et al.*, 2005).

Effect of contact time: The experiment of adsorption as a function of contact time was conducted at an initial metal concentration and result are shown in Fig. 7-9. The operating condition was maintained at pH 6, particle size of 2 mm and adsorbent loading of 1 g. Variations in adsorption were noticed as the contact time varied. The optimum equilibrium time for zinc removal were 150 min, (60-90 min), 60 and 180 min using waste tea, coconut husk, coconut shell and activated carbon, respectively. For nickel, optimum contact time were 180, 90, 90 and 180 min using waste tea, coconut husk, coconut shell and activated carbon, respectively while the optimum times for

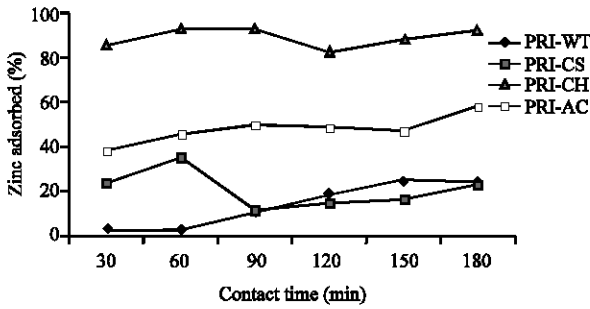


Fig. 7: Effect of contact time on adsorption of zinc

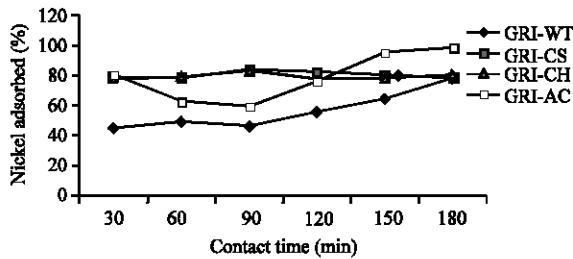


Fig. 8: Effect of contact time on adsorption of nickel

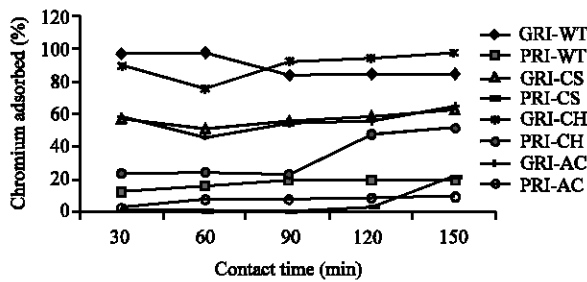


Fig. 9: Effect of contact time on adsorption of chromium

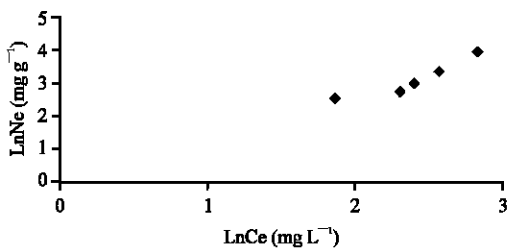


Fig. 10: Adsorption of zinc on waste tea

chromium were (60-90 min), 150, 150 and 180 min in the same order. This results show the importance of optimum contact time for each adsorbent. The study showed that the rate of metal uptake by the adsorbents was rapid and about 75% or more of the Cr, Ni and Zn accumulated on the adsorbents within 30 min. Results indicate removal efficiency increased with an increase in contact time before equilibrium is reached. This could be because of the greater availability of the various functional groups on

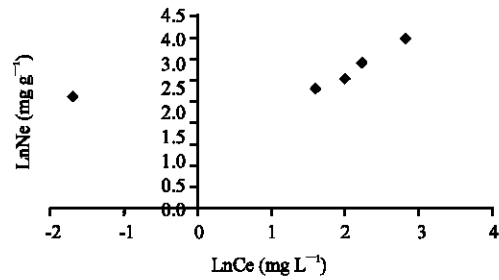


Fig. 11: Adsorption of zinc on coconut shell

the surface of the adsorbents which are required for interaction with anions and cations. This improved the binding capacity and the process proceeded rapidly. This experiment is important as equilibrium time is one the important parameters for an economical wastewater treatment system. This result obtained in this study is similar to the finding of Rao *et al.* (2002).

However, in some cases, adsorption was noticed to slow down in later stages because initially a large number of vacant surface sites may be available for adsorption and after some time the remaining vacant surface sites may be difficult to occupy due to repulsive forces between solute molecules of the solid and the adsorbent. Similar results have been observed by other investigators (Chand, 1999; Saravanne and Sundrajan, 2002; Narsi *et al.*, 2004).

CONCLUSIONS

In conclusion, it has been shown that the use of coconut husk, coconut shell and waste appears to be technically feasible, eco-friendly with high efficiency in the removal of heavy metals from wastewaters. Besides it is composed entirely of agricultural waste and this helps in the reduction of waste generation. They adsorbed comparatively like the expensive traditional activated carbon. The necessity of the study is justified considering the physicochemical analysis of the effluents in which the metal concentration did not conform with the limit of discharge stipulated by Federal Ministry of Environment, Nigeria.

Further studies on the use of other agriculture wastes and chemical modification of these low-cost adsorbents in removing heavy metals in effluents are ongoing in our research group and will be reported in subsequent papers. Also studies on the regeneration of the adsorbents using eco-friendly reagents therefore leading to the re-use of the adsorbents is being investigated.

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