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SOLID – LIQUID SORPTION STUDIES OF Ni, Cd and Pb ON UNMODIFIED AND MODIFIED AVOCADO PEAR SEED

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ABSTRACT
The batch removal of liquid-phase Ni, Cd and Pb ions on to solid-phase unmodified and mercaptoacetic acid-modified avocado pear seed grind was studied at room temperature. The percentage efficiency of the removal of the metal ions was found to be dependent on initial metal ion concentration of the adsorbate solution. Adsorbent modification enhanced adsorbent performance for Ni, Pb and Cd. Maximum percentage efficiencies of the ions adsorbed were 88.8%, 88.8% and 90.6% on the unmodified adsorbent and 90.67%, 89.02% and 90.53 on the modified adsorbent for Ni, Cd and Pb ions respectively. The trend of adsorption for single metal ion systems was Pb > Ni > Cd. Adsorption isotherms, namely Langmuir, Freundlich and Temkin were applied to adsorption data. Isotherm parameters showed that all the isotherms correlated the adsorption data well. All the three isotherms used to fit experimental data gave correlation values that lie between 0.935 and 0.999. The kinetic evaluation of the sorption showed that the data correlated well with the pseudo second order model.

Keywords: Avocado peer seed, unmodified, unmodified, kinetics, equilibrium, intra-particle diffusion.

INTRODUCTION
Metallic species mobilized and released into the environment through anthropogenic activities tend to persist indefinitely, circulating and eventually distribute throughout the food chain, thus, creating environmental concerns. This is a direct consequence of their non-biodegradability[1]. Metals that are exemplified by their relatively high atomic mass, and high density and that exhibit toxicity even at low concentrations are termed as heavy metals. Heavy metals have no known biological functions. Rather, they are toxic to living tissues[2] and have large bio-concentration factors in plants and marine organisms[3]. It is therefore necessary to have them removed from waste media before discharge into the natural environment. Conventional methods, among which are ion-exchange, chemical precipitation, chemical oxidation/reduction, flotation, coagulation/flocculation, membrane technologies and adsorption widely employed in the removal of heavy metals from industrial wastewaters[4] have been found to have limitations such as: unpredictable metal ion removal, formation of sludge, clogging of membrane surfaces , non-re-generatability of raw materials, high cost of procurement, installations and operations[5] ;. However, adsorption has edge over the other technologies on account of its simple design, cheapness, adsorbent re-generatability, little or no-sludge formation, availability of raw materials, effectiveness and efficiency. Activated carbon is the most utilized adsorbent for the adsorptive treatment of aqueous media[6-7]; It has been found to be highly effective, showing excellent sorption efficiency when used as adsorbent of heavy metals[8];. Nonetheless, it is limited by its relatively high production cost, low selectivity and regeneration problems, thereby necessitating the search for other alternatives that are cheap and readily available. Investigations have shown that, living and non-living biomaterials, which includes cellulose based agricultural by-products are capable of being used alongside or as alternatives to activated carbon. Being that they offer the advantages of high efficiency, cheapness and availability, re-generatability, high metal recovery and elimination of chemical and biological sludge[9-11].
Given the negative environmental and human impacts of heavy metals, which cannot be overemphasized especially their continuous accumulation in the aquatic and marine environments, there is a need for a continuous search for low cost adsorbent materials that can be conveniently and efficiently used for heavy metal removal from aqueous media. This work is therefore designed to probe the extent

to which avocado seed grind can remove some metal ions singly and when they are mixed.

MATERIALS AND METHOD

Adsorbent and Adsorbate Preparation

Avocado seeds obtained from an open retail market in Nigeria were chopped in bits, sun dried and ground into a powdery form. 300 g of the sample was soaked in 0.3M solution of nitric acid for 24 hours. The acid- soaked sample was then washed repeatedly and thoroughly with distilled water and oven dried at 60°C. 150 g of the washed sample was sieved to obtain different particle sizes of 75 µm, 150 µm, 300 µm and 600 µm.

1000mg/L stock solutions of the metal ions were prepared from their salts from which working solutions of 5, 10, 15, 20 and 25 mg/L were prepared. Adsorbate for experiments; Ni, and Cd ions, were obtained from BDH Chemicals Ltd, Poole, England, while Pb ion was from Avondale Laboratories, Beaumont close, Banbury, Oxon, England. All of which were analytical grade salts of their chlorides and nitrates respectively.

Experimental Procedure

0.2 g portion of the 300 µm dried powdered unmodified and modified avocado pear seed (adsorbent) were separately and accurately weighed using an electronic weighing balance and transferred into test-tubes for the test on the effect of initial metal ion concentrations of 5, 10, 15, 20 and 25 mg/L working solutions. 10 ml of the metal ion solutions was then added to each of test tubes for unmodified and modified adsorbent. The test-tubes were tightly stoppered and subjected to shaking on a mechanical shaker at 200 rpm for 1 hour. The above process was repeated for the 20 mg/L working solutions of the metal ions for 20, 30, 40, 50 and 60 min for the effect of contact time. After each adsorption, the mixtures were centrifuged at 3500 rpm for 5 min and decanted. The supernatant was then collected and analyzed for absorbance using the atomic absorption spectrophotometer. All the experiments were carried out at an ambient temperature.

RESULTS AND DISCUSSION

Equilibrium studies

The extent of adsorption of the metal ions by the adsorbate was estimated with three isotherms, namely: Langmuir, Freundlich and Temkin. The linearized forms of the equations used are:

Langmuir isotherm: $\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$ (1)

Where: q_e = Amount adsorbed at equilibrium
q_m = Maximum amount adsorbed
C_e = Final concentration of metal ion in solution
K_L = Langmuir or equilibrium constant for adsorption

Freundlich isotherm: $\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$ (2)

Where, K_F and n are Freundlich constants

Temkin isotherm: $q_e = B \ln A + B \ln C_e$ (3)

B = $\frac{RT}{b_T}$ and b_T = adsorption potential of the adsorbent ($Jmol^{-1}$)
A = Temkin isotherm constant (dm^3g^{-1}),
R = molar gas constant = $8.314 Jmol^{-1}K^{-1}$
T = Absolute temperature (K)

The variation of initial metal ion concentration with adsorption is shown in Figure 1. There is a linear correlation of the two variables as adsorption increased with increase in initial metal ion concentration for all the metals. The linear increase depicts that the adsorbing material has corresponding surface pores to accommodate adsorbent particles arising from increasing concentration. The linear increase is also an indication that the avocado seed powder has adsorbent capacity for the metal ions in solution as particle concentration keeps increasing within the limits of maximum surface capacity.

The plots for the isotherms and the adsorption parameters of the equilibrium models are shown in Figures 2 to 7 and Table 1 respectively. The results of the isotherm parameters in Table 1 show that; though the Langmuir model had a good correlation coefficient (R^2> 0.9) indicative of a best fit modelling, the q_{max} and K_L values for Ni and Cd did not show a positive and direct relationship to the calculated R^2 values. The q_{max} and K_L values for both ions are negative, thus showing that monolayer process was less favourable for the metal ions. The case of Pb is different with this model as the parameters are all positive, though lower for the modified sample. The favourability of the sorption was confirmed using the standard Gibbs energy of reaction which is a criterion of spontaneity in relation to the Langmuir constant K_L in the equation,[12],[13].

$\Delta G^0 = -RT \ln K_L$ (4)

ΔG^0 was found to be greater than zero ($\Delta G^0 > 0$) for the Langmuir constant applied to equation (4), it implies that the monolayer process was not spontaneous for Ni and Cd as also indicated by the negative q_{max} and K_L values. On the other hand, ΔG^0 of Pb was less than zero ($\Delta G^0 < 0$), which implies that the process was spontaneous.

The Freundlich parameters are however all positive with very high R^2 values. Though the adsorption capacity value is low for all metals, the results are indicative of a dominating multilayer process on a heterogeneous surface for all metals considered in the work. While monolayer and multilayer processes are concurrent[14], they are also competitive, depending on the prevailing factors affecting the adsorption. The Freundlich parameters for the modified sample are also observed to be lower than the unmodified as with the Langmuir except for Pb. The modified functional group may not have contributed more to the adsorption than the original adsorbent material. This may likely occur because the electronegativity of the sulphur (2.5) in the thiolic[15] functional group in the modified adsorbent is less than that of oxygen (3.5) in the unmodified cellulosic hydroxyl (-OH) group. It is then very likely that the hydroxyl surface will adsorb the metal ions more than the thiolic surface by stronger electrostatic interaction. The predominating multilayer adsorption is indicative of heterogeneous surfaces on the adsorbing material.

The results of the Temkin model for the metal ions show that the adsorption potential of the material used was good in the sense that single- and double-digit energy values were observed for Ni and Cd, and for Pb respectively. Temkin isotherm assumes that fall in the heat of adsorption is linear rather than logarithmic, as implied in Freundlich equation. b_T is related to the heat of adsorption, ΔQ as shown in equation (5),

$b_T = \Delta Q = -\Delta H$.   (5)

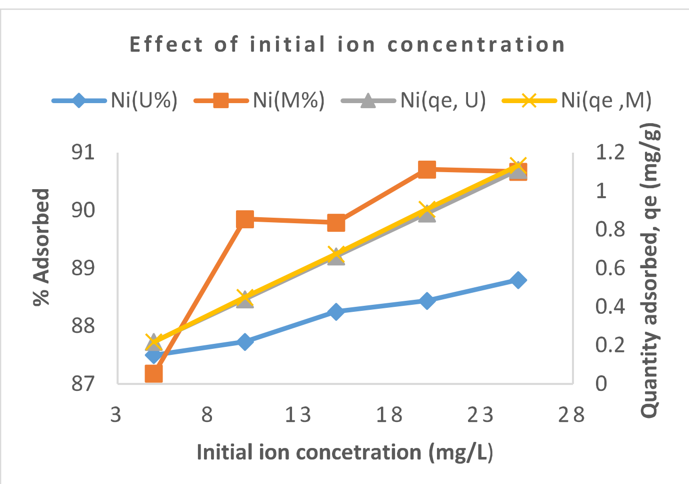

Figure 1. Plot of effect of initial metal ion concentration on the adsorption Ni, on unmodified and modified avocado pear seed

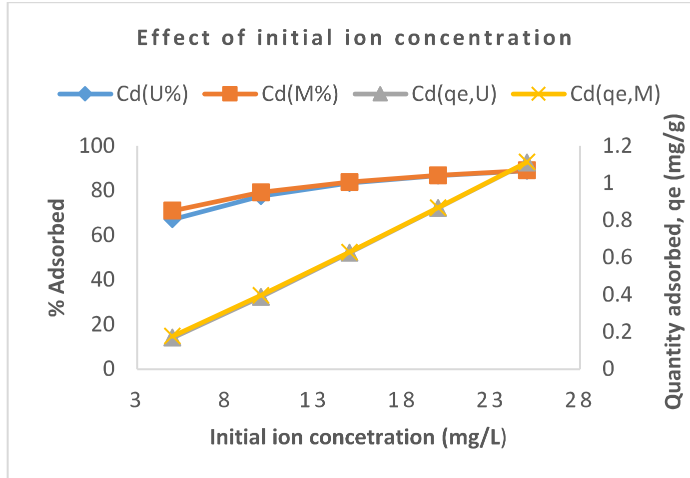

Figure 2. Plot of effect of initial metal ion concentration on the adsorption Cd, on unmodified and modified avocado pear seed

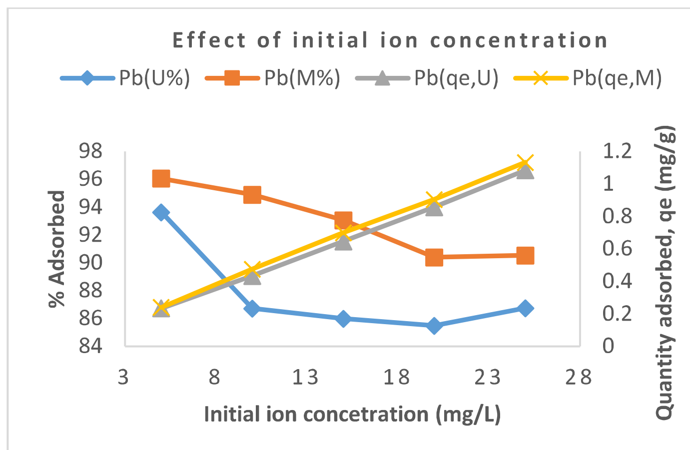

Figure 3. Plot of effect of initial metal ion concentration on the adsorption Cd, on unmodified and modified avocado pear seed

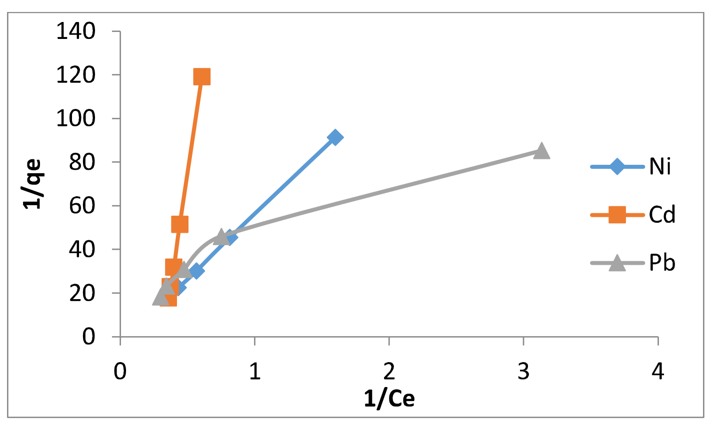

Figure 4: Langmuir isotherm for the adsorption of Ni, Cd and Pb on unmodified avocado pear seed

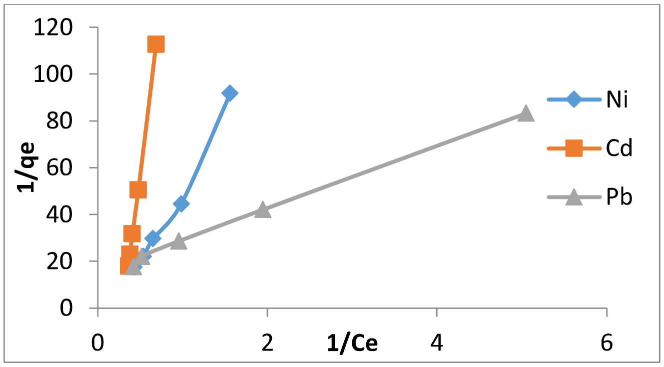

Figure 5: Langmuir isotherm for the adsorption of Ni, Cd and Pb on modified avocado pear seed

For a positive value of b_T it implies that the adsorption process is exothermic, while a negative value means that it is endothermic. Since the values of b_T for all the metal ions considered are positive, it implies that the adsorption is exothermic; in which case, there is a decrease in the heat of adsorption as the concentration of metal ions is increased. Temkin model also indicates the bonding energy or interaction between the adsorbate and adsorbent. The high values of b_T indicates that there were strong and sufficient binding energies for adsorbate/adsorbent interaction that resulted in the release of adsorption heat in line with the assumptions of the model

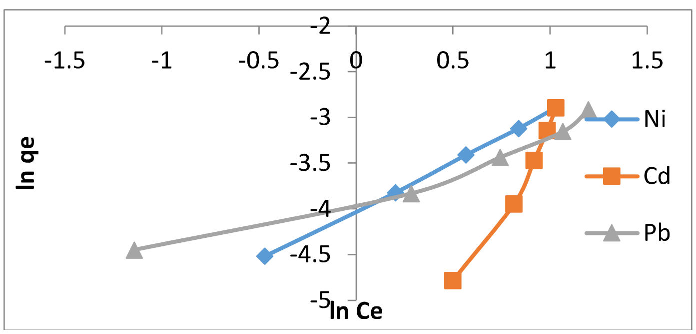

Figure 6: Freundlich isotherm for the adsorption of Ni, Cd and Pb on unmodified avocado pear seed

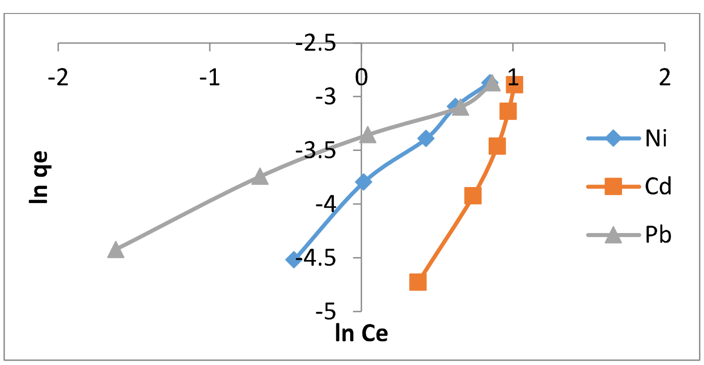

Figure 7: Freundlich isotherm for the adsorption of Ni, Cd and Pb on modified avocado pear seed.

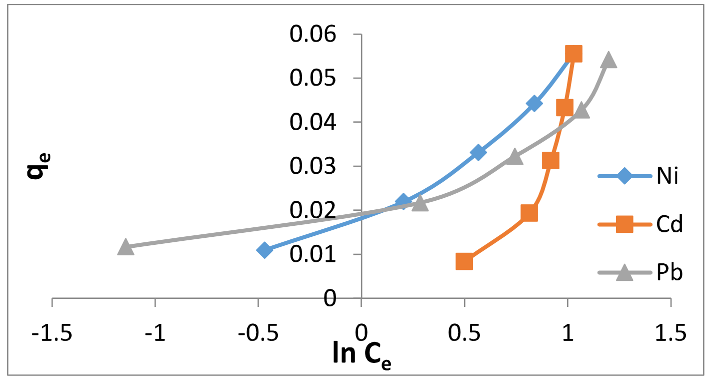

Figure 8: Temkin isotherm for the adsorption of Ni, Cd and Pb on unmodified avocado pear seed

Kinetics of Adsorption

The kinetics of solution processes remain a necessary and definite determinant of the type of boundary or interfacial interaction in adsorption. Metal ions in solution must diffuse or be agitated to have a concentration gradient that favours the increase of the ions on the adsorbent surface. The rate of diffusion or convectional motion of adsorbate particles is therefore a driving force to accomplish effective adsorption. Over the years, different rate models have been proposed to determine surface processes in adsorption. In this work the pseudo second order kinetics and the intra-particle models were applied to the adsorption data. The results of the application are shown in figures 9 and 10 for the unmodified and modified adsorbents respectively. The kinetic parameters are shown in Table 2. The results for the unmodified avocado seed powder showed that the adsorption of all the three metals followed the pseudo second order(PSO) model with correlation coefficients very close to unity. The calculated q_e values were also found to be close to the experimental values in many cases: thus, the adsorption could well be described by the model[16]. The predominant interactions in this case are electrostatic between surface groups and the partitioning solution metal ions.

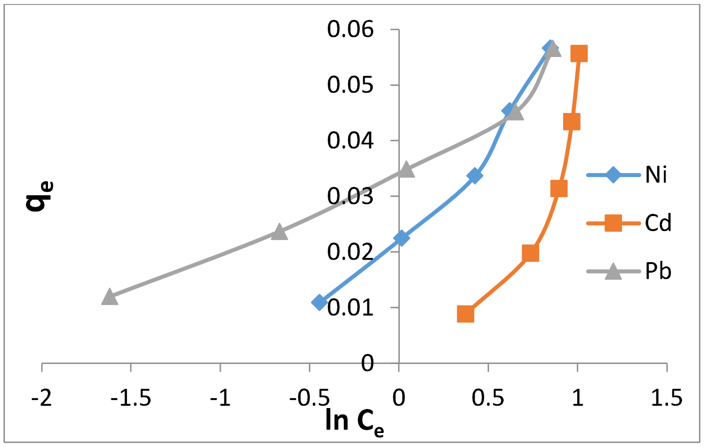

Figure 9: Temkin isotherm for the adsorption of Ni, Cd and Pb on modified avocado pear seed

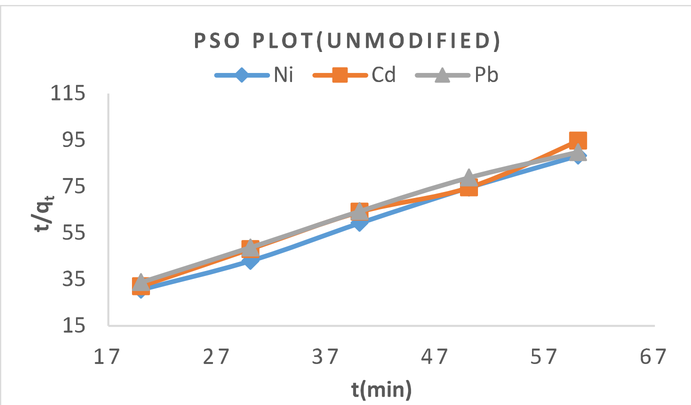

Figure 10. Pseudo second order plot of adsorption of Ni, Cd and Pb on unmodified avocado pear seed

The intra-particle diffusion model is used to determine the diffusional mechanistic steps involved in particle transport through the pores of the adsorbent surface.

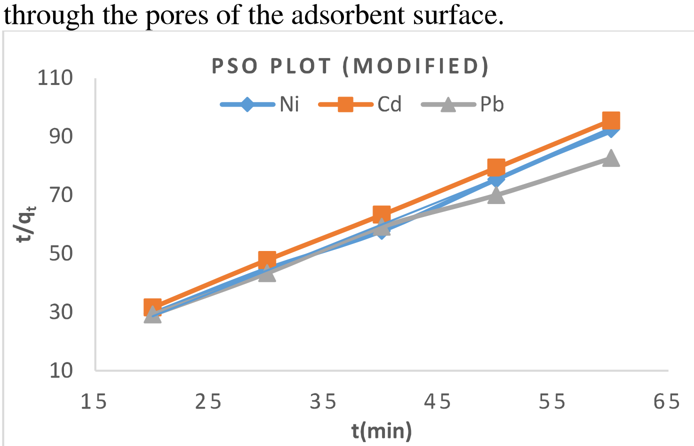

Figure 11. Pseudo second order plot of adsorption of Ni, Cd and Pb on modified avocado pear seed

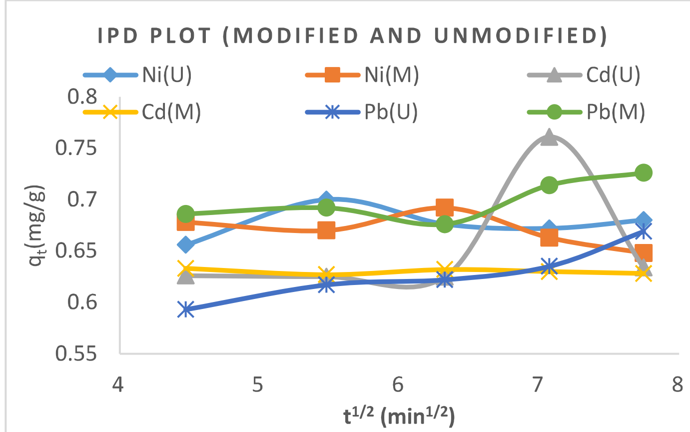

Figure 12. Intra-particle diffusion plot of adsorption of Ni, Cd and Pb on unmodified and modified avocado pear seed

Pores of a surface could be microporous, mesoporous and macroporous. The linearity of the plot confirms the mechanism of a single step of microporous intra-particle diffusion; the multilinearity of the plot indicates that the particle transport proceeds by more than one single step, in which case the process no longer conforms to the intra-particle diffusion mechanism and thus it would not be the rate limiting diffusion kinetics. In this work, the results of the intra-particle diffusion were multilinear in all cases, which then implies that the diffusion were multistep processes; and for this reason, it is not the rate limiting diffusion mechanism of the adsorption. The rate constants are also low and some are negative, indicative of the fact that intra-particle diffusion was not a predominant mechanism.

CONCLUSION

The solid-liquid adsorption of three metal ions, Ni, Cd and Pb from aqueous solution was carried out by batch method using unmodified(U) and modified(M) avocado peer seed powder. Adsorption was carried out as a function of the initial metal ion concentration and the contact time. Equilibrium sorption was evaluated using three models, namely: Langmuir, Freundlich and Temkin isotherms; while the kinetics was evaluated using the pseudo second order and the intraparticle diffusion models. The quantity of metal ions adsorbed on to the unmodified(U) and modified(M) avocado peer seed powder bore a positive linear relationship with initial metal ion concentration for all the metals considered. The percent of metal ions removed from solution increased with increase in initial metal ion concentration for Ni and Cd. Maximum percent adsorption for the metals are: Ni (88.8%U, 90.67%M), Cd (88.8%U, 89.02%M) and Pb (93.62%U, 96.04%M). This observation shows that the adsorption was higher for the modified than the unmodified avocado peer seed powder; however, that of Pb ions decreased with increase in metal ion concentration. The sorption correlated well with the pseudo second order kinetic model with R2 values greater than 0.99 for all the metal ions. The intraparticle diffusion model was multilinear in application, which indicated that it was not the rate limiting mechanism for particle diffusion on the pore of the sorbent surface. The results have shown that avocado peer seed powder can be effectively used to remove Ni, Cd and Pb metal ions from their aqueous solutions in the unmodified and the modified forms.

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DISCLOSURE STATEMENT

No potential conflict of interest was reported by the authors.

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