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Temperature and pH influence in sequestering cadmium, nickel and lead ions from synthetic wastewater using fluted pumpkin seed coat

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ABSTRACT

The use of agricultural wastes in the treatment of metal-bearing effluents is one of the recent techniques that had been found to be environmental friendly. This work recommended the coat of fluted pumpkin seed a good biosorbent through adsorption process in a batch experiment. Variation of important operational parameters such as pH and temperature were used to explore their effect using 1 g of 250 µm size of both unmodified and mercaptoacetic acid modified fluted pumpkin seed coat at contact time of 1 hr with initial metal ions concentration of 100 mg/l. The adsorption efficiency of the metals was pH as well as temperature dependent with nearly 100% adsorption by both unmodified and modified fluted pumpkin seed coat. Specifically, cadmium was adsorbed more strongly at low pH of 2, 4 & 6 by the unmodified coat of the fluted pumpkin seed while it was at higher pH of 10 by the modified seed coat. The same is applicable for nickel which indicated higher adsorption at 2 by the unmodified seed coat and 10 by the modified one while higher adsorption for lead was shown at pH of 2 for both unmodified and modified ones. Maximum adsorption was equally achieved at low temperature (303K) by both unmodified and modified seed coats, though unmodified seed coat showed slightly higher adsorption than the modified seed coat. The values of E_a, ΔS^0_{ads}, ΔH^0_{ads} *and* ΔG^0_{ads} *gotten indicated that the adsorption process is by physical adsorption, spontaneous, feasible and exergonic (release of free energy), endothermic and occur with increasing degree of orderliness.*

Key words: *Adsorption, metal sequestering, temperature, pH and fluted pumpkin seed coat*

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I. Introduction

Inadequate treatment of metal contaminated wastewater before discharge from industries and other sources has become one of the most serious environmental problems which need to be harnessed. Heavy metals such as cadmium lead and nickel are important environment pollutants, especially in areas of high anthopogenic activities (USEPA, 2000; Holan & Volesky, 1994). These metals are markedly very toxic even at low concentrations. According to (WHO, 1997) the maximum permissible limit for cadmium in wastewater before discharge is given as 0.1mg/L for surface water, land for

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irrigation and drinking water. The limit for nickel is 0.1mg/L for surface water, 0.2mg/L for irrigation land and 0.01mg/L for drinking water, while lead is 0.05mg/L for surface water, 0.1mg/L for irrigation land and 0.001mg/L for drinking water. In order words, these metals are needed in very trace amount in order to avoid threat. Therefore the sequestering of these metals is highly crucial from the standpoint of environmental pollution control (Puranik & Paknikar, 1999; Yan & Viraraghavan, 2003). Recently waste biomass has been in use in sequestering metals bearing wastewater because of the economic constraints that are associated with the conventional method (Bossrez et al., 1997; Yu & Kaewsarn, 1999). In this work, the coat of fluted pumpkin seed was used in sequestering metals from wastewater. According to (Agatemor, 2000) the proximate composition of the coat of the fluted pumpkin seed was classified as a lingo-cellulosic material, hence the interest in finding out its feasibility in sequestering heavy metals from solutions. The effect of pH and temperature was evaluated for achieving maximum uptake of these metals using the coat of the fluted pumpkin seed. The equilibrium and thermodynamic modeling were also fitted to data to determine proper metals adsorption mechanism.

II. Materials and Methods

The fluted pumpkin seed coat was bought from Umuahia Main Market, Abia State and processed to get the coat. The coat was grounded into tiny particle size using manual grinder and sieved through a test-sieve shaker after washing with de-ionized water and drying in an oven at 50 ^{0}C for 12hrs to get 250 μm mesh size. It was then activated by soaking in 2% (v/v) dilute nitric acid solution for 24 hours, filtered, rinsed severally with de-ionized water and allowed to dry in the oven at 105 ^{0}C for about 6 hours. Hence labeled unmodified sample. About 10g portion of the activated sample was modified using mercarptoacetic acid by soaking the sample into 1000cm^3 of 0.3 mol. mercarptoacetic acid for 2hrs at 25^{0}C, filtered, rinsed with de-ionized water and finally dried at 50^{0}C for 12hrs. 100mg/l concentration of Cd^{2+}, Ni^{2+} and Pb^{2+} prepared as an aliquot from the stock solution of 1000mg/l was used. To determine the effect of pH on Cd^{2+}, Ni^{2+} and Pb^{2+} adsorption from their aqueous solutions, 50cm^3 portions of the metal ion solutions of 100mg/l were introduced into various 250ml flask containing 1 gram of both unmodified and modified samples after varying the metal ion solutions with 0.1M HCl for low pH and 0.1M NaOH for higher pH in order to obtain pH ranges of 2, 4, 6, 8 and 10 respectively at 25 ^{0}C. After 1hr, the solution mixtures were filtered, and the final metal ion concentrations in the filtrate were determined by AAS (Buck model 200A). Moreover, to determine the effect of temperature on the metal ions adsorption from aqueous solutions, experiment was performed in a constant speed shaking water bath and the effect of these temperature variations [303K (30^{0}C), 323K (50^{0}C), 342K (70^{0}C), 363K (90^{0}C) and 383K (110^{0}C)] on adsorption were investigated. The experimental procedure was repeated on temperature as that of pH at pH of 7.5. The described procedures for each parameter were triplicated for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} onto unmodified and modified fluted pumpkin seed coat. The amounts of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed by both unmodified and modified seed coats during the series of batch investigations were determined using a simplified mass balance equation expressed as (Bhatti et al., 2007):

$$Q_e = C_o - C_e \quad (01)$$

Where Q_e = amount adsorbed (mg/g) by the adsorbents at equilibrium or metal ion concentration on adsorbent at equilibrium

C_e = metal ion concentration (mg/l) (final concentration) in the solution (of the filtrate) at equilibrium

C_o = initial metal ion concentration (mg/l) in solution used.

III. Results and Discussion

The pH effect on Cd^{2+}, Ni^{2+} and Pb^{2+} adsorption at various concentrations is shown in Table 01 and equally in Figure 01.

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Table 01. Concentrations of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed by unmodified and modified fluted pumpkin seed coat from aqueous solutions at various pH and at a temperature of 298 K

	Unmodified FPS			Modified FPS		
pH	Cd2+ (mg/g)	Ni2+ (mg/g)	Pb2+ (mg/g)	Cd2+ (mg/g)	Ni2+ (mg/g)	Pb2+ (mg/g)
2	99.999+0.001	78.984+0.053	99.999+0.002	96.154+1.155	96.634+1.057	94.760+1.496
4	99.999+0.001	78.900+0.015	99.994+0.000	99.124+0.173	96.672+0.925	88.560+1.277
6	99.999+0.001	78.844+0.010	99.993+0.001	99.368+0.282	99.640+0.502	86.030+2.023
8	99.995+0.001	78.800+0.030	99.993+0.001	99.392+0.293	99.903+0.519	96.890+2.449
10	99.992+0.002	78.800+0.030	99.992+0.001	99.648+0.407	99.740+0.547	90.832+0.260

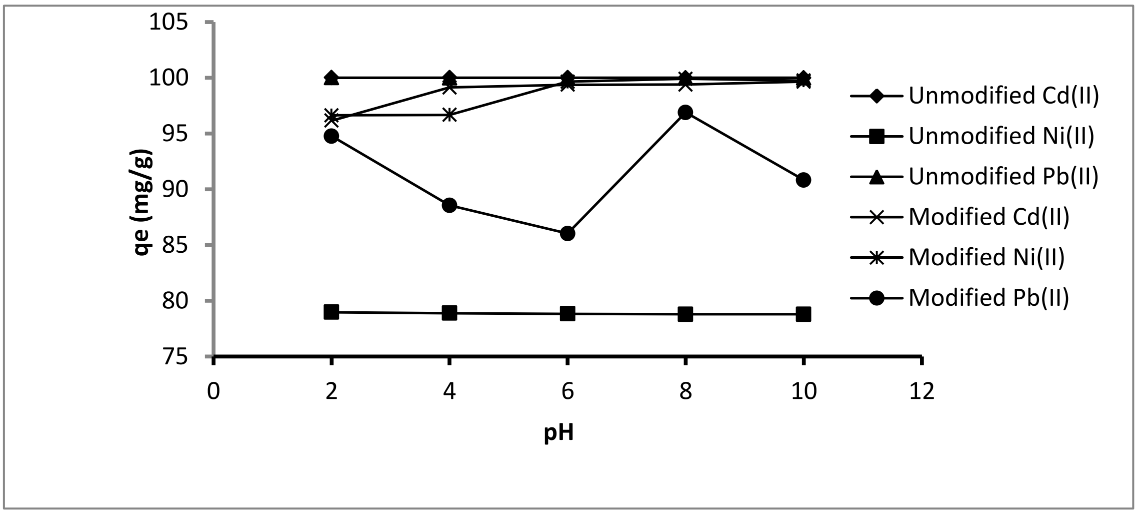

Figure 01. The plot showing the effect of pH on the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified fluted pumpkin seed coat.

It can be seen from Table 01 that the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified fluted pumpkin seed coat was more favoured at low pH of 2 while the concentrations of these metal ions adsorbed by the modified seed coat were found to decrease as a result of modification i.e. at pH of 10 for Cd^{2+} adsorption and 8 for Ni^{2+} and Pb^{2+} adsorption. Fig. 01 shows the trend of the variation of the amount of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed with various pH of the solutions. Since maximum Cd^{2+}, $Pb^{2+}$and Ni^{2+} sequestered by the modified seed coat were mainly observed at pH of 8 and 10 (Table 01), this shows that at an increased pH, the soluble metal ions became precipitated, the functional groups on the cell wall with negative charge increase due to deprotonation of the metal binding sites, which promotes the metal uptake (Sag et al., 1995). It has been reported that at highly acidic pH solutions, metal ions compete with H^+ on the binding sites of cells and adsorption is lowered (Nasir et al., 2007) but this assertion is not applicable for metal ions adsorption by the unmodified seed coat that showed maximum adsorption a low pH. Higher adsorption at lower pH may be due to increased protonation (H^+) by the neutralization of the negative charges at the surface of the biosorbent, which facilitates diffusion process and provides more active sites of the biosorbent (Mittal et al., 2007).

Table 02. Concentrations of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed by unmodified and modified fluted pumpkin seed coat from aqueous solutions at various temperatures

	Unmodified FPS			Modified FPS		
T (K)	Cd^{2+} (mg/g)	Ni^{2+} (mg/g)	Pb^{2+} (mg/g)	Cd^{2+} (mg/g)	Ni^{2+} (mg/g)	Pb^{2+} (mg/g)
303	99.986±0.018	99.999±0.023	99.872±0.088	99.833±0.486	99.879±0.156	99.008±3.094
323	99.962±0.006	99.979±0.023	99.720±0.020	98.934±0.084	99.520±0.005	90.695±0.624
343	99.953±0.003	99.972±0.020	99.641±0.015	98.766±0.009	99.487±0.152	90.527±0.700
363	99.931±0.001	99.869±0.026	99.587±0.039	98.190±0.248	99.450±0.036	90.198±0.846
383	99.902±0.020	99.821±0.048	99.555±0.054	98.004±0.332	99.320±0.094	90.025±0.924

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Table 02 shows the variation of the concentrations of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed by fluted pumpkin seed coat from aqueous solutions at various temperatures. From Table 02, it is evident that the extent of adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} from aqueous solutions by fluted pumpkin seed coat decreased with increase in temperature and with modification. This indicated that the adsorption of these heavy metal ions by the seed coat favours the mechanism of physical adsorption. For a physical adsorption mechanism, the extent of adsorption is expected to decrease with increase in temperature but for a chemisorption mechanism, the extent of adsorption is expected to increase with increase in temperature.

The effect of temperature on the amount of heavy metal ions adsorbed by fluted pumpkin seed coat was studied using the Arrhenius equation, which can be written as follows,

$$logk = logA - \frac{E_a}{2.303RT} \qquad (02)$$

Where, k is the rate constant for the adsorption process, A is the pre-exponential factor, E_a is the activation energy for the adsorption process, R is the gas constant and T is the temperature. From equation 02, a plot of log k versus 1/T should be linear with slope equal to $E_a/2.303R$ and intercept equal to log A. Fig. 02 shows the Arrhenius plots for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified fluted pumpkin seed coat.

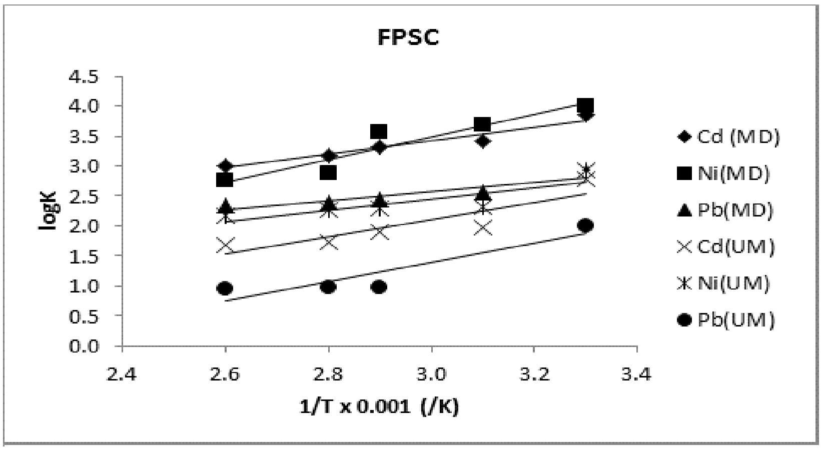

Figure 02. Variation of logk with 1/T for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified fluted pumpkin seed coat.

Table 03. Transition state parameters for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified fluted pumpkin seed coat

System	Ions	Slope	logA	E_a(J/mol)	A	R^2
FPS	Cd(MD)	1.1454	-0.0143	21.42	0.9662	0.9412
	Ni(MD)	1.8810	-2.1582	35.17	0.0056	0.8962
	Pb(MD)	0.7570	0.2993	14.16	2.0534	0.8497
	Cd(UM)	1.4410	-2.222	26.95	0.0048	0.7780
	Ni(UM)	0.9495	-0.4026	17.75	0.3799	0.7276
	Pb(UM)	1.6027	-3.4233	29.97	0.0003	0.8347

Parameters deduced from the plots are presented in Table 03. From the results obtained, R^2 values ranged from 0.7276 to 0.9412 indicating an excellent degree of fitness of the adsorption data to the Arrhenius model; E_a values ranged from 14.16 to 35.17 J/mol. indicating that the values are within the range of values expected for the mechanism of physical adsorption. Enthalpy and entropy changes for the adsorption of metal ions by unmodified and modified fluted pumpkin seed coat were estimated using the transition state equation (2) (Sag et al., 1995).

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$$log\frac{k}{T} = log\frac{R}{Nh} + \frac{\Delta S^0_{ads}}{2.303R} \quad (03)$$

Where k is the adsorption rate constant, T is the temperature, R is the gas constant, N is the Avogadro's number, h is the plank constant, ΔS^0_{ads} and ΔH^0_{ads} is the standard entropy and enthalpy changes for the adsorption process. Figure 03 shows the transition state plot for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified fluted pumpkin seed coat.

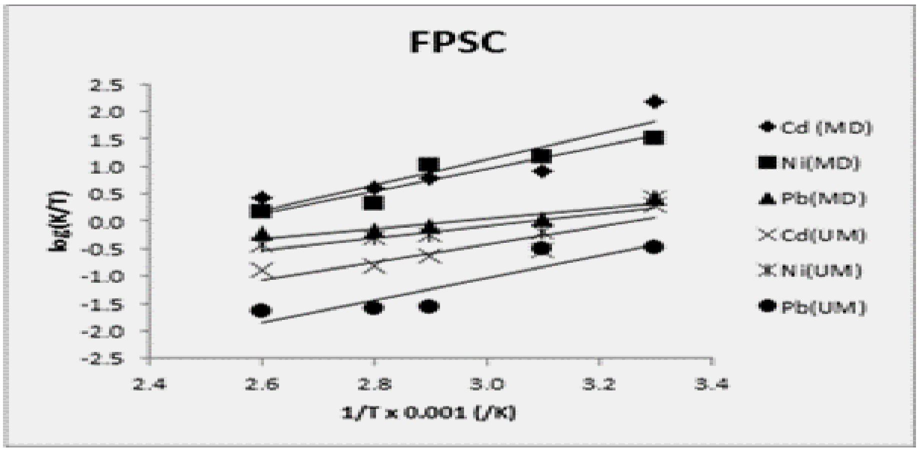

Figure 03. Variation of log(k/T) with 1/T for the absorption of Cd^{2+}, Ni $^{2+}$and Pb^{2+} by unmodified and modified fluted pumpkin seed coat.

Table 04. Transition state parameters for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified FPS, OBS and KNP wastes.

System	Ions	Slope	Intercept	ΔH^0 (J/mol)	ΔS^0 (J/mol)	R^2
FPS	Cd (MD)	2.3089	-5.8042	44.21	-436.83	0.7949
	Ni(MD)	2.0292	-5.1282	38.85	-423.88	0.9064
	Pb(MD)	0.9039	-2.6667	17.31	-376.75	0.8902
	Cd(UM)	1.5879	-5.188	30.40	-425.03	0.8098
	Ni(UM)	1.0977	-3.3728	21.02	-390.27	0.7830
	Pb(UM)	1.9968	-7.0261	38.23	-460.22	0.8089

Thermodynamic parameters deduced from the plots are presented in Table 04. From the results obtained, it can be seen that ΔS^0_{ads} values are negative indicating that the adsorption of the studied ions occur in a state of orderliness while the positive values obtained for ΔH^0_{ads} indicated that the adsorption process is endothermic. Also the Gibb's free energy (ΔG^0_{ads}) was calculated from equation (03), (04) and (05) (Yahaya et al., 2009)

$$\Delta G^0_{ads} = -RTlnK \quad (04)$$

$$\ln k = \frac{\Delta S^0_{ads}}{2.303R} - \frac{\Delta H^0_{ads}}{2.303RT} \quad (05)$$

Where, $\frac{\Delta S^0_{ads}}{2.303R}$ is equals to intercept and $\frac{\Delta H^0_{ads}}{2.303RT}$ is equals to slope

The values obtained from Table 05 shows that the ΔG^0_{ads}values for the adsorption of these metal ions are negative indicating that the adsorption process is spontaneous, feasible and exergonic (release of free energy) (Ho et al., 2000).

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Table 05. The Gibb's free energy (ΔG^0_{ads}) for metal ions adsorption onto unmodified and modified fluted pumpkiln seed coat at initial concentration of 100 mg/l in variation with temperature (K)

Temperature	Cd^{2+}	Ni^{2+}	Pb^{2+}	Cd^{2+}	Ni^{2+}	Pb^{2+}
K	Unmodified			Modified		
303	-128754	-118230	-139408	-132315	-129912	-114138
323	-443187	-126036	-148613	1411052	-136874	-121673
343	-145755	-133842	-157817	-149788	-145352	-111294
363	-154255	-141646	-167022	-158525	-153830	-136743
383	-162756	-149452	-166942	-167262	-153830	-136743

IV. Conclusion

On the basis of the experimental results, fluted pumpkin seed coat was found to be very effective in Cd^{2+}, Ni^{2+} and Pb^{2+} sequestering from aqueous solution especially when unmodified. Cd^{2+}, Ni^{2+} and Pb^{2+} uptake by fluted pumpkin seed coat were considerable affected by operational variables. The extent of adsorption increases with low pH for the unmodified samples and high pH for the modified ones and at decreased temperature. The mechanism of adsorption is by physical process. Adsorption of the studied ions occurs in a state of orderliness and the adsorption process is endothermic.

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