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Kinetic studies of oil bean seed shell in the adsorption of toxic heavy metals from their solutions

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ABSTRACT

The unmodified and mercaptoacetic acid modified oil bean seed shells were used in the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} from their aqueous solutions. Adsorption was carried out in a batch process at various contact time with initial metal ions concentration of 100 mg/l using 1 g of 250 µm size of the shell at temperature of 25 ^{0}C and pH of 7.5. Adsorption equilibrium was established in about 10 minutes for the unmodified and 90 minutes for the modified. Kinetic studies revealed that the adsorption of some of the heavy metal ions by the oil bean seed shell fitted the Elovich adsorption model excellently except in the adsorption of Cd^{2+} by the unmodified shell that showed lower R^2 value.

Key words: Adsorption kinetics, Elovich model, heavy metals, oil bean seed shell, pseudo-first-order, pseudo-second-order.

INTRODUCTION

Applications of metals for commercial purposes largely generate metallic waste products which become nuisance to the environment. These problems have to be harnessed especially in our developing country (Nigeria) where the pollution free environment is very difficult to maintain. Most often these liquid wastes are not adequately discharged causing a lot of discharged liquid wastes (wastewaters) from domestic houses, industries, agricultural or commercial processes [1, 2]) to the environment without reference to environmental issues. Some pollutants from these liquid wastes such as heavy metals are non-biodegradable hence tend to persist indefinitely, circulating and eventually accumulating throughout the food chain, becoming a serious threat to the environment. However some metals such as cadmium, nickel and lead are markedly more toxic even at very low concentrations [3]. The most severe form of cadmium toxicity in human is ”itai-itai”, a disease characterized by excruciating pain in the bone[4, 5]. Some other health implications of cadmium in humans include kidney dysfunction, hepatic damage and hypertension [6]. Toxic levels of lead in man have been associated with encephalopathy, anemia, seizures, coma mental retardation and biazarre behavior [7, 8]. Long-term exposure of nickel can cause decreased body weight, heart damage, liver damage and skin irritation [9]. In other words, the inadequate discharged of these liquid wastes may not be wholesome hence, their removal is vital from the stand point of environmental pollution control [10, 11]. The disadvantages associated with the adoption of conventional method of treating metal bearing wastewaters [12] has led to the invention of adsorption processes using natural adsorbents or agricultural waste products which has some major advantages [13]. This work studied the effectiveness of adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by both unmodified and modified oil bean seed shell via variations in the contact time. The kinetic or rate of adsorption based on pseudo first-order, second-order and Elovich model equations were also studied.

MATERIALS AND METHODS

The *Pentaclethra macrophylla* was obtained from Umuahia main Market, Abia State and processed to get the shell. The shell was grounded into tiny particle size using manual grinder and sieved through a test-sieve shaker after washing with deonized water and drying in 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 15 g portion of the activated sample was modified using mercarptoacetic acid by soaking the sample into 1000 cm^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 12 hence, labeled modified sample.

2.1 Preparation of adsorbate solutions (metal ion solutions)

All the chemicals used in the experiment were analytical grade reagents.

$CdCl_2$, $NiSO_4.6H_2O$ and $Pb(NO_3)_2$ salts were used as the source of Cd^{2+}, Ni^{2+} and Pb^{2+} and all the solutions were made in deionized water. The solutions of Cd^{2+}, Ni^{2+} and Pb^{2+} were prepared from a stock solution containing 1000 mg/l of Cd^{2+}, Ni^{2+} and Pb^{2+} respectively. This was done by dissolving one gram (1 g) of each salt in 1000 cm^3 of deionized water and made up to the mark of the volumetric flask. Each of these solutions represented the metal ion solution (wastewater) of 1000 mg/l concentration. From the stock solutions of 1000 mg/l, various aliquots (5, 4, 3, 2, 1 and 0.5) cm^3 were pipetted into beakers and made up to the mark of 50 ml volume with deionized water to give a range of concentrations between 100 and 10 mg/l (i.e. 100, 80, 60, 40, 20and 10) mg/l. The initial concentration of metal ion solutions used for the biosorption study on investigating the effects of time was 100 mg/l (prepared as an aliquot from the stock of 1000 mg/l of the various metal ions). On the other hand, concentrations of 80, 60, 40, 20 and 10 mg/l (prepared from stock by serial dilution) as initial concentrations were used to investigate the effect of variation in the initial concentrations of metal ions on biosorption.

BATCH ADSORPTION EXPERIMENTS

Equilibrium adsorption experiments were performed in a batch process under the following experimental conditions: contact time (10, 30, 60, 90 and 120 minutes).

3.1 Effect of contact time on the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+}

The experiment was also performed to determine the adsorption capacity of the oil bean seed shell at various time intervals of 10, 30, 60, 90 and 120 minutes, 50 cm^3 of each of these metal ion solutions of initial concentration 100 mg/l were placed into various flasks containing 1 g (250 µm size) of each of the adsorbents. The flasks were agitated for various time intervals of 10, 30, 60, 90, and 120 minutes, at temperature of 25 ^{0}C and pH of 7.5. After each adsorption contact time, the solution mixture of each flask was filtered with Whatman 42 filter paper and filtrate collected into sample bottles. The equilibrium (final) concentration of each metal ion was determined using Atomic Absorption Spectrophotometer (Buck model 200A). The described procedures for each parameter were carried out (repeated) for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} onto unmodified and modified *Pentaclethra macrophylla* seed shell. The amounts of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed by the adsorbents during the series of batch investigations were determined using a simplified mass balance equation as expressed by [14]:

$$Q_e = C_o - C_e \qquad (1)$$

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

RESULTS AND DISCUSSION

4.1Effect of contact time on adsorption.

Table 1 shows the variation of the concentrations of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed by oil bean seed shell from aqueous solution at various time intervals. From Table 1, it can be seen that the concentrations of heavy metal ions adsorbed by the oil bean seed shell were found to increase at a shorter time (10 min) by the unmodified oil bean seed shell though Pb^{2+} adsorption by the shell of the oil bean maintained constant increase i.e. from 10 – 120 minutes. However, adsorptions of Cd^{2+}, Ni^{2+} and Pb^{2+} by the shell on modification were also found to increase with increase in time interval though adsorption of these metal ions by the oil bean seed shell did not closely follow a definite pattern indicating that modification had effect on the adsorption capacity of the shell.

From the results (Table 1), it is an indicative that the concentrations of heavy metal ions adsorbed do not vary regularly with time. In some cases, the amount increases with time while in others, it decreases with time. The average impact of time on the adsorption capacity of heavy metal ions depends on the number of adsorption sites available and on the strength of adsorption and desorption mechanism.

Table 1: Concentrations of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed by oil bean seed shell from aqueous solutions at various time and at 298 K

t (min)	Unmodified oil bean seed shell			Modified oil bean seed shell		
	Cd^{2+} (mg/g)	Ni^{2+} (mg/g)	Pb^{2+} (mg/g)	Cd^{2+} (mg/g)	Ni^{2+} (mg/g)	Pb^{2+} (mg/g)
10	98.782$\pm$ 0.324	99.986$\pm$2.290	99.999 $\pm$ 0.000	95.620$\pm$ 1.070	98.142$\pm$ 0.198	85.300$\pm$ 1.668
30	98.467$\pm$ 0.184	99.642 $\pm$ 2.137	99.999 $\pm$ 0.000	98.644 $\pm$0.282	98.464 $\pm$0.054	85.620 $\pm$1.525
60	98.580$\pm$ 0.234	91.888 $\pm$ 1.331	99.999 $\pm$ 0.000	98.714 $\pm$0.314	98.658 $\pm$0.033	88.380 $\pm$0.290
90	98.340$\pm$ 0.127	91.807 $\pm$ 1.367	99.999 $\pm$ 0.000	99.674 $\pm$0.743	98.850 $\pm$0.118	93.664 $\pm$2.073
120	96.114$\pm$ 0.869	90.999$\pm$ 1.729	99.999 $\pm$ 0.000	97.412 $\pm$0.269	98.812 $\pm$0.101	92.181 $\pm$1.410

Kinetic studies:

Several kinetic models including pseudo-first-order, pseudo-second-order and intra-particle diffusion models are common kinetic models that can be used to examine the controlling mechanism involved in the adsorption of Cd^{2+}, Pb^{2+} and Ni^{2+} by unmodified and modified oil bean seed shell.

The pseudo-first-order equation is given as [15]:

$$log(q_e - q_t) = log(q_e) - \frac{k_1 t}{2.303} \quad (1)$$

Whereq$_e$ and q_t are the amount of heavy metal ions adsorbed at equilibrium and at time, t (respectively mg/g) and k_1 is the first-order rate constant (min^{-1}). From equation 1, a plot of log(q_e – q_t) versus t should be linear if a pseudo-first-order kinetic is obeyed. However, when adsorption data obtained for oil bean seed shell were fitted into the model expressed by equation 1, values of R^2 obtained from the plots (plots not shown) were very low indicating that the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by oil bean seed shell is not consistent with a pseudo-first-order kinetics.

According to [16], a pseudo-second-order adsorption rate equation can be expressed as follows,

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2)$$

Where k_2 is the rate constant of pseudo-second-order adsorption ($gmg^{-1}min^{-1}$), q_e and q_t are the adsorption capacity at equilibrium and at time, t, respectively. Introducing boundary conditions to equation 1, i.e. t = 0 to t=t and q_e = 0 to q_t = q_t, integrated form of equation 2 was obtained (equation 3) and upon simplification, equations 4 and 5 were obtained.

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_t} + k_2 t \quad (3)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \quad (4)$$

$$\frac{1}{q_t} = \frac{1}{h} + \frac{1}{q_e}(t) \quad (5)$$

The implication of equation 5 is that a plot of 1/q_t versus t should be linear with slope and intercept equal to q_e and $\frac{1}{h}$ (h = $k_2 q_e^2$) respectively. Fig. 1 shows pseudo-second-order kinetic plots for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by oil bean seed shell. Adsorption parameters obtained from the plots are presented in Table 2. From the results obtained, it can be seen that values of R^2 are very close to unity indicating the application of a pseudo-second-order model to the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by oil bean seed shell. It is also evident from the results that values of k_2 calculated from the plots are relatively low. It was also observed that h and k_2 values for the adsorption of Ni^{2+} and Pb^{2+} by modified oil bean seed shell were higher than those obtained from the unmodified shell. The reverse was however observed for the adsorption of Cd^{2+} by the shell. On the other hand, the adsorption of Ni^{2+} displayed a decrease of h and k_2 values due to modification of the shell. According to [17], a pseudo-first and -second order kinetics cannot reveal the mechanism of adsorption therefore, a model of Elovich was also used to test for the adsorption mechanism of the studied adsorbates. Elovich adsorption model can be expressed as follows [18]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad (6)$$

Where α is the initial adsorption rate ($mgg^{-1}min^{-1}$) and β is the desorption constant (gmg^{-1}) during any one experiment. [19] had earlier proposed that $\alpha\beta t >> t$ and if the boundary conditions are applied (i.e t=0 and $q_t = q_t$ at t = t), the Elovich equation becomes,

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{7}$$

The implication of equation 7 is that a plot of q_t versus ln(t) should be linear with slope and intercept equal to $\frac{1}{\beta}$ and $\frac{1}{\beta} ln(\alpha\beta)$ respectively. Fig. 2 shows Elovich equation for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified oil bean seed shell. Values of Elovich constants deduced from the plots are presented in Table 3. From the results obtained, it can be seen that the adsorption of some of the heavy metal ions by the oil bean seed shell fitted the Elovich adsorption model excellently except in the adsorption of Cd^{2+} by the unmodified shell that showed lower R^2 value.

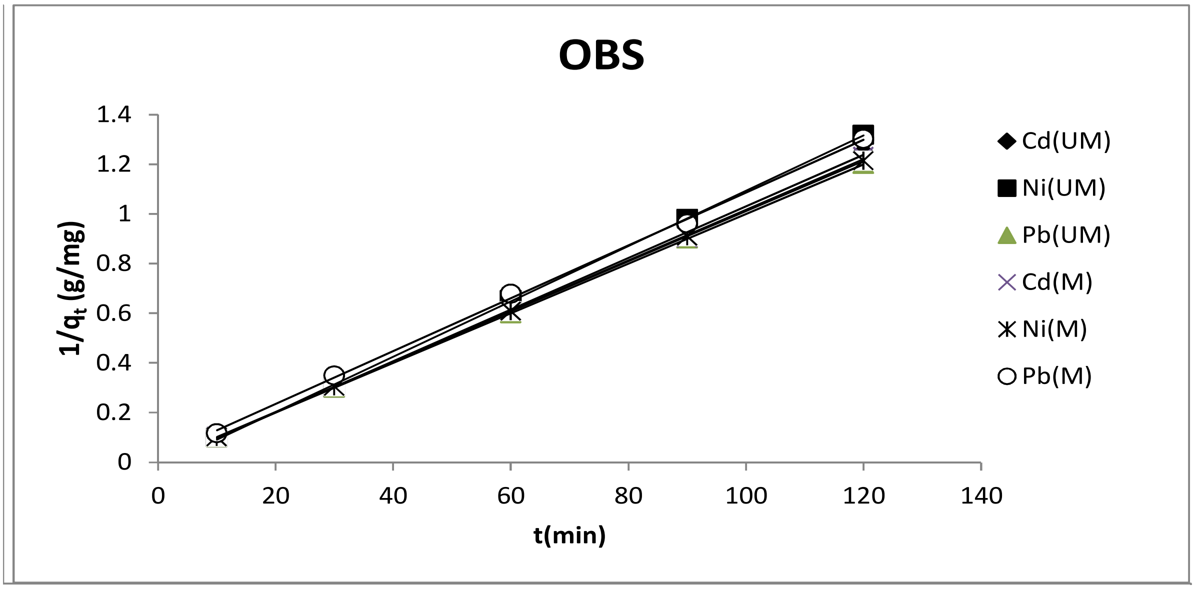

Fig.1: Variation of $1/q_t$ with t (pseudo-second-order kinetic) for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified FPS oil bean seed shell

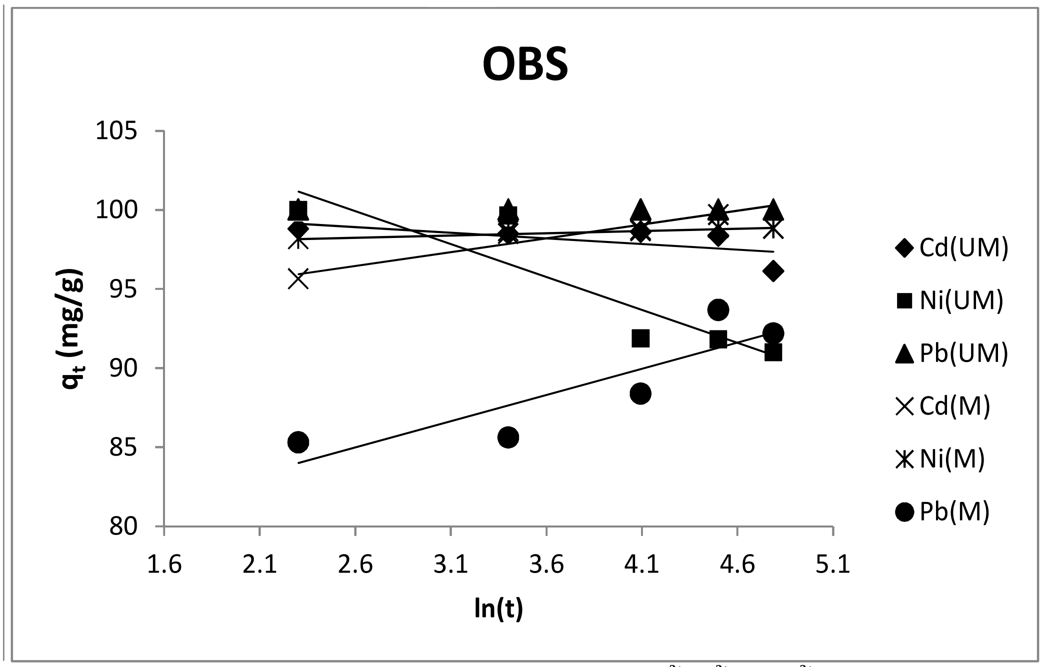

Fig. 2: Variation of q_t with ln(t) (Elovich adsorption model) for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified oil bean seed shell

Table 2: Pseudo-second-order adsorption parameters for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified oil bean seed shell

System	Ions	Slope	q_e	*h*	k_2	R^2
OBS	Cd(UM)	0.0104	-0.0081	-1.24E+02	-1.34E-02	0.9996
	Ni(UM)	0.0111	-0.0202	-4.95E+01	-6.10E-03	0.9997
	Pb(UM)	0.0100	4.00E-16	2.50E+15	2.50E+11	1.0000
	Cd(M)	0.0102	-0.0017	-5.88E+02	-6.12E-02	0.9996
	Ni(M)	0.0101	0.0014	7.14E+02	7.29E-02	1.0000
	Pb(M)	0.0106	0.0226	4.42E+01	4.97E-03	0.9990

Table 3: Elovich parameters for the adsorption of Cd^{2+}, Ni^{2+} and Pb^{2+} by unmodified and modified oil bean seed shell

System	Metal ion	Slope	Intercept (I)	β	Iβ	α	R^2
OBS	Cd(UM)	0.7126	100.78	1.4033	141.43	1.88E+61	0.4161
	Ni(UM)	-4.1523	110.71	-0.2408	-26.66	-1.09E-11	0.8288
	Pb(UM)	-	-	-	-	-	-
	Cd(M)	1.7431	91.93	0.5737	52.74	1.40+23	0.9078
	Ni(M)	0.2892	97.48	3.4578	337.07	7.0449E+145	0.9778
	Pb(M)	3.3175	76.37	0.3014	23.02	3.2E+10	0.7581

CONCLUSION

The results of the work indicated that the oil bean seed shell is capable of adsorbing toxic heavy metals from their aqueous solutions. The batch studies clearly suggest that the shell of the oil bean seed exhibit almost 100% adsorption especially when unmodified. The kinetic evaluation suggests that the uptake of toxic heavy metals fitted Elovich model.

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