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Sequester of lead (II) ion from its aqueous solution by native pulverized locust beans (*Parkiabiglobosa*) hull

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Abstract: *In this work, natural pulverized locust beans hull exhibited high sorption capacity, four influence conditions studied at 30±2^0 C; the suspensions shaken at constant 130 rpm and analyzed with absorption spectrophotometer (AAS; Perkin-Elmer model Analyst 2000). Maximum equilibrium mg/g sorption attained within 30mins at optimum equilibrium of pH 7.0. Lagergren pseudo-first-order and pseudo-second-order kinetic models were examined; Pb^{2+} adsorption better explained by the Ho pseudo-second-order model. Mathematical description sorption equilibrium Langmuir and Freundlich models were proposed, Langmuir R^2 = 0.9998 > R^2 = 0.1274 Freundlich isotherm, suggested that the Langmuir isotherm provide a good model for the locust beans hull lead (II) ions adsorption process.*
Keywords: *Adsorption,Kinetics, Lignocellulosic,Natural pulverized beans hull,Sequester*

I. Introduction

Water takes highest proportion in human body and it is an essential natural resource needs for human and plants for sustainable life, but increase industrialization has led to contamination/pollution of most every (surface and ground) water body by different deadly toxic heavy metals, whereasseveral acute and chronic effects causes to human, aquatic life and plants had been known and reported.

Industrial uses of metals and other domestic processes have released substantial amount of potentially toxic heavy metals into the atmosphere, the aquatic and terrestrial environment [1]. Industrial effluents are discharged directly into the drainage system without treatment by many industries. The implication of this is the pollution of surface water with consequent effects on human health [2]. Heavy metals toxicity can result in damage or reduced mental and central nervous function, lower energy level, and damage to blood composition, lungs, kidneys, liver and other vital organs. High level of Pb exposure may cause problems in the synthesis of hemoglobin, compromise the kidneys, gastrointestinal tract, joints and the reproductive system and result in an acute or chronic damage to the nervous system [3, 4].

It isnecessary to sequester these deadly substances from heavy metal-bearing effluent before being discharged into environment due to their non-biodegradability and toxicity, considerable attention had been established, because most of the heavy metals salts are soluble in water and form aqueous solutions and consequently cannot be separated by ordinary physical separation means separation [4, 5].

Hence conventional techniques for removing dissolved heavy metal include ion-exchange [6], precipitation [7], biochemical technology[8], reverse osmosis [9] electro-dialysis [10], adsorption[11] and so forth. Several studies have been reported on different functional groups polysaccharides,protein,lignin and cellulose contains biomass in sequester metals ions from aqueous and heavy metal bearing effluents by different researchers to mention few: hazelnut shells[12], black gram husk[13], eggshells[14], rice bran[15], almond shell [16], sawdust[17], African white star apple [18], giant reed based[19],and seed oil shell[20] .

In this study, the adsorption behaviors including pH influence, kinetics, sorption isotherms and dosage influence were investigated to evaluate the effectiveness of native pulverized locust beans hull in removal of Pb^{2+} from its aqueous solution.

II. Materials And Methods

2.1 Sorbent preparation

Native locust beans (Parkiabiglobosa) hull were collected from local locust beans food condiment production site, in Agosasa, Ipokia local government, Ogun State, Nigeria. Locust beans hull were extensively washed with deionized water to remove dirt and other particulate matter that might interact with sorbed metal ion and air dried and pulverized into powdery form, using local mortar and pestle and sieved with a mesh to maximum particle size of 2mm. The native pulverized locust beans hull, which is the prepared biosorbent, was stored in air-tight, moisture-free containers and bussequently used for biosorption studies.

2.2 Preparation of metal ion solution

Stock solution (1000mg/L) of lead was prepared by dissolving required amount of analytical grade lead nitrate salt ($Pb(NO3)_2$) in deionized and double distilled water. Working solution ($100mg/dm^3$–$500mg/dm^3$) concentrations of Pb(II) ions were prepared by appropriate dilution of the stock solution.

2.3 Batch experiments

The batch experiments were conducted in 100 mL Erlenmeyer flasks containing 25 mL of lead solution. A weighed amount of native pulverized locust beans hull was added to lead solutions. The mixtures were shaken on a rotary shaker at 130 rpm for 1hour at $30{\pm}2^0$ C. The influence of pH (4.0 – 9.0), initial metal concentration (100 – 500 mg/L), adsorbent dose (0.4 – 2.4 g/L) and influence of contact time (30 – 180 min) was investigated in order to find the optimum conditions for the lead metal biosorption. After equilibrium, the solution suspensions were filtered and the supernatants were subsequently analyzed for residual Pb(II) ions concentrations with atomic absorption spectrophotometer (AAS; Perkin-Elmer model Analyst 2000).

Amount of metal adsorbed by 1.0 g of the biomass was calculated from the following mass balance equation:

$$\mathbf{q} = \frac{\text{Co}-\text{Ce V}}{1000\ \text{W}} \quad (1)$$

Where q is the amount of metal uptake (mg/g), C_o and C_e are the initial and final metal ions concentrations(mg/L), M is the amount of pulverized locust beans hull (g) and V is the volume of the solution (mL). The Pb concentration removal percentage can be calculated as follows:

$$\textbf{\% removal} = \left(\frac{\text{Co}-\text{Ct}}{\text{Co}}\right)\times \mathbf{100} \quad (2)$$

Where C_t (mg/l) is liquid-phase concentration of Pb (II) ions at timet.

III. Results And Discussion

3.1 Influence of pH on Pb(II)ionremoval

Severalauthors have reported that pH has a significate influence on the solubility, speciation and biosorption capacity of heavy metal, It also affects the metal adsorption or loading/influencing surface properties of biomass, metal speciation ion in solution and degree of ionization [21].It not only influences the states of the functional groups on the surface of the biomass, but also the existing form of the metal ions in solution. 99.2% lead ions was adsorbed onto native pulverized locust beans hull at pH 4, from pH 5 to pH 6 decreases in sorption percent observed; 98.3% and 98.5% respectively and sharply increase of 0.9% transpired at pH 7, 99.4% and gradually decrease in adsorption occurred at pH 8 to pH 9 and lead precipitate observed, could be due to increase OH^- ions in the adsorption medium [22]. The different pHsorption profile for various heavy metal ions may be related to the nature of chemical interactions of each metal with the biomass [23].

3.2 Influence of initial Pb(II) ion concentration

The initial metal ion concentration provides an important force to overcome all mass transfer resistances of the metal between aqueous and solid phase [24]. Pb(II) adsorption capacity at different initial Pb(II) ions concentrations under determined optimum pH7 and temperature 30 ± 2^0 C studied.

As the initial lead concentration increased from 100 – 200mg/L, the metal uptake capacity increased from 99.4mg to 99.8mg of lead per gram of native pulverized locust beans hull, while decrease in adsorption occurred from 300mg/L to 96.57mg/g and increase in adsorption was observed from 400mg/L to 99.7% and slight change occurred at 500mg/L to 98.9%.

3.3 Influence of dosage

Fig. 1 shows the plot of amount of lead adsorbed (qe) against the quantity of native pulverized beans hull (g) examined. From the figure, it is observed that the amount of lead metal adsorbed increases from 98.12 to 99.13%. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active binding sites on the surface of the adsorbent [25].

3.4 Influence of contact time

Equilibrium metal sorption of 99mg/g was set-in, in the first 30minutes, same adsorption of metal mg/g observed throughout the selected contact time, assumed that native pulverized locust beans hull available active binding sites has been saturated before the 180mins.

3.5 Sorption kinetic model:

In present research, two models were applied to understand sorption kinetic; the pseudo-first-order model, described by Lagergren[26], the pseudo-second-order model by Ho and McKay[27].

Lagergren model equation can be expressed as:

$$\log(q_e\text{-}q_t) = \log(q_e) - \frac{k1t}{2.303} \quad (3)$$

Where qt is the amount of metal ions adsorbed (mg/g) at any given time t (min), qe is the amount of metal ions adsorbed (mg/g) at equilibrium and K_1 is the pseudo-first-order reaction rate constant for adsorption (min^{-1}).

The Ho pseudo-second-order equation as:

$$\frac{t}{qt} = \frac{1}{K2qe2} + \frac{t}{qe} \quad (4)$$

Where qt is the amount of metal ions adsorbed (mg/g) at any given time t (min), qe is the amount of metal ion adsorbed (mg/g) at equilibrium and K_2 is the Ho pseudo-second-order reaction rate constant for adsorption (g $(mgmin)^{-1}$).

$$h = K_2q_e^2 \quad (5)$$

In equation (5), h can be regards as the initial sorption rate as q/t when t approaches zero.

3.6 Isotherm model:

Langmuir and Freundlich adsorption isotherms were used in this present study and the equations (6), (7), (8) and (9) below give details respectively.

$$q = \frac{KCeb}{(1+KCe)} \quad (6)$$

Where, Ce is the equilibrium solution phase concentration (mmol kg^{-1}), q the equilibrium solid phase concentration (mmol kg^{-1}), k is the enthalpy related constant, b is the Langmuir isotherm sorption capacity (mmol kg^{-1}).

Linearized form of equation 6 written as:

$$\frac{Ce}{q} = \frac{1}{Kb} + \frac{Ce}{b} \quad (7)$$

Fig. 4 shown the plot $\frac{1}{qe}$ versus $\frac{1}{Ce}$that gives Langmuir isotherm, where $\frac{1}{b}$ is the slope and $\frac{1}{Kb}$ is the intercept.

Equations (8) and (9) give non-linear and linear Freundlich equations respectively.

$$qe = K_fCe^{1/n} \quad (8)$$

$$loqe = \log K_f + (\frac{1}{n})\log Ce \quad (9)$$

Where K_f is the sorption capacity constant and n is the intensity constant, qe and Ce are the same as earlier stated in equation 6.

The results of 1/n, n, K_f and R^2 showing in tab. 2 were calculated from the Plot of log qe versus log Ce shown in fig.5, where slope is the value of 1/n and intercept is equal to log K_f.

As seen in tab.1., the R^2 values for the both pseudo-order models; pseudo-second-order has the highest significant for the model, where chemical binding reaction controls the sorption kinetic mechanism, thus, for this work; the kinetic of Pb^{2+} adsorption better explained by the pseudo-second-order model.Similarly,the correlation coefficient and other parameters values of pseudo-first-order kinetic are lower than in the case of pseudo-second-order kinetic model. Based on the R^2 values obtained for both isotherms models shown in tab.2, the high value of 0.9998 for Langmuir compare to that of Freundlich model, suggested that the Langmuir isotherm provide a good model for the adsorption process.

[28] in their findings, concluded that, if the metal ions are taken up independently on a single type of binding site in such a way that the uptake of the first metal does not affect the sorption of the next ion, the sorption process would follow the Langmuir metal adsorption equation, meanwhile, this research is in accordance with aforementioned authors proved. Moreover, the K_L (separation factor)value obtained in this study, revealed that the adsorption is favourable as K_L value is greater than 0 but less than 1 and sorption capacity, q_{max}which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage showed that the order of adsorption affinity on native pulverized locust beans hull.According to[29], n value between 1and 10 represent beneficial adsorption, thus, n value in this research adsorbent was beneficial and large value for 1/n indicates larger change in effectiveness over different equilibrium concentration. Also, when 1/n >1.0, the change in adsorbed concentration is greater than the change in the solute concentration[30]. Furthermore, the values of 1/n less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentration and vice versa [31]. In this research work, the value of 1/n obtained was found to be less than unity, which agrees with the results discussed above.

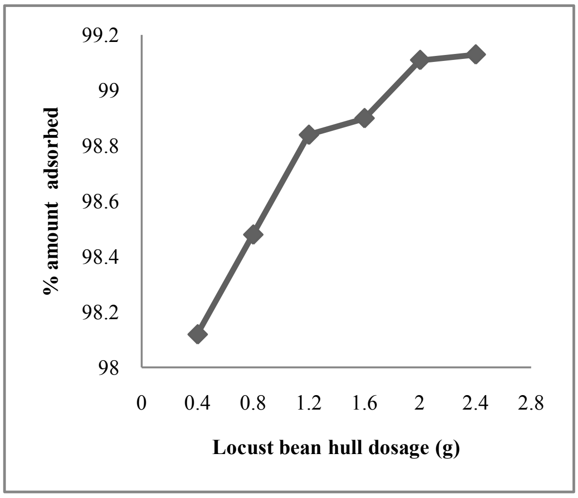

Fig.1: Influence of adsorbent dosage on Pb^{2+}sorption,pH 7at 30±2^{0}C.

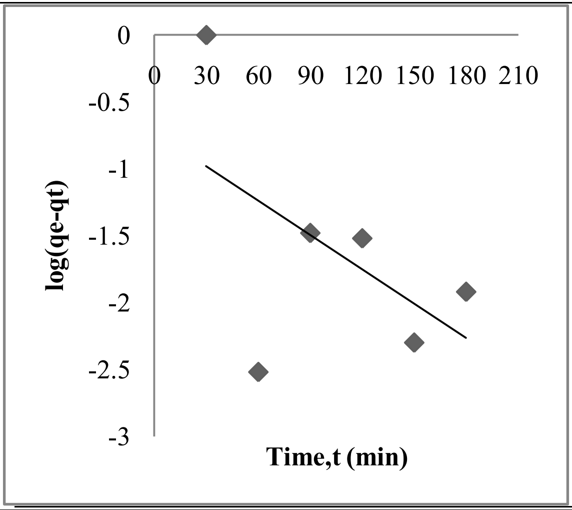

Fig.2: Pseudo-first-order for the adsorption of $Pb^{2+}$by native pulverized locust beans hull, pH7 at 30±2^{0}C.

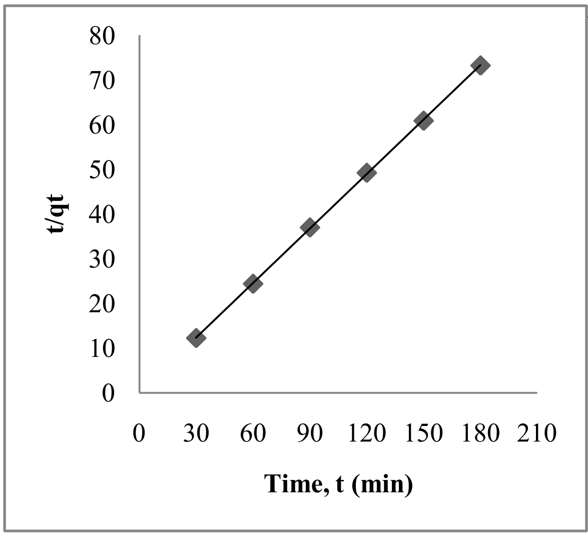

Fig.3: Pseudo-second-order for the adsorption of Pb^{2+} bypulverized locust beans hull, pH 7 at 30±2^{0}C

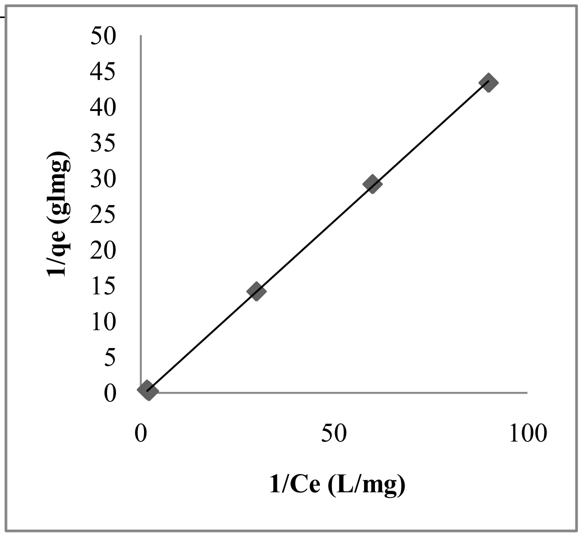

Fig.4: Langmuir isotherm for the adsorption of Pb^{2+} by adsorbent, pH7 at 30 ±2^{0}C.

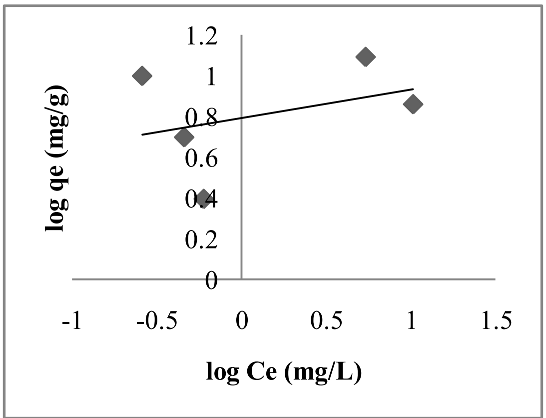

Fig.5: Freundlich isotherm for the adsorption of Pb^{2+} bynative pulverized locust beans hull, pH7 at 30±2^{0}C.

Table 1: Kinetic parameter obtained for pseudo-first order and pseudo-second order model for sorption of lead (II) ions by native pulverized locust beans hull, pH 7.0, at 30±2^{0}C.

metal ion		Pseudo-first order model					Pseudo-second order model				
		q_e (cal)mg/g	K_1 (min^{-1})	R^2	q_e(exp)mg/g		q_e (cal)mg/g	h (mg/g.min)	K_2 (g/mg.min)	R^2	qe(exp)mg/g
Pb (II)		0.1882	0.0198	0.2868	2.468		2.4558	18.98	3.1463	0.9999	2.468

Table 2: Isotherm parameter obtained for Langmuir and Freundlich model for sorption of lead (II) ions by native pulverized locust beans hull, pH7.0 at 30±2^{0}C.

Metal ions		Langmuir isotherm parametes					Freundlich isotherm parameters			
		q_{max}	b	K_L	R^2		1/n	n	K_f	R^2
Pb(II)		10.64	1.06	0.009	0.9998		0.1445	7.1189	6.192	0.1274

IV. Conclusion

Mathematical kinetic and isotherms sorption results obtained provide a better understanding of the sorption phenomena and indicate a very promising potential usefulness of abundant lignocellulosic locust beans hull, in the removal of lead ions from its aqueous solution and other effluent bearing toxic heavy metals from the environment. Thus, it can be concluded that, this inexpensive, available and effectiveParkiabiglobosahull, would be useful to remove heavy metals in aqueous media.

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