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Kinetics and Equilibrium Adsorption Study of Lead onto *Strychnos spinosa* Leaves

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Abstract: Adsorption of lead (II) ions onto powder prepared from renewable plant material which is *Strychnos spinosa*was investigated with the variation in the parameters of contact time, the amounts of adsorbent, lead (II) ion concentration and temperature. The experimental data were analyzed using Langmuir, Temkin and Freundlich equations. The adsorption data were found to fits Freundlich, Langmuir and Temkin models. The experiments showed that the highest removal rate was 96.79% for lead (II) ion under optimal conditions. The kinetic data for the adsorption process obeyed pseudo-second order rate equation. The *Strychnos spinosa* leaves powder investigated in this study exhibited a high potential for the removal of lead (II) ion from aqueous solution.

Key words: Lead · Adsorption isotherms · Adsorbent · *Strychnos spinosa*

INTRODUCTION

Lead is one of the four heavy metals that have the most damaging effects on health. Heavy metals can pose health hazards if the concentration exceeds allowable limits. Even when the concentration does not exceed the allowable limits, there is still a potential for long-term contamination [1]. Heavy metals can enter the human body through contact with contaminated tools, water and hand-to-mouth contamination [2].

Lead is a heavy metal which occurs naturally. Exposure to lead can damage the brain, kidney, bones and the nervous system resulting in behavioral disorder [2]. Lead can also cause reproductive problems, high blood pressure, nervous disorders and memory problems in adults. In extremely bad cases, it can lead to sudden attack, comma and death [3].

The exploitation of gold in Zamfara, Nigeria has yielded great benefits as well unexpected environmental pollution. In 2009, hundreds of children had died from exposure to lead [3].

One hundred and sixty three (163) Nigerians, most of which are children died, others went blind and deaf in 2010 as a result of illegal gold mining in Zamfara state of northern Nigeria. Also in 2011, over 4,000 children were contaminated due to mining activities in Dareta and Gaidanbuzu villages of Zamfara state [3].

The conventional methods for the removal of heavy metals from waste water are often inadequate. There is need for the search and development of new improved and cheap methods for treating waste water.

Recently, the search for low cost metals binders (adsorbent) has increased. Locally available materials such as agricultural waste or industrial by-products can servers as adsorbents for the removal of metals.

The removal of Cr (VI) using rice husk was investigated and result showed that the maximum uptake (66%) was obtained at pH of 2 and adsorbent dose of 70g/l and the adsorption isotherms fits the Freudlich model with constants $k_F$value of 2.863 [4].

The binding efficiency of tobacco dust for heavy metals shows that it exhibited strong capacity for metals such as Pb (II), Cd (II), Zn (II) and Ni (II) [5].

The use of biomass from *Ficusreligiosa* leaves was reported by and the biosorption data were found to fit Langmuir adsorption model [6].

The use of cotton stalk and apricot seeds for the sorption of Cu (II) and Pb (II) ions were investigated. The adsorption efficiency of the two agricultural products was in the order cotton > apricot seeds with adsorption order of Pb (II) > Cu (II) [7].

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The adsorptive capacity of neem leaves for Cu (II), Ni (II),Pb (II) and Zn (II) ions was studied. After 120 minutes contact time, the leaves achieved percent removal of 76.8, 67.6, 58.4 and 41.45 for Cu (II), Ni (II), Zn (II) and Pb (II) ions, respectively. The results obtained were for 1.0g adsorbent dose which showed that neem leaves are good adsorbent for metal ions [8].

The objective of this study was to evaluate the feasibility of using *Strychnos spinosa* tree leaves for the removal of Pb(II) ion from aqueous solution.

Experimentation

Adsorbent: *Strychnos spinosa* leaves were collected at adjacent road 9, University of Jos senior Staff Quarters, Bauchi ring road, Jos, Plateau State. Samples were washed with distilled water and air–dried. Dry leaves were grounded to fine powder by a mortar and pestle. The sample was then sieved through a 125µm mesh size sieve and stored in plastic bag for further use.

Adsorbate: Solution of Pb (II) ion of concentration ranging 20 to 60 mg/l was prepared. All the chemicals used were of analytical reagent grade.

Determination of the Effect of Initial Lead (II) Ions Concentration: 0.5g of *Strychnos spinosa* leaf biomass weighed accurately was added to each 100ml solution of lead (II) ion. Five lead (II) ion solutions of different concentration 20, 30, 40, 50 and 60mg/l. The mixture was shaken constantly for 60 minutes. At the end of each equilibrium time, the mixture was filtered and the concentration determined using the AAS (Spectrometer). The procedure was repeated for each concentration of lead (II) ion solutions prepared.

Effect of Adsorbent Dose: Various doses of 1.0, 1.5, 2.0, 2.5 and 3.0g of the sample were added to the respective lead (II) solutions of optimum concentration (i.e. concentration with the highest adsorption) of 60mg/l prepared at room temperature. The lead (II) uptake efficiency was investigated.

Effect of Contact Time: 0.5g of the *Strychnos spinosa*leaf was mixed with 100ml solution of initial concentration 60mg/l. The mixture was shaken constantly for the time period of 30, 60, 90, 120 and 150mintutes each. At the end of each contact time period, the mixture was filtered and the concentration of the filtrate was determined using the AAS (Spectrometer).

Effect of Temperature: 0.5g of the *Strychnos spinosa* leaf was mixed with 100ml solution of initial concentration 60mg/l. The mixture was shaken constantly and maintain at different temperatures of 30, 40, 50, 60 and 70°C. Each was then filtered and stored for AAS (Spectrometer) analysis for remaining metal ions.

Calculation of the Metal Adsorption Uptake: For each experimental condition examined, the lead adsorption percentage was determined/calculated using the formula

$$R = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

where

R = The metal adsorption percentage

C_i = The initial metal concentration in mg/l

C_e = The final metal ion concentration at equilibrium in mg/l

For each experimental condition examined the lead uptake of optimum value was calculated using the formula

$$q_e = \frac{(C_i - C_e)\,V}{M_s} \qquad (2)$$

where

q_e = The lead uptake in mg/g

C_i = The initial lead concentration in mg/l

C_e = The final lead concentration in mg/l

V = The volume of the lead solution in contact with the biomass in litre

M_s = Weight of the biomass in grams.

Adsorption Kinetics: The kinetic data were tested using pseudo- first order model, a pseudo- second order model [9] and an intra-particle diffusion [10] model to investigate the mechanism of biosorption and potential rate controlling steps such as mass transport and chemical reaction processes.

Thermodynamic Parameters: In order to study the feasibility of the adsorption process, the thermodynamic parameters such as Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) change of the adsorption were estimated.

RESULTS AND DISCUSSION

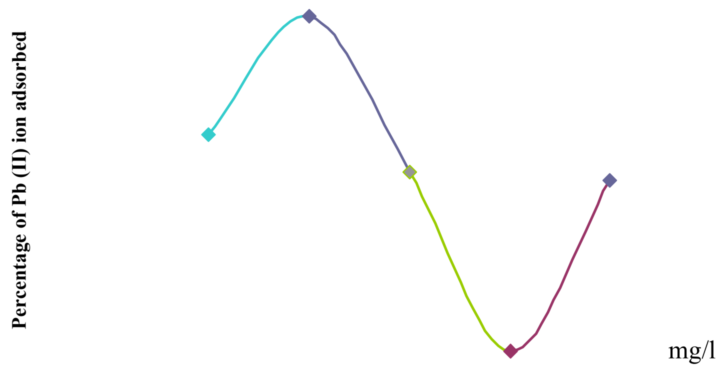

Fig. 1: Effect of initial Concentration on the adsorption of Pb (II) ion by *Strychnos spinosa*

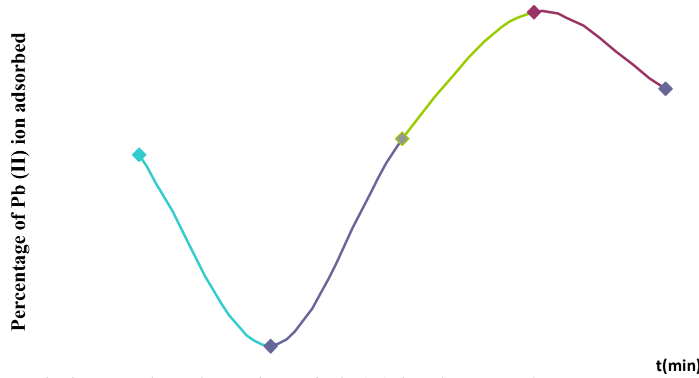

Fig. 2: Effect of contact time variation on the adsorption of Pb (II) ion by *Strychnos spinosa*

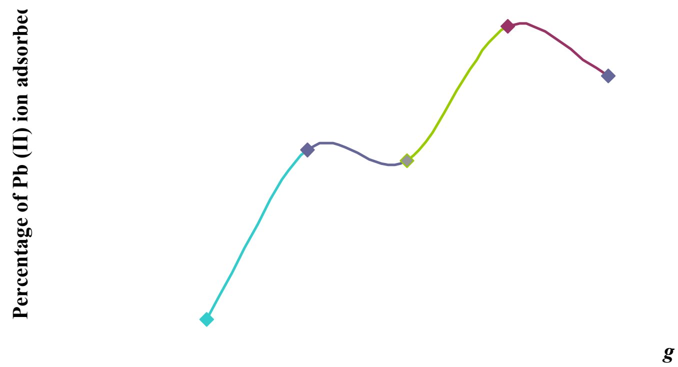

Fig. 3: Effect of dosage on the adsorption of Pb (II) ion by *Strychnos spinosa*

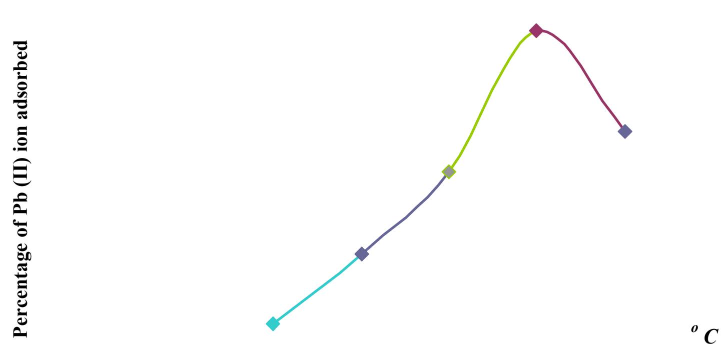

Fig. 4: Effect of temperature on the adsorption of Pb (II) ion by *Strychnos spinosa*

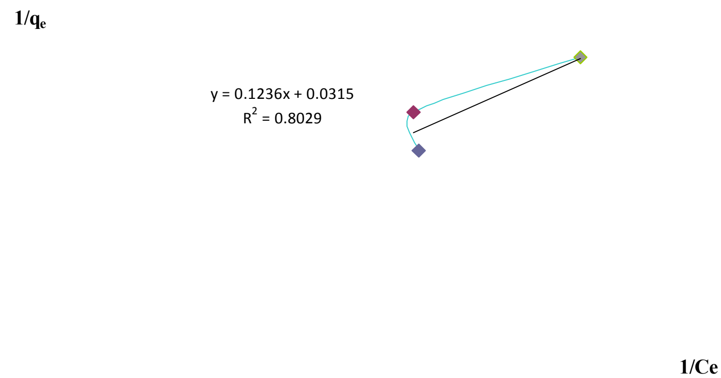

Fig. 5: Langmuir isotherm for adsorption of Pb (II) ion by *Strychnos spinosa*

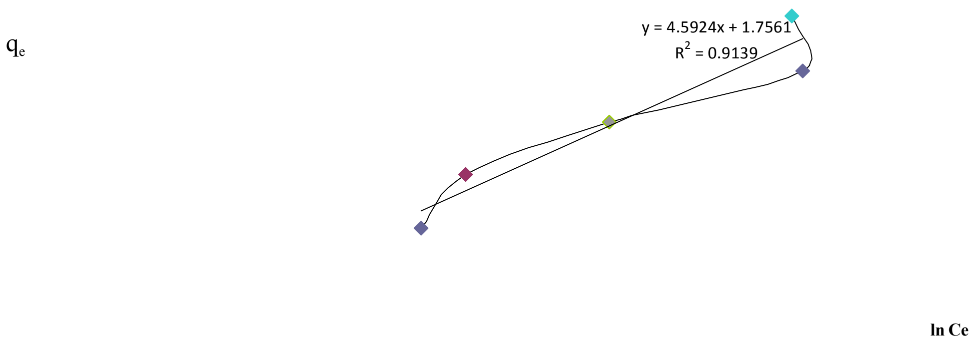

Fig. 6: Temkin isotherm for adsorption of Pb (II) ion by *Strychnos spinosa*

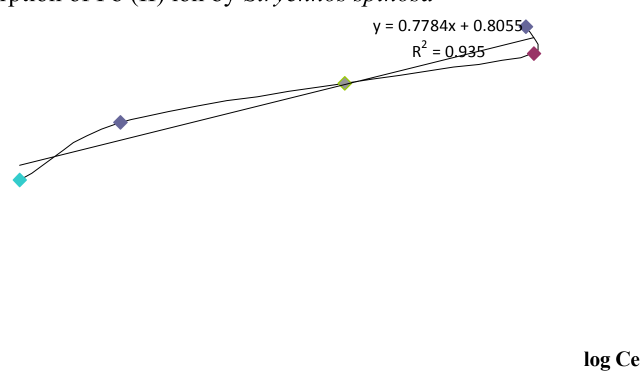

Fig. 7: Freundlich isotherm for adsorption of Pb (II) ion by *Strychnos spinosa*

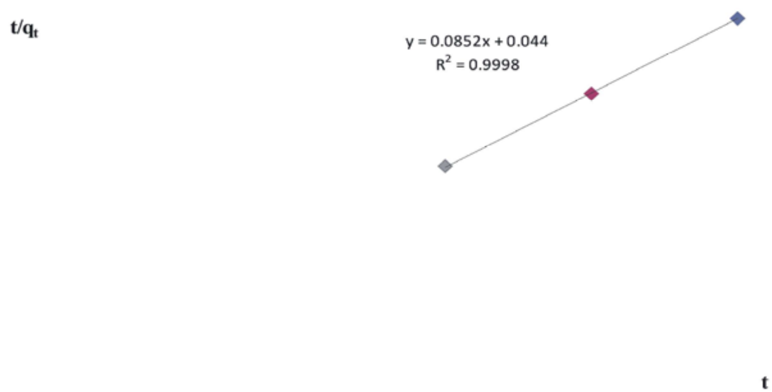

Fig. 8: Pseudo-second order of adsorption of Pb (II) ion by Strychosspinosa

Table 1: Adsorption isotherm for lead (II) ion onto *Strychnos spinosa*

Adsorption isotherms	Parameters	Value
Langmuir isotherm	$q_{max,}$ (mg/g)	31.746
	$b_,$ (L/mg)	0.255
	R^2	0.803
Freundlich isotherm	$k_{F,(}$ (mg/g),	6.390
	n	1.285
	R^2	0.935
Temkin isotherm	A_T, (L/mg)	1.466
	b_T, (mg/g)	539.494
	RT,(k.j/mol)	2477.572
	R^2	0.914

Table 2: Kinetic parameters for adsorption of Pb (ii) ion onto *Strychnos spinosa*

Kinetic Model	Parameters	Value
Pseudo-second order	$k_{2,}$ (g/mg.min)	0.1649
$q_{e,}$ (mg/g)	11.7370	
R^2	0.999	

Table 3: Thermodynamic treatment of sorption process

Temperature (K)	ΔGkj/mol	ΔSkj/mol.K	ΔH^0 kj/mol	E_a, kj/mol
303	-9.404	0.019	-3.647	-3.610
313	-9.594			
323	-9.784			
333	-9.974			
343	-10.164			

The relevant parameters used in this study were contact time, temperature, adsorbent dosage and initial ion concentration. The results of varying these parameters on the adsorption of 0.5g of the *Strychnos spinosa*leaves are discussed below.

The results of the initial lead ion concentration showed that up to 96.79% of the lead ions was adsorbed at initial metal ions concentration of 40mg/l after 60 minutes. The efficiency was increased as the initial metal ion concentration increased. The gradual increase in the efficiency of the biomass showed nearness to saturation of the available binding sites on it.

The rate of lead ion adsorption was found to be very rapid during the initial 120 minutes (98.11%). Thereafter, the rate of lead removal wasdecreased considerably. During the initial stage of adsorption, a large number of vacant surface sites were available for adsorption. After a lapse of sometimes, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between the biosorbate molecules on the solid surface and in the bulk phase, besides, the metal ions were biosorbed into the mesopores that got almost saturated with lead ions during the initial stage of biosorption.

Increase in the adsorbent dose resulted to an increase in the efficiency percentage removal of lead ion. This is probably due to increase in number of available adsorption sites as the adsorbent dose increased.

The adsorption was increased with increasing temperature which indicated the increase in the mobility of large metal molecules with increasing temperature.Due to the high swelling power of *Strychnos spinosa* leaf, increase in temperature produced a high swelling effect within the internal structure of adsorbent enabling metal ion to penetrate further.

The adsorption isotherm was obtained from data deduced from effect of initial lead concentration. According to the correlation values (R^2), Freundlich isotherm model best fitted for adsorption of lead (II) ion than Temkin and Langmuir isotherms, respectively.

The kinetic data for the studied biosorption process was analysed by fitting pseudo- second order. It showed excellent linearity with correlation coefficient (R^2>0.99) which implies that it is highly significant. Over the past few years, a pseudo-second order kinetic model has been considered to be among the most appropriate [11].

The thermodynamic treatment of the sorption data indicates that ΔGvalues were negative at all temperatures investigated. The negative values of ΔGindicates the thermodynamically feasible and spontaneous nature of the adsorption process. The decrease in ΔG values shows a decline in the feasibility of the adsorption with increasing temperature. The positive value of ΔS showed increased in randomness at the solid/liquid interface during the adsorption. The nature of E_a was found to be -3.61KJ and indicates the exothermic nature of the adsorption process. The probability of lead (II) ions to stick on the surface of the biomass is very high as $\Delta S < 1$, this value confirms that physical sorption is the predominant mechanism [12].

CONCLUSION

The successful application of *Strychnos spinosa* leaves as an adsorbent for the removal of lead (II) ion from aqueous solution has further strengthened the call for the use of biomass to replace the use of conventional and expensive method for the removal of metals from wastewater.

The results clearly established that *Strychnos spinosa* leaf biomass can be used as an alternative, environmentally friendly, inexpensive and also effective adsorbent for the removal of lead (II) ion from aqueous solution.

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