Chemistry Research Journal, 2017, 2(4):171-178

Available online <u>www.chemrj.org</u>



Research Article

ISSN: 2455-8990 CODEN(USA): CRJHA5

Adsorption of Cr(lll), Pb(ll) and Cd(ll) ions from aqueous solution by Monkey bread (*Piliostigma thonningii*) seed pod

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Abstract The potential of *piliostigma thonningii* seed pod (a plant waste) as an adsorbent in the removal of Cd(II), Cr(III) and Pb(II) ions from aqueous solution was investigated in this study. The influences of initial metal ion concentration, pH and temperature on the adsorption process were investigated in a batch study. Maximum percentages of each of the metals adsorbed were 89% for Cd(II), 92 % for Cr(III) and 98 % for Pb(II) ions at a fixed temperature of 303 K. The trend of the heavy metal adsorption follows: Pb(II) > Cr(III) > Cd(II), indicating that lead(II) was best adsorbed by the adsorbent. From the two isotherm models applied to the experimental adsorption data, Freundlich model was found to give best description to the experimental data. The feasibility of the process was assessed using different thermodynamic parameters viz; ΔG_{ads} , ΔH_{ads} and ΔS_{ads} . Results obtained showed that the ΔH values (J/mol) were 30.49, 35.94 and 47.40 while ΔS values (J mol⁻¹ K⁻¹) were 99.02, 117.07 and 154.73 for Cd(II), Cr(III) and Pb(II) ions respectively, indicating the endothermic nature of the process and further revealed increased randomness at solid/solution interface. This increased randomness at the solid-solution interface thus indicates that physisorption is the likely predominant mode of the adsorption process. The negative ΔG values at the different studied temperatures suggest that the adsorption process was spontaneous.

Keywords Adsorbent, Adsorption, Adsorption isotherms, heavy metal ions, piliostigma thonningii

Introduction

Water pollution is one of the most serious environmental problems facing the modern society [1, 2]. Wastewaters contain varying degree of heavy metals, which are known for their non-degradability and toxicity. It is, therefore, essential to control discharge of heavy metals into water bodies and natural streams since they are highly toxic even at very low concentrations. They are released into the environment through different anthropogenic routes such as photographic development, ceramics, alkaline batteries, electroplating and metal plating works [3]. They pose severe threats to human health when released to the environment due to their high toxicity and are capable of exerting their toxic effects even at low concentrations. Occupational levels of metals exposure have been observed to constitute risk factors for chronic lung disease and testicular degradation [4].

Water insoluble chromium(III) compounds and chromium metals are not considered health hazards while the toxicity and carcinogenic properties of chromium(VI) had been known for a long time. The acute toxicity of chromium(VI) is due to its strong oxidative properties. Chromium salts (chromates) are also the cause of allergic reactions in some cases. Therefore, contact with products containing chromates can lead to allergic contact dermatitis and irritant dermatitis, resulting in ulceration of the skin, sometimes referred to as "chrome ulcers" [5].



Cadmium had been known to cause damages to some specific structure of the functional units of the kidney [6]. Chronic inhalation or oral exposure of animals to cadmium results in effects on the kidney, liver, lungs, bone, immune system, blood and nervous systems [7]. The Reference Dose (RFD) for cadmium in drinking water is 0.05 mg/kg/day and RFD for dietary exposure to cadmium is 0.001 mg/kg/day and both are based on significant proteinurea in humans [8].

Lead poisoning also known as plumbism is a type of metal poisoning and a medical condition in humans and other vertebrates caused by increased levels of lead. According to Staudinger *et al.* [9], lead is particularly toxic to children causing potentially permanent learning and behavioural disorders. Symptoms include abdominal pain, headache, anemia, irritability and in severe cases seizer, coma and death. The toxicity of lead can lead to loss of memory or concentration, depression, nausea, abdominal pain, loss of coordination, numbness and tingling in the extremities [10].

For these reasons, it is imperative to focus attention on the development of improved friendly methods and low cost adsorbents for toxic heavy metal removal. Various techniques are in use for the removal of heavy metals from the industrial discharge but adsorption technology has been found to show high efficiency in detoxifying effluents. Adsorption utilizes the ability to accumulate heavy metals from waste water by either metabolically mediated or physiochemical pathway of uptake [11].

This work is therefore aimed at exploring the adsorptive behaviour of *piliostigma thonningii* seed pod, a plant waste, towards the removal of the following heavy metal ions: lead(II), cadmium(II) and chromium(III) from aqueous solution. The selection of this novel adsorbent in the removal of aforementioned metal ions is due to its cheapness, non-toxicity and ease of availability,

Materials and Methods

Materials

All the chemicals used were of analytical grades. Stock solutions of each of lead(II) nitrate, cadmium(II) chloride and chromium(III) chloride were used as adsorbates and solutions of various concentrations (10, 20, 30, 40 and 50 mg/L) were obtained by serially diluting the stock solutions with deionized water. The adsorbent, *Piliostigma thonningii* seed pod was washed at the first step and then rinsed copiously with deionized water. After drying at 100 $^{\circ}$ C, it was grounded and screened (using screen with mesh size 40 µm) followed by activation by soaking in 0.3 M HNO₃ with continuous stirring for 30 min and left undisturbed for 24 hr and then filtered, dried in the oven at temperature of 75 $^{\circ}$ C for 6 hr and kept in plastic containers in readiness for the adsorption process.

Adsorption experiments

Sorption experiments were carried out as a function of pH, initial metal ions concentration and temperature using adsorbent dosage of 0.15 g and adsorbate volume of 25 ml (0.025 L). Stock solutions of 1000 mg L⁻¹ of each of the metal ions Cd(II), Pb(II) and Cr(III) used for the adsorption study were prepared from the salt of the individual ions. From the stock solutions, various working concentrations of 10 mg/L, 20 mg/L, 30 mg/L, 40 mg L⁻¹ and 50 mg L⁻¹ of each of the metal ions were prepared by serial dilution. The effect of initial metal ion concentration on equilibrium adsorption of the Pb(II), Cd(II) and Cr(III) ions by the adsorbent was carried out by introducing 25 cm³ of various concentrations (10 mg L⁻¹, 20 mg L⁻¹, 30 mg L⁻¹, 40 mg L⁻¹ and 50 mg L⁻¹) of the metal ions into different 100 cm³ Erlenmeyer flasks containing 0.15 g of the adsorbent of particle size 40 µm. The flasks were shaken for 2 h in a thermostated mechanical shaker maintained at a temperature of 30 ^oC and at a pH 6.0. At the end of the contact time (2 h), the suspension was centrifuged at 3000 rpm for 10 min and the mixtures filtered rapidly into separate sample bottles [12]. The residual metal ion concentration in the filtrate was determined using Atomic Absorption Spectrophotometer. Concentration of blank solution (without adsorbent) was also measured.

The effect of pH on adsorption of the metal ions was studied by varying the pH of the metal solution using 0.1 M solutions of HCl and NaOH to adjust the pH to the required pH and pH values of 2.0, 4.0, 5.0, 6.0, 7.0 and 8.0 were obtained. Exactly 25 cm³ portions of 50 mg L⁻¹ of each of the metal ion solutions were introduced into different 100 cm³ Erlenmeyer flasks containing 0.15 g of the adsorbent of particle size 40 μ m. The mixtures were shaken



intermittently in a thermostated mechanical shaker maintained at 30 °C for 2 h and then filtered. The residual metal ion concentration of each filtrate was finally determined using VPG Buck scientific 210/211 Atomic Absorption Spectrophotometer (AAS).

The effect of temperature on the adsorption process was carried out using 0.15 g of dry adsorbent at initial concentration 50 mg/L, allowing sufficient time of 120 min for adsorption equilibrium to reach. The studies were performed at different temperatures of 303 K, 313 K, 323 K, 333 K and 343 K. At the end of the contact time (2 h), the suspension was centrifuged at 3000 rpm for 10 min and supernatants were filtered rapidly through Whatman No. 42 filter paper into separate sample bottles. The lead, cadmium and chromium ions concentration in the filtrate were determined using VPG Buck scientific 210/211 Atomic Absorption Spectrophotometer. Generally, the described procedure for each parameter was carried out in triplicates and mean residual concentration taken. The amount adsorbed q_e (mg/g) and percentage adsorption, % R were both calculated from the average residual metal ions concentration in solution using the relations [13, 14]:

$$q_e = \frac{Co - Ce}{m} * V$$
(1)

$$% R = \frac{C_o - C_e}{C_o} \times 100$$
(2)

Where C_o and C_e are the initial and the final metal ion concentrations (mg/L), V is the volume of the sample (L) while m is the dry mass of adsorbent (g).

Results and Discussion

Effect of pH

The pH of an aqueous solution is an important factor governing both the availability of metal ions in solution as well as the number of binding sites on the adsorbent [15, 16]. The experiments were conducted below pH 8.5 to avoid possible hydroxide precipitation which may erroneously present a higher adsorption capacity for the metal ions by the adsorbent. The biosorption capacity increased with increasing pH and optimum pH for removal of Cd(II), Cr(III) and Pb(II) by the adsorbent occurred at pH 6, 7 and 4 with the adsorption capacities of 4.69 mg/g, 4.83 mg/g and 4.99 mg/g. The trend of the heavy metal removal therefore follows: Pb(II) > Cr(III) > Cd(II).



Figure 1: Effect of pH on the adsorption of the metal ions onto P. thonningii seed pod

Effect of initial metal ion concentration

The initial metal ion concentration provides an important driving force to overcome mass transfer resistance of all molecules between the aqueous and the solid phases [17, 18]. Figure 2 shows the variation of removal efficiencies with initial metal ion concentrations. The metal ion concentrations chosen in our study ranged from 10 mg/L to 50 mg/L. For the fixed adsorbent mass of 0.15 g/L used in the study, it was observed that as metal ion concentrations increase, the removal efficiencies of the adsorbents decreased from 47.75% to 47.6%, 66.5% to 66.4 % and 48.75 to 48.40% for Cd(II), Cr(III) and Pb(II) ions respectively. This shows that increasing the initial heavy metal concentrations in the solutions at the fixed adsorbent mass of 0.15 g decreased the percentage metal removal. This may be explained on the basis that the increase in the number of ions competing for the fixed available binding sites and also limited active sites on the adsorbent at higher metal ion concentrations.



adsorbent material has a finite number of adsorption sites, and that as the metal concentrations increase, these sites become saturated. Therefore, more metal ions were left un-adsorbed in solution at higher concentration levels [19].



Figure 2: Effect of the initial metal ion concentration on the percentage metal ion adsorbed onto P. thonningii seed pod

Adsorption Isotherms

A good representation of the dynamic adsorption separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases [20]. The nature of interaction between the adsorbate and adsorbent, i.e. favorable or unfavorable, can be determined from the isotherm shape.

In order to quantify the amount of metal ions adsorbed by the adsorbent and to determine the mechanism of the adsorption process onto the adsorbent, the experimental data were applied to Langmuir and Freundlich isotherm equations. The constant parameters of the isotherm equations for this adsorption process were calculated by regression using linear forms of the isotherm equations.

The Langmuir Isotherm model

The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. This isotherm predicts monolayer coverage of the adsorbate (metal ions) on the outer surface of the adsorbent and assumes that there is no lateral interaction between the adsorbed molecules [21]. The Langmuir equation can be presented by the well known equation [22].

$$\frac{c_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{c_e}{q_{max}} \tag{3}$$

Where q_e is the adsorption capacity in mg of adsorbate per gram of adsorbent, C_e is the residual (equilibrium) metal ions concentration in solution, q_{max} is the maximum adsorption capacity corresponding to the monolayer coverage and K_L is the Langmuir isotherm constant, which expresses the intensity of the adsorption process. Plots of C_e/q_e vs C_e were all linear but of negative slope as depicted in figure 3 and this shows that the experimental adsorption data did not follow the Langmuir adsorption isotherm model.



Figure 3: Langmuir isotherm plot for adsorption of the metal ions onto P. thonningii seed pod



Equilibrium Freundlich isotherm

This model proposes heterogeneous energetic distribution of active sites, accompanied by the interaction between adsorbed molecules. The linearized form of Freundlich adsorption isotherm is represented as [23, 24].

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e$$

 K_F and n are Freundlich constants describing both the intensity and capacity of the adsorption process respectively. Figure 4 is linear plots of ln q_e vs ln C_e according to Freundlich Isotherm equation. The constants K_F and 1/n were calculated from the intercept and slope of the linear Freundlich isotherm plots and are represented in table 1. K_F shows the ease of removal and separation of the heavy metal ions from aqueous solutions. In all cases reported here, the range of the values of n was within 0.96 to 0.99 for the adsorption of the metal ions indicating beneficial adsorption for the system under study. This Freundlich type behavior is indicative of the surface heterogeneity of the adsorbent, i.e. the adsorptive sites (surface of the studied adsorbent) are made up of small heterogeneous adsorption patches that are homogeneous in themselves. According to Anusiem *et al.* [25], the fit of experimental adsorption. The high R^2 values suggest an excellent fitting of experimental data into Freundlich model. The calculated Freundlich constants and the R^2 values are presented in table 1.



Figure 4: Freundlich isotherm plot of $\ln q_e$ vs $\ln C_e$ for adsorption of the metal ions onto P. thonningii seed pod

Table 1: Freundlich isotherm constants for adsorption of Cd(II), Cr(III) and Pb(II) ions by the adsorbent

Constants	Metal ions					
	Cr(III)	Cd(II)	Pb(II)			
K _F	0.077	0.080	0.091			
n	0.97	0.96	0.99			
\mathbf{R}^2	0.999	0.999	0.999			

Adsorption Thermodynamics

k

The thermodynamics of adsorption of lead(II), cadmium(II) and chromium(III) ions by *piliostigma thonningii* were investigated at temperature range of 303 K to 343 K and with metal ion concentration of 50 mg/L and the results are represented in Figure 5.

In order to evaluate the activation energy for the process, the Arrhenius equation was used (equation 5)

$$= Aexp(-E_a/RT)$$

Where k is the adsorption rate constant obtained from the slope of kinetic plot, Ea is the activation energy of adsorption, R is the gas constant and T is the temperature in Kelvin.

(5)

(6)

Transforming equation (5) to natural logarithmic form becomes $\ln k = \ln A - Ea/RT$

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The plot of ln k versus 1/T should produce a straight line with slope equal to -Ea/RT, from which the Ea values of 35.94, 30.49 and 47.40 in J/mol for Cr(III), Cd(II) and Pb(II) ions respectively were obtained.

The thermodynamic parameters (ΔH and ΔS) for the adsorption process were calculated using the following equations:

$\Delta G = -RT \ln K$	(7)
$\ln K = -\Delta G / RT = -[\Delta H - T\Delta S] / RT$	(8)
$\ln K = -\Delta H/RT + \Delta S/R$	(9)

The plot of ln K Vs 1/T should produce a straight line with slope equal to $-\Delta H/R$ and the intercept $\Delta S/R$, from which ΔH and ΔS can be calculated from the linear plots respectively. The observed thermodynamic values are given in table 2.

The negative values of ΔG at all temperatures indicated that the adsorption process was spontaneous and that the adsorbent sites have affinity for the metal ions. The positive values of ΔH give an indication that the adsorption process was endothermic while the positive values of ΔS showed an increase in randomness at the solid/solution interface after metal ions adsorption on the adsorbent surface.



Figure 5: The plot of lnK versus 1/T for the adsorption of metal ions onto P. thonningii seed pod

 Table 2: Thermodynamic parameters for the adsorption of metal ions onto *P. thonningii* seed pod. at temperatures 303K, 313K, 323K, 333K and 343K

Metal ions	ΔH(J/mol)	ΔS(J/mol)	ΔG(303 K)	ΔG(313 K)	ΔG(323K)	ΔG(333K)	ΔG(343K)
			(kJ/mol)	(kJ/mol	(kJ/mol)	(kJ/mol)	(kJ/mol)
Cd(II)	30.49	99.02	-29.972	-30.962	-31.952	-32.943	-33.933
Cr(III)	35.94	117.07	-35.436	-36.606	-37.777	-38.948	-40.119
Pb(II)	47.40	154.73	-46.835	-48.383	-49.930	-51.477	-53.024

Conclusion

Use of *P. thonningii* seed pod., an agricultural waste as an adsorbent for adsorption of Cd(II), Cr(III) and Pb(II) ions fron aqueous solution has been explored under batch adsorption study. The study was subjected to different pH's to determine the optimum pH for adsorption of each of the metal ions since they are bound to exist strong electrostatic attraction between the negatively charged adsorbent and the positively charged metal ions at different pH... The amount of metal ions adsorbed was found to vary with initial metal ion concentration and temperature. The adsorption data fitted well to the Freundlich isotherm model and the recorded maximum percentage removals were 66.5%, 66.5% and 48.75% for Cr(III), Pb(II) and Cd(II) ions respectively at 323K. Thermodynamic assessment of the process revealed that the adsorption process was endothermic and spontaneous.



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