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Biosorptive removal of Pb^{2+} and Cd^{2+} onto novel biosorbent: Defatted *Carica papaya* seeds

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ABSTRACT

Carica papaya seeds, an agricultural waste in Nigeria, were defatted to obtain defatted *C. papaya* seed biosorbent. The Fourier Transformed Infrared spectrum of defatted *C. papaya* seed biosorbent suggests the presence of C=O, –OH of carboxylic acid, lactonic and amide band functional groups. The adsorption of metal ion onto defatted *C. papaya* seed biosorbent led to small shifts in the IR bands. The adsorption capacity of defatted *C. papaya* seed biosorbent was evaluated to be 1666.67 mg/g for Pb^{2+} and 1000.00 mg/g for Cd^{2+}. In binary metal ion solution, the defatted *C. papaya* seeds showed decreased adsorption capacity for either metal ion. The influence of different particle sizes was found to have negative impact on the adsorption capacity of *C. papaya* seed biosorbent in the removal of Pb^{2+} and Cd^{2+} from aqueous solution. The adsorption of both metal ions was observed to follow the Freudlich model better than the Langmuir model suggesting that the adsorption of both metal ions was on multisites on the defatted *C. papaya* seed biosorbent. The adsorption was found to be highly feasible, spontaneous and exothermic in nature. Optimization results suggests 5 m^3 of 100 mg/L of Pb^{2+} and Cd^{2+} requires 43.3 and 49.2 kg of defatted *C. papaya* seeds to remove 95% of the metal ions from aqueous solution.

1. Introduction

Heavy metals such as Pb and Cd are pollutants of very high priority concern in the scientific community because apart from being toxic to the entire ecosystem, they are non-biodegradable. They have the ability to bioaccumulate in biological species even at very low concentrations [1]. Exposures to Lead and cadmium has been reported to have deleterious health effects on humans including damage to liver, kidney and a painful disease called "itai–itai" [1,2].

These metals get into natural surface and ground waters from industrial effluents such as those from the oil and gas, plastic, pharmaceutical, storage-battery manufacture, paper and pulp, mining, electroplating, lead smelting, other metallurgical finishing, automobile industry, agricultural run-off, chemical spills and municipal wastewaters [1]. Various traditional methods of removing heavy metals from waste-waters have been reported including the use of precipitation and coagulation, chemical oxidation, sedimentation, filtration, osmosis, ion exchange, etc [3].

Adsorption technology is currently being used extensively for the removal of heavy metals from aqueous solutions because it is a cleaner, more efficient and cheaper technology. A review of some recent low cost adsorbents has been done by Yurtsever and Sengil [1]. In Nigeria, *Carica papaya* fruit is a delicacy which is usually eaten with or without meals. The seeds are often times discarded as waste. The fruits have tremendous nutritional value and contain 1.5% protein, 0.1%

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Table 1 – Values of surface acidity and pH_{PZC} of defatted *C. papaya* seeds using Boehm's titration.

Sample	Carboxylic	Lactonic	Phenolic	Acidic value	Basic value	pH_{PZC}
	Meq/g of DPS adsorbent					
DPS adsorbent	0.098 ± 0.013	0.117 ± 0.009	1.864 ± 0.022	2.078	0.587	6.25

fat, 7.1% carbohydrates, and 35.0 calories per 100 g edible fruit. They also contain high levels of calcium, iron, sodium, potassium, β-carotene, vitamin B2, niacin, and vitamin C [4–6].

C. papaya seeds, the fruit, leave, and latex are used medicinally. The main medicinal use of *C. papaya* seeds is as a digestive agent. It is prescribed for people who have difficulty digesting protein and is used to break up blood clots after surgery, this is due to the presence of enzyme papain in the plants latex [7]. The seeds are reported to contain 24.3 g protein, 25.3 g fatty oil, 32.5 g total carbohydrate, 17.0 g crude fiber, 8.8 g ash, 0.09% volatile oil, a glycoside, caricin, and the enzyme, myrosin per 100 g of the seeds. With reversed-phase partition column chromatography, the oil from the seeds of *C. papaya* was found to contain the following acids: lauric, 0.4%; myristic, 0.4%; palmitic, 16.2%; stearic, 5.0%; arachidic, 0.9%; behenic, 1.6%; hexadecenoic, 0.8%; oleic, 74.3%; and linoleic, 0.4% [8,9]. It has been concluded that papaya seed oil is a potential source of high oleic oil and its full potential should be exploited [10].

With the vast array of biosorbents currently available for removal of metal ions, there is the dearth of information on the adsorptive potential of *C. papaya* seeds even though Basha et al. [11] have used the trunk of the plant to adsorb Hg^{2+}. Recently, we showed that defatting *C. papaya* seeds enhances its ability as an biosorbent to remove methylene blue from aqueous solution with an adsorption capacity as high as 1250 mg/g [12]. Furthermore the usefulness of the lipids, which have been mentioned above, makes it very crucial that the seeds are defatted before use as biosorbent. As a follow up on this, this work demonstrates the use of novel defatted *C. papaya* seeds as biosorbent in the adsorption of Pb^{2+} and Cd^{2+} from aqueous solution.

Some variables that affect the adsorption capacity of defatted *C. papaya* seed biosorbent, such as particle size, pH, adsorbent dose, initial dye concentration, temperature, and time were studied.

2. Materials and methods

2.1. Preparation and characterization of defatted C. papaya seed biosorbent

C. papaya seeds, collected from open markets in Nigeria, were sun dried for 7 days after which they were crushed and defatted using the soxhlet extraction method with hexane as solvent. The air dried sample was then called Defatted *C. Papaya* Seeds (DPS). Fourier Transformed Infrared Spectroscopy (FTIR) of defatted *C. papaya* seed biosorbent was carried out using the KBr method as described by Prahas et al. [13]. SHIMADZU 8400S FTIR instrument in the vibrational absorption range of 4000–600 cm^{-1} was employed. Boehm titration and pH drift (or pH_{pzc} – pH at point of zero charge) methods were adopted for surface chemistry [13]. The specific surface area of defatted *C. papaya* seed biosorbent was calculated as described in [12,14] and was found to be 143.27 m^2/g.

2.2. Adsorption studies

Standard solutions of Pb^{2+} and Cd^{2+} were prepared from their nitrate salts. In studying the effect of initial metal ion concentration, 50 mL of both metal ion in the range of 10–500 mg/L and 0.5 g of defatted *C. papaya* seed biosorbent were agitated for 2 h at 180 rpm at 298 K. The effect of temperature on the adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seed biosorbent was studied by repeating the procedure for initial concentration at 313 K and 323 K. The thermodynamic parameters, ΔH^o, ΔS^o and ΔG^o for the adsorption process were obtained from the relation $\ln b = \Delta S/R - \Delta H/RT$ with all the letters having their usual meanings.

The effect of biosorbent dose was carried out by taking known weights of the defatted *C. papaya* seed biosorbent ranging from 0.1 g to 3.0 g into glass bottles containing 50 mL of 250 mg/L each of Pb^{2+} and Cd^{2+}. These mixtures were agitated for 2 h at 180 rpm at room temperature (298 K). The effect of pH on adsorption capacity of defatted *C. papaya* seed biosorbent was studied by dispersing 0.5 g each of defatted *C. papaya* seed biosorbent in 50 mL of 250 mg/L of both metal

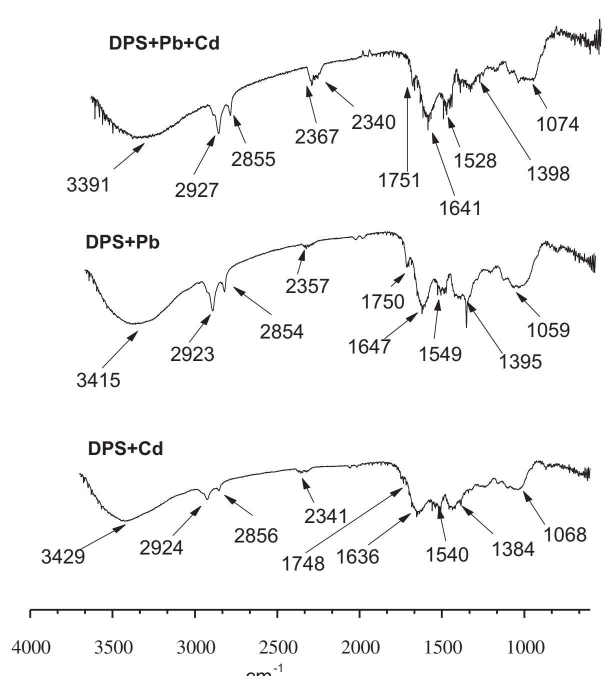

Fig. 1 – Fourier Transformed Infrared Spectroscopy plots of defatted *C. papaya* seed biosorbent and metal loaded defatted *C. papaya* seed (DPS) biosorbent.

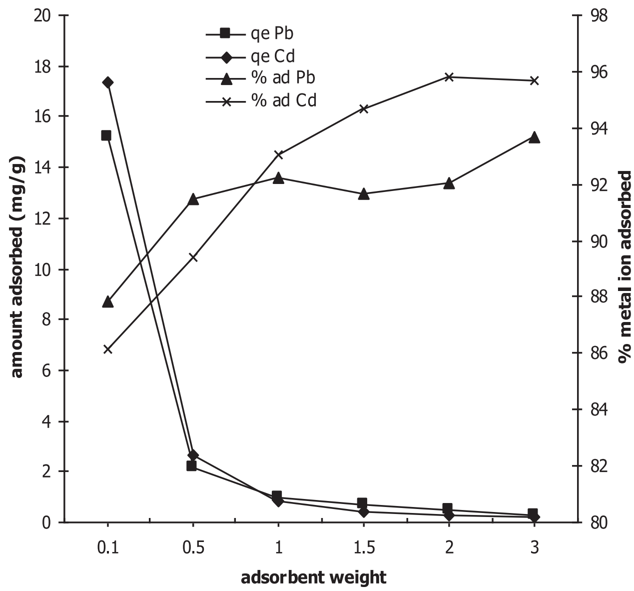

Fig. 2 – Effect of defatted *C. papaya* seed biosorbent dose on adsorption of Pb^{2+} and Cd^{2+}.

ions contained in a series of glass bottles and adjusting the pH of the adsorbate solution with either 0.01 M NaOH or 0.01 M HNO_3 in the range of 3–8. These were agitated for 2 h at 180 rpm at room temperature (298 K).

The effect of particle size on adsorption was studied with four different particle sizes (75, 300, 500 and 750 μm) of defatted *C. papaya* seed biosorbent by dispersing 0.5 g of each particle size in 50 mL of 250 mg/L containing Pb^{2+} and Cd^{2+}. These were agitated for 2 h at 180 rpm at 298 K and samples were taken out of the shaker at predetermined time intervals between 0.5 and 120 min to study the effect of contact time.

The samples collected were then analyzed for Pb^{2+} and Cd^{2+} using the Atomic Absorption Spectroscopy (AAS) instrument. The amounts of metal ions adsorbed by the adsorbents were calculated by difference using the formula:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

Where q_e is the adsorption capacity of various adsorbents, Co is the initial concentration of Pb^{2+} (mg/L), C_e is the equilibrium concentration of Pb^{2+} (mg/L), V is the volume of sample used (L), W is the weight of adsorbent used (g).

The pseudo second order kinetic model (equation (1)) was used to analyze kinetic data obtained.

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (\text{non} - \text{linear}) \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (\text{linear}) \tag{3}$$

where q_e is the amount of metal ion adsorbed at equilibrium (mg/g), q_t is the amount of metal ion adsorbed at time t (min) in mg/g and k_2 is the rate constant of the PSOM for sorption of both metal ions. Kinetic data were further used to investigate the rate-determining step occurring in the present adsorption system using Bangham's equation [15].

$$\log\left(\log\left(\frac{C_o}{C_o - q_t m}\right)\right) = \log\left(\frac{k_o m}{2.303V}\right) + \alpha \log(t) \tag{4}$$

where V is the volume of solution (L) and $\alpha < 1$) and k_0 (g) are constants, m is the weight (g) of defatted *C. papaya* seed biosorbent used for the adsorption reaction, and t is time (min).

The Langmuir and Freudlich isotherm (equations (5) and (7) respectively) models were used to study the adsorption isotherms of defatted *C. papaya* seed biosorbent.

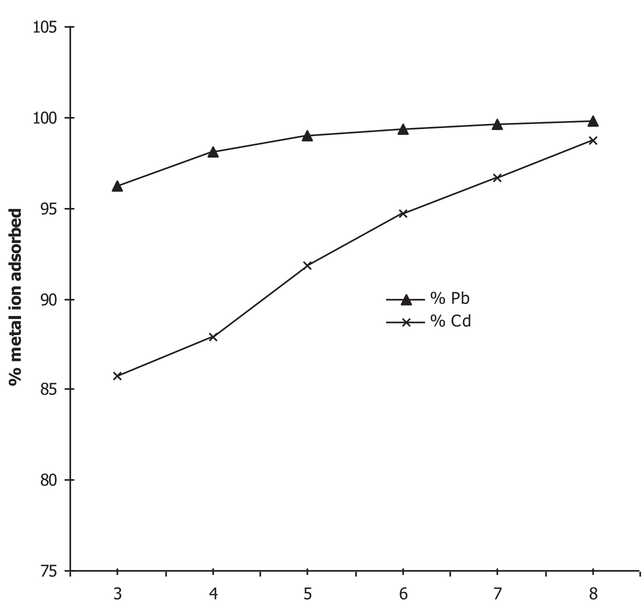

Fig. 3 – Effect of pH on the adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seed biosorbent.

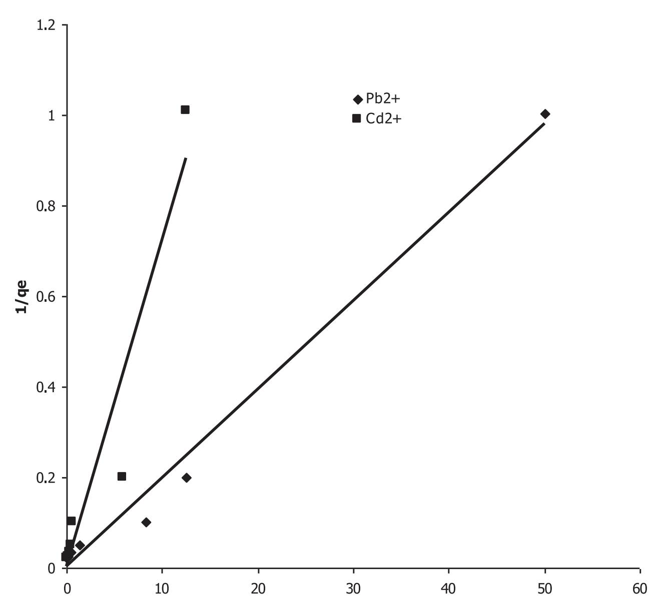

Fig. 4 – Langmuir isotherm plot for the adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seed biosorbent.

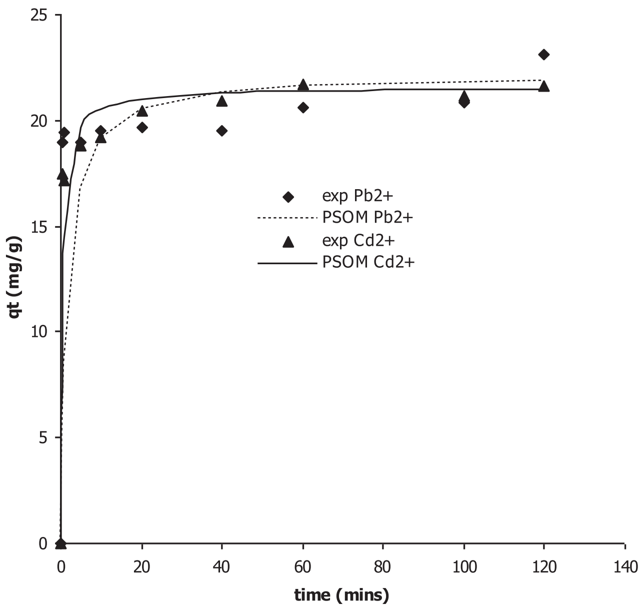

Fig. 5 – Pseudo-second order kinetic model plots for the adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seed biosorbent.

$$q_e = \frac{Q^o b C_e}{1 + bC_e} \quad \text{(Non-linear form)} \tag{5}$$

$$\frac{Ce}{q_e} = \frac{1}{Q^o b} + \frac{Ce}{Q^o} \quad \text{(Linear form)} \tag{6}$$

$$q_e = K_F Ce^{1/n} \quad \text{(Non-Linear form)} \tag{7}$$

$$\log q_e = \log q + 1/n \log C_e \quad \text{(linear form)} \tag{8}$$

Samples were collected in duplicate and the averages of the results were used for analysis. All filtrates were analyzed using Atomic Absorption Spectrophotometry (AAS)-Perkin Elmer Analyst 200A, 2003 model. The pH for all experiments was 5.0 except for effect of pH where the pH was varied from 3.0 to 8.0. This is irrespective of the pH_{PZC} (6.25) to avoid metal ion precipitation.

3. Result and discussions

3.1. *Physicochemical analysis*

Table 1 shows some of the physicochemical properties of defatted *C. papaya* seed biosorbent. Table 1 show that the acidic functional groups of the biosorbent are more than the basic groups suggesting that the biosorbent is well suited for the removal of cationic species from aqueous solutions. Fig. 1 shows the Fourier Transformed Infrared spectra of defatted *C. papaya* seed biosorbent (DPS) with metal Pb^{2+} and Cd^{2+}. Defatted *C. papaya* seed biosorbent spectrum has been well discussed in our previous work [12]. In order to study the effect of interaction between metal ions and adsorptions sites on defatted *C. papaya* seed biosorbent, $Pb^{2+}$and Cd^{2+} on defatted *C. papaya* seed adsorbent was used. It was observed that there were several small shifts in peaks when Pb^{2+} and Cd^{2+} were adsorbed onto defatted *C. papaya* seed the biosorbent. The wave number in the range 3429-3344 cm^{-1} is -OH stretch. Some observed shifts include the shift in –OH band from 3344 cm^{-1} in defatted sample to 3429, 3415, and 3391 cm^{-1} and S=O band in defatted sample from 1057 to 1068, 1059, and 1074 cm^{-1} for DPS + Cd, DPS + Pb and DPS + Pb + Cd samples respectively. The medium absorption band at 2930 cm^{-1} and 2380 cm^{-1} are the υ_{C-H} stretching and υ_{N-H} group respectively. There were also other observed small shifts in these bands when Pb^{2+}, Cd^{2+} and Pb^{2+}+ Cd^{2+} were adsorbed onto DPS (Fig. 1). The 1750 cm^{-1} band observed in the defatted sample (indicative of five ring lactone) [12] showed a shift to 1748, 1750, 1751 cm^{-1} for DPS + Cd, DPS + Pb and DPS + Pb + Cd samples respectively.

In the defatted sample spectrum, a sharp and distinct absorption was observed at 1650 cm^{-1} (C=O stretching). This is a clear indication of the presence of α,β-unsaturated ketone, β-keto (enolic) esters, Lactones, quinones and carboxylic acids

Table 2 – Equilibrium isotherm parameters for the adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seeds.

	Langmuir model			Freudlich model		
	Qo (mg/g)	b (L/g)	r^2	k_f (mg/g)	1/n	r^2
Pb^{2+}	1666.67	0.031	0.9888	16.90	0.54	0.8938
Cd^{2+}	1000.00	0.014	0.9149	8.77	0.60	0.8931

	Langmuir parameters at different temperatures					
	Pb^{2+}			Cd^{2+}		
	Qo (mg/g)	b (L/g)	r^2	Qo (mg/g)	b (L/g)	r^2
298 K	1666.67	0.03	0.9888	1000.00	0.01	0.9149
313 K	40.32	1.59	0.9997	129.87	0.11	0.9395
323 K	30.12	2.29	0.9993	49.50	0.31	0.9632

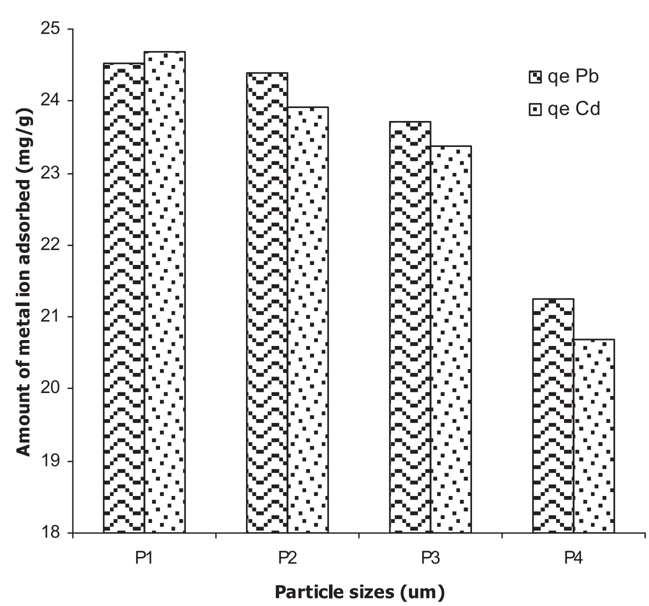

Fig. 6 – Effect of particle size on the adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seed biosorbent.

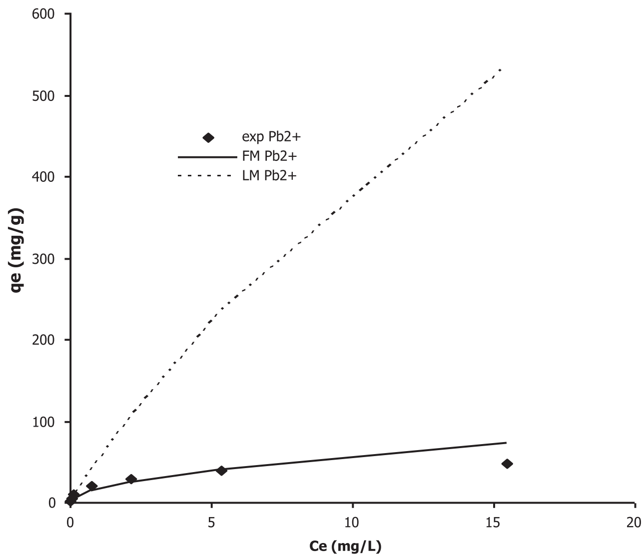

Fig. 7 – Langmuir (LM) and Freudlich (FM) isotherm model plots for the adsorption of Pb^{2+} onto defatted *C. papaya* seed biosorbent.

[12]. On adsorption of Cd^{2+}, Pb^{2+} and Pb^{2+}+ Cd^{2+}, this band shifted to 1636, 1647 and 1641 cm^{-1}. This is a clearly suggests the involvement of α,β-unsaturated ketone, β-keto (enolic) esters, Lactones, quinones, amide and carboxylic acid functional groups in the adsorption of Pb^{2+} and Cd^{2+}. Ansari et al. [16] have also observed similar hypsochromic shifts when they adsorbed Cd^{2+} on *Polypogon monspeliensis* waste biomass.

3.2. *Effect of pH*

Fig. 2 shows the effect of pH on the adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seed biosorbent. It was observed that there was no significant increase in percentage of metal ion

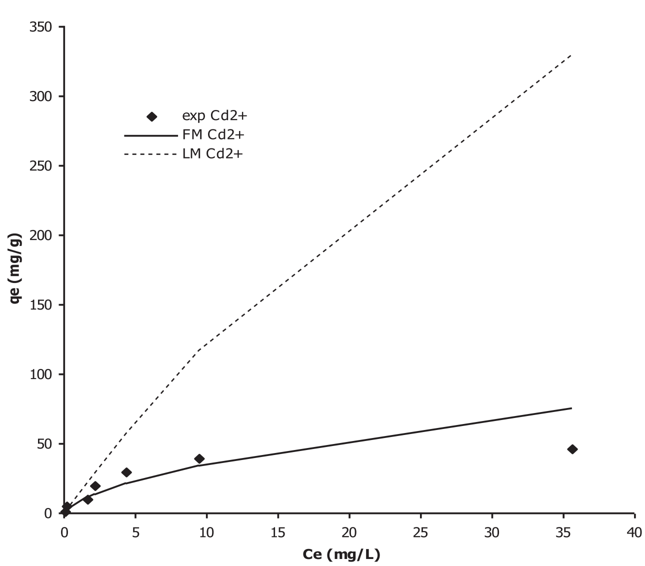

Fig. 8 – Langmuir (LM) and Freudlich (FM) isotherm model plots for the adsorption of Cd^{2+} onto defatted *C. papaya* seed biosorbent.

Table 3 – Effect of binary metal ions on the adsorption capacity of defatted *C. papaya* seed biosorbent for Pb^{2+} and Cd^{2+}.

pH	C_e (mg/L)		q_e (mg/g)	
Pb^{2+}:Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
100:100	15.78	9.66	8.32 (16.7%↓)	8.93 (9.2%↓)
100:50	22.05	5.37	8.98 (10.1%↓)	4.39 (11.8%↓)
50:100	18.72	9.80	3.10 (37.9%↓)	8.93 (9.2%↓)

↓ = percentage decrease of adsorption capacity.

adsorbed especially for Pb^{2+} with change in pH (Pb^{2+} removal from aqueous solution increased from 96 to 99% and Cd^{2+} from 85 to 98%). Similar observation was been made by Puangsri et al. [10] when they adsorbed Hg^{2+} on *C. papaya* wood. This might suggests that adsorption of the metal ions onto defatted *C. papaya* seed biosorbent is not largely influenced by pH. This could mean that ion-exchange mechanism is not strictly the mechanism by which the metal ions are being adsorbed onto the surface of defatted *C. papaya* seed biosorbent. It is possible that the lone pair of electrons (Lewis base) on some of the functional groups present on the surface of the defatted *C. papaya* seed biosorbent may have played a major role in the removal of the metal ions by (Lewis acid) defatted *C. papaya* seed biosorbent. It is therefore thought that there could have been the formation of inner–sphere complexes between DPS adsorbent and metal ion. However, percentage of Pb^{2+} adsorbed onto defatted *C. papaya* seed biosorbent was more than for Cd^{2+} because of the larger ionic size of Pb^{2+} (less strongly hydrated) compared with Cd^{2+} (more strongly hydrated).

3.3. *Effect of biosorbent dose*

Fig. 3 shows the amount of Pb^{2+} and Cd^{2+} adsorbed with varying defatted *C. papaya* seed biosorbent weights in 250 mg/L of the single metal ion in aqueous solution. Increasing biosorbent dosage decreased the amount of both metal ions adsorbed with Pb^{2+} being more adsorbed than Cd^{2+} (Fig. 3). However, the percentage of metal ion adsorbed was observed to follow the reverse trend. Similar trend have been observed by Ho et al. [17] and Ho and Ofomaja [18]. It is possible that the change in the solid-liquid ratio from 0.003 to 0.1 may have directly resulted in this trend since amount adsorbed, q_e,has an inverse proportionality function to weight of biosorbent but a direct proportionality function to percentage adsorbed (Equation (1)). 0.5 g of defatted *C. papaya* seed biosorbent was chosen for use in this work not because it gave the highest adsorption capacity but because it showed sufficiently high percentage of metal ions adsorbed which were not significantly different from those obtained at higher dosage of defatted *C. papaya* seed biosorbent.

3.4. *Effect of contact time*

Fig. 4 suggests that increasing contact time increased the amount of metal ions adsorbed on defatted *C. papaya* seed biosorbent. Both metal ions showed very high initial sorption rates (13.8 mg g^{-1} min^{-1} for Pb^{2+} and 44.4 mg g^{-1} min^{-1} for

Table 4 – Ratios of adsorption capacity for the adsorption of Pb^{2+} and Cd^{2+} onto defatted *Carica papaya* seeds.

$Pb^{2+}:Cd^{2+}$	Q^{mix}/Q^{o} Pb^{2+}	Q^{mix}/Q^{o} Cd^{2+}	Q^{o}/Q^{m}_{cd}	Q^{o}/Q^{m}_{pb}
100:100	0.833	0.908	1.10	1.20
100:50	0.899	0.881	1.14	1.20
50:100	0.621	0.908	1.10	1.61

Cd^{2+}). The higher initial sorption rate of Cd^{2+} is expected because of the smaller ionic radii of Cd^{2+} which enables it to initially compete favorably with Pb^{2+} for same adsorption site on defatted *C. papaya* seed biosorbent. The ionic radii (Pauling) of the metal ions are Cd^{2+} (0.97Å) and Pb^{2+} (1.20 Å). It has been noted that the smaller the ionic diameters, the higher the initial adsorption rate [19]. The overall Pseudo second order kinetic rate was low but was faster for Cd^{2+} (0.028 g mg^{-1} min^{-1}) than for Pb^{2+} (0.096 g mg^{-1} min^{-1}) for same reason adduced before even though the adsorption capacity of DPS is more for Pb^{2+} than for Cd^{2+} (22.17 mg/g for Pb^{2+} and 21.55 mg/g for Cd^{2+}). The adsorption failed the pseudo-first order kinetic model implying that adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seed biosorbent is not only time dependent but also concentration dependent. From Bangham's equation we observed that the adsorption is not strictly by pore diffusion but there could also be the contribution of film diffusion as seen from the reduced linearity of the Bangham plots ($Pb^{2+} r^2 = 0.6434$ and Cd^{2+} $r^2 = 0.8997$-plots not shown) [15].

Recently, Wu et al. [20], introduced the "approaching equilibrium factor", R_w, into the Pseudo-second order kinetic model (PSO). Calculations using the modified PSO kinetic model for data obtained in this study suggest that R_w for the adsorption of Pb^{2+} and Cd^{2+} is 0.013 and 0.004 respectively. This implies that the adsorption of Cd^{2+} approaches equilibrium faster than Pb^{2+}. This further supports the rate constants and initial sorption rates obtained for the adsorption of both metal ions onto defatted *C. papaya* seed biosorbent in this study. The half-life ($t_{0.5}$) for the adsorption process was found to be 1.61 min and 0.48 min for Pb^{2+} and Cd^{2+} respectively [20].

3.5. *Effect of initial metal ion concentration*

Fig. 5 shows the Langmuir isotherm plots for the adsorption of Pb^{2+} and Cd^{2+} on defatted *C. papaya* seed biosorbent. Increasing initial metal ion from 50 to 500 mg L^{-1} increased amount of both metal ion adsorbed onto defatted *C. papaya* seed biosorbent. This observed trend is because there is increasing concentration gradient between the biosorbent and the adsorbate. The adsorption capacity of defatted *C. papaya* seed biosorbent for Pb^{2+} was observed to be 1666.67 mg/g and for Cd^{2+} it was 1000.00 mg/g (Table 2). Adsorption capacities obtained in this study are higher than those obtained from biosorbents in recent times; Ponkan peel(112.1 mg/g for Pb^{2+} [21]), macrofungus biomass (38.4 mg/g for Pb^{2+} and 27.3 mg/g for Cd^{2+} [22]), Almond Shell (9.00 for Pb^{2+} and 7.00 mg/g for Cd^{2+} [23]), and Zeolite (175 mg/g for Pb^{2+} and 137 mg/g for Cd^{2+} [24]), potassium hydroxide treated pine cone powder (19.22 mg/g for Cu^{2+} and 26.27 mg/g for Pb^{2+} [25]). This shows the strong future potential of this biosorbent in removing metal ions from waste water.

With increasing particle size (75 < 300 < 500 < 750 μm) of defatted *C. papaya* seed biosorbent, adsorption capacity decreased (Fig. 6). This is consistent with literature that the smaller the particle sizes of an adsorbent, the greater the rate of diffusion and adsorption. However, intra-particle diffusion is reduced as the particle size reduces, because of the shorter mass transfer zone, causing a faster rate of adsorption [26,27]. With the portion of defatted *C. papaya* seed biosorbent not sieved, adsorption capacity for both metal ions was observed to be slightly higher (≈14.3%).

Fitting experimental data to Langmuir and Freudlich equilibrium models nonlinear regression, it was observed that the Freudlich gave better fit than Langmuir (Figs. 7 and 8). This implies that the adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seed biosorbent is on heterogeneous adsorption sites on the surface of defatted *C. papaya* seed biosorbent which further strengthens the fact that defatted *C. papaya* seed biosorbent has multi-adsorption sites as shown from the FTIR analysis.

3.6. *Effect of binary mixture*

The effect of binary mixture of metal ions on the adsorption capacity of defatted *C. papaya* seed biosorbent is shown in Table 3. It was observed that the simultaneous presence of either metal ion decreased the adsorption capacity of defatted *C. papaya* seed biosorbent for either metal ion. The values of Q^{mix}/Qo for both Pb^{2+} and Cd^{2+} were found to be less than unity as shown in Table 3 suggesting that the simultaneous

Table 5 – Thermodynamic parameters for the adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seed biosorbent.

	$-\Delta H^o$ (kJ mol^{-1})	$-\Delta S^o$ (J mol^{-1})	r^2	$-\Delta G^o$ (kJ mol^{-1} K^{-1})		
				298 K	313 K	323 K
Pb^{2+}	12.32	73.56	0.9286	34.61	35.35	36.09
Cd^{2+}	19.30	61.63	0.9956	4.55	4.57	4.58

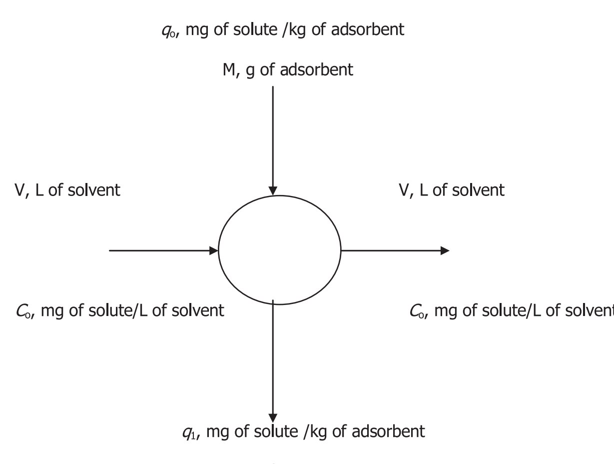

Fig. 9 – Schematic diagram for a single-batch adsorber.

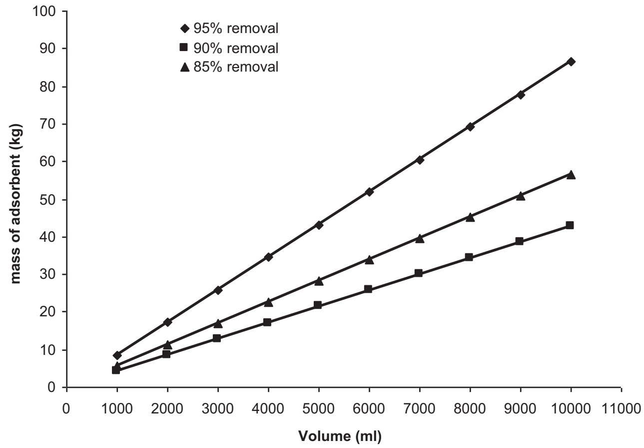

Fig. 10 – Predicted defatted *C. papaya* biosorbent mass against volume of wastewater containing 100 mg/L Pb^{2+}.

presence of both metal ion reduced sorption of the metal ions through competition for adsorption sites on the DPS biosorbent. Furthermore, It has been observed that $Q^o_{cd}/Q^m_{cd} < Q^o_{pb}/Q^m_{pb}$ (Table 4) suggesting that Cd^{2+} adsorption onto defatted *C. papaya* seed biosorbent is more affected by the simultaneous presence of a competing metal ion than Pb^{2+}. This tendency of Pb^{2+} to effectively compete for adsorption sites on colloidal surface has been previously described in the presence of Cd^{2+} [28].

3.7. *Thermodynamics of adsorption*

Table 5 shows data for the various thermodynamic parameters in the adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seed biosorbent. The table suggests that the adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seed biosorbent is highly feasible, spontaneous and exothermic in nature. ΔG^o was found to increase slightly with increasing temperature with the adsorption of Pb^{2+} onto defatted *C. papaya* seed biosorbent being more feasible and spontaneous than that for Cd^{2+} (Table 5).

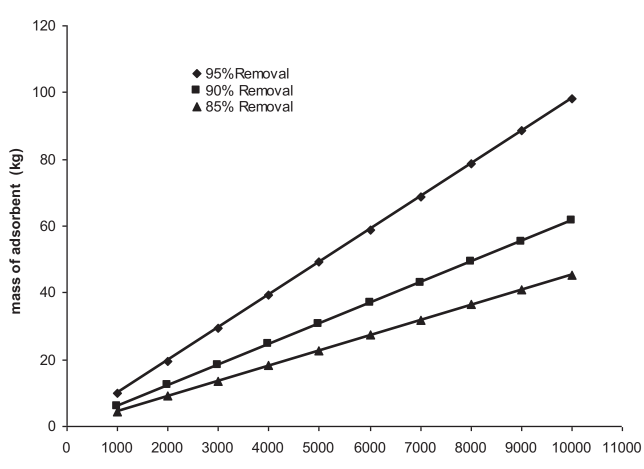

Fig. 11 – Predicted defatted *C. papaya* biosorbent mass against volume of wastewater containing 100 mg/L Cd^{2+}.

3.8. *Mechanism of adsorption*

From the Fourier Transformed Infrared (FTIR) studies of defatted *C. papaya* seed biosorbent, it was observed that the acidic groups were more than the basic and may have been basically responsible for the adsorption of Pb^{2+} and Cd^{2+} onto defatted *C. papaya* seed biosorbent in the following manner:

For the phenolics it is

$$S{-}OH + M^{2+} \rightleftharpoons S{-}O{-}M^{+} + H^{+}$$

For carboxylic acid

$$S{-}COOH + M^{2+} \rightleftharpoons S{-}COOM^{+} + H^{+}$$

The lone pair of electrons on the Lactone and amide present in the biosorbent may have been involved in the adsorption of metal ions from aqueous solution.

3.9. *Optimization of adsorbent weight*

Adsorption process is known to proceed by various mechanisms: external mass transfer of solute onto the surface of the adsorbent followed possibly by intra-particle diffusion mechanism.

Thus, to predict the adsorber size and efficiency in the removal of an adsorbate by an adsorbent, an empirical procedure based on the adsorption equilibrium is designed. Adsorption equilibrium is a dynamic concept based on the equal rate of both adsorption and desorption process taking place on the adsorbent's surface. The complex nature of adsorption has made it impossible to use a single adsorption theory to explain all adsorption systems. However, adsorber design engineering requires equilibrium data. Vadivelan and Kumar [29] have previously predicted the efficiency of a single batch adsorber for the adsorption of methylene blue onto rice husk using equilibrium data obtained.

The design objective is to reduce the adsorbate of volume V (L) from an initial concentration of C_o to C_1 (mg/L). The amount of the adsorbent is M and the solute loading changes from qo (mg/kg) to q_1 (mg/kg). At time $t = 0$, $q_o = 0$ and as time proceeds the mass balance equates the dye removed from the

Table 6 – Mass of defatted *C. papaya* seed biosorbent for the removal of various percentages of 100 mg/L Pb^{2+} from various volumes of aqueous solutions.

Volume (L)	95% Removal	90% Removal	85% Removal	80% Removal	70% Removal
	Mass of defatted *C. papaya* seed adsorbents (kg)				
1000	8.65	5.64	4.28	3.45	2.42
2000	17.31	11.28	8.56	6.89	4.85
3000	25.96	16.92	12.83	10.34	7.27
4000	34.62	22.56	17.11	13.79	9.69
5000	43.27	28.19	21.39	17.24	12.12
6000	51.92	33.83	25.67	20.68	14.54
7000	60.58	39.47	29.95	24.13	16.96
8000	69.23	45.11	34.23	27.58	19.39
9000	77.89	50.75	38.50	31.03	21.81
10,000	86.54	56.39	42.78	34.47	24.23
1,000,000	8654.08	5638.76	4278.30	3447.27	2423.23

Table 7 – Mass of defatted C. *papaya* seed biosorbent for the removal of various percentages of 100 mg/L Cd^{2+} from various volumes of aqueous solutions.

Volume (L)	95% Removal	90% Removal	85% Removal	80% Removal	70% Removal
	Mass of defatted C. *papaya* seed adsorbents (kg)				
1000	9.83	6.14	4.55	3.60	2.47
2000	19.66	12.29	9.10	7.21	4.94
3000	29.49	18.43	13.65	10.81	7.42
4000	39.32	24.58	18.20	14.41	9.89
5000	49.15	30.72	22.75	18.02	12.36
6000	58.98	36.86	27.30	21.62	14.83
7000	68.81	43.01	31.85	25.22	17.30
8000	78.64	49.15	36.40	28.82	19.77
9000	88.47	55.29	40.95	32.43	22.25
10,000	98.30	61.44	45.50	36.03	24.72
1,000,000	9829.74	6143.88	4549.51	3603.07	2471.87

liquid to that adsorbed by the adsorbents. The mass balance for the adsorption system in Fig. 9 can be written as:

$$V(C_0 - C_1) = M(q_0 - q_1) = Mq_1 \qquad (9)$$

Under equilibrium conditions,
$C_1 \rightarrow C_e$ and $q_1 \rightarrow q_e$

From adsorption studies and from model results in this work it was observed that Freundlich model gave better robust fit to equilibrium data. On this basis, Freudlich isotherm equations was used in the designed of the amount of defatted C. *papaya* seed biosorbent required to remove a certain percentage of metal ion from various volumes of wastewater.

The equations include:

For Freundlich isotherm

$$\frac{M}{V} = \frac{(C_o - C_e)}{q_1} = \frac{(C_o - C_e)}{q_e} = \frac{(Co - Ce)}{k_f C_e^{1/n}} \qquad (10)$$

Figs. 10 and 11 show the plot for the predicted amount of defatted C. *papaya* seed biosorbent required to remove certain percentage of 100 mg/L of Pb^{2+} or Cd^{2+} from specific volumes of wastewater solutions in a single-batch adsorber. For example to remove 95% of 100 mg/L Pb^{2+} from 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 m^3 aqueous solution using defatted C. *papaya* seed biosorbent, requires 8.65, 17.31, 25.96, 34.61, 43.27, 51.92, 60.58, 69.23, 77.89, 86.54 and 8654.08 kg of defatted C. *papaya* seed biosorbent (Table 6). For adsorption of Cd^{2+} under same adsorption conditions it is 9.83, 19.66, 29.49, 39.32, 49.15, 58.98, 68.81, 78.64, 88.47, 98.30, 9829.74 kg of defatted C. *papaya* seed biosorbent (Table 7).

4. Conclusion

The use of a new biosorbent, defatted C. *papaya* seeds, in the adsorption of Pb^{2+} and Cd^{2+} gave an adsorption capacity of 1666.67 mg/g and 1000.00 mg/g respectively. The adsorption of both metal ions was found to be highly feasible, spontaneous and exothermic in nature. The adsorption of both metal ions was found to approach equilibrium in ≈20 min of contact time. Its exceptionally high adsorption capacity suggests the strong potential of this biosorbent in the removal of metal ions from aqueous solution.

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