

Original Research Article

Biosorption of Cd²⁺ from aqueous solution using Papaya (*Carica papaya*) seed: Equilibrium and Kinetic studies

¹Kabir. A. Sanusi, ²Babayo A. Umar and ³Sayed Abdullahi

Abstract

^{1,2}Faculty of Science, Department of Chemical Sciences, Federal University Kashere, Gombe State

²School of Prelim and Gen. Studies, Dept. of Social Sciences, Federal Polytechnic Mubi, Adamawa State

*Corresponding Author's E-mail: adebayokabir@gmail.com

Biosorption of Cd (II) ions onto raw biomass of the Papaya (*Carica papaya*) seed has been studied using the batch equilibrium adsorption method. The sorption characteristics of the adsorbent were investigated under various experimental conditions, such as pH, contact time, concentration of Cd (II), sorbent mass and temperature. The FT-IR analysis showed that likely functional groups responsible for the adsorption are carboxyl, carbonyl, amides and hydroxyl groups. The pH for optimum adsorption is 5.0. Equilibrium data fit well to the Langmuir isotherm. The estimated maximum adsorption capacity was found to be 63.58 mg/g at 308 K and 90.95 mg/g at 328 K. The kinetic data obeyed the pseudo second-order model. Taking into account its good adsorption capacity, ease of sample treatment, as well as availability, the biomass of *Carica papaya* seed is a promising cost-effective biosorbent for Cd²⁺ removal from aqueous environment.

Keywords: Biosorption, Papaya seed, cadmium, equilibrium, kinetics, isotherm, adsorption capacity

INTRODUCTION

Virtually every industrial activity utilizing heavy metals in their production process introduces metal ions into the environment via their effluents or waste. These industrial processes include: electroplating, plastic manufacturing, mining, paint pigment production, alloy preparation, lead, silver, cadmium, and cadmium-nickel batteries manufacture, and metallurgical practices. These industrial activities have introduced metals such as copper (Cu), nickel (Ni), lead (Pb), mercury (Hg), chromium (Cr), zinc (Zn) and cadmium (Cd) and many others into the environment at levels which are above the permissible levels. The health hazards posed by many of these metals have been previously investigated and documented (Olu-Owolabi et al. 2012b).

Cadmium is one the toxic elements listed by The Agency for Toxic Substances and Disease Registry (ATSDR). Cadmium is highly toxic non-essential metal which accumulates in the kidneys of mammals and can cause kidney dysfunction. Cadmium may interfere with

the metallothionein's ability to regulate zinc and copper concentrations in the body. Epidemiological studies have revealed that Cd²⁺ may contribute to some forms of cancer in humans and low exposures may result in kidney damage (Al-Ashimi and Al-Shafar, 2013).

Several technologies are presently been utilized for the removal of these metals from industrial wastewater in order to prevent their release into the environment. Conventional technologies used include: chemical precipitation, coagulation, chemical/electrochemical reduction, solvent extraction, and electrolysis (Olu-Owolabi et al., 2012a). But these techniques are limited by techno-economic consideration as well as environmental friendliness. Some of these methods do not possess removal efficiencies which are sufficient for meeting the ever increasing environmental requirements been set by regulatory bodies. Also, the possibility of secondary contamination from concentrated sludge and other secondary pollutants is a subject of concern when

utilizing these conventional techniques. The ability of biomaterials to remove heavy metals through biosorption has proved to be highly efficient, easy to handle, environment-friendly, and economically feasible. This has attracted plenty of attentions in recent years because biomaterials are: (i) available in abundance and cheap, (ii) easy to obtain and process, and (iii) available as waste type or nuisance (Olu-Owolabi et al., 2012b).

Thus, extensive research has been directed to the investigation of low cost materials such as agricultural and industrial waste or by-products for the removal of heavy metals. These materials include: rice husk (Das and mondel, 2011), soya bean hulls, cotton seed hulls, rice straw, sugarcane bagasse (Marshall and Champagne, 1995), grape bagasse (Hafne et al., 2008), coconut shell and husk (Harneed, 2010), mango peel (Iqbal et al, 2009), petiolar felt sheath of palm (Iqbal et al., 2002), maize barn (Singh et al., 2006), cocoa pod (Olu-Owolabi et al., 2012a) and moss plant (Olu-Owolabi et.al., 2012b). However, some major limitations of these biosorptions are that some of them have not yielded satisfactory results (high metal adsorption capacity) and others that yielded good results may not locally be available.

Nigeria is the world's 7th largest producer of *Carica papaya* seed (350,000 metric tons per annum in 2009) (ICO, 2011). As domestic waste, they are commonly found in refuse dumps where they attract flies and rodents, which can be regarded as unsightly, environmentally undesirable and a non-productive use of resources. After industrial processing of the fruits, considerable amounts of papaya seeds are discarded as waste (Norhafzah et al., 2011). Due to challenges facing the proper disposal of agricultural waste, *Carica papaya* (pawpaw) seed as with several other agricultural by-products have been identified as an environmental problem in Nigeria and some other African countries like Ghana and Codevoire (Horsfall et al., 2004). Studies by Egila et al. (2011) identified *Carica papaya* seed (CPS) as a promising biosorbent for metal removal from highly acidic solutions.

There has been no reported work on Cd²⁺ removal from aqueous solution using the *Carica papaya* seed (CPS). Studies by Egila et al. (2011) and Ong et al. (2010) identified *Carica papaya* seed (CPS) as a promising biosorbent for metal removal from highly acidic solutions. This may be an indication of the ability of the papaya seed biomass to equally adsorb Cd²⁺ from aqueous solution. Since CPS is abundantly available at no cost, and Cd²⁺ pollution of surface waters is a major international challenge, the CPS was investigated for the development of a CPS-based procedure for the removal of Cd²⁺ from aqueous solution.

In this study, the sorption behavior of Cd²⁺ from aqueous solution using CPS was studied under various conditions; contact time, solution pH, temperature and sorbent dose, and sorbate concentration, with the aim of

determining the mechanism for the removal of Cd²⁺ from aqueous solution by *Carica papaya* seed (CPS).

METHODOLOGY

Sampling, pre-treatment and characterization of biosorbent material

The *Carica papaya* seed was obtained in February 2013 from Igboho (18°34'18" W; 18°46'25"S), Oyo State, Nigeria; washed severally with tap water and deionized water to remove impurities, then air-dried, ground, sieved through a 0.5 mm mesh size sieve, and the sieved particles were used for the study. This was called the raw PS (CPS). The Specific Surface Area (SSA) of the sample was determined using the methods of Sears (1956) and Iler (1978). The bulk density and specific gravity of the CPS sample was determined as described by Olu-Owolabi et al. (2012a). The pH at the point zero charge (pH PZC) was determined as described by Unuabonah et al. (2008). The determination of RBL surface properties is necessary because the particle sizes are most likely heterogeneous and these properties aid in estimating the degree of metal sorption. The SSA of CPS has been determined as 25.352 m²/g, while the bulk density and specific gravity are 0.625 g/cm³ and 0.194 g/cm³, respectively. The pH PZC value is 7.01. This is important because it marks the pH where the surface functional groups do not contribute to the pH of the solution, and in an applied electric field, the electrophoretic mobility of the particles would be zero (Sposito, 1989).

The Fourier Transform Infrared (FTIR) spectra of the CPS biosorbent were obtained using Perkin Elmer Spectrum 1 FTIR spectrophotometer. About 0.1 g of the processed dry CPS biosorbent in powder form along with KBr were ground into fine particles and pressed to make pellets with was used to obtain the FT-IR spectrum in the scanning frequency from 4500 to 500 cm⁻¹.

Biosorption procedures

The synthetic metal ion (Cd²⁺) solution was prepared from Anala R grade $CdCl_2 \cdot 2\frac{1}{2}H_2O$. A stock solution of 1000 mg/L was prepared by dissolving 2.0319g of the salt 200cm³ in distilled water and then made up to mark in a 1L standard volumetric flask. Working solutions of various concentrations were prepared from this stock solution as required.

Replicate batch experiments were used to determine metal sorption capacity of the biomass in 60 mL polyethylene bottles by contacting approximately 1.0 g of the CPS biomass with 20 mL of metal solution, except where otherwise stated, for determining effect of pH, time, and temperature and sorbate concentration. The

sorbent-sorbate mixtures were shaken on a mechanical shaker during the course of the adsorption experiment and concentrations of metal in the filtrate solutions were determined using the Buck Scientific 205 Atomic Absorption Spectrometer (AAS) with air-acetylene flame on absorbance mode.

The quantity of metal adsorbed by CPS after each specified incubation period was calculated using the following equation:

$$q_e = \frac{(C_o - C_e)V}{M} \quad 2.1$$

where; C_o and C_e are the initial and equilibrium sorbate concentrations in solutions; q_e , V and M are the amount of sorbate adsorbed (mg/g), volume of the solution (mL) used for incubation and mass (g) of sample, respectively. To obtain insights into the surface properties and degree of affinity of CPS, sorption data were tested against the Langmuir and Freundlich equilibrium isotherms using the linear forms of these models in Eqs. (2.2) and (2.3).

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad 2.2$$

$$\text{Freundlich: } \log q_e = \log K_f + n \log C_e \quad 2.3$$

where; Q_o is the maximum adsorption capacity per unit weight of sorbent, b is a solute-surface interaction energy-related parameter, while q_e and C_e are the amount of solute adsorbed per unit mass of the adsorbent (mg/g) and equilibrium metal concentrations in the solution (mg/L); where K_f and n are the Freundlich model capacity factor and the isotherm linearity parameter, respectively.

In describing the kinetics of the biosorption, the pseudo-first-order, pseudo-second-order, Elovich, and Intra-particle diffusion models have been applied to the biosorption data. The Lagergren pseudofirst-order and pseudo second-order rate equations (Lagergren, 1898) were tested using their simplified equations in (2.4) and (2.5) respectively:

$$\log (q_e - q_t) = \log q_e - (k_1 t / 2.303) \quad 2.4$$

Where q_e and q_t are the amounts of metals sorbed (mg/g) at equilibrium and at time t , respectively; and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). The q_e and rate constants k_1 were calculated from the slope and intercept of the plot of $\log (q_e - q_t)$ vs. t .

$\frac{t}{q_t} = (1/K_2 q_e^2) + (t/q_e) \quad 2.5$
Where k_2 is the rate constant of pseudo-second-order sorption. The pseudo-second-order rate constants k_2 and q_e values were calculated from the slope and intercept of the plots t/q vs. t .

The Elovich model equation (Demirbas et al., 2004) in Eq. (2.6) was used.

$$Q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad 2.6$$

where a is the initial adsorption rate (mg/g/min) and b is the desorption constant (g/mg) during any one experiment.

The linearized form of the intra-particle diffusion model equation (Ofomaja et al., 2009) was used as shown in Eq. (2.7).

$$\log R = K_{id} + \alpha \log (t) \quad 2.7$$

Where R is percentage metal ion adsorbed, t is contact time, α is gradient of linear plots and depicts the adsorption mechanism, K_{id} is intra-particle diffusion rate constant (h^{-1}).

RESULTS AND DISCUSSION

Fourier Transform Infrared (FT-IR) spectroscopy

FT-IR spectra of unloaded CPS biomass showed several absorption peaks between the scanning frequency range of 4000-500 cm^{-1} (Figure 1). The broad band around 3379 cm^{-1} is indicative of the stretching band of the carbonyl double bond from carboxylic acids and their salts, a stretching vibration of free hydroxyl functional groups of the aromatic and aliphatic origin and possibly N-H stretch of amides. Also, the numerous free hydroxyl groups in the polysaccharide structure of its wall may explain the presence of the band. The two sharp absorption bands at 2923 and 2854 cm^{-1} are indicative of C-H stretch likely from aliphatic (alkane and methylene) groups. The sharp band at 1747 cm^{-1} is characteristic of the C=O stretch of carbonyl double bond either from free or esterified carboxyl groups. However, a distinct absorption band at 1651 cm^{-1} has been assigned to amide-I of protein secondary structures. A peak at 1161 cm^{-1} indicates the presence of -SO₃H group stretching vibration. The strong band around 1087 cm^{-1} is due likely to the C-OH bond and -C-C- stretchings, which are characteristic for polysaccharides. Similar observations have been reported by Pehlivan *et al.* (2007), Olu-Owolabi *et al.* (2012b), and Unuabonah *et al.* (2013).

Effect of pH on adsorption

pH is an important biosorption parameter because it affects the activities of functional groups present on the surface of the biosorbent which are responsible for adsorption, and affects competitive adsorption of ions to sorption sites (Olu-Owolabi *et al.*, 2012b). Establishing the capacity of CPS as new biosorbent material for Cd²⁺ requires knowing the optimum pH for adsorption. This was determined by equilibrating the sorbent-sorbate mixture containing 300 mg/L of Cd²⁺ at pH values between 3 and 8. Thus, various biosorbents have various optimum sorption pH for different metals.

As shown in Figure 2, the uptake of Cd²⁺ ions is pH dependent. At the low pH value of 3.0, CPS adsorbed

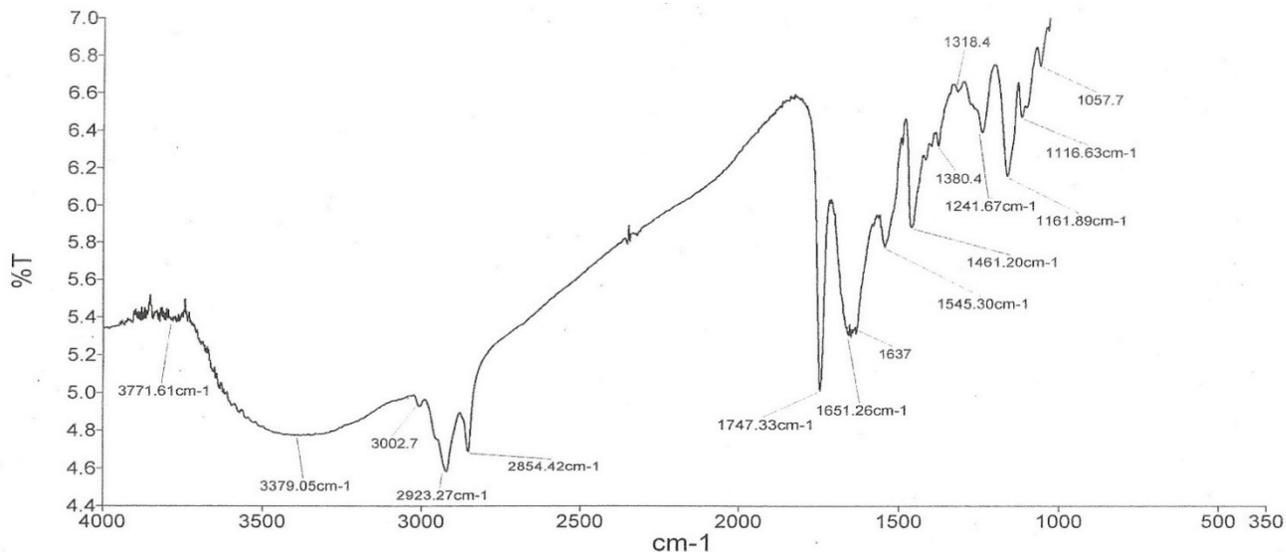


Figure 1. FT-Infra-red Spectra of *Carica papaya* seed adsorbent (CPS)

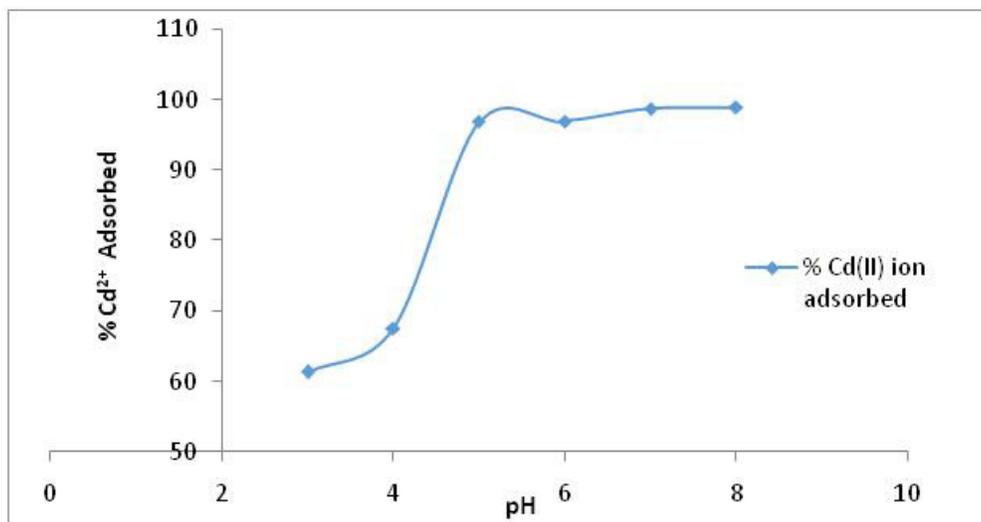


Figure 2. The effect of pH on the adsorption of Cd^{2+} onto *Carica papaya* seed (CPS).

lower amount (58.4 mg/g or 61.3%) of Cd^{2+} onto its surface active adsorption sites. With increase in solution pH, the quantity adsorbed increased steadily until pH 5.0 (73.2 mg/g or 96.91%) and 6.0 (74.8 mg/g or 96.96%) where the quantities of Cd^{2+} adsorbed made a plateau on the graph before precipitation of Cd^{2+} ions set in. In summary, steady increment in adsorption was observed from pH 3.0 to 5.0, indicating that more Cd^{2+} ions were adsorbed on CPS surfaces as pH increased. Then adsorption reached a plateau between pH 5.0 and 6.0. The optimum pH for adsorption of Cd^{2+} was recorded at pH 5.0. Above this pH, there was an apparent increase in adsorption of Cd^{2+} . This has been attributed mainly to solvation and hydrolysis of Pb^{2+} ion products leading to precipitation of Cd^{2+} from solution. In aqueous solutions

of pH less than 5, Cd^{2+} ions exist as either Cd^{2+} or $\text{Cd}(\text{OH})^+$ or both. However, the formation of Cd^{2+} hydrolysis products begins to occur at pH values between 5 and 6, and this brings about precipitation. Due to this reason all the experiments were carried out at pH 5.

Adsorption kinetics

The efficiency of CPS to remove Cd^{2+} metal from solution can be assessed by the rate of Cd^{2+} adsorption, and may be linked to its efficiency to cleanup waste water. The effect of time (15, 30, 60, 180, 360, and 1440 min) on Cd^{2+} sorption was determined by equilibrating the CPS-sorbate aliquot at pH 5.0 using 300 mg/L Cd^{2+} solution.

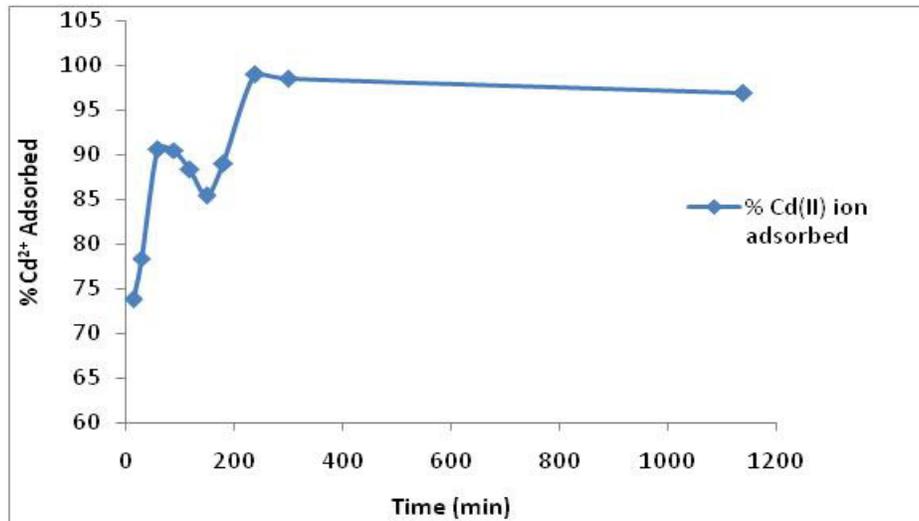


Figure 3. The effect of time on the adsorption of Cd^{2+} onto *Carica papaya* seed (CPS).

Table 1. Adsorption Kinetics

Model	Calculated Parameters	Experimental Values	r
Pseudo-first-order	$q_e = 23.65\text{mg/g}$ $K_1 = 0.0095\text{g/mg/min}$	$q_e = 78.15\text{mg/g}$	0.858
Pseudo-second-order	$q_e = 78.65\text{mg/g}$ $K_2 = 0.0032\text{g/mg/min}$	$q_e = 78.15\text{mg/g}$	0.989
Elovich	$q_e = 65.73\text{mg/g}$ $\beta = 0.19$	$q_t = 78.15\text{mg/g}$	0.823
Interparticle diffusion	$R = 80.36\%$ 0.091 $K_{id} = 1.645$	$R = 76.15$	0.702

From the adsorption rate curve (Figure 3), it was observed that Cd^{2+} adsorption was rapid and nearly completed in 60 min with 90.45% (88.92 mg/g) of the total Cd^{2+} in solution adsorbed. As time elapsed, there was little or no adsorption until after 240 min when the percentage of Cd^{2+} adsorbed increased to 90.10% (87.6 mg/g). This trend of adsorption may be explained thus: the initial rapid increase in Cd^{2+} uptake is due to the fact that a large number of vacant CPS surface sites are available for adsorption during the initial stage and since these have very high affinity for Cd^{2+} , they are filled rapidly; after this initial rapid adsorption, the remaining vacant surface sites become very difficult to occupy due

to the repulsive forces between the solute molecules on the solid and bulk phases. This result has shown that the breaking of these repulsive forces barrier and further adsorption are time dependent as seen after 240 min. Hence, the time required to attain a rapid equilibrium is 60min. However, a contact time of 240 min has been employed for every other study because of this possibility of further adsorption. Similar trend was observed by Jimoh *et al.* (2011) and Olu-Owolabi *et al.* (2012b).

Four kinetics models have been used to test the mechanism that controlled the sorption process: the pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion models. Table 1 showing the

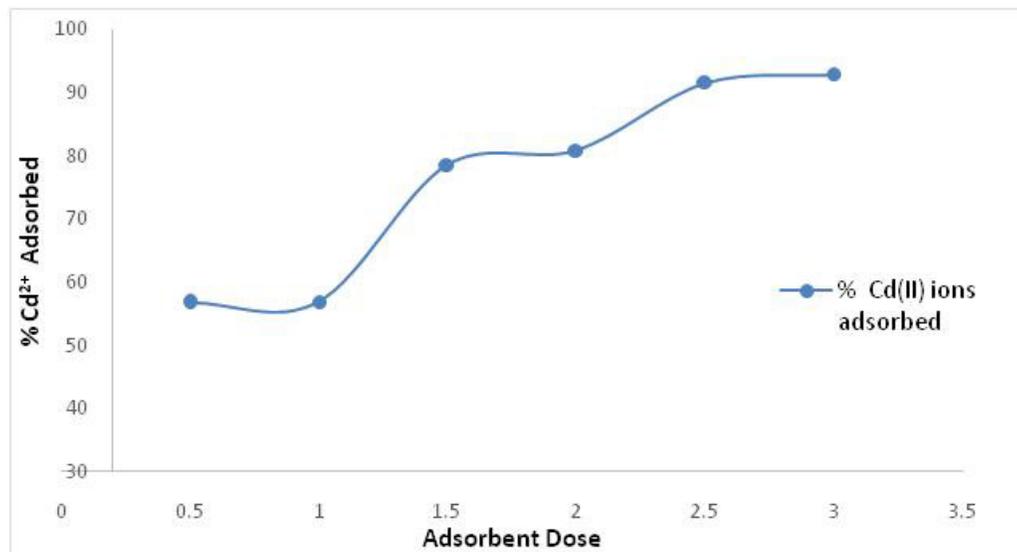


Figure 4. The effect of varying biosorbent dose on the adsorption of Cd²⁺ onto *Carica papaya* seed (CPS).

comparative fits of the various models indicate that the kinetics data fit the pseudo-second-order kinetics better than for pseudo-first-order kinetics because the r^2 value as well as the experimental q_e value of the pseudo-second-order is better correlated implying that Cd²⁺ adsorption is controlled by chemisorption involving sharing or exchange of electrons between sorbent and sorbate (Feng et al., 2011). Intra-particle diffusion and Elovich models gave further insight into the kinetics models. Elovich curve, which did not pass through the origin (figure not shown), indicates there is some degree of boundary layer control. The linear intra-particle model also suggests that intra-particle diffusion is not the rate-controlling step (Olu-Owolabi et al., 2012b).

Effect of adsorbent dose

The effect of adsorbent dose on adsorption was evaluated by equilibrating the sorbent-sorbate mixture with 300 mg/L of Cd²⁺ at pH 5.0 using varying masses in the range of 0.5–3.5 g. It was observed (Figure 4) that increasing the biomass dosage from a range 0.5 g through 3.50 g increased the percentage of Cd²⁺ removal from aqueous solution from 56.78% to over 92.90%, while on the other hand, the equilibrium adsorption capacity, q_e , per mass of CPS was found to decrease (89.25–19.43 mg/g) with increase biomass dose. Similar reports are found in literature (Ofomaja et al., 2009). It is apparent that by increasing the amount of CPS, available sorption sites for sorbent-solute interaction is increased due to increased available surface negative charges and decrease in the electrostatic potential near the CPS surface which favors sorbent-solute interaction; hence,

leading to the noticed increased percentage Cd²⁺ removal from the aliquot solution. Unuabonah et al. (2008) have attributed the q_e decrease with increasing mass to the decreasing total surface area of the adsorbent and an increase in diffusion path length due to aggregation of CPS particles, and as the weight of the CPS increased, the aggregation becomes increasingly significant.

Adsorption isotherms and thermodynamics

The effects of sorbate concentrations and temperature on adsorption were done using varying Cd²⁺ concentrations between 100 and 600 mg/L at $35 \pm 2^\circ\text{C}$ and $55 \pm 2^\circ\text{C}$. Results (Figure 5) show that increase in reaction temperature from 308 to 328K, did not seem to affect amount of Cd²⁺ adsorption onto the surface of RBL at lower concentrations until maximum sorption which occurred at 400 mg/L of Cd²⁺ concentration in solution. Then increase in temperature led to an increase in the amount of Cd²⁺ metal adsorbed (from 77 mg/g to 90 mg/g) as concentration of the metal increased from 400 mg/L to 500 mg/L, while there was no noticeable change in amount of Cd²⁺ metal adsorbed at 298 K. Thus, temperature enhanced the reactions between of Cd²⁺ ions and the CPS surface functional groups. However, further increase in Cd²⁺ concentration at the higher temperature did not cause any increase in adsorption. Thus, to increase rate and efficiency of adsorption of Cd²⁺ on CPS as well as reduce the effect of the repulsive forces discussed in Section 3.3, high reaction temperature is recommended.

Langmuir and Freundlich adsorption isotherms (Table 2) were used to assess the CPS adsorption capacity and

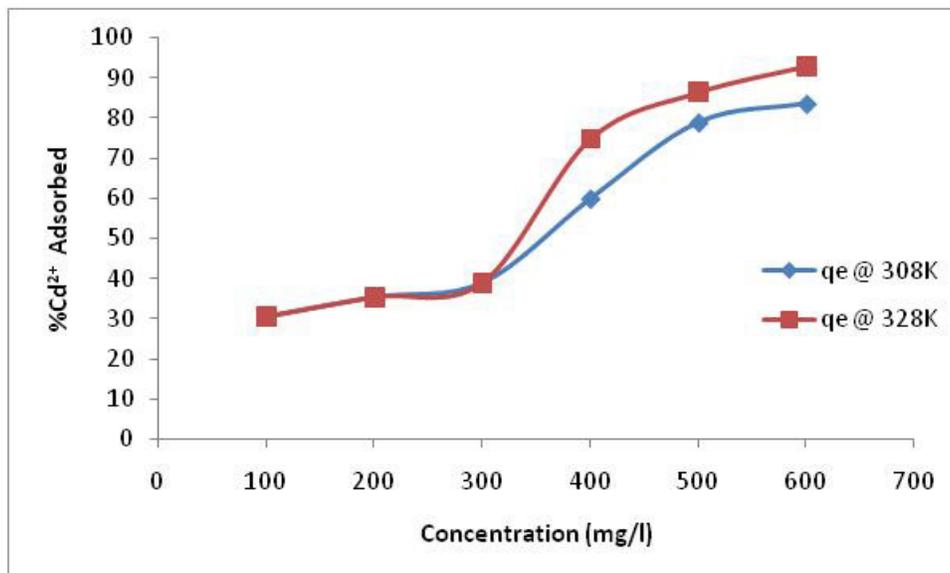


Figure 5. The effect of initial sorbate concentration on the adsorption of Cd²⁺ onto *Carica papaya* seed (CPS).

Table 2. Adsorption Isotherm Parameters

Isotherms	Calculated	Experimental	r ²	r ²
	Parameters	Values	308 ⁰ K	328 ⁰ K
Langmuir	Q ₀ = 63.58mg/g @ 308 ⁰ K	q _e = 70.21mg/g	0.993	0.858
	Q ₀ = 90.95mg/g @ 328 ⁰ K	q _e = 89.81mg/g		
	b = 0.195g/mg/min			
Freundlich	n = 16.13 @ 308 ⁰ K	q _e = 78.15mg/g	0.989	0.99

n = 7.58 @ 328⁰K
 K_f = 49.66 @ 308⁰K
 K_f = 49.66 @ 308⁰K

surface sorption properties. Langmuir isotherm, which is based on the assumption that all sites possess equal affinity for the sorbate while forming a sorbate monolayer on the biosorbent surface at saturation, gave better fit to the sorption data than the Freundlich model which assumes sorption on heterogeneous surfaces (Hameed, 2010). The estimated monolayer adsorption capacity (Q₀) is 63.58mg/g and 90.95 mg/g at 308 K and 328K respectively.

CONCLUSION

The ability of *Carica papaya* seed biosorbent to remove Cd²⁺ from aqueous solution was investigated in equilibrium, kinetics and thermodynamics studies. The

results obtained show that the biomass of *Carica papaya* seed has an optimum pH for Cd²⁺ adsorption at 5.0, nearly attains maximum adsorption within 1 h at 308 K, and obeys the pseudo-second order kinetics with an exothermic reaction. Adsorption increased with increase in temperature. The Langmuir isotherm described the equilibrium data better than other isotherms indicating adsorption is monolayer with monolayer adsorption capacity of 63.58 mg/g at 308 K and 90.95 mg/g at 328 K. The FT-IR analysis showed that possible functional groups responsible for metal adsorption are carboxyl, carbonyl, amides, hydroxyl and possibly other smaller groups that cannot be identified using only FT-IR spectra. Taking into account its good adsorption capacity, ease of sample treatment, as well as availability, the biomass of *Carica papaya* seed is a promising cost-effective

biosorbent for Cd²⁺ removal from aqueous environment.

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