



## Sorption of Hg(II) onto *Carica papaya*: Experimental studies and design of batch sorber

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### ABSTRACT

A novel sorbent, *Carica papaya*, was evaluated for sorption of Hg(II) from aqueous solution under the varying conditions of contact time, metal ion concentration, sorbent dose and pH. The results indicate that sorption equilibrium was established in about 120 min. The Hg(II) sorption was strictly pH dependent, and maximum removal was observed at pH 6.5. The sorption interaction of Hg(II) onto *C. papaya* obeyed the pseudo-second order rate equation. The batch biosorption rate for the system based on an intraparticle diffusion rate parameter derived from the plots of Hg(II) sorbed versus the square root of time indicated that the adsorption mechanism was predominantly intraparticle diffusion but there was also a dependence on pore size as the Hg(II) diffuses through macro-, meso-, and microspores. The sorption isotherm data provided a very good fit to the Langmuir isotherm equation with a monolayer sorption capacity of 155.6 mg g<sup>-1</sup> and the regression coefficient ( $R^2$ ) 0.9959 with low S.E. and SSE values. A design procedure was proposed using the Langmuir isotherm to design a two stage sorption system to minimize the amount of biomass required for the treatment of Hg(II) solution using *C. papaya*. Desorption studies indicated that the maximum percent recovery of Hg(II) was 96.7 ± 0.80 with 0.1 N HCl and 99.0 ± 0.49 with 1% KI.

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## 1. Introduction

Aqueous heavy metal pollution represents an important environmental problem due to its toxic effects and accumulation throughout the food chain. Mercury is generally considered to be one of the most toxic metals found in the environment. Mercury causes damage to the central nervous system and chromosomes, impairment of pulmonary function and kidney, chest pain and dyspnoea. The major sources of mercury pollution in the aquatic environment are industries such as chloralkali, paint, pulp and paper, oil refining, electrical, rubber processing and fertilizer [1,2]. Elevated levels of mercury in waters from anthropogenic emission sources have also been documented, indicating that the atmospheric transport and deposition is an important source of contamination [3]. In the environment, mercury is found in its elemental form and in various organic compounds and complexes. One of the most toxic mercury chemical species is mercury dichloride (HgCl<sub>2</sub>) because this substance easily forms organomercury

complexes with proteins [4]. The most frequently used methods for preconcentration of mercury from natural waters are those employing columns on which chelating agents have been immobilized, solvent extraction, electrochemical precipitation and solid phase extraction [5]. However, the application of such processes is often restricted because of technical and/or economic constraints.

Adsorption as a wastewater treatment process has been found to be an economically feasible alternative for metal removal. Activated carbon is one of the most well known adsorbents [6–8] but the high cost of the process has limited its use. A search for a low-cost and easily available adsorbent has led to the investigation of materials of biological origin as potential metal biosorbents. Biosorption is becoming a potential alternative to the existing technologies for the removal and/or recovery of toxic metals from wastewater [9–12].

Successful metal biosorption has been reported by a variety of biological materials including, micro algae and seaweeds, bacteria, fungi and crop residues [13–15]. One category of biowastes on which little attention has been paid as low-cost metal biosorbents is the woody plant wastes. The few reported cases include pine bark and needles [16], ground-up tree fern [17], petiolar felt-sheath of palm [18] and papaya wood [19,20]. Also, there is a lack of detailed critical analysis for the sorption of metals onto these biosorbents even though high sorption capacities have been obtained in several

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**Nomenclature**

$C_i$	metal concentration at the solid/liquid interface ( $\text{mg L}^{-1}$ )
$C_0$	initial concentration of adsorbate in solution ( $\text{mg L}^{-1}$ )
$C_n$	equilibrium concentration in $n$ th stage sorption system ( $\text{mg L}^{-1}$ )
$C_{n-1}$	initial concentration in $n$ th stage sorption system ( $\text{mg L}^{-1}$ )
$h$	initial biosorption rate in pseudo-second model ( $\text{mg g}^{-1} \text{min}^{-1}$ )
$k_1$	Lagergren's rate constant ( $\text{min}^{-1}$ )
$k_2$	pseudo-second order biosorption rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ )
$K_1$	intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-0.5}$ )
$K_2$	intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-0.5}$ )
$K_3$	intraparticle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-0.5}$ )
$K_F$	Freundlich isotherm constant ( $\text{L g}^{-1}$ )
$K_L$	Langmuir isotherm equilibrium binding constant ( $\text{L mg}^{-1}$ )
$n$	exponent in Freundlich isotherm
$q_e$	equilibrium sorption capacity ( $\text{mg g}^{-1}$ )
$q_i$	observed sorption capacity of batch experiment $i$
$q_{\text{max}}$	maximum sorption capacity ( $\text{mg g}^{-1}$ )
$q_t$	sorption capacity at time $t$ ( $\text{mg g}^{-1}$ )
$Q_i$	estimated sorption capacity of batch experiment $i$
$R_L$	Langmuir separation factor
$R^2$	regression coefficient
S.E.	standard error
SSE	sum of squares error
$t$	biosorption time (min)
$V$	volume of metal solution (L)
$W$	mass of sorbent (g)
$W_1$	mass of sorbent required in stage 1 (g)
$W_2$	mass of sorbent required in stage 2 (g)

cases. The present work relates to sorption properties of papaya wood, which is generated as a waste in papaya plantations and has otherwise no commercial value, for Hg(II) removal and recovery. The aim of the present work was to study the biosorption capacity of *Carica papaya* for the removal of Hg(II) from aqueous solution under different experimental conditions and the evaluation of their performance using kinetics and isotherms. For these purposes, the removal capacity, desorption efficiency and various factors affecting the sorption, such as contact time, initial pH of the solution and metal concentration, were investigated with the batch equilibration technique.

## 2. Materials and methods

### 2.1. Preparation of sorbent

Papaya (*C. papaya*) wood was obtained from the felled trunk of matured trees. The trunk was debarked, cut into small pieces ( $2 \text{ cm} \times 2 \text{ cm}$ ), soaked in boiling water for about 45 min, thoroughly washed under tap water, and left for 3–4 h in distilled water, changed 4–5 times. The washed wood pieces were ground into fibers (diameter: 0.005–0.02 cm; length: 0.2 cm) and oven dried at  $80^\circ\text{C}$  and used for sorption studies. Major chemical constituents

of the papaya wood are  $4.96 \pm 0.68\%$  protein,  $30.11 \pm 2.67\%$  crude fiber and  $5.92 \pm 1.02\%$  mineral ash, and the crude fibre comprises lignin and cellulose, indicating the presence of high amounts of hemicellulose and attached polysaccharides.

### 2.2. Sorption experiments and analytical method

A 1.354 g of mercuric chloride ( $\text{HgCl}_2$ ) was dissolved in 1 L of distilled water to obtain a stock solution having  $1000 \text{ mg L}^{-1}$  of Hg(II). The stock solution was diluted to obtain test solutions of desired strength. The effect of pH on biosorption was investigated in the pH range of 2–9 with initial Hg(II) concentration of  $200 \text{ mg L}^{-1}$  and solid to liquid ratio of  $1.0 \text{ g L}^{-1}$ . The pH of the solution was adjusted with 0.1 N HCl or NaOH. The effect of biomass concentration on the removal of Hg(II) at  $200 \text{ mg L}^{-1}$  concentration was studied employing 0.05, 0.1, 0.5, 1, 2, 3 and  $5 \text{ g L}^{-1}$  of biomass. After attaining equilibrium, the aqueous phases were separated from the biosorbent by filtration through 0.45 mm Whatman filter paper and the concentration of Hg(II) ions in the filtrate was determined.

Kinetic studies of Hg(II) sorption by the *C. papaya* were accomplished to estimate the time necessary to reach the sorption equilibrium. The experiments were carried out in continuously stirred (200 rpm) beakers, adding 0.1 g of dried biomass into 100 mL of solutions ( $120, 160$  and  $200 \text{ mg L}^{-1}$  of Hg(II)). The pH (6.5) of the solution monitored continuously during the kinetic experiments with a pH electrode and adjusted with  $\text{HNO}_3$  or NaOH solution, if deviations were observed. Samples (5 mL) were taken out at predetermined time intervals, filtered and the filtrates stored for Hg(II) analysis.

Batch equilibrium sorption experiments were carried out at room temperature ( $30 \pm 2^\circ\text{C}$ ) in 250 mL Erlenmeyer flasks containing mercuric chloride solutions (100 mL) of known concentrations, which varied from 40 to  $240 \text{ mg L}^{-1}$ . Accurately weighed 0.1 g of biomass was added to each flask and the mixtures were agitated on the rotary shaker. The solution pH (6.5) was adjusted to the required value by using  $\text{HNO}_3$  or NaOH. After 24 h of agitation, which is more than sufficient time required for equilibrium, the solution was separated from the biomass by membrane filtration. The change in Hg(II) concentration due to sorption was determined with spectrophotometer (Shimadzu UV-1201). The formation of a pink colored product when rhodamine 6G is treated with tetraiodomercurate(II) is used to determine mercury ( $10\text{--}50 \mu\text{g}$ ) in a final volume of 50 mL. It is reported that the reaction occurs instantly over the pH range of 1–7 and when the system is stabilized with gelatin, the absorbance remains unchanged at 575 nm for minimum 24 h [21].

All the biosorption experiments were repeated twice to confirm the results. The data were the mean values of two replicate determinations. Control experiments, processed without the addition of biosorbent, confirmed that the sorption of metals on the walls of glass flasks or in the filtration systems was negligible.

### 2.3. BET analysis

The surface area, pore volume and pore size of *C. papaya* were measured by surface area analyzer (Micromeritics, ASAP 2010) and were presented in Ref. [20].

### 2.4. FTIR studies

Infrared spectra of unloaded and Hg(II) loaded biomass of *C. papaya* was obtained using a Fourier Transform Infrared Spectrometer (FTIR GX 2000, PerkinElmer). For the FTIR study, 30 mg of finely ground biomass was palletted with 300 mg of KBr (Sigma) in order to prepare translucent sample disks.

### 2.5. Desorption and regeneration

The mercury loaded sorbent was separated and gently washed with deionized water to remove any unadsorbed Hg(II). The Hg(II) loaded sorbent samples were desorbed by agitating for 3 h with 100 mL of dilute HCl (0.1 N) or potassium iodide solution (1%) and desorption was determined at intervals of 30 min. The desorbed wood was washed and the regenerated biomass was used in five sorption–desorption cycles to determine reusability of the wood.

### 2.6. Hg(II) uptake capacities

The amount of Hg(II) sorbed at equilibrium,  $q_e$  ( $\text{mg g}^{-1}$ ), which represents the metal uptake, was calculated from the difference in metal concentration in the aqueous phase before and after sorption, according to the following equation:

$$q_e = \frac{V(C_i - C_e)}{W} \quad (1)$$

where  $V$  is the volume of Hg(II) solution (L),  $C_i$  and  $C_e$  are the initial and equilibrium concentration of Hg(II) in solution ( $\text{mg L}^{-1}$ ), respectively and  $W$  is the mass of dry sorbent (g).

### 2.7. Non-linear regression analysis

All the constants in kinetic as well as isotherm models were evaluated by non-linear regression using DATAFIT® software (Oakdale Engineering, USA). The optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the equation to the experimental data [22]. Apart from the correlation coefficient ( $R^2$ ), the sum of squares error (SSE) and the standard error (S.E.) of the estimate were also used to measure the goodness-of-fit. SSE can be defined as

$$\text{SSE} = \sum_{i=1}^m (Q_i - q_i)^2 \quad (2)$$

and S.E. can be defined as

$$\text{S.E.} = \sqrt{\frac{1}{m-p} \sum_{i=1}^m (Q_i - q_i)^2} \quad (3)$$

where  $q_i$  is the observation from the batch experiment  $i$ ,  $Q_i$  is the estimate from the isotherm for corresponding  $q_i$ ,  $m$  is the number of observations in the experimental isotherm and  $p$  is the number of parameters in the regression model. The smaller S.E. value indicates the better curve fitting.

## 3. Results and discussion

### 3.1. Effect of pH on Hg(II) sorption

The solution pH has been reported to be the most important variable governing the biosorption of metal ions by sorbents [15,23]. In order to establish the effect of pH on the sorption of Hg(II) ions onto *C. papaya*, batch equilibrium studies at different pH values were carried out in the range of 2.0–9.0. As seen from Fig. 1, the mercury uptake is small at low pH. Between pH values 3.0 and 7.0 the metal sorption increases sharply, attaining values that remain almost constant for pH values in the range of 7.0–9.0. The low metal sorption at pH below 3 may be explained on the basis of active sites being protonated, resulting in a competition between  $\text{H}^+$  and  $\text{M}^{2+}$  for occupancy of the binding sites [24]. A sharp increase in the sorption occurred in the pH range of 3.0–6.5 can be

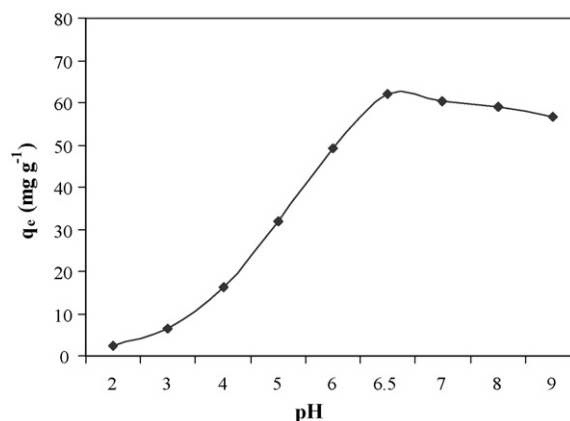


Fig. 1. Effect of pH on Hg(II) sorption onto *C. papaya* (initial Hg(II) concentration:  $200 \text{ mg L}^{-1}$ , contact time: 5 h, solid to liquid ratio (s/l):  $1.0 \text{ g L}^{-1}$ ).

explained as follows: at low pH values, excess  $\text{H}^+$  ions present in solution competes with Hg(II) ions for active sites leading to less Hg(II) removal.

However, when the pH was increased the concentration of  $\text{H}^+$  ions decreases, but the concentration of Hg(II) ions remains the same leading to increased uptake [25]. Further increase in sorption was insignificant as the optimum sorption reached at pH 6.5, when the pH was increased beyond 6.5, Hg(II) showed a trend of declining sorption. This may be attributed to the decreased solubility of Hg(II) at high pH.

### 3.2. Effect of solid/liquid ratio on sorption

The effect of the solid/liquid ratio (s/l) on the Hg(II) sorption is studied at room temperature and at pH 6.5. Various s/l ratios including 0.05, 0.1, 0.5, 1.0, 2.0, 3.0 and  $5.0 \text{ g L}^{-1}$  are used to determine the optimum quantity of biomass needed for maximum sorption, while keeping the volume and the initial concentration of the metal solution constant (figure not shown). From  $200 \text{ mg L}^{-1}$  Hg(II) ion solution, the bulk sorption was achieved with  $1.0 \text{ g L}^{-1}$  *C. papaya*. Further increment in sorbent dose did not cause significant improvement in sorption. This may be due to the binding of almost all ions to the sorbent and the establishment of equilibrium between the ions bound to the sorbent and those remaining unadsorbed in the solution. Different  $\text{Hg}^{2+}$ /biomass ratios were obtained by increasing the quantity of *C. papaya* biomass while the ion concentration and the solution volume was kept constant. The change in  $\text{Hg}^{2+}$ /biomass ratio with the quantity of mercury sorbed by *C. papaya* is given in Table 1. A decrease in  $\text{Hg}^{2+}$ /biomass ratio was linked with increase in the sorption of mercury because of increase in the sorption surface area of *C. papaya*. Goyal et al. [26] also obtained similar results.

Table 1

Effect of change in  $\text{Hg}^{2+}$ /biomass ratio on sorption at the constant initial Hg(II) concentration of  $200 \text{ mg L}^{-1}$ , pH 6.5

Biomass concentration ( $\text{g L}^{-1}$ )	$\text{Hg}^{2+}$ /biomass ratio	Hg(II) sorbed ( $\text{mg g}^{-1}$ )
0.05	4.0	$12.64 \pm 0.16$
0.1	2.0	$28.95 \pm 0.09$
0.5	0.4	$47.62 \pm 0.11$
1	0.2	$62.18 \pm 0.14$
2	0.1	$65.17 \pm 0.05$
3	0.06	$66.25 \pm 0.07$
5	0.04	$67.54 \pm 0.13$

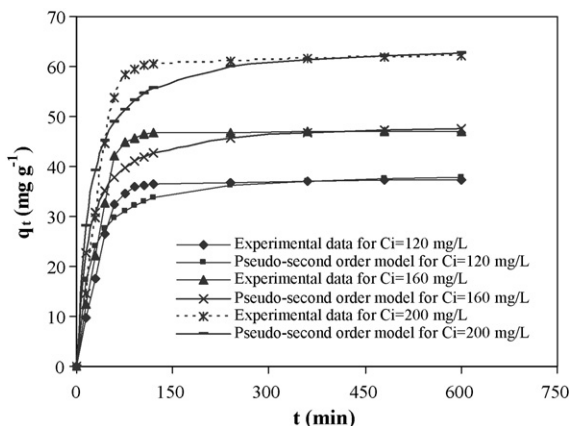


Fig. 2. Experimental and predicted kinetics from pseudo-second order model for sorption of Hg(II) onto *C. papaya* (pH: 6.5, solid to liquid ratio (s/l): 1.0 g L<sup>-1</sup>).

### 3.3. Effect of contact time

The batch experiments carried out to study the relationship between contact time and mercury uptake by *C. papaya* show that the equilibrium time is always reached in 120 min at various initial Hg(II) concentrations. Fig. 2 shows the effect of initial Hg(II) concentration on sorption capacity at different contact time. It was observed that sorption capacity varies with varying initial Hg(II) concentration, however, the removal rate is same. It can be noticed that the contact time significantly affects the Hg(II) uptake; the metal sorption increases sharply in the first 60 min and tapers off there after, as equilibrium is approached. This relatively rapid mercury uptake indicates that the sorption process occurs mainly on the surface of the sorbent. The uptake of heavy metal ions by biosorbents has often been observed to occur in two stages: the first rapid and quantitatively predominant and the second slower and quantitatively insignificant, has been extensively reported in literature [27]. The rapid stage is probably due to the abundant availability of active sites on the biomass, and with the gradual occupancy of these sites, the sorption becomes less efficient in the slower stage [28]. The fast mercury uptake by the *C. papaya* may be attributed to its porous and mesh structure, which provides ready access and large surface area for the sorption of metals on the binding sites [19].

According to these results, it was set a contact time of 5 h in order to ensure that equilibrium conditions are attained. This equilibrium time is clearly shorter than those usually employed for the sorption of Hg(II) by other sorbent materials. Times of 24 h are proposed for the sorption by chemically modified chitosan [29], pinus pinaster bark [30] or ion exchange resins [31]. Even longer times, from 80 to 120 h, are necessary with some carbonaceous materials [32]. The rapid kinetics has a significant practical importance, as it will facilitate smaller reactor volumes ensuring efficiency and economy.

### 3.4. Dynamic modeling

The transient behavior of the batch sorption process at different initial concentrations was analyzed using the pseudo-first-order [33] and pseudo-second order [34] kinetic models and is expressed as follows.

Pseudo-first order rate equation:

$$q_t = q_e[1 - \exp(-k_1 t)] \quad (4)$$

Pseudo-second order rate equation:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (5)$$

where  $k_1$  (min<sup>-1</sup>) and  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) are pseudo-first order and pseudo-second order rate constants, respectively.  $C_i$  is the initial concentration of sorbate in solution (mg L<sup>-1</sup>) and  $q_t$  (mg g<sup>-1</sup>) is the sorption capacity at time  $t$ .

The pseudo-first order considers the rate of occupation of sorption sites to be proportional to the number of unoccupied sites. It was observed from Lagergren plot (figure not shown) that at all initial Hg(II) concentrations (120, 160 and 200 mg L<sup>-1</sup>) the sorption data were well represented by the Lagergren model only for the first 60 min and thereafter it deviates from theory. In other words, the sorption data were well represented only in the region where rapid sorption took place, i.e., for the first 60 min. Ho and McKay [34] reported similar observation as the sorption data were represented well by the Lagergren first-order model only for the rapid initial phase that occurs for a contact time of 0–30 min for basic dyes onto peat particles. This confirms that it is not appropriate to use the Lagergren kinetic model to predict the sorption kinetics for the entire sorption period in the present case. The predicted rate constants at different initial Hg(II) concentrations and their corresponding correlation coefficient ( $R^2$ ), S.E. and SSE values are shown in Table 2.

The kinetic data were further analyzed using a pseudo-second order relation proposed by Ho and McKay [34] and Fig. 2 shows the predicted kinetics for Hg(II) onto *C. papaya*. The pseudo-second order rate constant  $k_2$ , the calculated  $h (= k_2 q_e^2)$  value, and the corresponding  $R^2$ , S.E. and SSE values are given in Table 2. It was observed that at all initial Hg(II) concentrations and for the entire sorption period, correlation coefficient ( $R^2$ ) values were found to be higher, and ranged from 0.9952 to 0.9962, while S.E. values were low and ranged from 0.2157 to 0.7129. The high  $R^2$  and low S.E. and SSE values confirm that the sorption kinetic data were well represented by pseudo-second order model for the entire sorption period and thus supports the assumption behind the model that the sorption is due to chemisorption, which is in good agreement with the sorption equilibrium data well represented by Langmuir isotherm equation. Also from Table 2, it was observed that the  $R^2$  values increases with decreased initial Hg(II) concentration, which shows good agreement of the pseudo-second order model at lower Hg(II) concentration.

Further, the kinetic constants were correlated with the major operating variables such as initial Hg(II) concentration before applying the kinetic models for process design or optimization. Thus the effect of initial sorption rate  $h$  (mg g<sup>-1</sup> min<sup>-1</sup>) and the pseudo-second order rate constant  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) on the initial

Table 2  
Kinetic constants for Hg(II) onto *C. papaya* by non-linear regression analysis

Kinetic model	Initial Hg(II) concentration (mg L <sup>-1</sup> )		
	$C_i = 120$	$C_i = 160$	$C_i = 200$
Pseudo-first order			
$k_1$ (min <sup>-1</sup> )	0.0140	0.0082	0.0078
$R^2$	0.9012	0.8921	0.9024
S.E.	0.3963	0.4820	0.3998
SSE	1.5707	2.3232	1.5986
Pseudo-second order			
$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	0.0372	0.0339	0.0281
$h$ (mg g <sup>-1</sup> min <sup>-1</sup> )	2.0978	2.7855	3.3222
$q_e$ (mg g <sup>-1</sup> )	38.91	49.09	64.76
$R^2$	0.9962	0.9958	0.9952
S.E.	0.4766	0.7129	0.2157
SSE	1.0667	0.7129	0.4654

Hg(II) concentration were obtained by plotting the data in logarithmic coordinates (figure not shown). The relation between  $k_1$  and  $C_i$  was not estimated, because kinetic study confirms that the sorption data were better represented by pseudo-second order kinetics than by pseudo-first order kinetics. It was observed that the trend line for initial sorption rate increase with initial concentration while the trend line for the pseudo-second order rate constant decrease with increased initial concentration (figure not shown). Ho and McKay [34] and Kumar et al. [35] observed the trend lines for initial sorption rate and the pseudo-second order rate constant decrease with increased initial concentration for dye particles on peat surface and fly ash, respectively. The relations between  $k_2$  and  $h$  and initial Hg(II) concentration are given by the equations.

$$k_2 = -0.5354 C_i - 0.3077 \quad R^2 = 0.9267, \quad \text{S.E.} = 0.0236 \quad (6)$$

$$h = 0.9040 C_i - 1.5547 \quad R^2 = 0.9962, \quad \text{S.E.} = 0.0087 \quad (7)$$

### 3.4.1. Intraparticle diffusion modeling

In order to investigate the mechanism of the sorption of Hg(II) onto *C. papaya*, intraparticle diffusion-based mechanism has been studied. In the present work, diffusion controlled mechanisms were considered to be more appropriate [36]. The mechanism of sorption is generally considered to involve three steps, one or any combination of which can be the rate-controlling mechanism: (i) mass transfer across the external boundary layer film of liquid surrounding the outside of the particle; (ii) sorption at a site on the surface (internal or external) and the energy will depend on the binding process (physical or chemical); this step is often assumed to be extremely rapid; (iii) diffusion of the sorbate molecules to a sorption site either by a pore diffusion process through the liquid filled pores or by a solid surface diffusion mechanism.

According to previous studies, the intraparticle diffusion plot may represent multi-linearity, representing the different stages in sorption [37–39]. Sorption kinetic data were processed to determine whether intraparticle diffusion is rate limiting for the sorption of Hg(II) from the plot between the amount of Hg(II) sorbed,  $q_t$  ( $\text{mg g}^{-1}$ ) versus  $t^{0.5}$  ( $\text{min}^{0.5}$ ) (Fig. 3). The plots obtained showed multi-linearity with three distinct phases: external surface sorption (phase 1), initial linear portion (phase 2) and plateau (phase 3). The first, sharper portion was attributed to the diffusion of Hg(II) through the solution to the external surface of sorbent, or the boundary layer diffusion of solute molecules. The second portion described the gradual sorption stage, where intraparticle diffusion was rate limiting. The third portion was attributed to the final equilibrium stage for which the intraparticle diffusion started to slow

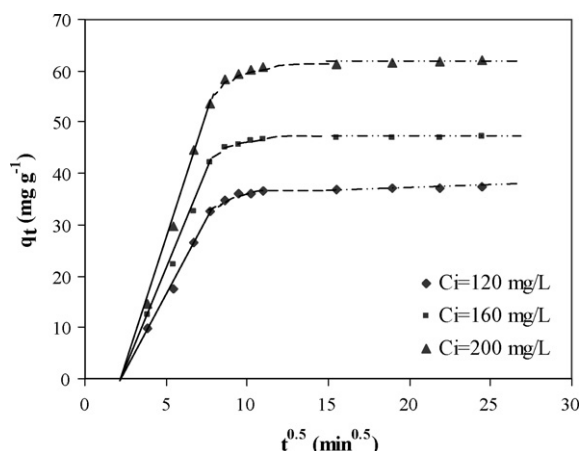


Fig. 3. Intraparticle diffusion plot of Hg(II) sorption onto *C. papaya*.

**Table 3**

The intraparticle diffusion rate parameters of Hg(II) with different initial concentrations by non-linear regression analysis

Kinetic model	Initial Hg(II) concentration ( $\text{mg L}^{-1}$ )		
	$C_i = 120$	$C_i = 160$	$C_i = 200$
$K_1$ ( $\times 10^{-2} \text{ mg g}^{-1} \text{ min}^{-0.5}$ )	3.7626	4.7672	6.2261
$R^2$	0.9940	0.9848	0.9967
S.E.	0.3963	0.4820	0.3998
SSE	1.5707	2.3232	1.5986
$K_2$ ( $\times 10^{-2} \text{ mg g}^{-1} \text{ min}^{-0.5}$ )	3.6218	4.6409	6.0243
$R^2$	0.9012	0.8921	0.9024
S.E.	0.9477	1.5785	1.1989
SSE	1.7963	4.9834	2.8748
$K_3$ ( $\times 10^{-2} \text{ mg g}^{-1} \text{ min}^{-0.5}$ )	1.7887	2.2632	2.9702
$R^2$	0.8874	0.8814	0.8318
S.E.	2.8010	3.8268	4.9335
SSE	46.088	78.090	73.019

down due to the extremely low Hg(II) concentration left in the solution. The rate of uptake might be limited by concentration of the sorbate and its affinity to the sorbent, diffusion coefficient of the Hg(II) in the bulk phase, the pore-size distribution of the sorbent.

As seen from Fig. 3 the plot was not linear over the whole time range, implying that more than one process affected the sorption. Previous studies showed that such plots might present a multi-linearity [38,40], which indicated that two or more steps occurred. The multiple nature of the plot (Fig. 3) could be explained by boundary layer diffusion, which gave the first portion and the intraparticle diffusion that gave further two linear portions. Fig. 3 shows that the straight line did not pass through the origin and this further indicated that the intraparticle diffusion was not only the rate-controlling step [40–43]. It could be deduced that there were three processes that controlled the rate of sorption but only one was rate limiting in any particular time range. The slope of the linear portion indicated the rate of the sorption. The lower slope corresponded to a slower sorption process. One could observe that the diffusion in bulk phase to the exterior surface of sorbent, which started at onset of the process, was the fastest. The second portion of the plot seemed to refer to the diffusion into mesopores and the third one with the lowest slope to adsorption into micropores. This implied that the intraparticle diffusion of Hg(II) molecules into micropores was the rate-limiting step in the sorption process on *C. papaya*, particularly over long contact time periods. As seen in Table 3, there were small differences in the slope of the first and second portions of the plot and the slopes generally increased with initial concentrations, which corresponded to an enhanced diffusion of Hg(II) from the exterior surface of adsorbent and through macropores and mesopores, respectively.

### 3.5. Effect of initial Hg(II) concentration on sorption

The metal uptake mechanism is particularly dependent on the initial metal concentration: at low concentrations metals are adsorbed by specific sites, while with increasing metal concentrations the specific sites are saturated and the exchange sites are filled [44]. The Hg(II) sorption capacity of the *C. papaya* biomass is presented as a function of the equilibrium concentration of Hg(II) within the aqueous sorption medium (figure not shown). The initial concentration was changed in the range of 40–240  $\text{mg L}^{-1}$ . The amount of Hg(II) ions adsorbed per unit mass of the sorbent (i.e., equilibrium sorption capacity,  $q_e$ ) increased from 10 to 70.82  $\text{mg g}^{-1}$  with the initial concentration, ranged from 40 to 240  $\text{mg L}^{-1}$ , as expected. This might be due to higher availability of Hg(II) ions in the solution. Moreover, higher initial concentration provides increased driving force to overcome all mass transfer resis-

tance of metal ions between the aqueous and solid phases resulting in higher probability of collision between Hg(II) ions and sorbent.

Various sorbents (organic and biologic), having a wide sorption capacity range for heavy metal ions, have been reported. Chen and Wilson [45] used a living *E. coli* strain for bioaccumulation of Hg(II) and the highest bioaccumulation level was obtained as 17.6 mg g<sup>-1</sup> dry biomass. Saglam et al. [46] have found maximum sorption capacity for immobilized live and heat-inactivated fungal mycelia of *Phanerochaete chrysosporium* as 83.10 and 102.15 mg Hg(II) g<sup>-1</sup>, respectively, whereas the amount of Hg(II) ions adsorbed onto the plain carboxymethylcellulose beads was 39.42 mg g<sup>-1</sup>. Ozer et al. [47] reported that the sorption capacity of *Rhizopus arrhizus* and a living *E. coli* strain was 71 and 17.6 mg Hg(II) g<sup>-1</sup>, respectively. Shah and Devi [48] used a dithizone-anchored poly(vinyl pyridine) support and they reported a specific sorption capacity of up to 144.42 mg Hg(II) g<sup>-1</sup>. Liu et al. [49] achieved 72.21 mg Hg(II) g<sup>-1</sup> sorption capacity with *N*-(hydroxymethyl)-thioamide resin. Jyo et al. [50] reported 40.12 mg Hg(II) g<sup>-1</sup> with phosphoric acid-treated poly(glycidylmethacrylate-co-divinyl-benzene) beads.

### 3.6. Sorption isotherm models

Analysis of equilibrium data is important for developing an equation that can be used to compare different biosorbents under different operational conditions and to design and optimize an operating procedure. To examine the relationship between sorption and aqueous concentration at equilibrium, various sorption isotherm models are widely employed for fitting the data [51,52]. In the present investigation the equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. The main reason for the extended use of these isotherm models is that they incorporate constants that are easily interpretable.

The Langmuir sorption isotherm [53,54] is given by the following equation:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (8)$$

In this model,  $q_{\max}$  (mg g<sup>-1</sup>) is the amount of sorption corresponding to complete monolayer coverage, i.e., the maximum sorption capacity and  $K_L$  (L mg<sup>-1</sup>) is the Langmuir constant. For Langmuir type sorption process, to determine if the sorption is favorable or not, a dimensionless separation factor is defined as [55]

$$R_L = \frac{1}{1 + K_L C_i} \quad (9)$$

If  $R_L > 1$ , the isotherm is unfavorable;  $R_L = 1$ , the isotherm is linear;  $0 < R_L < 1$ , the isotherm is favorable;  $R_L = 0$ , the isotherm is irreversible.

The Freundlich model [56] is expressed as

$$q_e = K_F C_e^{1/n} \quad (10)$$

In this model, the mechanism and rate of sorption are functions of the constants  $n$  and  $K$  (L g<sup>-1</sup>). The value of  $n$ , of this model, falling in the range of 1–10 indicates favorable sorption [57]. The model constants of both Langmuir and Freundlich along with correlation coefficients ( $R^2$ ), S.E. and SSE values are listed in Table 4. It was observed that the equilibrium data fitted both the Langmuir and Freundlich expressions with a satisfactory correlation coefficient value of 0.9921 and 0.9959, respectively (figure not shown). However, the lower correlation coefficient as well as high standard errors for the Freundlich isotherm as compared to Langmuir confirms the non-applicability of this model for the Hg(II)/papaya wood system. High correlation coefficient values (0.9959) for the Langmuir isotherm predicts the monolayer coverage of Hg(II) on

**Table 4**

Isotherm constants for Hg(II) sorption on to *C. papaya* by non-linear regression analysis

Langmuir	Freundlich
$q_{\max}$ (mg g <sup>-1</sup> ) = 155.63	$K_F$ (L g <sup>-1</sup> ) = 0.1697
$K_L$ (L mg <sup>-1</sup> ) = 0.00427	$n_F$ = 1.2674
$R_L$ = 0.727	$R^2$ = 0.9921
$R^2$ = 0.9959	S.E. = 0.0713
S.E. = 0.0392	SSE = 0.0203
SSE = 0.0062	

papaya wood particles. The Langmuir model served to estimate the maximum metal uptake values where they could not be reached in the experiments and it contains the two important parameters of the sorption system ( $q_{\max}$  and  $K_L$ ) [58]. The  $q_{\max}$  is attributable to the maximum metal uptake upon complete saturation of the sorbent and  $K_L$  is a coefficient attributed to the affinity between the sorbent and sorbate. The  $q_{\max}$  is found to be 155.63 mg g<sup>-1</sup>, which is higher than the experimental value, 72.05 mg g<sup>-1</sup>. The separation factor ( $R_L$ ) values indicate (Table 4) that Hg(II) sorption on to papaya wood is favorable.

### 3.7. Design of batch sorption system from isotherm data

The Langmuir isotherm model was used to design a multistage sorber and for biomass optimization. The schematic diagram for a multistage is shown in Fig. 4. The solution to be treated contains  $V$  (l) of Hg(II) solution of initial concentration  $C_0$  (mg L<sup>-1</sup>). The Hg(II) concentration is to be reduced from  $C_{n-1}$  to  $C_n$  (mg L<sup>-1</sup>).  $W$  (g) of biomass with solid phase concentration of  $q_0$  was used to reduce the Hg(II) concentration on the biomass increases from  $q_0$  to  $q_n$  (mg g<sup>-1</sup>). The metal uptake process can be represented by a mass balance equation:

$$V(C_{n-1} - C_n) = W(q_n - q_0) \quad (11)$$

When fresh biomass is used at each stage, the amount of metal sorbed on the unit mass biosorbent for a desired amount of metal removal can be obtained by rearranging Eq. (11) as follows:

$$q_n = \frac{V}{W}(C_{n-1} - C_n) \quad (12)$$

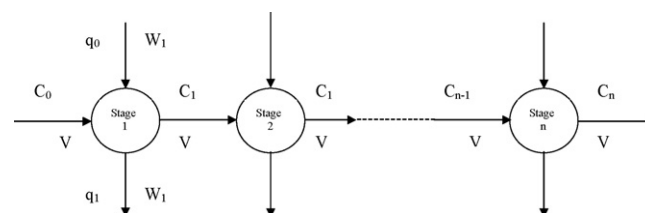
If the equilibrium metal uptake follows the Langmuir isotherm, the solid phase concentration for the desired amount of metal removal can be evaluated using the equation:

$$q_n = \frac{K_L q_m C_n}{1 + K_L C_n} \quad (13)$$

Combining Eqs. (12) and (13), the amount of biomass required for the desired metal removal can be predicted using Eq. (14) as follows:

$$W = \frac{V(C_{n-1} - C_n)}{(1 + K_L C_n)(K_L q_m C_n)} \quad (14)$$

Eq. (14) can be used to determine the amount of biomass required for any given initial metal concentration and for any



**Fig. 4.** Schematic diagram for multistage batch sorption.

**Table 5**  
Biomass of *C. papaya* required for a series of sorption system ( $C_0$ : 550 mg L<sup>-1</sup>;  $C_2$ : 300 mg L<sup>-1</sup>)

Sorption system	$C_1$ (mg L <sup>-1</sup> )	Biomass required in stage 1, $W_1$ (g)					Biomass required in stage 2, $W_2$ (g)				
		100 L	200 L	300 L	400 L	500 L	100 L	200 L	300 L	400 L	500 L
1	525	0.031	0.118	1.482	1.975	2.469	0.817	1.634	2.452	3.269	4.086
2	500	0.067	0.260	1.691	2.255	2.819	0.726	1.453	2.179	2.906	3.632
3	475	0.112	0.431	1.932	2.576	3.220	0.636	1.271	1.907	2.543	3.178
4	450	0.165	0.639	2.208	2.944	3.679	0.545	1.090	1.634	2.179	2.724
5	425	0.231	0.892	2.504	3.338	4.173	0.454	0.908	1.362	1.816	2.270
6	400	0.312	1.205	2.808	3.744	4.679	0.363	0.726	1.090	1.453	1.816
7	375	0.413	1.593	3.202	4.269	5.337	0.272	0.545	0.817	1.090	1.362
8	350	0.539	2.082	3.628	4.837	6.047	0.182	0.363	0.545	0.726	0.908
9	325	0.700	2.703	4.120	5.493	6.866	0.091	0.182	0.272	0.363	0.454
10	300	0.908	3.505	4.707	6.276	7.845	0.000	0.000	0.000	0.000	0.000

desired amount of Hg(II) removal for any multistage system. The design parameters for a two stage batch sorption system are explained. The design objective is to treat 100 L of Hg(II) solution of initial metal concentration 550 mg L<sup>-1</sup> in the first stage. A series of equilibrium metal concentration from 525 to 300 mg L<sup>-1</sup> in 25 decrements was considered in stage one of a two stage sorption system. In the sorption system number one, the design objective is to reduce the initial metal concentration from 550 to 525 mg L<sup>-1</sup>. Similarly in the sorption system 2, 3, 4, 5, 6, 7, 8, 9 and 10, the design objective of the first stage is to reduce the initial metal concentration from 550 to 500, 475, 450, 425, 400, 375, 350, 325 and upto 300 mg L<sup>-1</sup>, respectively. The biomass required reducing the concentration from 550 to 300 mg L<sup>-1</sup> in a single stage sorber were shown in Table 5. For all the sorption system number, the design objective of the second stage is to reduce the equilibrium metal concentration in stage 1 to 300 mg L<sup>-1</sup>. The corresponding amount of biomass needed for the required amount of metal removal in stage 1 and stage 2 was calculated using Eq. (14). Based on the sorption system number that utilizes the minimum biomass dose to reduce the metal concentration from  $C_{n-1}$  to  $C_n$  can be predicted from the plot of total biomass does required in both stages of two stage sorption system versus the equilibrium concentration in stage one (figure not shown). It was observed that the 3rd two stage sorption system with equilibrium concentration of 350 mg L<sup>-1</sup> in stage one utilized minimum biomass of *C. papaya* to achieve the desired objective of reducing 100 L of metal solution from 550 to 300 mg L<sup>-1</sup>.

A similar two stage sorption systems were developed for different solution volumes to be treated for decreasing initial metal concentration from 550 to 300 mg L<sup>-1</sup>. The determined amount of biomass required in each stage for the different volumes of solution to be treated to reduce the initial metal concentration from 550 to 300 mg L<sup>-1</sup> were shown in Table 5. The minimum amount of *C. papaya* required for different volumes of metal solution to be treated was calculated from the plot on total amount of biomass required at both the stages versus sorption system number for different volumes of Hg(II) solution (figures not shown). The predicted optimum biomass required for two stage sorption system to reduce the metal concentration from 550 to 300 mg L<sup>-1</sup> for different metal solution volumes is given in Table 6. From Tables 5 and 6, at optimized condition, it was observed that a two stage sorption

**Table 6**  
Optimum biomass required for the treatment of different metal solution volume ( $C_0$ : 550 mg L<sup>-1</sup>;  $C_2$ : 300 mg L<sup>-1</sup>)

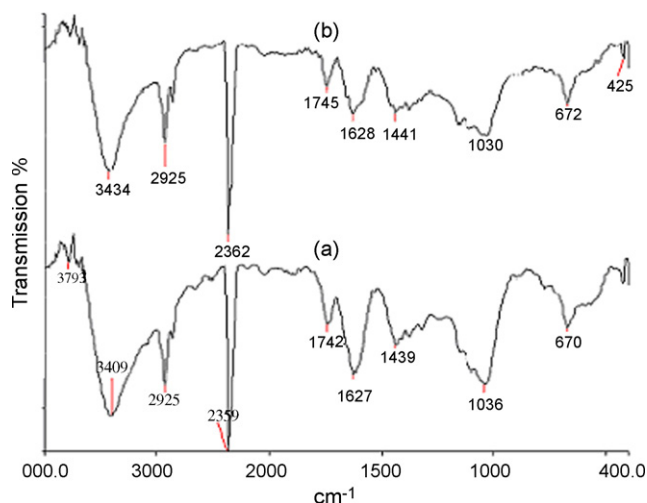
Volume of solution (L)	Optimum biomass (g)
100	0.71
200	1.728
300	3.842
400	5.122
500	6.403

system had reduced the biomass dose by 25.5% when compared to that of single stage sorption system.

### 3.8. FT-IR analysis

Various functional groups such as hydroxyl, carboxyl, sulfhydryl, sulfonate, etc. have been proposed to be responsible for sorption metal binding by different biosorbents and their importance for metal uptake depends on factors such as the quantity of sites, its accessibility, chemical state or affinity between site and metal [59]. FT-IR analysis was performed to confirm the presence of the above groups in *C. papaya*. The nature of the biosorbent–Hg(II) ions interaction was elucidated on the basis of FT-IR.

The FT-IR spectra of unloaded and Hg(II) loaded form of biosorbent in the range of 400–4000 cm<sup>-1</sup> were taken and presented in Fig. 5. The FT-IR spectrum of raw biomass showed several distinct and sharp absorptions at 3409 cm<sup>-1</sup> (indicative of primary amide, –CONH<sub>2</sub> group), 2925 cm<sup>-1</sup> (indicative of –CH stretching), 2359 cm<sup>-1</sup> (indicative of =N–H<sub>2</sub><sup>+</sup> group), 1742 cm<sup>-1</sup> (indicative of C=O stretching arising from lactones, quinones or carboxylic acids), 1627 cm<sup>-1</sup> (indicative of amide I band of amide bond in *N*-acetyl glucosamine polymer or of the protein peptide bond), 1439 cm<sup>-1</sup> (indicative of asymmetric and symmetric stretching of COO<sup>-</sup>) and the band at 1036 cm<sup>-1</sup> (indicative of sulfur compounds, S=O) [60,61]. The FT-IR spectra of papaya wood exposed to Hg(II) ions (Fig. 5(b)) indicated no shifts or change in any of the characteristic absorbance bands present in Fig. 5(a) with the exception of a peak shift at 3434, 2362 and 1645 cm<sup>-1</sup>. The spectra exhibited absorptions at approximately 3434 cm<sup>-1</sup> suggesting



**Fig. 5.** FT-IR spectra of raw (a) and Hg loaded (b) *C. papaya*.

**Table 7**

Sorption of Hg(II) from 200 mg L<sup>-1</sup> metal solution, pH 6.5, by 1.0 g L<sup>-1</sup> *C. papaya* biomass and metal desorption by 0.1 M HCl and 1% KI during five repeated sorption–desorption cycles, contact time 180 min each cycle of sorption and desorption

Cycle no.	Hg(II) sorbed (mg g <sup>-1</sup> )	Hg(II) desorbed with 0.1 N HCl (%)	Hg(II) desorbed with 1% KI (%)
1	52.47 ± 0.02	97.74 ± 0.54	99.40 ± 0.36
2	52.59 ± 0.04	97.96 ± 0.94	99.64 ± 0.59
3	51.62 ± 0.05	96.16 ± 1.35	99.31 ± 0.64
4	51.46 ± 0.03	95.86 ± 0.64	98.62 ± 0.46
5	51.43 ± 0.02	95.80 ± 0.53	98.49 ± 0.39

the occurrence of secondary amide, –CONH–. The peak that was observed at 2362 cm<sup>-1</sup> was attributed to P–H band. A medium strength absorption peak at 1645 cm<sup>-1</sup> can be assigned to primary –CONH<sub>2</sub> group amide I; mostly N–H bending [61]. The present results implied mainly involvement of amide groups in sorption of Hg(II) ions. Although slight changes on the other absorption frequencies were observed, it was difficult to interpret how these absorption peaks were related with Hg(II) sorption. It is likely that the oxidation of the biomass during Hg(II) sorption might result in changes in the absorption frequencies of the various functional groups present in the biomass.

### 3.9. Desorption and reuse

Desorption studies help elucidate the mechanism of sorption and recover metals from wastewater and sorbent. The desorption of the sorbed Hg(II) ions from *C. papaya* was studied in a batch system. Hg(II) ions sorbed onto *C. papaya* was eluted with 0.1 N HCl and 1% KI solution. The maximum percent recovery of Hg(II) was 96.7 ± 0.80 with 0.1 N HCl and 99.0 ± 0.49 with 1% KI. Higher desorption of Hg(II) by I<sup>-</sup> is due to the formation of relatively more stable iodide complexes of Hg(II) compared to the chloride complexes [2].

In order to show the reusability of the *C. papaya* sorption–desorption cycle of Hg(II) ions was repeated five times. The quantities of metals sorbed and desorbed were determined at the termination of each cycle for five repeated cycles (Table 7). No statistically significant difference in the sorption and desorption of Hg(II) was noted during one to five successive sorption–desorption cycles. From these results it may be concluded that desorption of Hg(II), on the treatment of *C. papaya* with 1% KI was almost complete. These results showed that *C. papaya* could be repeatedly used in heavy metal sorption studies.

## 4. Conclusions

Based on this study, a novel sorbent, *C. papaya* was identified as an effective sorbent for the removal of Hg(II) from aqueous solutions. Kinetics data tend to fit well in pseudo-second order kinetics, confirming the chemisorption of Hg(II) onto papaya wood. Analysis of mechanistic steps involved in the sorption process confirms that the sorption process is predominantly intraparticle diffusion controlled. The experimental sorption capacity of the *C. papaya* was 70.8 mg g<sup>-1</sup> at pH 6.5 and solid to liquid ratio of 1.0 g L<sup>-1</sup>. The equilibrium data followed Langmuir isotherm confirming the monolayer coverage of Hg(II) onto papaya wood particles. A simple procedure was proposed to design a two stage sorption system using the experimental equilibrium data of single stage sorption system. At optimized condition, it was observed that a two stage sorption system had reduced the biomass dose by 25.5% when compared to that of single stage sorption system. The FT-IR spectra of raw and mercury loaded papaya wood indicated that amide groups

were major binding sites of mercury. The main advantages of this sorbent are its rapid and high sorption–desorption property and reusability in repeated cycles. However, column studies are to be undertaken to scale up the process in order to apply *C. papaya* to the treatment of industrial wastewater and also the effect of various anions present in the wastewater. Some aspects required for scale-up were not taken into consideration in the present study. For instance, factors such as stirring speed and particle size, which may change the efficiency of Hg(II) removal, were not studied.

This work illustrated an alternative solution for the management of the unwanted biological material like *C. papaya*, which is a waste from papaya tree, when completes its fruit bearing life. Therefore, the use of *C. papaya* for the removal of heavy metals from contaminated waters may be a novel and cost-effective alternative.

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