



Cd(II) Adsorption from Aqueous Solution onto *Cucumis sativus* Peel: Equilibrium, Thermodynamic and Kinetic Study

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Abstract : *This paper reports the feasibility of using Cucumis sativus peel (CSP) for cadmium sorption from aqueous solution under different experimental conditions. Effect of various process parameters, viz. pH, adsorbent dose, contact time, initial concentration and temperature has been studied for the removal of cadmium. The applicability of different kinetic and isotherm models for the adsorption process was also evaluated. The isotherm modelling data fitted best to Freundlich model having regression coefficient (R²=0.999) showing monolayer adsorption on heterogenous surface. The governing kinetic mechanism in sorption process was pseudo second order model. Thermodynamic parameters revealed the feasibility, spontaneity and exothermic nature of adsorption. FTIR and SEM of CSP (before and after exhaustion) were recorded to explore number and position of the functional groups available for the binding of Cd(II) ions and surface morphology of adsorbent. Data reveal the involvement of functional group for binding the Cd(II) on the surface of adsorbent. In comparison to other adsorbents, the sorption capacity of the CSP for cadmium-contaminated effluents may prove to be economical and feasible.*

Keywords: Adsorption, *Cucumis sativus peel* (CSP), Cadmium, Removal, Kinetics, Isotherms.

Introduction

Contamination of aqueous environments by heavy metals is a worldwide environmental problem due to their geo-accumulation, bioaccumulation and biomagnifications by flora and fauna (Sternberg and Dorn, 2002). Being non-degradable, heavy metals pose health risks to humans when present beyond the permissible levels (Loghmanadham, 1997) and cause serious diseases such as kidney failure, anaemia, liver damage, cancer and brain damage. Heavy metals typically present in wastewater are cadmium, lead, chromium, copper, nickel, silver, tin and zinc.

Amongst all, Cadmium is a non-essential element and one of the most hazardous elements, classified as a "priority metal" from the stance of potential toxicological effects to human health and plants. Cadmium is frequently used in industrial processes such as electroplating, metallurgical processes, battery

production, mining, smelting, and alloy industries. Cadmium may be present in high concentrations in liquid industrial waste and is often deposited directly in the environment without any pre-treatment. Physicochemical methods conventionally used for the treatment of industrial wastewaters include coagulation and chemical oxidation, membrane separation, electrochemical treatment, filtration, flotation, softening and reverse osmosis (Saeed *et al.*, 2009). All these methods suffer from one or the other limitation, even none of these are successful in removing the metal from wastewater completely and also generate enormous quantity of toxic chemical sludge.

Adsorption systems are rapidly gaining prominence as treatment processes for dissolved metals (Yavuv *et al.*, 2006, Zhu *et al.*, 2007). The ability of biomaterials to remove heavy metals, through biosorption has been projected as an attractive alternative. Various

adsorbents have been tried effectively for metal removal from wastewater stream (Rao *et al.*, 2006, Ahluwalia and Goyal, 2007, Joush *et al.*, 2007) including plant materials, such as apple residues, sawdust, papaya wood, rice polish, tea-waste, sugarcane bagasse, rice husk, pine bark, hazel-nut shell, coconut husk, petiolar-felt sheath of palm, black gram husk, and wheat bran (Kurniawan *et al.*, 2006). Therefore, there is a need to find other more economically feasible, viable, eco-friendly biosorbents for the remediation of wastewaters polluted by toxic metals.

In an earlier study by Santhi and Manonmani (2011) activated carbon prepared from *Cucumis sativus* was used for the removal of a cationic dye from wastewater. In our present study, an effort was made to explore the feasibility of utilizing *C. sativus peels* (CSP) as biosorbent for the removal of Cd(II) from wastewater. The effects of pH, adsorbent dose, contact time and initial cadmium concentration were studied. The isotherm models and adsorption kinetic were used to evaluate the equilibrium experimental data, obtained from the study. FTIR and SEM were employed to evaluate the involvement of functional group and surface morphology of the biomass.

Materials and Methods

Preparation of biosorbent

CSP, is a low-cost and abundantly available agro-waste, known as cucumber. Collected CSP was extensively washed in running tap water for 1 h to remove dirt and other particulate matter, followed by washing in double-distilled water, changed repeatedly, oven-dried at 80°C for 24 h, ground and sieved to get particle size of 1.0-2.0 mm for metal adsorption experiments stored in desiccators.

All reagents including standard 1000 mgL⁻¹ Cd(II) solution used were of analytical grade (Merck, India). Deionized water (DW) was used throughout the experiments produced by Millipore Water purification system, (USA). The

experimental stock solution of Cd²⁺ (1000±2 mgL⁻¹) was prepared by dissolving Cd (NO₃)₂·4H₂O in DW and further dilutions were prepared from the stock solution.

Sorption procedure

Batch sorption experiments were performed at 25±1°C on an orbital shaker at 160 rpm using 250ml capped Erlenmeyer flasks. The pH of Cd(II) aqueous solution was adjusted to desired levels (pH 2-9) using 1molL⁻¹ HCl/NaOH. The efficiency for Cd(II) adsorption was studied at varying time intervals (10 min-24 h). After shaking the flasks for a definite time interval, the samples were filtered through Whatman No. 41 filter paper. Stock solution, diluted solution or filtrates of Cd(II) resulting from the experiments were analyzed on flame atomic absorption spectrometer (AAS, Perkin-Elmer AAnalyst 300, USA), using Electrode less discharge lamp (EDL) at 228.8nm and air/acetylene mixture as fuel. The detection limit of the method used for Cd was found to be 0.05mgL⁻¹.

Percent removal and amount of Cd(II) ions adsorbed at equilibrium was calculated using the following equations, respectively:

$$\% R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \left(\frac{C_0 - C_e}{m} \right) V \quad (2)$$

here C₀ and C_e are initial concentration and final equilibrium concentration of adsorbate (mgL⁻¹), q_e is the concentration adsorbed by adsorbent at equilibrium (mg adsorbate/g adsorbent), V is the volume of liquid (L) and m is mass of adsorbent(g).

Freundlich and Langmuir isotherm models were employed to interpret the equilibrium data. Similarly, kinetics of the biosorption was tested with Pseudo-first order, Pseudo-second order and Intra-particle diffusion kinetic models to explain the experimental data.

Results and Discussion

Influence of pH and contact time

Several studies have shown that the pH has been very imperative factor, affecting the metal adsorption on biomass (Kurniawan *et al.*, 2006). Not only do different metals have different pH optima for their sorption, these may also differ from one type of sorbent to the other (Saeed and Iqbal, 2003). Since the capacity of CSP is being reported as a new sorbent material and the effect of pH on the sorption of 25 mgL^{-1} of Cd(II) ion concentration by 1 gL^{-1} dose was studied at a range of 2-9 pH (Fig. 1). It was noted that percent Cd(II) sorption at pH 2 was 71.08% i.e. very low, increasing with the increase in pH from 2-5. The low metal sorption at pH 2 may be explained on the basis of protonation of active sites such as hydroxyl, phosphate, sulphate and amino groups resulting in hindrance of M^{2+} to occupy the binding sites (Saeed *et al.*, 2005). As the pH is increased the biosorbent surface gets deprotonated, which favour the adsorption of Cd(II). This process continues until the maximum 76.72% removal achieved at pH 5. Whereas at pH value higher than 9, adsorption studies could not be carried out due to precipitation of feebly soluble hydroxide of Cd(II) (Chen *et al.*, 2008) such as $\text{Cd}(\text{OH})^+$ and $\text{Cd}(\text{OH})_2$.

Fig. 2 shows adsorption capacity as a function of time for 25 mgL^{-1} Cd(II) concentration by 1 gL^{-1} dose at pH 5. The result revealed rapid sorption of 76.24% in the first 30 min of contact time and then maximum (82.36%) near the equilibrium at 150 min and after that slightly decreases. The majority of Cd(II) were removed within the first 30 min of contact time. After equilibrium, the adsorption rate slowly declined. Initially, the adsorption sites are open and the metal ions interact easily with the sites and hence a higher rate of adsorption is observed. Further, the driving force for biosorption, the concentration difference between the bulk solution and the solid-liquid interface is initially higher and this resulted in a faster adsorption rate. However,

after the initial period, a decrease in adsorption may be due to the slower diffusion of solute into the interior of the biosorbent (Zhu *et al.*, 2008). Plot of metal sorption as a function of time is single and continuous up to 300 min leading to saturation shows possibility of monolayer coverage of metal ion onto the adsorbent surface, after that adsorption capacity remains constant.

Effect of biosorbent dose and initial ion Concentration

Biomass level of $1-20 \text{ gL}^{-1}$ was employed to evaluate the maximum removal of metal from the least amount of biomass, with 25 mgL^{-1} concentration of Cd solution. Fig. 3 exhibit that the optimum percentage removal (88.08%) was obtained at a biomass level of 2 gL^{-1} , however, above this dose, percentage removal did not seem to increase significantly due to equilibrium limitation. The adsorption capacity decreased from $41.18-1.67 \text{ mgL}^{-1}$ when the biomass dose increased from $1-20 \text{ gL}^{-1}$. Similar observations have been documented earlier with varying biomass dosage (Shukla *et al.*, 2002).

Fig. 4 shows maximum removal efficiency of 83% as a function of initial Cd(II) ion concentration. For CSP, the removal of cadmium increased quickly over initial concentration $2-10 \text{ mgL}^{-1}$. However, as the initial Cd(II) concentration increased continuously the removal efficiency did not increase any more due to release of more Cd(II) ions in the solution because of the saturation of binding sites. This indicates that energetically less favourable sites become involved with increasing Cd(II) ion concentration in aqueous solution which can be attributed to the presence of sorption sites of different affinities (Sanchez *et al.*, 1999).

Equilibrium modelling

The Freundlich model (Freundlich, 1906) proposes a monolayer sorption with heterogeneous energetic distribution of active sites and with interaction between adsorbed molecules. Whereas the Langmuir isotherm

model (Langmuir, 1918) is based on the hypothesis that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules. The Freundlich and Langmuir equation [Eq. 3 and 4] are linearly expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (4)$$

where C_e (mgL⁻¹) is the equilibrium cadmium concentration in solution, q_e & q_m are the equilibrium and the maximum adsorption capacities (mg/g). Value of n (heterogeneity factor) and K_f (Freundlich Constant, Lg⁻¹ (Table 1) were found from slope and intercept of the plot between $\log q_e$ versus $\log C_e$ (Fig. 5a) provides an indication of the adsorption capacity of biosorbent and intensity of adsorption, respectively. Values of Langmuir constant q_{max} and K_L (Lg⁻¹) were calculated from slope and intercept of plots between C_e/q_e versus C_e (Fig. 5b) indicates uptake of Cd(II) as monolayer sorption and high binding energy for metal ion, respectively (Table 1).

From the correlation coefficient values of the tested isotherm models, it was concluded that sorption data of Cd(II) ions by CSP fits better in Freundlich model of monolayer adsorption on heterogeneous surface with different energetic distribution of active sites. The Freundlich exponent n gives an indication of the favourability of adsorption. In this study value of n is greater than unity which indicates the favourable adsorption of the Cd(II) ions on CSP. The Freundlich isotherm model is indicative of surface heterogeneity of the adsorbent, i.e. the adsorptive sites are made of small heterogeneous adsorption patches that are homogenous in themselves (Okafor *et al.*, 2012).

Thermodynamic study

Langmuir isotherm data for the adsorption of the Cd(II) were analysed for the thermodynamic parameters. The change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using following Eq. 5 and 6.

$$\Delta G^\circ = - RT \ln K_L \quad (5)$$

$$\log K_L = - \frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

The plot of $\ln K_L$ as a function of $1/T$ (Fig.6) yields a straight line from which ΔH° and ΔS° were calculated from the slope and intercept, respectively. The negative value of ΔG° indicates spontaneous adsorption and the degree of spontaneity of the reaction increases with increasing temperature (Table 1). The negative ΔH° value and positive ΔS° value as shown in Table 1, indicates exothermic process and increasing randomness at the solid/liquid interface, respectively.

Kinetics modelling

The prediction of kinetics is necessary for the design of sorption systems. Kinetics explains the dynamic of rate of reaction and factors affecting the reaction rates (Bulut and Tez, 2007). The pseudo-first-order and pseudo-second-order (Ho and McKay, 1999) equations can be written as Eq.7 and 8, respectively,

$$\log(q_e - q_t) = \log q_e - K_{1ad} t \quad (9)$$

$$\frac{t}{q_t} = \frac{1}{K_{2ad} q_e^2} + \frac{1}{q_e} t \quad (8)$$

q_e and q_t are adsorption capacities (mg/g) at equilibrium and at time t , respectively. K_{1ad} is the first order rate constant (Lmin⁻¹) and K_{2ad} is the rate equilibrium constant (gmg⁻¹min⁻¹) for

pseudo second order kinetics. K_{1ad} and q_e obtained from the plot of $\log (q_e - q_t)$ versus t (Lagergren, 1898) as best shown in Fig. 7a. For pseudo-second-order q_e and K_{2ad} ($\text{gmg}^{-1}\text{min}^{-1}$), were obtained from the slope and intercept of linear plots between t/q_t against t for the metal ion sorption (Fig. 7b) (Vadivelan and Kumar, 2005). This model suggests that the adsorption rate is proportional to the number of unoccupied site that are homogenous.

The intra-particle diffusion (Weber and Morris, 1963) model is expressed as Eq. 9

$$q_t = K_1 t^{0.5} + I \quad (9)$$

Value of "I" provides an insight about the thickness of the surface of biosorbent, as its low value is indicative of resistance in mass transfer. The linear plot (Fig. 8) deviated from origin, indicating intra-particle diffusion is not the sole rate-controlling step. The value of K_1 and I (Table 2) are in accordance with the observations of other similar studies (Demirbas *et al.*, 2004). Fig. 8 present multi-linear plots, then two or more steps influence the adsorption process such as external diffusion, intra-particle diffusion etc (Figaro *et al.*, 2009).

In the present study the correlation coefficient was not high for pseudo first order; however, the pseudo-second-order kinetic model (Ho and McKay, 2000) was successfully applied with very high correlation coefficients comparative to pseudo first order and intra particle diffusion model at all three temperatures (Table 1) for explaining the kinetics of the adsorption process. The rate of Cd(II) uptake increases rapidly with increasing temperature.

FTIR and SEM studies

To identify the type of possible Cd(II) binding sites on CSP, FTIR spectra (Perkin–Elmer 1760X) performed in spectral range of 4000-400 cm^{-1} before and after adsorption (Fig.9). The

spectrum of CSP was complex due to the existence of various functional groups on the surface of the biomass. The region between 2600 and 3600 cm^{-1} shows two major band stretches. A broad and strong band stretch was observed from 3000 to 3600 cm^{-1} , indicating the presence of free or hydrogen bonded –H groups (alcohols and carboxylic acids) on the surface of the adsorbent (Iqbal *et al.*, 2009). The region between 2250 and 2700 cm^{-1} showed the presence of R-NH_3^+ groups ($=\text{NH}^{+2}$, $\equiv \text{NH}^+$, $=\text{NH}^+$). A band at 1647.04 cm^{-1} indicated C=O stretching in carboxyl groups (Arslanoglu *et al.*, 2008), which shifted to 1650.89 cm^{-1} after Cd(II) adsorption. The peak at 1512.04 cm^{-1} showed the bending of N–H which shifted to 1519.75 cm^{-1} after Cd(II) adsorption. It can be concluded from this observation that nitrogen atom participated as an active site for Cd(II) removal. A shift of alcoholic group (–OH) at 3451.9 cm^{-1} -3433.4 cm^{-1} was observed when Cd(II) was loaded to CSP. The C=C group stretching at 2270.3 cm^{-1} shifted to 2268.7 cm^{-1} and C=O stretching shifted from 1723.7 to 1722.7 cm^{-1} and intensity were strengthened. The peak of C=O stretching of the carbonyl group shifted to 1658.2 cm^{-1} correspond for the change of this to carboxylate group. The C-C and C-O stretching shifted from 1593.7 to 1625.8 cm^{-1} and from 1102.6 to 1110 cm^{-1} , respectively after adsorption. The changes in FTIR spectrum of CSP after the adsorption of Cd(II) suggest the involvement of –OH, C=O and –NH groups in the adsorption process (Doshi *et al.*, 2007).

The surface morphology of biomass was analysed by Scanning Electron Microscope (SEM) (ZEISS, JSM-840A) before and after adsorption. The SEM of the biomass showed the irregular pattern at 20 μm indicating huge irregular surface with porous structure available for adsorption and after sorption of Cd(II) ion, the adsorbent surface became abnormal and a great deal of substance adhered to the surface

Table 1 Equilibrium, Kinetic and Thermodynamic Parameters for the adsorption of Cd(II) onto CSP at different temperatures.

Temp	Freundlich Isotherm			Langmuir Isotherm		
	R ²	n	K _f (Lmg ⁻¹)	R ²	q _m (mg g ⁻¹)	K _L
298K	0.975	1.287	3.741	0.765	3.597	27.8
308K	0.985	1.418	5.597	0.902	5.813	14.33
318K	0.993	1.485	6.546	0.935	7.142	11.66
Temp	Pseudo First Order Reaction			Pseudo Second Order Reaction		
	R ²	q _e (mg g ⁻¹)	K _{1ad} (min ⁻¹)	R ²	q _e (mg g ⁻¹)	K _{2ad} (g mg ⁻¹ min ⁻¹)
298K	0.900	1.489	0.007	0.998	4.695	0.023
308K	0.817	1.227	0.005	0.998	4.716	0.026
318K	0.825	1.218	0.007	0.999	4.807	0.029
Temp	Intra-Particle Diffusion					
	R ²	K _{id} (mg/g/min ^{1/2})	I			
298K	0.840	0.132	2.745			
308K	0.824	0.121	2.956			
318K	0.805	0.115	3.132			
Temp	Thermodynamic Parameters					
	G° (kJ/mol)	H° (kJ/mol)	S° (J/mol K)			
298K	-8.24	-2.125	8.686			
308K	-6.60					
318K	-6.09					

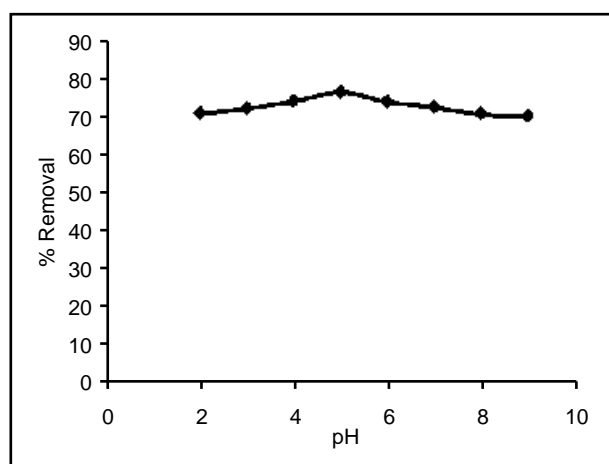


Fig. 1 Effect of pH on adsorption of Cd(II) onto CSP (25mgL⁻¹ Cd(II) conc, 1gL⁻¹CSP dose, pH 2-9, 60 min, 160 rpm at 25°C).

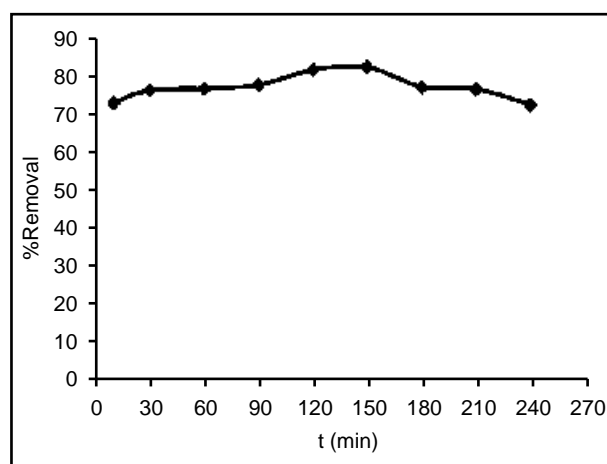


Fig. 2 Effect of contact time on adsorption of Cd(II) onto CSP (25mgL⁻¹ Cd(II) conc, 1gL⁻¹CSP dose, pH 5, 160 rpm at 25°C).

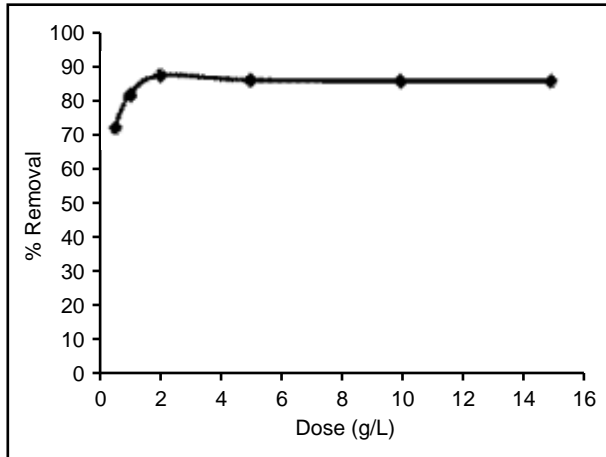


Fig. 3 Effect of adsorbent dose on Cd(II) sorption onto CSP (25mgL^{-1} Cd(II) conc, pH 5, 150min, 160 rpm at 25°C).

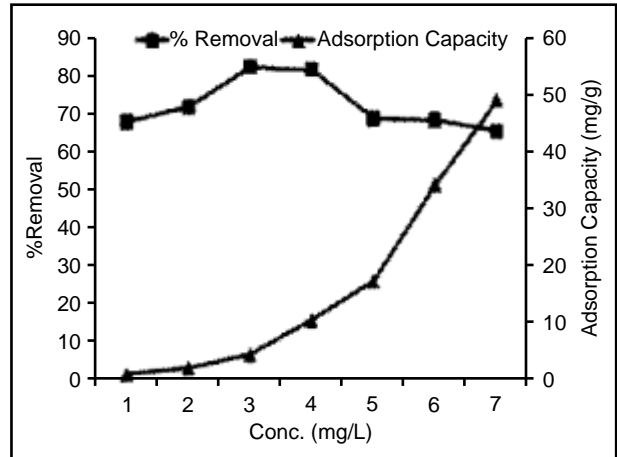


Fig. 4 Effect of initial ion concentration on Cd(II) sorption onto CSP (2gL^{-1} of CSP dose, pH 5, 150min, 160 rpm at 25°C).

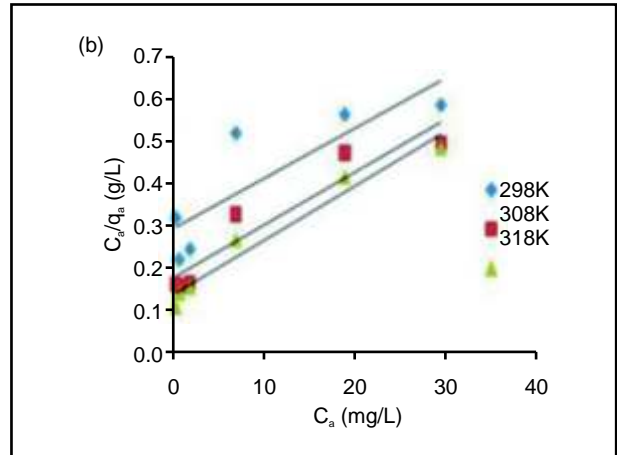
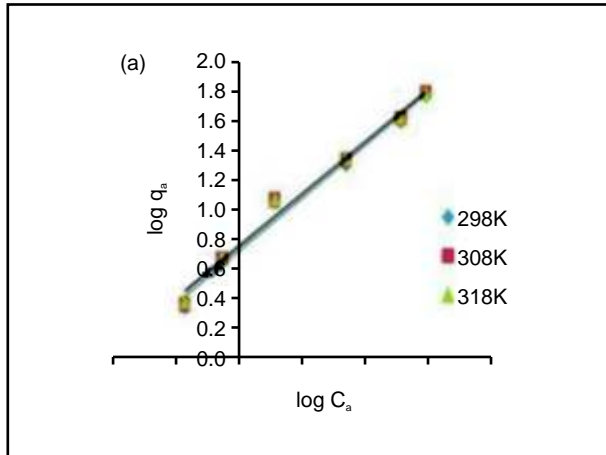


Fig. 5 Isotherms plots for (a) Freundlich and (b) Langmuir for adsorption of Cd(II) onto CSP.

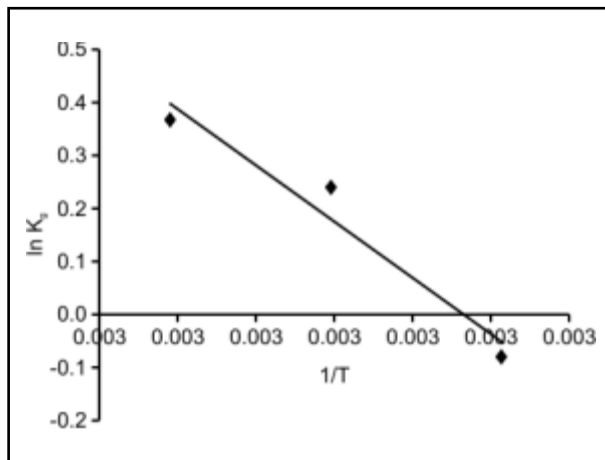


Fig. 6 Plot of $\ln K_L$ versus $1/T$ for determining thermodynamic parameters.

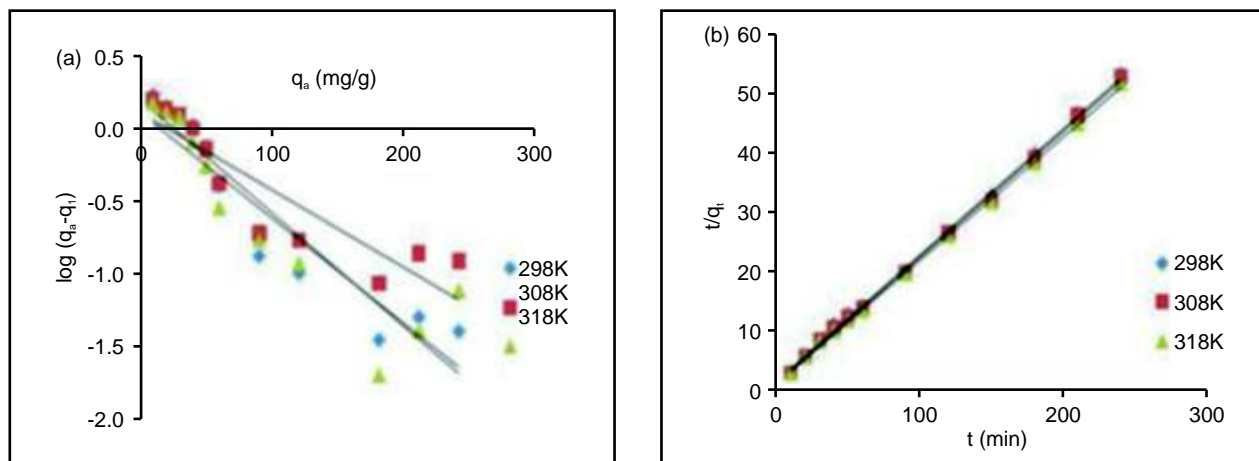


Fig. 7 Plots for Pseudo-first-order (a), Pseudo-second-order (b) kinetic models for adsorption of Cd (II) onto CSP.

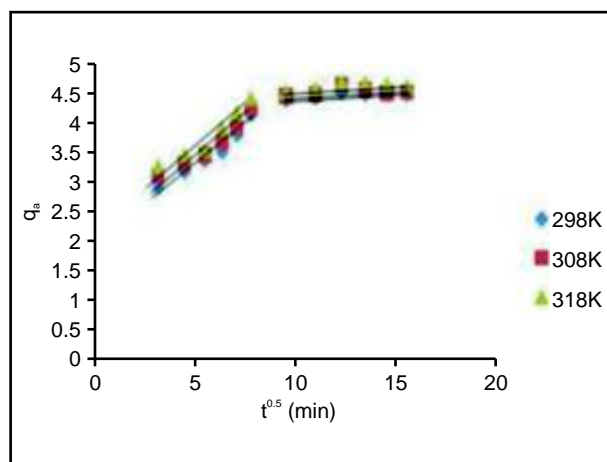


Fig. 8 Intra particle diffusion model for adsorption of Cd(II) onto CSP.

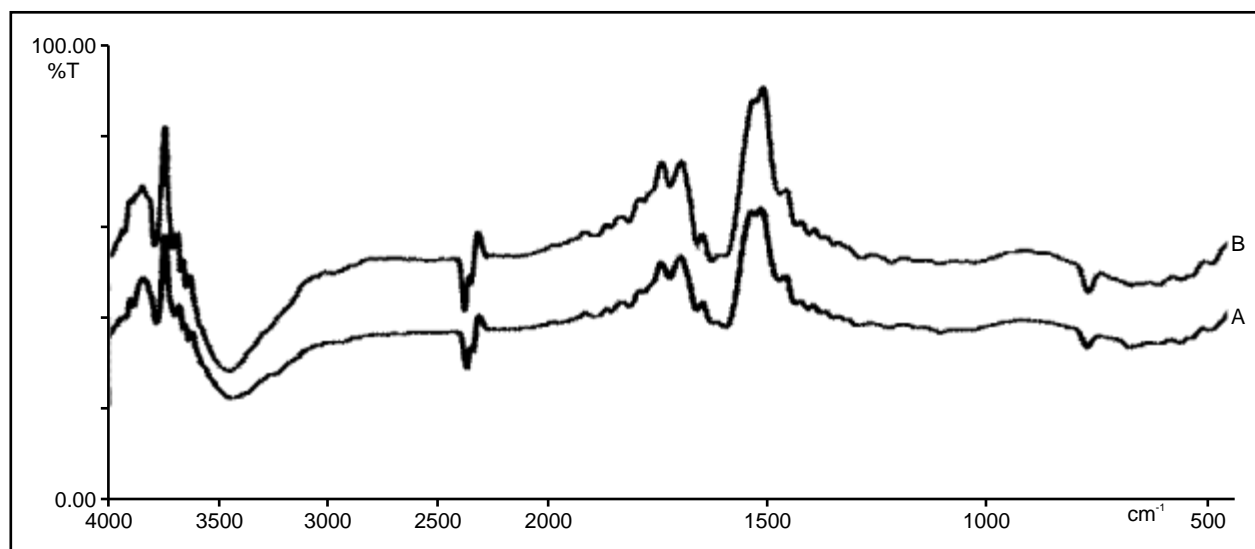


Fig. 9 FTIR spectra of (A) biomass of CSP and (B) Cd(II) loaded biomass of CSP.

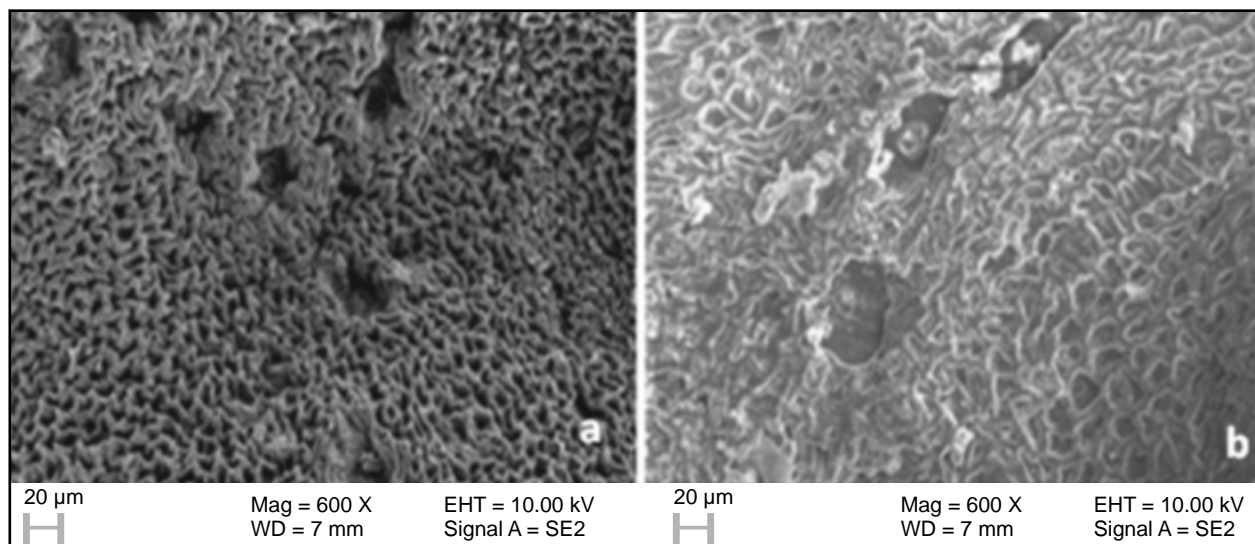


Fig. 10 SEM micrograph of CSP (a) before adsorption and (b) after adsorption of Cd(II) ions onto CSP.

showing agglomeration on it as shown in Fig. 10. These alternations in surface morphology are one of the evidence of Cd(II) sorption onto biomass. In the present investigation, performance of unmodified and new biosorbent CSP was evaluated for the removal of Cd(II) ions from aqueous solution. The Cd sorption onto CSP was highly influenced by pH and the favourable pH is 5. The contact time, initial concentration and temperature were also determining factor for the biosorption. The removal efficiency of 90.2% was achieved in 150 min of contact time with optimised conditions with initial ion concentration of 10mgL^{-1} . Batch studies displayed that equilibrium was explained by freundlich isotherm model and the adsorption process followed pseudo-second-order kinetics. Influence of temperature on biosorption showed that the process was spontaneous and endothermic in nature for all the temperature range evaluated. The probable interaction of Cd(II) ion and biosorbent were displayed by FTIR and SEM studies. The removal capacity of CSP was at par with commercially used other adsorbents prepared with other agro waste materials. Utilization of biomass in unmodified form will not only reduce the cost, but also lower the energy requirement in modifying the

biomass, thereby presenting a green chemistry option. The outcome of batch studies of biosorption characteristics from this work could be further utilised in the designing of the biosorption system for the actual wastewater treatment.

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