Removal of Cd(II) Ions from Simulated Wastewater by HCl Modified Cucumis sativus Peel: Equilibrium and Kinetic Study

Authors: Pandey, Ruchi, Ansari, Nasreen Ghazi, Prasad, Ram Lakhan, and Murthy, Ramesh Chandra

Source: Air, Soil and Water Research, 7(1)

Published By: SAGE Publishing

URL: https://doi.org/10.1177/ASWR.S16488

Libertas Academica
FREEDOM TO RESEARCH

Open Access: Full open access to this and thousands of other papers at http://www.la-press.com.

Air, Soil and Water Research

Removal of Cd(II) Ions from Simulated Wastewater by HCl Modified *Cucumis sativus* Peel: Equilibrium and Kinetic Study

Ruchi Pandey[1,2], Nasreen Ghazi Ansari[1], Ram Lakhan Prasad[2] and Ramesh Chandra Murthy[1]

[1]Analytical Chemistry Section, CSIR—Indian Institute of Toxicology Research, Lucknow, India. [2]Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi, India.

ABSTRACT: This paper describes the adsorption of Cd(II) ions from aqueous solutions by modified *Cucumis sativus* peel (CSP) by HCl treatment. The optimum pH, adsorbent mass, contact time, and initial ion concentration were determined. The maximum removal efficiency was 84.85% for 20 mg/L Cd(II) ion at pH 5. The adsorption isotherms were obtained using concentrations of the metal ions ranging from 5 to 150 mg/L. The adsorption process follows Langmuir isotherm and pseudo-second-order reaction kinetics. CSPs exhibit monolayer adsorption capacity of 58.14 mg/g at 298 K. The paper also discusses the thermodynamic parameters of the adsorption (the Gibbs free energy, entropy, and enthalpy). Our results establish that the adsorption process was spontaneous and endothermic under normal conditions.

KEYWORDS: adsorption, removal, isotherm, kinetics, thermodynamics

CITATION: Pandey et al. Removal of Cadmium (II) Ions from Simulated Wastewater by Modified *Cucumis sativus* Peel: Equilibrium and Kinetic Study. *Air, Soil and Water Research* 2014:7 93–101 doi:10.4137/ASWR.S16488.

RECEIVED: April 27, 2014. **RESUBMITTED:** July 4, 2014. **ACCEPTED FOR PUBLICATION:** July 14, 2014.

ACADEMIC EDITOR: Carlos A. Martinez-Huitle, Editor in Chief

TYPE: Original Research

FUNDING: The authors are grateful to Council of Science and Technology, Uttar Pradesh, India (GAP-271) for providing their financial support for this research work.

COMPETING INTERESTS: Authors disclose no potential conflicts of interest.

CORRESPONDENCE: ruchipandey3@gmail.com; murthyrc729@gmail.com

Introduction

The presence of cadmium ions in the aquatic environment beyond the permissible levels[1] has been of great concern to researchers because of their toxic, non-degradable, and other adverse effects on human being as well as on the flora and fauna.[2] Cadmium is frequently used in processes such as electroplating, metallurgical processes, production of batteries, smelting, alloy industries, and mine land waste.[3–5] Therefore, their level in industrial waste keeps on increasing and is often deposited directly in the environment without any pre-treatment. Thus for the treatment of industrial wastewater, a number of physicochemical methods, such as chemical oxidation and coagulation, filtration, electrochemical treatment, softening, flotation, and membrane separation (ie reverse osmosis),[6] are conventionally used. All these methods suffer from one or the other limitations,[7] which are, for instance, complicated treatment process, high cost, generation of enormous quantity of toxic chemical sludge, energy consumption, and incomplete removal of waste.[8,9]

Adsorption systems are rapidly gaining prominence as treatment process for dissolved metals, which is why they have been proposed as an attractive alternative to traditional techniques utilized in waste water treatment.[10] The bio-waste materials seem to be very effective and economical adsorbents because they are the natural adsorbents that occur in the environment with very favorable adsorption properties.[11] Till date, various adsorbents have been tried effectively for metal ion removal from the wastewater stream,[12–14] 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, wheat bran,[15] grass and bamboo leaves,[16] virgin chitin,[17] and modified chitin using kraft lignin.[18] Therefore, it is a need to find other more economically feasible, eco-friendly biosorbents for the remediation of polluted wastewater. Particularly for Cd(II) ion removal from aqueous solution, so many researchers have used different types of adsorbents including naturally occurring materials,[19,20] plant wastes,[13,21,22] modified plant wastes,[21,23] and microorganisms.[24,25]

This paper explores the potential of *Cucumis sativus* (cucumber) peels (CSPs) as a novel adsorbents for removal of Cd(II) ions from wastewater since it has not been studied earlier. Cucumber is a widely cultivated plant of family Cucurbitaceae. Its origin belongs to India,[26] where so many varieties have been observed, and these days, they are grown and used all over the world. Apart from their use in food items, a large amount of residue (peels) are also generated alongside, so it is important to explore their constructive use to minimize the amount of waste. The benefits of using CSP as an adsorbent are: it is freely available, easily processed, and adapted as an adsorbent because it might ensure high swelling capacities with excellent mechanical strength same as other biosorbents studied by Annadural.[27] 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 of the study.

Materials and Methods

Preparation of simulated wastewater. All reagents, including standard 1000 mg/L Cd(II) solution were used of analytical grade (Merck, India). Double distilled water (DDW) was used throughout the experiments produced by Millipore (Water purification system, USA). The experimental stock solution of Cd^{2+} (1000 ± 2 mg/L) was prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$ in DDW, and further dilutions were prepared from the stock solution.

Adsorbent preparation. Acid-modified CSP, treated with HCl was used in this study. The CSP is a low-cost and abundantly available agro-waste material. Collected CSP was extensively washed in running tap water for 1 hour to remove dirt and other particulate matter, followed by repeatedly washing in DDW. The washed peels were dried under sunlight for 2 days and afterward oven-dried at 80°C for 24 hours, grounded, and sieved to get particle size of 500 μm. The modification process was followed according to Argun et al[28] to enhance the number of negatively charged binding sites on the adsorbent surfaces, and to prevent the elution of tannin compounds, that would release color in the water and also greatly increase chemical oxygen demand (COD). An accurately weighed 25 g sample was poured into 250 mL of HCl solution, and then were shaken at 250 rpm for 4 hours at 298 K and left overnight. Finally, the mixture was filtered and washed several times with DDW until the pH of the solutions turns neutral. The modified CSPs were oven-dried at 85°C for 2 hours and the dried material was stored in desiccators for the next set of metal ion adsorption experiment. Determination of pH_{ZPC} was done through solid addition method;[29] particle density, bulk density, and porosity were determined using method described by Ekpete and Horsfall;[30] moisture content using ASTM 2867-99 method; and ash content using ASTM D2866-94 method. The proximate analysis of the modified CSP is shown in Table 1.

Sorption procedure. Batch adsorption experiments were performed at 25 ± 1°C on an orbital shaker at 250 rpm using 250 mL capped Erlenmeyer flasks. The pH of Cd(II) ion aqueous solution was adjusted to desired levels (pH: 2–9) using 1 mol/L HNO_3/NaOH. The Cd(II) ion removal efficiency of CSP was studied at varying time intervals. After shaking the flasks for a definite time duration, the samples were filtered through Whatman No. 41 filter paper. Stock solution, diluted solution, or filtrates of Cd(II) ion resulting from the experiments were analyzed on flame atomic absorption spectrometer (AAS, Perkin-Elmer AAnalyst 300, USA), using electrode less discharge lamp at 228.8 nm and air–acetylene mixture as fuel. The detection limit of the method used for Cd was found to be 0.05 mg/L.

Percent removal and amount of Cd(II) ions adsorbed at equilibrium were calculated using the following Equations 1 and 2, respectively:

$$\%R = \frac{C_0 - C_e}{C_0} \times 100, \tag{1}$$

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

where C_0 and C_e are initial concentration and final equilibrium concentration of adsorbate (mg/L), q_e is adsorption capacity at equilibrium (mg adsorbate/g adsorbent), V is the volume of liquid (L), and m is the mass of adsorbent (g). Freundlich and Langmuir isotherm models were employed to interpret the equilibrium data. Similarly, kinetics of the biosorption was tested using pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic models to explain the experimental data.

Effect of anions and cations. In real wastewaters, the metals of interest are usually found with a number of other ions. To study the effect of these anions and cations on Cd(II) ion

Table 1. Physical parameters of modified CSP.

pH^{ZPC}	PARTICLE DENSITY	BULK DENSITY (g/mL)	POROSITY (%)	MOISTURE CONTENT (%)	ASH CONTENT (%)
4.2	0.235	0.127	0.15	13.5	8.5

adsorption, various concentration (2, 5, 15, and 20 mg/L) of anions such as sulfate (SO$_4^-$), carbonate (CO$_3^{2-}$), chloride (Cl$^-$), nitrate (NO$_3^{2-}$), and cations like Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+} were added individually in the 20 mg/L Cd(II) ion solution in a conical flask and were shaken for a time period of 2 hours. The solution was filtered and the filtrate was analyzed for the remaining Cd(II) ion concentration.

Desorption procedure. Desorption process was performed as described by Sari and Tuzen,[31] using HNO$_3$/HCl in order to reuse CSP for next set of experiment, and the comparative effects of these eluents were also evaluated. To study the desorption effect, two sets of 25 mL of 20 mg/L of Cd(II) ions solution in flask were shaken for 1 hour with 1 g/L dosage of CSP. After that, solution in both flasks was filtered. The CSPs sustained on both the filter papers were washed repeatedly using HNO$_3$ and HCl (0.1, 0.5, and 1 mol/L) separately. The filtrate obtained through washing of exhausted CSP contain Cd(II) ions and the determination of the Cd(II) ion concentration in the final solution was performed by flame AAS.

Results and Discussion

Influence of pH and contact time. The pH of the solution is one of the most important factors to determine the adsorbent's efficiency as it not only affects surface charge of the adsorbent but also affects the degree of ionization and speciation of adsorbate.[32,33] The different adsorbents and metals both have unlike pH maxima for the removal study.[34] Thus to find out the optimum pH for the present study, 20 mg/L of Cd(II) ion concentration was treated with 1 g/L dose of CSP at a pH range of 2–9 (Fig. 1A). It was noted that percent Cd(II) ion sorption increased rapidly up to pH 5. The low metal sorption below pH 5 may be explained assuming protonation of active sites such as hydroxyl and amide groups resulting in hindrance of Cd(II) ions to occupy the binding sites.[35] In our previous study for the removal of Pb(II) ions from aqueous solution using unmodified CSP, we have performed fourier transform infrared (FTIR) analysis, in which existence of these functional groups was confirmed.[36] As the pH is increased, the biosorbent surface gets deprotonated, which favor the adsorption of Cd(II) ion. The reason can also be attributed to the pHzpc value, above which the surface of adsorbent is negative and below pHzpc value, the surface becomes positively charged. Here, obtained pHzpc value of modified CSP is 4.2, which means above this value, adsorption of Cd(II) ions is favored due to availability of negatively charged binding sites. This process continues until the maximum percentage removal achieved at pH 5 and after that up to pH 6 removal capacity remains constant. At pH >8, the products such as [Cd(OH)]$^+$ and [Cd(OH)$_2$] will be produced.[37,38] Thus in order to assure full utilization of the adsorption property of CSP as well as to avoid precipitation of Cd(II) ions, all the following experiments were conducted at pH 5.0.

Figure 1B shows adsorption capacity as a function of time for 20 mg/L Cd(II) concentration by 1 g/L dose at pH 5. It can be seen that the adsorption of Cd(II) ions is rapid during first 30 minutes of contact time and then maximize near

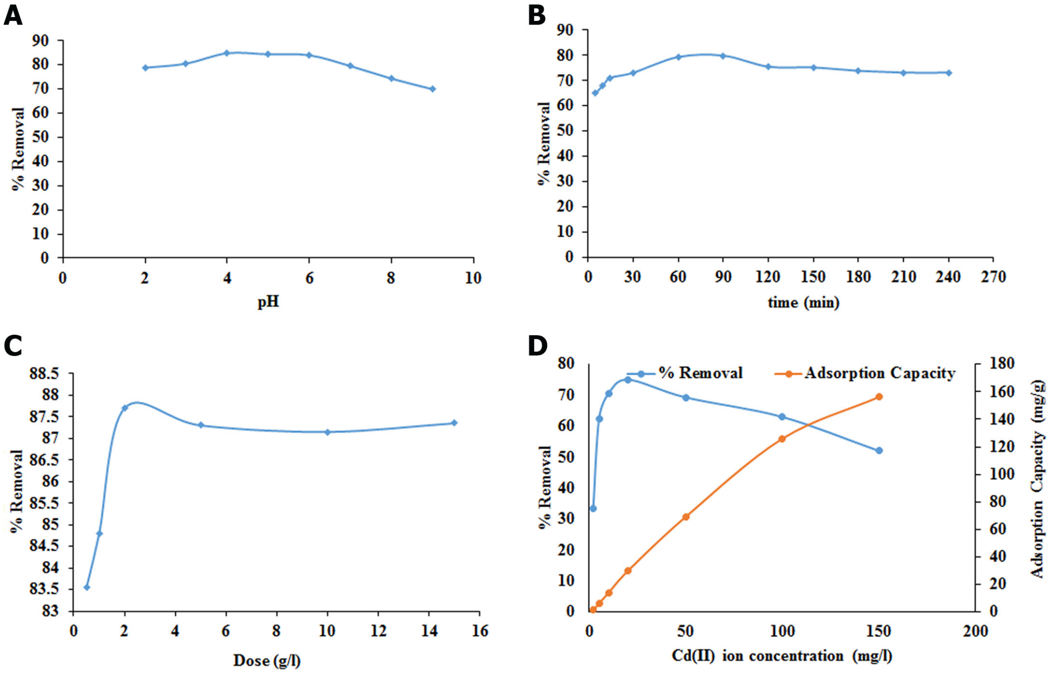

Figure 1. (**A**) Effect of pH for 20 mg/L Cd(II) ion using 1 g/L CSP dosage for 1 hour, (**B**) Effect of contact time for 20 mg/L Cd(II) ion concentration using 1 g/L CSP dosage at pH 5, (**C**) Effect of adsorbent dose for 20 mg/L Cd(II) ion concentration for 1 hour at pH 5, and (**D**) Effect of initial metal ion concentration at pH 5 on Cd(II) ion removal using modified CSP.

the equilibrium (150 minutes). The hasty removal at the early stage may be due to the high driving force that promotes the quick transfer of Cd(II) ions to the surface of CSP and the availability of the exposed surface area/active sites on the adsorbent.[39] With the further increase in time, the availability of the uncovered surface area and the remaining active sites decrease, and therefore, the driving force decreases. However, after the initial period, the decrease in adsorption may also be attributed to the fact that Cd(II) ions diffuse slowly into the intra-particle pores of the adsorbent.[40]

Effect of biosorbent dose and initial ion concentration. Biomass level of 0.5–15 g/L was employed to evaluate the maximum removal using the least amount of biomass, with 20 mg/L concentration of Cd(II) ion solution. Figure 1C shows that the optimum percentage removal of 87.7% was obtained at a biomass level of 2 g/L. This may be due to the good adsorbent surface area and pore volume availability at higher adsorbent dose providing more functional groups and active sites.[41] However, above this dose, percentage removal did not seem to increase significantly due to equilibrium limitation. Simultaneously, further increases in adsorbent dose above 2 g/L, the Cd(II) ion percentage removal gradually decreases. Figure 1D shows maximum removal efficiency of 83% as a function of initial Cd(II) ion concentration. For CSP, the Cd(II) ions percentage removal increased quickly over initial concentration of 2–20 mg/L. 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 and on the other hand saturation of binding sites. This indicates that energetically less favorable 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. On the other hand, metal uptake increases significantly with increasing metal ion concentration.

Equilibrium modeling. The capacity of an adsorbent can be described by equilibrium sorption isotherm, which is characterized by certain constants whose values express the surface properties and affinity of the adsorbent. The Freundlich model (1906), an empirical equation that assumes an infinite number of adsorption sites with a heterogeneous energy distribution of the active sites on adsorbent surface, has been used in its original form as in Equation 3:

$$q = k_F C_e^{1/n}, \tag{3}$$

where C_e (mg/L) is the equilibrium Cd(II) concentration in solution. k_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent, respectively.

The Langmuir isotherm model (1918) is probably the most widely applied adsorption isotherm, which is based on the hypothesis that metal uptake occurs on a homogenous surface through monolayer sorption without interaction between adsorbed molecules. This saturated monolayer isotherm is represented in Equation 4:

$$q = \frac{q_m k_L C_e}{1 + K_L C_e}, \tag{4}$$

$$R_L = \frac{1}{1 + K_L C_0}, \tag{5}$$

where q_m is the maximum adsorption capacity (mg/g) and k_L is an affinity constant related to the energy of adsorption and its value indicates the strength or affinity of the sorbate for solute.[42] Equation (5) demonstrates about the separation factor, R_L that is another essential parameter of Langmuir isotherm, provides significant information about the nature of adsorption. The R_L value indicates the type of the Langmuir isotherm,[43] irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). As shown in Table 2, the R_L values indicate the favorable biosorption. Adsorption equilibria of Cd(II) ion by CSP at different temperatures are well described by Langmuir and Freundlich isotherm models, as shown in Figure 2. The equilibrium constants and correlation coefficients (R^2) are presented in Table 2. The values of R^2 show better agreement with Langmuir model. The values of k_F and n (Freundlich constants) showed high adsorption capacity and favorability of adsorption with easy uptake respectively. From Figure 2, it is apparent that the maximum adsorption capacity obtained from the Langmuir isotherm increased with increasing temperature, and the value of q_m was 58.14 mg/g at 298 K and pH 5.0. All the data obtained by isotherm models reinforcing the applicability of the Langmuir model. The adsorption capacity of CSP is fairly high in comparison with other adsorbents at room temperature, as of Ficus religiosa (27.14 mg/g),[44] cassava tuber bark waste (26.3 mg/g),[23] rice husk (20.24, 16.18, and 11.12 mg/g),[21] *Lathyrus sativus* husk (35 mg/g),[45] grape stalk (27.88 mg/g),[22] wheat bran (15.71 mg/g),[46] and juniper fiber (29.5 mg/g).[47] In our previous study for Cd(II) ion removal

Table 2. Summary of isotherm parameters for Cd(II) ion sorption onto modified CSP.

FREUNDLICH ISOTHERM				LANGMUIR ISOTHERM			
TEMP (K)	k_F (mg$^{1-1/n}$ g^{-1} L$^{1/n}$)	1/n	R^2	k_L (mg/L)	q_m (mg/g)	R^2	R_L
298	3.02	0.80	0.8948	0.03	58.14	0.9963	9×10^{-4}
308	3.30	0.72	0.9855	0.05	66.66	0.9939	7×10^{-4}
318	6.17	0.63	0.9672	0.11	67.11	0.9993	7×10^{-4}

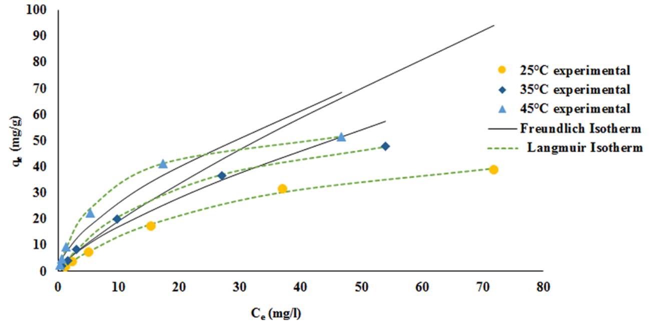

Figure 2. Freundlich and Langmuir adsorption isotherm for Cd(II) ion adsorption onto modified CSP at different temperatures.

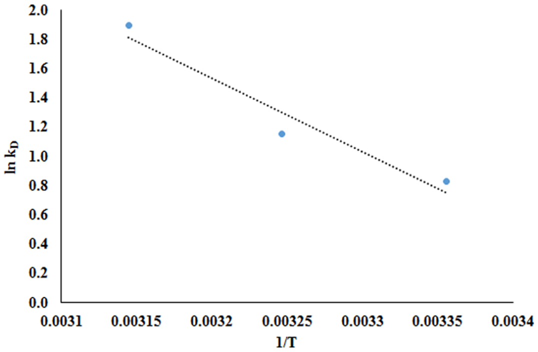

Figure 3. Plot of the ln K_D vs. temperature (1/T).

from aqueous solution using unmodified/virgin CSP, the obtained maximum adsorption capacity was 3.60 mg/g at 25 ± 1°C, which is very less compared to present work using acid modified CSP.[48]

Thermodynamic Study

In order to describe thermodynamic behavior of the biosorption of Cd(II) ions onto modified CSP, thermodynamic parameters including the change in free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were calculated from following equations:

$$\Delta G^0 = -RT \ln K_D, \qquad (6)$$

where R is the universal gas constant (8.314 J/mol K), T is temperature (K), and K_D (q_e/C_e) is the distribution coefficient.[31,49] The enthalpy (ΔH^0) and entropy (ΔS^0) parameters were estimated from the following equation:

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}. \qquad (7)$$

The plot of ln K_D as a function of $1/T$ (Fig. 3) yields a straight line from which ΔH^0 and ΔS^0 were calculated from the slope and intercept, respectively. The negative values of ΔG^0 indicate spontaneous adsorption,[50] and the degree of spontaneity of the reaction increases with increasing temperature (Table 3). The negative ΔH^0 value and positive ΔS^0 value, as shown in Table 3, indicate endothermic process and increasing randomness at the solid/liquid interface, respectively.

Kinetics modeling. The prediction of kinetics is necessary for the designing of sorption systems. Kinetics explains the dynamic of rate of reaction and factors affecting the reaction rates.[51] The linear form of the pseudo-first-order rate equation by Lagergren is given as follows:

$$\log(q_e - q_t) = \log q_{e-} \frac{K_{1ad}}{2.303} t, \qquad (8)$$

where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and at time t, respectively. The values of q_e (2.23, 1.25, and 1.13 mg/g) and first-order rate constant K_{1ad} (0.09, 0.06, and 0.05 L/min) were obtained from the plot of log (q_e−q_t) vs. t at temperatures 298, 308, and 318 K, respectively. While the lower correlation coefficient values R^2 (0.7925, 0.9511, and 0.9135) suggest that adsorption of Cd(II) ion by CSP does not follow the pseudo-first-order kinetic and this may be due to control of boundary layer in the beginning of the adsorption process.[52]

Experimental data were also tested for the pseudo-second-order kinetic model, which is given as following:

$$\frac{t}{q_t} = \frac{1}{K_{2ad} q_e^2} + \frac{t}{q_t}, \qquad (9)$$

where K_{2ad} is the rate equilibrium constant (g/mg min) for pseudo-second-order kinetics. For pseudo-second-order, q_e and K_{2ad} (g/mg min) were obtained from the slope and intercept of linear plots between t/q_t and t for the metal ion sorption (Fig. 4).[53] This model suggests that the adsorption rate is proportional to the number of unoccupied sites that are homogenous. The higher correlation coefficients, R^2, of the pseudo-second-order rate model are 0.998, 0.999, and 0.999 at 298, 308 and 318 K, respectively, suggesting that the kinetic modeling of the adsorbed Cd(II) ions, well follows the pseudo-second-order rate model. This means that the Cd(II) ion removal seems to be chemisorption process through sharing of electrons or by covalent forces through exchanging the electrons between adsorbent and adsorbate.[41] It can be observed that K_{2ad} increases as temperature rises (0.090, 0.16, and 0.19 g/mg min at 298, 308, and 318 K, respectively), thereby inferring that the adsorption reached equilibrium

Table 3. Thermodynamic parameters for adsorption of Cd(II) ions on modified CSP at different temperatures.

THERMODYNAMIC CONSTANT	TEMPERATURE (K)		
	298	308	318
ΔG^0 (kJ/mol)	−2.06	−2.95	−5.01
ΔH^0 (kJ/mol)		15.8	
ΔS^0 (J/mol K)		55.2	

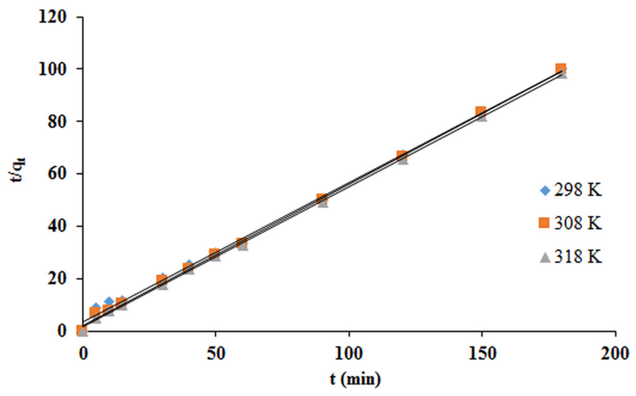

Figure 4. Plot of the pseudo-second-order kinetics at different temperatures.

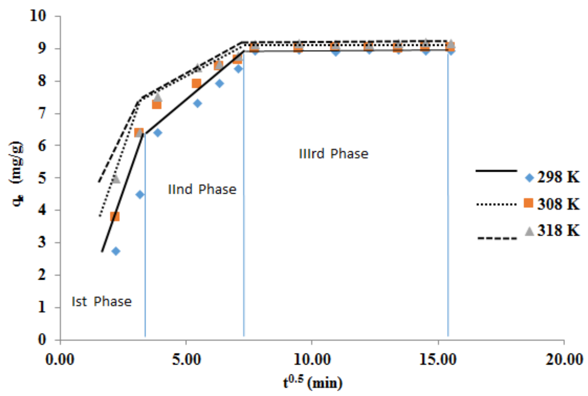

Figure 5. Plot of the intra-particle diffusion kinetics at different temperatures.

sooner at a higher temperature. This behavior could be attributed to an increased probability of the collision between metal ions and active binding sites and a decrease in the thickness of the boundary layer surrounding the adsorbent at high temperatures.[54] Thus, the mass transfer struggle of metal ions in the boundary layer decreased.[55]

Adsorption mechanism. The evaluation of rate controlling steps such as chemical reaction and mass transport is very advantageous to understand the mechanism that is involved in the adsorption phenomenon. The overall adsorption process can be divided into four steps.[56] In the first step, which is not directly involved with adsorbent, the transport of metal ion from the bulk to the boundary layer takes place. Second step is film diffusion, that is, transport of metal ions from the boundary layer to the external surface of the adsorbent. Third, transfer of ions from the surface to the intra-particular spaces present in adsorbent as active sites and this step is known as particle diffusion. Finally, at the fourth stage, interactions take place between the metal ions and the available adsorption sites on the internal surfaces of the adsorbent. Therefore, due to the slow rate of second and third steps, the rate controlling steps mainly depend on either film diffusion or particle diffusion. The intra-particle diffusion model widely used to predict the rate controlling step[57] and is expressed in Equation 10:

$$q_t = K_i t^{0.5} + I, \qquad (10)$$

where q_t is the amount of Cd(II) ion adsorbed at time t, i is the intercept at stage I and K_i is the intra-particle diffusion rate constant. The value of I provides an insight about the thickness of the boundary layer. The plots of q_t vs. $t^{0.5}$ at different temperature show multi-linearity characterizations (Fig. 5), indicating that three steps occurred in the adsorption process. All the intra-particle diffusion parameters are summarized in Table 4.

The larger slopes of the first sharp section represent the external surface adsorption and show that in the beginning, higher rate of metal ion removal is due to the immediate availability of large surface area and active adsorption sites. The second portion is the gradual adsorption stage, where intra-particle diffusion is rate-controlled.[58] The third and final equilibrium stage relates to the slowing down of intra-particle diffusion because of low solute concentrations in the solution. When the saturation occurs at the exterior surface for adsorption, the Cd(II) ions might have entered into the porous structure of the adsorbent. The deviation from the origin suggests that the intra-particle diffusion is not the only rate controlling step for the adsorption of Cd(II) ions onto CSP.

Effect of anions and cations on biosorption. Real/industrial wastewater often contains several other ions, including anions such as sulfate (SO_4^-), carbonate (CO_3^{2-}), chloride (Cl^-), nitrate (NO_3^{2-}), and cations such as Na^+, K^+, Ca^{2+}, Mg^{2+}, etc., which may interfere with the uptake of heavy metal ions by biosorbent. The effect of anions and cations on Cd(II) ion removal was studied, and the results were illustrated in

Table 4. Intra Particle Diffusion Parameters for the adsorption of Cd(II) ion on modified CSP at different temperatures.

	INTRA PARTICLE DIFFUSION								
	298 K			308 K			318 K		
	R^2	K_{id} (mg g^{-1} min$^{1/2}$)	I	R^2	K_{id} (mg g^{-1} min$^{1/2}$)	I	R^2	K_{id} (mg g^{-1} min$^{1/2}$)	I
Ist phase	0.993	1.7	−0.997	0.961	2.16	−0.886	0.934	1.045	2.97
IInd phase	0.818	0.415	5.31	0.781	0.265	6.68	0.766	0.143	7.72
IIIrd phase	0.907	−0.019	9.21	0.768	0.002	8.98	0.742	0.011	9.01

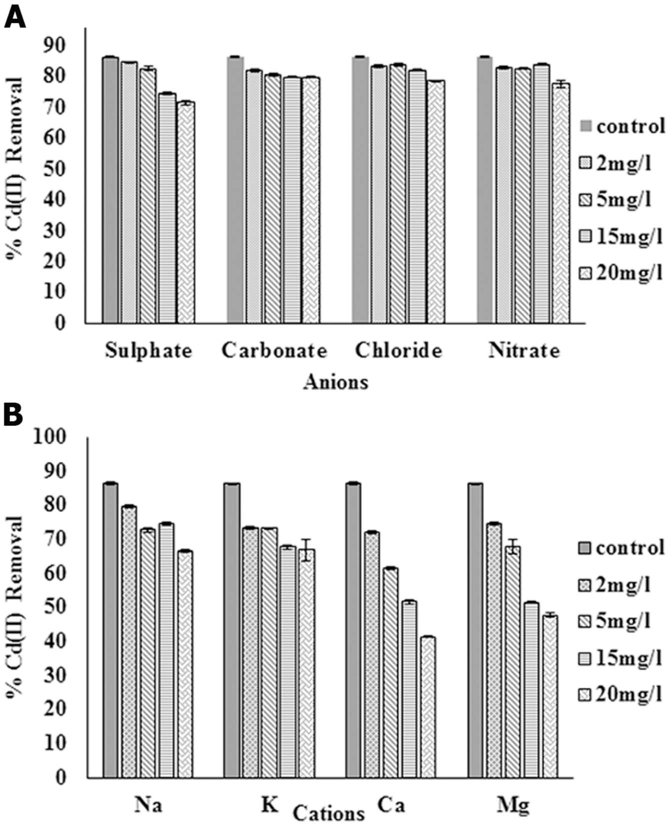

Figure 6. Effect of presence of anions (**A**) and cations (**B**) on Cd(II) ion uptake by modified CSP.

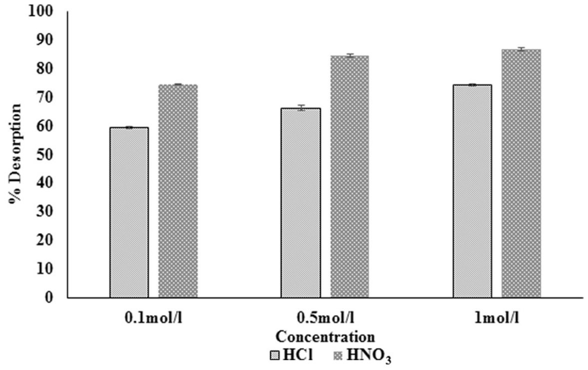

Figure 7. Desorption efficiency of modified CSP using HCl and HNO_3.

Figures 6A and 6B. It was apparent that the presence of anions did not significantly affect the Cd(II) ion removal (Fig. 6A). The removal efficiency was mainly affected by sulfate ions at 20 mg/L and the percentage removal was dropped 15% in comparison to control. The reason can be attributed to the fact that some anions can have an affinity toward the metal ions and form an insoluble or soluble complex. The displacements of these complexes are very difficult in the presence of the biosorbents.[59]

The effect of cation was investigated using their different concentrations. Results shown in Figure 6B demonstrate that presence of cations affects the percentage metal ion removal. The influence of Na^+ and K^+ on the adsorption of Cd(II) is very small in comparison to Ca^{2+} and Mg^{2+}. The presence of Ca^{2+} and Mg^{2+} at 20 mg/L caused removal percentage to drop by 39% and 30%, respectively, due to the competition between Cd^{2+} ions and $cations^+$ for the sites of binding on CSP.

Desorption study. It is evident from Figure 7 that the maximum desorption efficiency was 86.80% for Cd(II) using 1 mol/L HNO_3. Hydronium ions may replace Cd(II) ions on the metal loaded adsorbent, thus showing a behavior as a cation exchanger. The disposal problem of the loaded adsorbents is of most concern as they are hazardous in nature and this issue may be overcome to some extent by using desorption methods. Desorption allows the recovery of metal ions and regeneration of adsorbents. Regeneration of adsorbents promotes their reuse for the adsorption process, and finally the adsorbents must be incinerated.[60]

Conclusion

The present investigation shows the use of waste CSP for the Cd(II) ions removal from aqueous solution. The main benefits of procedure are: simplicity and ease way to prepare adsorbent, sensitivity, great adsorption efficiency with fast attainment of equilibrium. The Cd sorption onto CSP was highly influenced by pH and the favorable pH is 5. The Cd(II) ion uptake of 58.14 mg/g was achieved at optimized conditions in 90 minutes of contact time with initial ion concentration of 20 mg/L. Batch studies displayed that equilibrium was explained by Freundlich isotherm model and the adsorption process followed pseudo-second-order kinetics. Effect of temperature on biosorption showed that the process was spontaneous and endothermic in nature for all the temperature range evaluated. No significant effect on the uptake of Cd(II) ions by co-existing anions was observed, whereas cations, mainly Ca^{2+} and Mg^{2+} may interfere with the metal uptake. It was obvious from the desorption experiments that the increased concentration of eluting agent shows an impactful recovery of adsorbed metal ions and using 1 mol/L HNO_3, maximum desorption efficiency was achieved 86.80%. The removal capacity of CSP was at par with commercially used other adsorbents prepared with other agro-waste materials. Study of removal of Cd(II) ions shows that the CSP has the ability to adsorb Cd(II) from complex aqueous solution.

Acknowledgments

The authors are grateful to The Director, CSIR-IITR, Lucknow, and The Head, Department of Chemistry, BHU, Varanasi for taking interest in the study. The authors also express their gratefulness to all the technical staff for their help.

Author Contributions

Conceived and designed the experiments: RP. Analyzed the data: RP. Wrote the first draft of the manuscript: RP. Contributed to the writing of the manuscript: RCM. Agree with manuscript results and conclusions: NGA and RCM. Jointly developed the structure and arguments for the paper: RCM. Made critical revisions and approved final version: RLP and RCM. All authors reviewed and approved of the final manuscript.

REFERENCES

1. Loghman-Adham M. Renal effects of environmental and occupational lead exposure. *Environ Health Perspect*. 1997;105(9):928–938.
2. Sternberg SP, Dorn RW. Cadmium removal using *Cladophora* in batch, semi-batch and flow reactors. *Bioresour Technol*. 2002;81(3):249–255.
3. Li MS, Yang SX. Heavy metal contamination in soils and phytoaccumulation in a manganese mine wasteland, South China. *Air Soil Water Res*. 2008;1:31–41.
4. Wu J, Lu J, Chen T, et al. In situ biotreatment of acidic mine drainage using straw as sole substrate. *Environ Earth Sci*. 2010;60(2):421–429.
5. Bedoui K, Bekri-Abbes I, Srasra E. Removal of cadmium (II) from aqueous solution using pure smectite and Lewatite S 100: the effect of time and metal concentration. *Desalination*. 2008;223(1–3):269–273.
6. Iqbal M, Saeed A, Zafar SI. FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd(2+) and Pb(2+) removal by mango peel waste. *J Hazard Mater*. 2009;164(1):161–171.
7. Fu F, Wang Q. Removal of heavy metal ions from wastewaters: a review. *J Environ Manage*. 2011;92(3):407–418.
8. Barakat MA. New trends in removing heavy metals from industrial wastewater. *Arabian J Chem*. 2011;4(4):361–377.
9. Eccles H. Treatment of metal-contaminated wastes: why select a biological process? *Trends Biotechnol*. 1999;17(12):462–465.
10. Tor A, Danaoglu N, Arslan G, Cengeloglu Y. Removal of fluoride from water by using granular red mud: batch and column studies. *J Hazard Mater*. 2009;164(1):271–278.
11. Ciesielczyk F, Bartczak P, Wieszczycka K, Siwińska-Stefańska K, Nowacka M, Jesionowski T. Adsorption of Ni(II) from model solutions using co-precipitated inorganic oxides. *Adsorption*. 2013;19(2–4):423–434.
12. Madhava Rao M, Ramesh A, Purna Chandra Rao G, Seshaiah K. Removal of copper and cadmium from the aqueous solutions by activated carbon derived from *Ceiba pentandra* hulls. *J Hazard Mater*. 2006;129(1–3):123–129.
13. Ahluwalia SS, Goyal D. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresour Technol*. 2007;98(12):2243–2257.
14. Jusoh A, Shiung LS, Ali N, Noor MJMM. A simulation study of the removal efficiency of granular activated carbon on cadmium and lead. *Desalination*. 2007;206(1–3):9–16.
15. Kurniawan TA, Chan GYS, Lo W-H, Babel S. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Sci Total Environ*. 2006;366(2–3):409–426.
16. Pandey R, Prasad RL, Ansari NG, Murthy RC. Utilization of NaOH modified *Desmostachya bipinnata* (Kush grass) leaves and *Bambusa arundinacea* (bamboo) leaves for Cd(II) removal from aqueous solution. *J Environm Chem Eng*. 2014. doi:10.1016/j.jece.2014.06.015.
17. Schleuter D, Günther A, Paasch S, et al. Chitin-based renewable materials from marine sponges for uranium adsorption. *Carbohydr Polym*. 2013;92(1):712–718.
18. Wysokowski M, Klapiszewski Ł, Moszyński D, et al. Modification of chitin with kraft lignin and development of new biosorbents for removal of cadmium(II) and nickel(II) ions. *Mar Drugs*. 2014;12(4):2245–2268.
19. Gupta VK, Sharma S. Removal of cadmium and zinc from aqueous solutions using red mud. *Environ Sci Technol*. 2002;36(16):3612–3617.
20. Dávila-Rangel JI, Solache-Ríos M, Badillo-Almaraz VE. Comparison of three Mexican aluminosilicates for the sorption of cadmium. *J Radioanal Nucl Chem*. 2005;267(1):139–145.
21. Kumar U, Bandyopadhyay M. Fixed bed column study for Cd(II) removal from wastewater using treated rice husk. *J Hazard Mater*. 2006;129(1–3):253–259.
22. Martínez M, Miralles N, Hidalgo S, Fiol N, Villaescusa I, Poch J. Removal of lead(II) and cadmium(II) from aqueous solutions using grape stalk waste. *J Hazard Mater*. 2006;133(1–3):203–211.
23. Horsfall M Jr, Abia AA, Spiff AI. Kinetic studies on the adsorption of Cd2+, Cu2+ and Zn2+ ions from aqueous solutions by cassava (*Manihot esculenta* Cranz) tuber bark waste. *Bioresour Technol*. 2006;97(2):283–291.
24. Lodeiro P, Cordero B, Barriada JL, Herrero R, Sastre de Vicente ME. Biosorption of cadmium by biomass of brown marine macroalgae. *Bioresour Technol*. 2005;96(16):1796–1803.
25. Liu Y-G, Fan T, Zeng G-M, et al. Removal of cadmium and zinc ions from aqueous solution by living *Aspergillus niger*. *Trans Nonferrous Met Soc China*. 2006;16(3):681–686.
26. Renner SS, Schaefer H, Kocyan A. Phylogenetics of *Cucumis* (Cucurbitaceae): cucumber (*C. sativus*) belongs in an Asian/Australian clade far from melon (*C. melo*). *BMC Evol Biol*. 2007;7:58.
27. Annadural G, Juang RS, Lee DJ. Adsorption of heavy metals from water using banana and orange peels. *Water Sci Technol*. 2003;47(1):185–190.
28. Argun ME, Dursun S, Ozdemir C, Karatas M. Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics. *J Hazard Mater*. 2007;141(1):77–85.
29. Kumar A, Prasad B, Mishra IM. Adsorptive removal of acrylonitrile by commercial grade activated carbon: kinetics, equilibrium and thermodynamics. *J Hazard Mater*. 2008;152(2):589–600.
30. Ekpete OA, Horsfall M JNR. Preparation and characterization of activated carbon derived from fluted pumpkin stem waste (*Telfairia occidentalis* Hook F). *Res J Chem Sci*. 2011;1(3):10–17.
31. Sari A, Tuzen M. Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass. *J Hazard Mater*. 2009;164(2–3):1004–1011.
32. Sekar M, Sakthi V, Rengaraj S. Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from coconut shell. *J Colloid Interface Sci*. 2004;279(2):307–313.
33. Mahmoud ME, Osman MM, Ahmed SB, Abdel-Fattah TM. Enhanced removal of lead by chemically and biologically treated carbonaceous materials. *Sci World J*. 2012:604198.
34. Saeed A, Iqbal M. Bioremoval of cadmium from aqueous solution by black gram husk (*Cicer arientinum*). *Water Res*. 2003;37(14):3472–3480.
35. Saeed A, Iqbal M, Akhtar MW. Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). *J Hazard Mater*. 2005;117(1):65–73.
36. Pandey R, Ansari NG, Prasad RL, Murthy RC. Pb(II) removal from aqueous solution by *Cucumis sativus* (Cucumber) peel: kinetic, equilibrium & thermodynamic study. *Am J Environ Prot*. 2014;2(3):51–58.
37. Schneider IAH, Rubio J, Smith RW. Biosorption of metals onto plant biomass: exchange adsorption or surface precipitation? *Int J Miner Process*. 2001;62(1–4):111–120.
38. Chen G, Zeng G, Tang L, et al. Cadmium removal from simulated wastewater to biomass byproduct of *Lentinus edodes*. *Bioresour Technol*. 2008;99(15):7034–7040.
39. Wu Y, Zhang S, Guo X, Huang H. Adsorption of chromium(III) on lignin. *Bioresour Technol*. 2008;99(16):7709–7715.
40. Zhu B, Fan T, Zhang D. Adsorption of copper ions from aqueous solution by citric acid modified soybean straw. *J Hazard Mater*. 2008;153(1–2):300–308.
41. Li Y, Du Q, Wang X, et al. Removal of lead from aqueous solution by activated carbon prepared from *Enteromorpha prolifera* by zinc chloride activation. *J Hazard Mater*. 2010;183(1–3):583–589.
42. Deng L, Su Y, Su H, Wang X, Zhu X. Sorption and desorption of lead (II) from wastewater by green algae *Cladophora fascicularis*. *J Hazard Mater*. 2007;143(1–2):220–225.
43. Adeogun A, Idowu M, Ofudje A, Kareem S, Ahmed S. Comparative biosorption of Mn(II) and Pb(II) ions on raw and oxalic acid modified maize husk: kinetic, thermodynamic and isothermal studies. *Appl Water Sci*. 2013;3(1):167–179.
44. Rao KS, Anand S, Venkateswarlu P. Adsorption of cadmium from aqueous solution by *Ficus religiosa* leaf powder and characterization of loaded biosorbent. *CLEAN Soil Air Water*. 2011;39(4):384–391.
45. Panda GC, Das SK, Chatterjee S, Maity PB, Bandopadhyay TS, Guha AK. Adsorption of cadmium on husk of *Lathyrus sativus*: physico-chemical study. *Colloids Surf B Biointerfaces*. 2006;50(1):49–54.
46. Nouri L, Ghodbane I, Hamdaoui O, Chiha M. Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran. *J Hazard Mater*. 2007;149(1):115–125.
47. Min SH, Han JS, Shin EW, Park JK. Improvement of cadmium ion removal by base treatment of juniper fiber. *Water Res*. 2004;38(5):1289–1295.
48. Pandey R, Ansari NG, Murthy RC, Prasad RL. Cd (II) Adsorption from Aqueous Solution onto *Cucumis sativus* Peel: Equilibrium, Thermodynamic and Kinetic Study. *Journal of Ecophysiology & Occupational Health*. 2013;13:75–84.
49. Sarı A, Tuzen M, Soylak M. Adsorption of Pb(II) and Cr(III) from aqueous solution on Celtek clay. *J Hazard Mater*. 2007;144(1–2):41–46.
50. Ho Y-S, Ofomaja AE. Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent. *Biochem Eng J*. 2006;30(2):117–123.
51. Bulut Y, Tez Z. Removal of heavy metals from aqueous solution by sawdust adsorption. *J Environ Sci*. 2007;19(2):160–166.
52. Boudrahem F, Aissani-Benissad F, Aït-Amar H. Batch sorption dynamics and equilibrium for the removal of lead ions from aqueous phase using activated carbon developed from coffee residue activated with zinc chloride. *J Environ Manage*. 2009;90(10):3031–3039.
53. Vadivelan V, Kumar KV. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *J Colloid Interface Sci*. 2005;286(1):90–100.

54. Alfaro-Cuevas-Villanueva R, Hidalgo-Vazquez AR, Cortes Penagos Cde J, Cortes-Martinez R. Thermodynamic, kinetic, and equilibrium parameters for the removal of lead and cadmium from aqueous solutions with calcium alginate beads. *Sci World J*. 2014;2014:647512.
55. Apiratikul R, Madacha V, Pavasant P. Kinetic and mass transfer analyses of metal biosorption by *Caulerpa lentillifera*. *Desalination*. 2011;278(1–3):303–311.
56. Özer A, Gürbüz G, Çalimli A, Körbahti BK. Biosorption of copper(II) ions on *Enteromorpha prolifera*: application of response surface methodology (RSM). *Chem Eng J*. 2009;146(3):377–387.
57. Wang L, Zhang J, Zhao R, Li Y, Li C, Zhang C. Adsorption of Pb(II) on activated carbon prepared from *Polygonum orientale* Linn.: kinetics, isotherms, pH, and ionic strength studies. *Bioresour Technol*. 2010;101(15):5808–5814.
58. Cheung WH, Szeto YS, McKay G. Intraparticle diffusion processes during acid dye adsorption onto chitosan. *Bioresour Technol*. 2007;98(15):2897–2904.
59. Benaïssa H, Elouchdi MA. Removal of copper ions from aqueous solutions by dried sunflower leaves. *Chem Eng Process: Process Intensif*. 2007;46(7):614–622.
60. Demirbas E, Dizge N, Sulak MT, Kobya M. Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. *Chem Eng J*. 2009;148(2–3):480–487.