



## Sodium hydroxyethylcellulose succinate: an efficient ion exchanger to remove Cd(II) from single and binary metal system

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### ABSTRACT

This work deals with the use of a suporsorbent, i.e., sodium hydroxyethylcellulose succinate (HEC-Suc-Na), for the removal of Cd(II) ions from aqueous solution. HEC-Suc was fabricated via esterification of HEC with succinic anhydride in the presence of dimethylaminopyridine (DMAP) as a catalyst. The treatment of HEC-Suc conjugate with saturated NaHCO<sub>3</sub> solution provided HEC-Suc-Na (sodic form). These acidic and sodic forms of the sorbent were characterized by Fourier transform infrared and energy-dispersive spectroscopy. The surface morphology and charge on the surface of sorbent were monitored by SEM and pH corresponding to point of zero charge. Sorption data conformed well to the pseudo-second-order kinetic and Langmuir isotherm model. Maximum sorption capacity of HEC-Suc-Na for Cd(II) removal as calculated by Langmuir model was 714.2 mg g<sup>-1</sup>. Moreover, no significant decrease in the sorption capacity of the sorbent was found after five regeneration cycles suggesting its repeated use. Thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) showed negative values that indicate spontaneity and exothermic nature of the sorption process. Removal of Cd(II) in presence of Ni(II) was also studied.

*Keywords:* Cadmium; Ion-exchange; Modified cellulose; Regenerability

### 1. Introduction

The water bodies are extremely polluted due to various activities of modern age such as industrialization, use of pesticides, metal plating, mining, battery manufacture, smelting, tanneries, petroleum refining, paint manufacture, pigment manufacture, printing and so on [1,2]. Therefore, the status quo of surface and ground water is alarming and needs fruitful approaches for the treatment of contaminated water. In this account, the heavy metals are of major concern because their accumulations beyond certain limit pose a serious threat to the ecosystem.

Cadmium is one of the most toxic heavy metals and is well documented for its negative effects on human health. It has been reported as a root cause for various diseases and

disorders such as cancer, nausea, erythrocyte destruction, salivation, diarrhea, muscular cramps, renal degradation, skeleton deformity and pulmonary problems renal disturbances, lung insufficiency, bone lesions and hypertension in humans [3].

Numerous technologies for removing heavy metal ions from wastewater have been industrialized. Some important methodologies include chemical precipitation, adsorption, solvent extraction, ion-exchange and reverse osmosis [4–8]. Ion-exchange process is a relatively simple, efficient and eco-friendly technique for the extraction of toxic heavy metal ions from the industrial wastewater, tannery effluents and sewages [9,10]. In order to meet water glitches due to heavy metals and dyes, special attention has been focused on the use of modified and unmodified cellulosic sorbents as an alternative to replace the conventional adsorbents, with their both environmental and economic benefits [11,12]. Due to

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their potential for heavy metals uptake and low cost, these are found to be suitable sorbents.

Being smart materials, cellulose ether derivatives find extensive commercial applications in pharmaceuticals and several other industries [13]. Therefore, present study is projected for the use of a cellulose ether derivative sodium hydroxyethylcellulose succinate (HEC-Suc-Na) for effective removal of Cd(II) from aqueous solution. The study is also aimed to investigate the effects of sorbent dosage, contact time, pH, temperature and initial concentration on the sorption capacity of the sorbent to remove Cd(II) from aqueous solution. Application of various kinetic and isotherm models to the sorption data is another aim of this study. Besides this, our interest is also focused to estimate various thermodynamics parameters such as  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ , which predict feasibility and spontaneity of sorption. Furthermore, sorption of Cd(II) in presence of Ni(II) and regeneration studies of the sorbent are also aimed.

## 2. Experimental

### 2.1. Reagent and materials

Hydroxyethylcellulose (Natrosol hydroxyethylcellulose, HE10K, Belgium), Cd(NO<sub>3</sub>)<sub>2</sub>, NaHCO<sub>3</sub>, HNO<sub>3</sub> and NaOH were obtained from Fluka. HEC was dried at 110°C for 2 h before use. The solvents used were of analytical grade.

### 2.2. Synthesis of HEC-Suc conjugate and HEC-Suc-Na

HEC-Suc was synthesized by esterification of HEC with succinic anhydride using 4-dimethylaminopyridine by a reported method [14]. HEC-Suc synthesized showed fairly high degree of substitution (DS 2.78) as calculated by acid–base titration after saponification as opted elsewhere [15]. The HEC-Suc was converted into its sodic form (HEC-Suc-Na) by treating it with saturated NaHCO<sub>3</sub> solution. The HEC-Suc-Na was used for the removal of Cd(II) from aqueous solution.

### 2.3. Characterization of HEC-Suc conjugate and HEC-Suc-Na

Fourier transform infrared (FT-IR) spectra were recorded by using the pellet prepared by mixing the sample with KBr. This pellet was dried at 60°C for 30 min, under vacuum, prior to analysis. IR-Prestige-21 (Shimadzu, Japan) spectrometer was used to get FT-IR spectra. Thermogravimetric analyses of acidic (HEC-Suc) and sodic form of sorbent (HEC-Suc-Na) was carried out on a SDT Q 600 thermal analyzer (TA Instruments, USA) from ambient to 1,000°C under N<sub>2</sub> at the onset of 10°C/min. Scanning electron microscope (SEM) images and energy-dispersive spectroscopic (EDS) analyses of the sorbent HEC-Suc-Na were recorded before and after metal uptake using SEM (Nova, NanoSEM 450) equipped with a low-energy Everhart–Thornley detector (ETD) and Oxford energy-dispersive X-ray (EDX). For this purpose, the samples were prepared by dispersing HEC-Suc-Na and HEC-Suc-Cd (sorbent after Cd(II) uptake) in deionized water followed by drying their 20 µL volume on separate aluminum stubs. Surface charge of HEC-Suc-Na was monitored by calculating the pH<sub>pzc</sub> (pH corresponding to the point of zero charge), which was found to be 4.2.

Above this pH, surface of the sorbent has negative charge, which favors metal uptake.

### 2.4. Sorption and regeneration studies

Batch experiments were performed by stirring 100 mL of distilled water (DW) containing metal ion solutions of known concentration and 20 mg of the sorbent. The amount of metal ions removed by the sorbent  $q_e$  (mg g<sup>-1</sup>) was calculated by Eqs. (1) and (2):

$$q_e = \frac{C_i - C_f}{m} \times V \quad (1)$$

$$\text{Percentage uptake} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where  $C_i$  and  $C_f$  are the initial and final Cd(II) concentration in mg/L, respectively.  $V$  (L) and  $m$  (g) are the volume of solution and mass of adsorbent, respectively.

Effects of initial metal ion concentration and sorbent dosage on sorption capacity of the sorbent were studied by stirring Cd(II) (110–290 mg L<sup>-1</sup>) with 20 mg sorbent and Cd(II) (140 mg L<sup>-1</sup>) with sorbent dosage (20–80 mg), respectively, for 30 min at a speed of 150 rpm at 298 K. Effects of pH, contact time and temperature on Cd(II) removal from aqueous solution were investigated in the range 2.0–7.0, 5–120 min and 298–343 K, respectively, by stirring fixed amount of HEC-Suc-Na (20 mg) with DW (100 mL) containing Cd(II) (140 mg L<sup>-1</sup>) under optimal conditions. The pH of Cd(II) solution was adjusted by using 1 M HNO<sub>3</sub> and 1 M NaOH. Flame atomic absorption spectrophotometer (FAAS; AA 6300, Shimadzu, Japan) was used to determine the equilibrium concentration of Cd(II) at wavelength 228 nm.

To carry out regeneration studies, the sorbent, HEC-Suc-Na (20 mg), was first stirred with Cd(II) (140 mg L<sup>-1</sup>) for 30 min. After Cd(II) uptake, the sorbent obtained was stirred overnight with brine solution (100 mL). Then the sorbent obtained after filtration was completely washed with DW until negative AgNO<sub>3</sub> test. The recovered sorbent was then air-dried. This regenerated sorbent was again used for Cd(II) uptake. These sorption–regeneration studies were carried out five times. Acidic form of the sorbent, i.e., HEC-Suc, was also analyzed for Cd(II) sorption under optimal conditions.

Sorption of Cd(II) from binary metal solution was carried out to study potential of the sorbent for the removal of Cd(II) in the presence of Ni(II). Binary solution (100 mL) containing Cd(II) (140 mg L<sup>-1</sup>) and Ni(II) (100 mg L<sup>-1</sup>) was stirred with the sorbent under optimal conditions (20 mg, 30 min, 298 K). Removal of Cd(II) from binary solution was carried out at pH 6 because Cd(II) have maximum sorption capacity at this pH in single metal system. To optimize Ni(II) concentration used for competitive studies, sorbent (20 mg) was stirred with solution (100 mL) containing Ni(II) (40–220 mg L<sup>-1</sup>) for 30 min at a speed of 150 rpm and 298 K. For each metal ion, metal ion uptake in the supernatant was determined by using FAAS in the presence of other metal ion. Equilibrium concentration of Ni(II) was determined at wavelength 232 nm using FAAS.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of HEC-Suc conjugate and HEC-Suc-Na

HEC-Suc was synthesized by esterification of HEC with succinic anhydride under homogeneous reaction conditions in *N,N*-dimethylacetamide (DMAc). The HEC-Suc was then converted into HEC-Suc-Na by treating it with saturated  $\text{NaHCO}_3$  solution. HEC-Suc-Na and HEC-Suc were found insoluble in hot and cold water, dimethylsulphoxide (DMSO), ethanol and methanol and so on, and it provided the basis for its use for the removal of metal ions from aqueous solution.

The FT-IR (KBr) spectra of HEC-Suc and HEC-Suc-Na are shown in Fig. 1. The bands stretched at 1,728 and 1,726  $\text{cm}^{-1}$  are showing the presence of ester carbonyl groups in

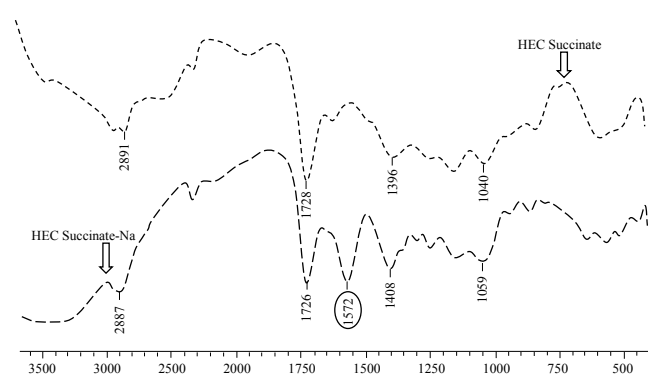


Fig. 1. FTIR (KBr, transmittance) spectra of HEC-Suc and HEC-Suc-Na.

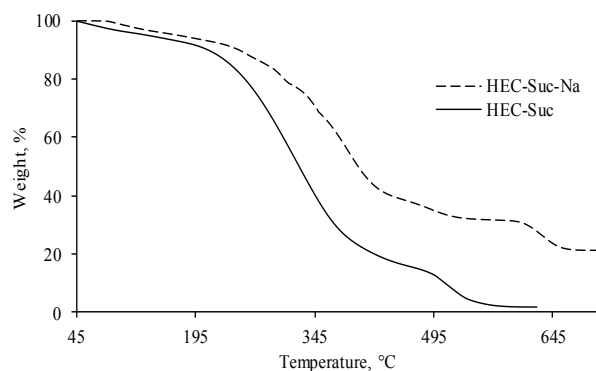


Fig. 2. Overlay TG curves of HEC-Suc and HEC-Suc-Na indicating thermal stability imparted in sodic form of sorbent throughout the degradation profile.

HEC-Suc and HEC-Suc-Na, respectively. However, the band appearance at 1,572  $\text{cm}^{-1}$  in the spectrum of HEC-Suc-Na is for carboxylate anion illustrating sodium salt formation.

Thermal stability of HEC-Suc and HEC-Suc-Na was checked by thermal analyses of the two polysaccharidic materials, which is an important property to get information about stability, storage, handling and predictions of performance parameters [16]. Fig. 2 shows the overlay of TG curves of HEC-Suc and HEC-Suc-Na. Thermal decomposition temperatures initial degradation temperature (Tdi), maximum degradation temperature (Tdm) and final degradation temperature (Tdf), which were obtained for each degradation step from differential thermogravimetry (DTG) curves, give comparison of thermal stability as shown in Table 1.

Two-step degradation profiles were witnessed by thermograms of HEC-Suc and HEC-Suc-Na. The degradation maxima (Tdm) of HEC-Suc and HEC-Suc-Na were found to be 320°C and 386°C, respectively, for first and major step degradations. Thus, an increase in Tdm value in going from HEC-Suc to HEC-Suc-Na was 66°C, which indicates that higher thermal stability was incorporated after conversion of HEC-Suc into sodic form. Likewise, Tdi value of this step for HEC-Suc-Na was almost 64°C higher than HEC-Suc. Literature also revealed that organic compounds containing metal are thermally more stable than without metal [17]. It is therefore inferred that the increased thermal stability of sorbent could be of commercial importance indicating its potential use for effluents with high temperatures.

Surface morphology of the sorbent (HEC-Suc-Na) was studied by SEM-EDS analyses before and after Cd(II) uptake (Fig. 3). Surface morphology of both the acidic (HEC-Suc) and sodic form (HEC-Suc-Na) of the sorbent showed rough and inhomogeneous surface. Presence of Na ions and Cd ions in the sorbent before and after sorption was confirmed by EDS plots, respectively.

#### 3.2. Sorption studies

##### 3.2.1. Effect of the initial metal concentration

The effect of initial concentration of heavy metal ion on the extent of its sorption was investigated. Fig. 4(a) demonstrates the effect of initial Cd(II) ion concentration on the sorption capacity of HEC-Suc-Na from aqueous solution. The sorption capacity of the sorbent increased with increase in initial metal ion concentration, and later on, it became constant. This can be attributed to mass transfer driving force and availability of sufficient sorption sites and fewer metal ions during early stages. The maximum sorption capacity was reached at 140  $\text{mg L}^{-1}$  for DW solution. This Cd(II) ion concentration was used for further sorption studies.

Table 1  
Thermal decomposition data of HEC-Suc and HEC-Suc-Na sorbent

| Sample     | Step | Tdi (°C) | Tdm (°C) | Tdf (°C) | Weight loss (%) at Tdf | Char yield (weight %) |
|------------|------|----------|----------|----------|------------------------|-----------------------|
| HEC-Suc    | I    | 174.26   | 320.22   | 462.39   | 77.10                  | 1.86% at 625°C        |
|            | II   | 470.71   | 513.81   | 551.62   | 12.17                  |                       |
| HEC-Suc-Na | I    | 237.79   | 386.01   | 531.21   | 63.10                  | 21.11% at 730°C       |
|            | II   | 593.97   | 628.76   | 667.33   | 10.13                  |                       |

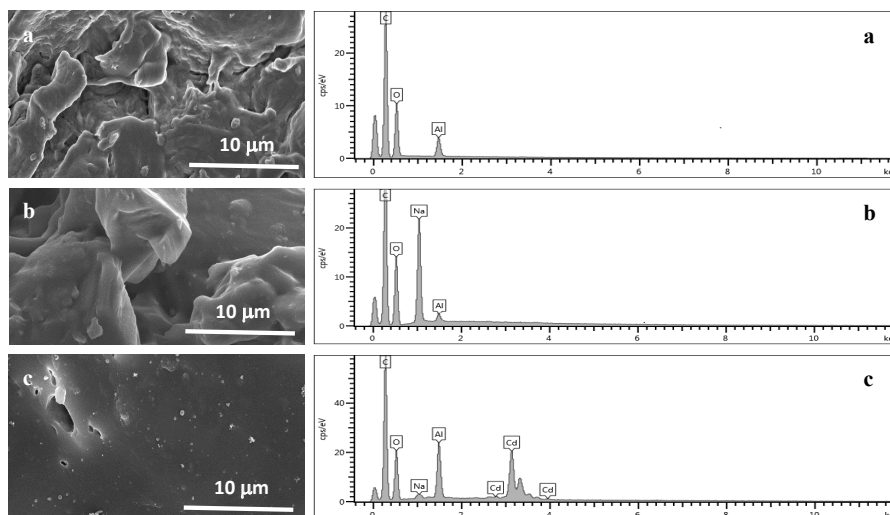


Fig. 3. SEM-EDS of HEC-Suc (a), HEC-Suc-Na (b), and Cd (II) adsorbed HEC-Suc-Na (c).

### 3.2.2. Effect of the sorbent dosage

The effect of sorbent (HEC-Suc-Na) dosage was studied for the removal of Cd(II) from aqueous solutions. Fig. 4(b) shows that the increased sorbent dosage resulted in a rapid uptake of metal ions attributable to the availability of more active sorption sites. Sorption capacity ( $\text{mg g}^{-1}$ ) was observed to be maximum at optimal sorbent dosage. It decreased in later stages of the process due to unavailability of Cd(II) ions to be exchanged with the sorbent (HEC-Suc-Na) surface sites. It can be witnessed from the plot (see Fig. 4(b)) that a sorbent dosage of 20 mg showed maximum sorption capacity. Therefore, this amount of HEC-Suc-Na was processed for further sorption analyses.

### 3.2.3. Effect of pH on Cd uptake

The pH of adsorption medium affects the charge on surface of sorbent and solution chemistry [18]. To study the effect of pH, the pH was varied within the range of 2.0–7.0. Fig. 5(a) shows that at lower pH, Cd uptake was insignificant but as the pH was changed from 4.0 onward, the Cd uptake increased abruptly. It was due to the fact that at lower pH high concentration of  $\text{H}^+$  ions causes the protonation of HEC-Suc-Na to form acidic HEC-Suc leaving no exchange sites for Cd(II) uptake. However, at pH values higher than  $\text{pH}_{\text{PZC}}$  (4.2 for HEC-Suc-Na), carboxylic functional group becomes deprotonated providing anionic sites for binding Cd(II) ions. The experiment revealed maximum uptake at pH 6.0.

### 3.2.4. Effect of temperature

The effect of temperature on sorption of Cd(II) ions using HEC-Suc-Na was studied to predict the endothermic or exothermic nature of the sorption process. As the temperature was increased from 298 to 343 K, the sorption capacity was reduced by  $55 \text{ mg g}^{-1}$  (Fig. 5(b)). Hence, the process of sorption for Cd(II) was found to be exothermic in nature. The reason for decreased ion-exchange at high temperature was high mobility of Cd(II) ions, which decreased adsorbate-adsorbent interaction.

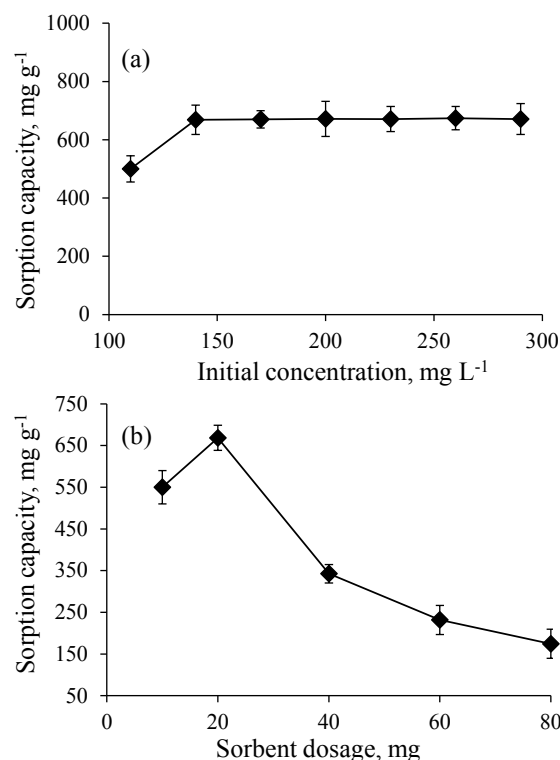


Fig. 4. Sorption capacity as a function of initial concentration of Cd(II) (a) and sorbent dosage (b).

### 3.2.5. Effect of contact time

The effect of contact time on the rate of Cd(II) uptake by HEC-Suc-Na is illustrated in the Fig. 5(c). Plot showed (see Fig. 5(c)) that 90% Cd(II) was removed in early 25 min, and equilibrium was achieved within 30 min. This rapid uptake at early stages of sorption was attributed to the presence of sufficient sorption sites on the surface of the sorbent (HEC-Suc-Na) and involvement of ion-exchange process.

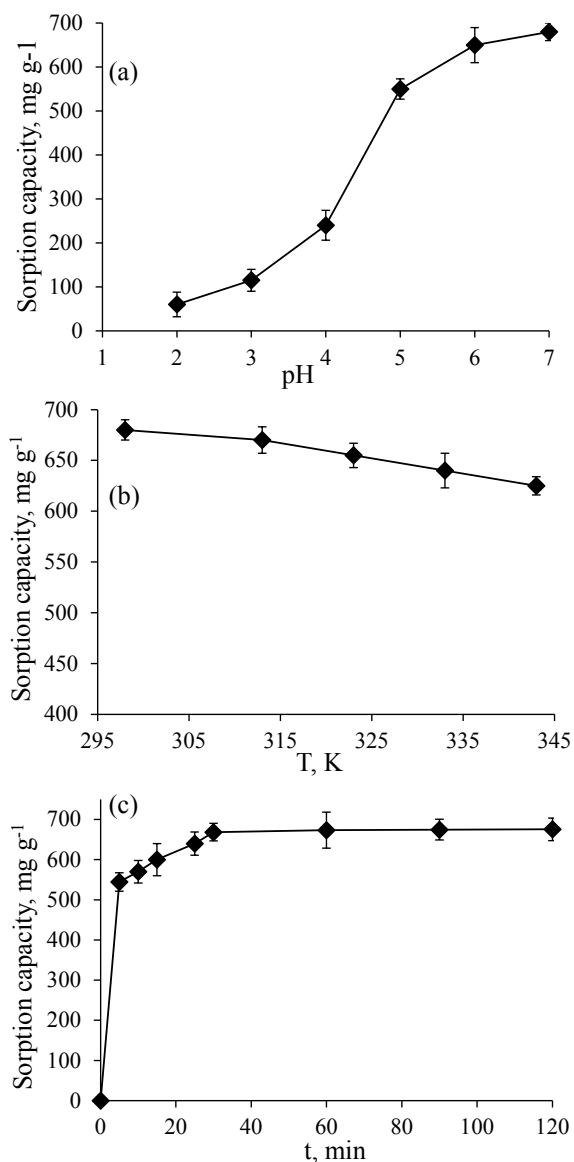


Fig. 5. Sorption capacity as a function of pH (a), temperature (b), and contact time (c).

### 3.2.6. Kinetic modeling

Kinetics of the sorption of Cd(II) on the HEC-Suc-Na was investigated to gain insight into the mechanism of the sorption because such studies are essential for designing wastewater treatment systems. Two kinetics models, i.e., pseudo first order and the pseudo second order, were used in this regard. Linear form of pseudo-first-order kinetic model is given by relation in Eq. (3):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (3)$$

where  $q_e$  is amount of metal ion sorbed at equilibrium, and  $q_t$  is amount of metal sorbed at time  $t$ ;  $k_1$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant. Table 2 shows the values of  $k_1$ ,  $q_e$  and  $R^2$ . Pseudo-first-order model (Fig. 6(a)) did not provide the

Table 2  
Freundlich, Langmuir, pseudo-first-order, pseudo-second-order, ion-exchange model and thermodynamic parameters for Cd(II) removal from aqueous solution using HEC-Suc-Na

| Models                   | Parameters  | Cd(II)  |
|--------------------------|---|---------|
| Experimental             | $q_e$ ( $\text{mg g}^{-1}$ )                          | 669.0   |
|                          | $Q_{\max}$ ( $\text{mg g}^{-1}$ )                     | 714.20  |
| Langmuir parameters      | $Q_{\max}$ ( $\text{mmol g}^{-1}$ )                   | 6.3688  |
|                          | $b$ ( $\text{mg L}^{-1}$ )                            | 0.1261  |
|                          | $b$ ( $\text{mmol L}^{-1}$ )                          | 14.145  |
|                          | $R^2$   | 0.9979  |
| Freundlich parameters    | $R_L$   | 0.0536  |
|                          | $n$   | 25.188  |
|                          | $k_F$   | 544.46  |
| Pseudo second order      | $R^2$   | 0.4450  |
|                          | $q_e$ ( $\text{mg g}^{-1}$ )                          | 666.66  |
|                          | $k$   | 0.0008  |
| Pseudo first order       | $R^2$   | 0.9999  |
|                          | $q_e$ ( $\text{mg g}^{-1}$ )                          | 233.8   |
|                          | $k_1$   | 0.082   |
| Ion-exchange model       | $R^2$   | 0.8963  |
|                          | $S$ ( $\text{min}^{-1}$ )                             | 0.0637  |
|                          | $R^2$   | 0.9987  |
| Thermodynamic parameters | $\Delta S^\circ$ ( $\text{J mol}^{-1}\text{K}^{-1}$ ) | -100.99 |
|                          | $\Delta H^\circ$ ( $\text{kJ mol}^{-1}$ )             | -38.90  |
|                          | $\Delta G^\circ$ ( $\text{kJ mol}^{-1}$ )             | -8.73   |
|                          | $R^2$   | 0.9949  |

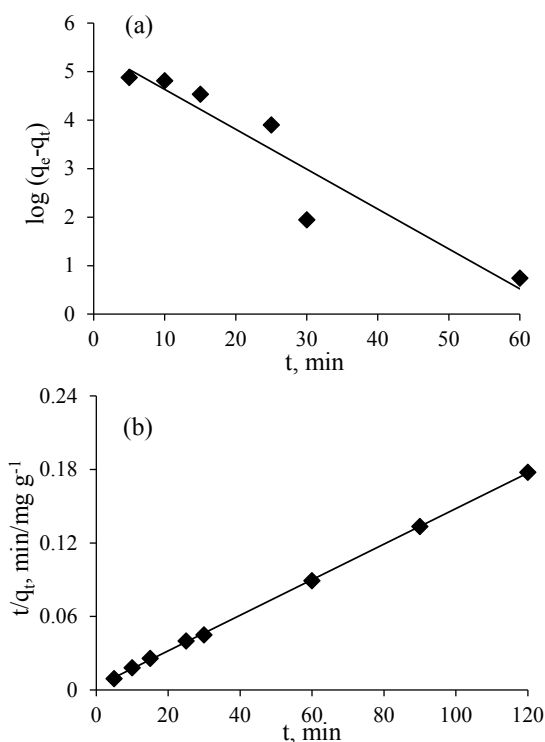


Fig. 6. Pseudo-first-order model (a) and pseudo-second-order model (b) for sorption of Cd(II) from aqueous solution by the sorbent (HEC-Suc-Na).



best fit to experimental data as evidenced from less values of correlation coefficient ( $R^2$ ) and deviation of experimental values of sorption capacity from values calculated from pseudo-first-order model. Therefore, pseudo-second-order kinetic model was fitted to kinetic data. Linear form of pseudo-second-order kinetic model is given by relation given in Eq. (4):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \quad (4)$$

where  $q_t$  and  $q_e$  are amounts of metal sorbed at time  $t$  and equilibrium;  $k$  is rate constant ( $\text{g mg}^{-1} \text{min}^{-1}$ ). To fit this model to experimental data, values of  $t/q_t$  were plotted against  $t$ . A straight line with high correlation coefficients was obtained (Fig. 6(b)). The values of  $q_e$  and  $k$  (Table 2) are calculated from slope and intercept of the straight line, respectively. The  $q_e$  evaluated from the pseudo-second-order plot matched well with experimental values. Therefore, pseudo-second-order kinetic model can be considered as a best model to evaluate the dynamic uptake of Cd(II) ion by HEC-Suc-Na and showed association of chemisorption mechanism to the rate-limiting step.

### 3.2.7. Sorption isotherm

The equilibrium sorption isotherms provide information about sorption mechanisms of any sorbent–sorbate system. A sorption isotherm demonstrates the distribution of sorbed molecules between the sorbate (liquid phase) and the sorbent (solid phase) at the equilibrium stage. The sorption data obtained from the sorption process of Cd(II) ions by HEC-Suc-Na (sorbent) from DW solutions was fitted to Freundlich and Langmuir isotherm. Linear form of Freundlich isotherm is given below in Eq. (5):

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (5)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is equilibrium sorption capacity, and  $C_e$  ( $\text{mg L}^{-1}$ ) is equilibrium metal ions concentration. The values  $n$  (sorption intensity),  $k_F$  (Freundlich constant) and  $R^2$  are enlisted in the Table 2. The low values of correlation coefficient show that Freundlich isotherm (Fig. 7(a)) offered less validity toward sorption data. Therefore, the data was fitted to the Langmuir model, linear form of which is given as Eq. (6):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} \times b} \quad (6)$$

where  $q_e$  ( $\text{mg g}^{-1}$ ) is equilibrium sorption capacity, and  $C_e$  ( $\text{mg L}^{-1}$ ) is equilibrium metal ions concentration. To fit Langmuir model to experimental data values of  $C_e/q_e$  were plotted against  $C_e$ . Straight line with high correlation coefficient was obtained (Fig. 7(b)). The values  $Q_{\max}$  (maximum sorption capacity/g of sorbent) and  $b$  (Langmuir constant) were calculated from slope and intercept of the straight lines, respectively. Maximum sorption capacities of HEC-Suc-Na for

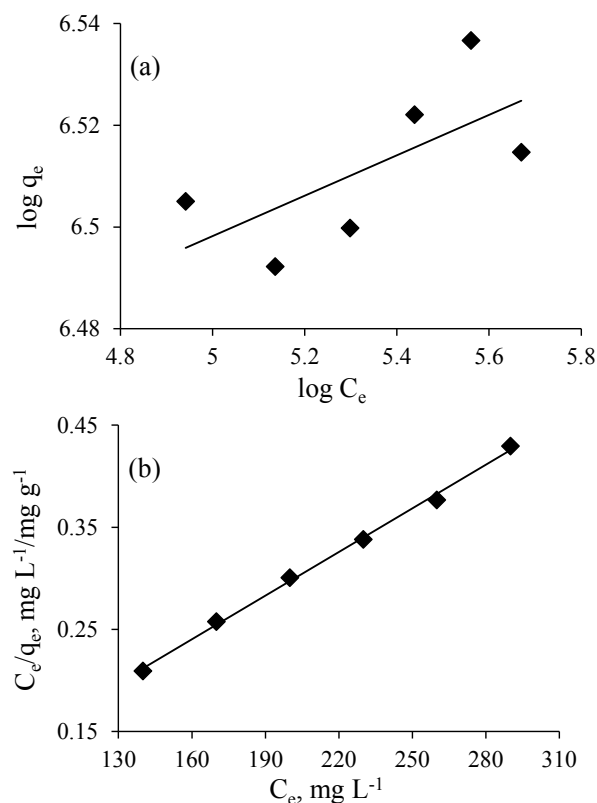


Fig. 7. Freundlich sorption isotherm (a) and Langmuir sorption isotherm (b) models for sorption of Cd(II) from aqueous solution.

Cd(II) uptake was found to be  $714.2 \text{ mg g}^{-1}$  (Table 2). Validity of this model to kinetic data is evidence of monolayer formation, i.e., chemisorption. The separation factor ( $R_L$ ) values can be used to predict whether the adsorption is favorable or unfavorable [19] and is given in Eq. (7):

$$R_L = \frac{1}{1 + bC_i} \quad (7)$$

$R_L$  values ranging from 0 to 1 indicate favorable adsorption (Table 2).

### 3.2.8. Ion-exchange mechanism

The higher Cd uptake during initial rapid phase of sorption was due to involvement of ion-exchange mechanism. It can be witnessed from the fact that acidic form of the sorbent (HEC-Suc) showed negligible Cd uptake (15.2%) while its modification to sodic form (HEC-Suc-Na) provided increased Cd uptake (97.1%) (see section 3.2.10). This was due to the fact that sodic form of the sorbent (HEC-Suc-Na) furnished sufficient  $\text{Na}^+$  ions for exchange of Cd(II) ions. Moreover, fitting of pseudo-second-order kinetic model and Langmuir isotherm model to the sorption data was also an evidence of contribution of ion-exchange mechanism during sorption process. Furthermore, involvement of ion-exchange mechanism

during the sorption process can also be evidenced from fitting of ion-exchange model [20] to the experimental sorption data. Rate equation that considers sorption of a metal ion from aqueous solution through ion-exchange mechanism is given by Eq. (8):

$$\log(1-F) = -\frac{S}{2.303}t \quad (8)$$

where  $F = q_t/q_c$ ;  $q_t$  and  $q_c$  are amounts of metal sorbed at time  $t$  and equilibrium, respectively, and  $S$  ( $\text{min}^{-1}$ ) is a constant. Values of  $\log(1-F)$  are plotted against  $t$ . Straight lines of high values of correlation coefficient are obtained that further verified involvement of ion-exchange mechanism during sorption of Cd(II) (Fig. 8(a), Table 2).

Additionally, it has been noted that sorption capacity values are higher than the theoretical sorption capacity of the sorbent as calculated from stoichiometric ratios of incoming and outgoing cations. Therefore, it is suggested that ion-exchange mechanism is accompanied by the precipitation of Cd(II) on the surface of the sorbent due to high Cd(II) concentration and pH.

### 3.2.9. Thermodynamic parameters determination

The results obtained from the experiments conducted to study the effect of temperature on the sorption of Cd(II) using HEC-Suc-Na from aqueous solution were used to evaluate thermodynamics parameters by using Eqs. (9)–(11):

$$K_c = \frac{C_{\text{ads}}}{C_c} \quad (9)$$

$$\Delta G^\circ = -RT \ln K_c \quad (10)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

where  $C_c$  is the equilibrium concentration of metal ion;  $C_{\text{ads}}$  is the amount of metal sorbed; and  $K_c$  is the sorption equilibrium constant. The straight line was obtained by plotting values of  $\ln K_c$  against  $1/T$  ( $\text{K}^{-1}$ ) (Fig. 8(b)). Entropy change ( $\Delta S^\circ$ ) and enthalpy change ( $\Delta H^\circ$ ) were measured from slope and intercept of this straight line, respectively. The decreased randomness at the adsorbent–adsorbate interface was predicted from the negative value of entropy change ( $\Delta S^\circ$ ), and the negative values of  $\Delta G^\circ$  and  $\Delta H^\circ$  illustrate the feasibility and exothermic nature of sorption process, respectively (Table 2).

Sorption capacity of different sorbents available in literature for Cd(II) removal is summarized in Table 3. The super-sorbent developed and discussed herein showed highest sorption capacity value for Cd(II) removal among the structurally related modified polysaccharidal sorbents.

### 3.2.10. Sorption and desorption (regenerability)

The sorption–desorption studies play an important role in real situations of wastewater treatment and thus help to evaluate inexpensive sorbents. In this study, HEC-Suc-Na

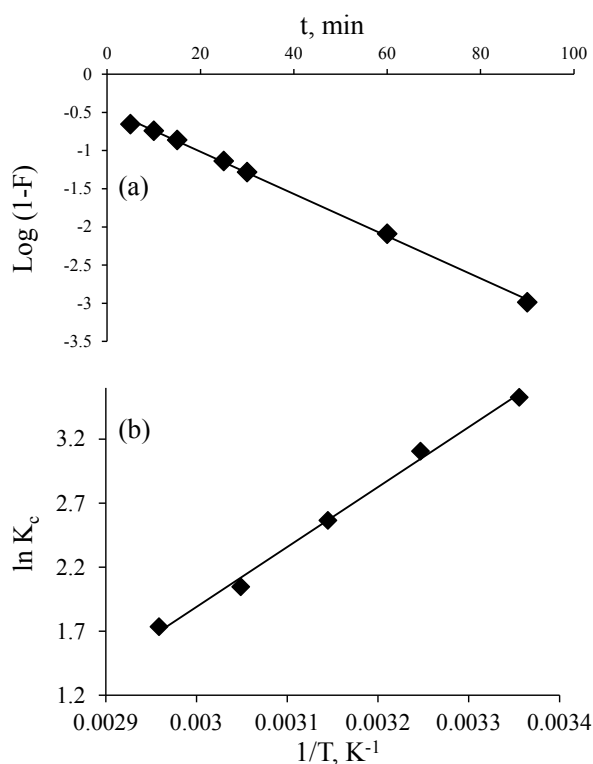


Fig. 8. Ion-exchange model (a) and effect of temperature on equilibrium constant (b) for sorption of Cd(II) from aqueous solution by the sorbent.

Table 3  
Comparison of HEC-Suc-Na for Cd(II) removal from DW solution with other reported sorbents

| Sorbent (treatment)   | Sorption capacity ( $\text{mg}\cdot\text{g}^{-1}$ ) | Reference     |
|---|---|---------------|
| Spent grain (modified with sodium hydroxide, pH 5.3–5.6, 298 K, 2 h)                    | 17.3  | [21]          |
| Sugar beet pulp   | 24.4  | [22]          |
| Mercerized cellulose (modified with succinic anhydride, 10 min)                         | 250   | [23]          |
| Filter aid cellulose (modified with succinic anhydride, sodic)                          | 185.2 from DW                                       | [24]          |
| Poly(vinyl alcohol)/chitosan  | 126.6   | [25]          |
| Bagasse pith (200°C and 400°C under steam with $\text{SO}_2$ and $\text{H}_2\text{S}$ ) | 149.9   | [26]          |
| Sugarcane bagasse (modified with succinic anhydride)                                    | 196   | [27]          |
| Chitosan encapsulated magnetic $\text{Fe}_3\text{O}_4$ nanoparticles                    | 200   | [28]          |
| Thiocarbamoyl chitosan  | 666.7   | [29]          |
| Pullulan (modified with succinic anhydride, 15 min)                                     | 476.2 from DW                                       | [14]          |
| Chitosan-stabilized nano zero-valent iron   | 124.74  | [30]          |
| Hydroxyethylcellulose (modified with succinic anhydride)                                | 714.2   | Present study |

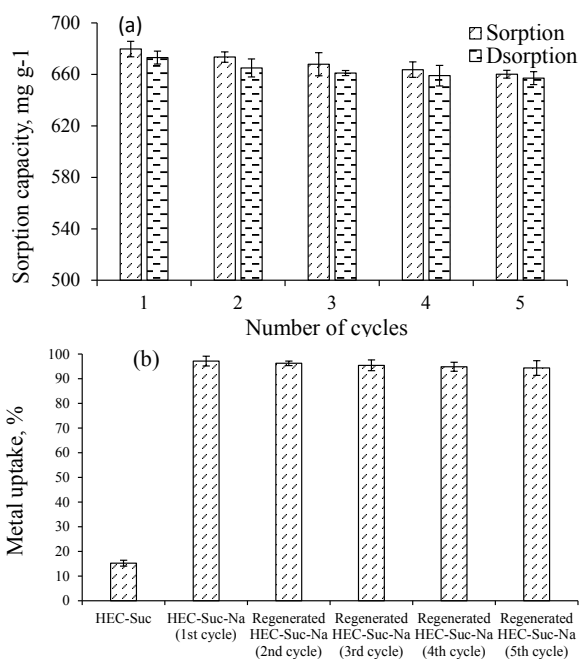


Fig. 9. Sorption capacity as a function of number of sorption-desorption cycles (a) and percentage Cd uptake by the acidic (HEC-Suc) and sodic form of sorbent (HEC-Suc-Na, 1st–5th cycles) (b).

was regenerated by using brine. The sorbent was regenerated, and almost all Cd(II) ions were removed from the sorbent surface with insignificant reduction in sorbent activity. The results of sorption–desorption experiments are represented in Fig. 9(a). After five cycles, 19.7 mg g<sup>-1</sup> reduction for Cd(II) in the sorption capacity of the HEC-Suc-Na was observed for Cd(II). A graph was plotted between percentage Cd(II) uptake and number of sorption–desorption cycles as illustrated in Fig. 9(b). It showed a slight decrease in percentage Cd(II) uptake (2.9%) after five cycles.

### 3.2.11. Competitive adsorption from binary system

Mostly removal of single metal ion from aqueous solutions is considered but it is necessary to study simultaneous removal of more than one heavy metal ions. It is because effluents from several industries contain various metal ions. In case of multicomponent system, factors affecting the sorption capacity are nature of adsorbent (metal binding site, presence of different functional groups) and metallic properties (concentration, ionic size, standard redox potential and electronegativity). This is why potential of HEC-Suc-Na for competitive uptake of Cd(II) from binary mixture Ni(II) + Cd(II) was evaluated. Purpose was to simulate system containing both Ni(II) and Cd(II) such as wastewater from Ni–Cd batteries effluent. Optimum amount of sorbent was added to binary mixture containing Ni(II) + Cd(II) and agitated at pH 6.0 for 30 min at 298 K. Table 4 shows sorption capacities of both metal ions in single and binary component system. Sorption capacity value for both metal ions in single metal system was found to be greater than binary system. It can be

Table 4

Sorption capacities for Cd(II) and Ni(II) from single metal system and binary system by HEC-Suc-Na

| Metal ion | System          | $q_e$ (mg g <sup>-1</sup> ) | $q^{\text{mix}}/q^0$ |
|-----------|-----------------|-----------------------------|----------------------|
| Ni(II)    | Ni(II) alone    | 500                         | –                    |
| Cd(II)    | Cd(II) alone    | 714.2                       | –                    |
| Ni(II)    | Ni(II) + Cd(II) | 126.6                       | 0.9676               |
| Cd(II)    | Ni(II) + Cd(II) | 357.2                       | 0.6774               |

attributed to the fact that single metal system lacks competition for sorption sites on the surface of sorbent. Simultaneous metal removal from binary mixture showed higher sorption capacity values for Cd(II) over Ni(II). This was probably due to greater ion-exchange capability of Cd(II) over its competing Ni(II). Difference in ionic radii, ionic charge and electrode potential of these metal ions is the reason for preferential adsorption Cd(II) over its competing Ni(II) [31]. Moreover, effect of ionic concentrations [32] on the adsorption process may be seen through the ratio of sorption capacity for a metal ion along with other ion ( $q^{\text{mix}}$ ) to the sorption capacity when present alone ( $q^0$ ) in the aqueous system. In binary system under study,  $q^{\text{mix}}/q^0$  was less than 1, which showed decrease in the sorption capacity of both ions in presence of each other. Results of competitive sorption for binary metal system are illustrated in Table 4. Sorption capacity values for single metal system for both metal ions are calculated by Langmuir model.

## 4. Conclusions

A supersorbent HEC-Suc-Na was explored for the uptake of Cd(II) ions from aqueous solution. Sorbent showed highest value of sorption capacity for Cd(II) removal from aqueous solution as compared with other reported polysaccharidal sorbents. Fitting of pseudo-second-order kinetic, Langmuir isotherm and ion-exchange models suggested that removal of Cd(II) followed ion-exchange mechanism. The sorbent was regenerated using green conditions with no significant decrease in sorption capacity. This suggests that sorbent can be used repeatedly before need to be replaced. Results of competitive removal show that HEC-Suc-Na is an excellent sorbent for the removal of Cd(II) from aqueous environments contaminated with high amounts of heavy metals such as Cd(II) and Ni(II).

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