MODIFIED HYDROXYETHYLCELLULOSE: A REGENERABLE SUPER-SORBENT FOR Cd^{2+} UPTAKE FROM SPIKED HIGH-HARDNESS GROUNDWATER

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A benign super-sorbent, *i.e.*, the sodic form of succinylated hydroxyethylcellulose (HEC-Suc-Na), was investigated for the sorption efficiency to remove cadmium (Cd) from spiked high-hardness groundwater (HGW). Hydroxyethylcellulose succinate (HEC-Suc) was synthesized and converted into its sodic form by treating with saturated NaHCO$_3$ solution. Batch-wise methodologies were used to sorb Cd^{2+} from HGW solution by HEC-Suc-Na. The results show that more than 90% Cd^{2+} removal was achieved within the first 30 min at pH 6 from HGW at 298 K. The Langmuir isotherm model and the pseudo-second order kinetic model provided the best fit for the sorption data of Cd^{2+} uptake. The estimation of the thermodynamics parameter indicated the spontaneous and exothermic nature of the sorption. As compared with other polysaccharidal sorbents, HEC-Suc-Na suggested its highest efficiency for Cd^{2+} uptake from HGW (666.66 mg g^{-1}). The sorbent showed high selectivity for Cd removal over background ion naturally present in HGW. The sorbent was easily regenerated using mild conditions and used for Cd^{2+} uptake over three cycles with no significant decrease in its sorption capacity. It suggests the possibility for manifold use of the sorbent before it needs to be replaced.

Keywords: adsorption, cadmium uptake, groundwater, hydroxyethylcellulose, regenerability, succinylation

INTRODUCTION

Heavy metals cause environmental contamination, which affects human health badly.[1] Cd is one of the most hazardous metals among the highly toxic heavy metal.[2] According to WHO, the permissible limit of cadmium in drinking water is 0.003 mg L^{-1}. Any concentration of Cd greater than this affects human health. Owing to its non-biodegradable nature, it accumulates in human vital organs and poses serious health hazards, including cancer, mental disorder, renal, lung and liver dysfunction.[3] Industries that discharge Cd into water streams include Ni-Cd batteries, mining, smelting, electroplating and metallurgy.[4]

Precipitation, adsorption, ion exchange, filtration, electrochemistry, chelation and reverse osmosis are some methods for the elimination of Cd from an aqueous environment. Chemical methods used for the removal of heavy metals are more expensive and less efficient.[5] Ion exchange stands on top among these methods due to its selectivity, efficiency and regenerability.[6]

Recently, cellulose-bearing materials, such as saw dust,[7] plant barks, fruit peels,[8] agricultural waste,[9] *etc.*, have been investigated for the removal of heavy metal ions. The advantages of these sorbents include their low cost, renewable nature and abundance. However, these low-cost sorbents contain functional groups of several types and it is difficult to decide that which functional group is responsible for the removal of metal ions from aqueous solutions. Another disadvantage associated with the use of low-cost sorbents, such as agricultural waste material, is their low sorption capacity. Therefore, it is currently very important to use sorbents containing a single type of functionalities, so that it can be established which functionalities are responsible for metal uptake. Moreover, new sorbents to be introduced must be more selective and efficient with higher sorption capacity.

Cellulose, a naturally occurring biopolymer, which is renewable, biocompatible and nontoxic, has ample hydroxyl (OH) groups that have affinities for heavy metal ions.[10,11] Chemically modified cellulose has excellent heavy metal removal capacity due to incorporation of new functional groups with better ion exchange properties.[12,13] However, intermolecular hydrogen bonds among hydroxyl groups of unmodified cellulose decrease its sorption capacity.[14] Chemical modification of cellulose includes direct conversion of the hydroxyl groups of cellulose into some useful functional groups with more binding sites.[15,16] Many researchers have used succinylated cellulose as a sorbent for the removal of heavy metal ions from aqueous solution and acquired useful results.[17-21]

So far, cellulose ether derivatives have not been exploited for heavy metal uptake. Keeping in mind the presence of free hydroxyls outside of the main cellulose chains, hydroxylethylcellulose (HEC) is reported for metal uptake after modification. Therefore, HEC-succinate (HEC-Suc) was synthesized, followed by its conversion to the sodic form (HEC-Suc-Na) by treatment with $NaHCO_3$. Then, HEC-Suc-Na was used for the removal of Cd^{2+} from HGW solution. The effects of contact time, pH, initial concentration and temperature on the sorption capacity have been investigated. To assess the feasibility of sorption, thermodynamic parameters, such as, $\Delta G°$, $\Delta H°$ and $\Delta S°$, were estimated. Kinetic studies were carried out to establish the mechanism of Cd^{2+} removal from HGW. Furthermore, the reproducibility of the novel super-sorbent HEC-Suc-Na was also investigated.

EXPERIMENTAL
Materials

Natrosol hydroxyethylcellulose (HE10K, Belgium) was purchased from a local market. HEC was dried at 110 °C for 2 h before use. Cadmium nitrate, NaOH, HCl, $NaHCO_3$ and diethylether provided by Fluka were of analytical grade. The chemical characteristics of the HGW, collected from Sargodha city suburbs (pH 7.3, Total Hardness = 1425 mg L^{-1} (as $CaCO_3$), Magnesium Hardness = 926.5 mg L^{-1}, Calcium Hardness = 498.5 mg L^{-1}, Total Alkalinity = 563.2 mg L^{-1}, P-Alkalinity (CO_3^{-2}) = 0 mg L^{-1}, M-Alkalinity (HCO_3^{-1}) = 563.2 mg L^{-1}, Chlorides = 1435 mg L^{-1}, Sulphates = 197.2 mg L^{-1}, Nitrates = 28 mg L^{-1}, Phosphates = 20.3 mg L^{-1}, Bicarbonates = 699 mg L^{-1}, Carbonates = 0 mg L^{-1}, Iron = 0.134 mg L^{-1}) were determined using different analytical techniques that are widely used for routine water analysis.

Synthesis of HEC-Suc conjugate and HEC-Suc-Na

HEC-Suc was synthesized by esterification of HEC with succinic anhydride using dimethylaminopyridine by a reported method.[22] HEC-Suc showed a fairly high degree of substitution (DS 2.84) as calculated by acid-base titration after saponification by a method adopted elsewhere.[23] The HEC-Suc was converted into its sodic form (HEC-Suc-Na) by treating it with saturated $NaHCO_3$ solution.[24] The HEC-Suc-Na was used for the removal of Cd^{2+} from HGW. In the FTIR spectrum of HEC-Suc, the appearance of distinct ester carbonyl signals at 1728 cm^{-1} is the indication of successful succinylation of HEC. Moreover, the appearance of the characteristic carboxylate anion peak at 1587 cm^{-1} in the spectrum of HEC-Suc-Na is a direct indication of sodium salt formation. The surface charge of HEC-Suc-Na was monitored by calculating the pH_{ZPC} (pH corresponding to the point of zero charge), which was found to be 4.2. Above this pH, the surface of the sorbent has negative charge, which favors metal uptake.

Sorption experiments

The stock solution of Cd^{2+} (1000 mg L^{-1}) was prepared in HGW and diluted to required concentrations. The pH of the solutions was adjusted using HCl (0.1M) and NaOH (0.05M) solutions. The concentration of Cd^{2+} was recorded by using an atomic absorption spectrophotometer (AAS) AA 6300 (Shimadzu, Japan) at 228.8 nm wavelength using flame (air-acetylene). In order to optimize sorbent dosage, 10, 20, 40, 60, 80 and 100 mg of the sorbent were added to Cd^{+2} (100 mg/L) solutions and stirred at 298 K for 30 min at a speed of 130 rpm in HGW. It was found that the sorption capacity was maximum for 20 mg sorbent dose. So, this optimized amount of sorbent was chosen for further studies. To optimize the pH for Cd^{2+} uptake, the optimized amount of the sorbent (20 mg) was stirred over a range of 5-120 min in HGW (100 mL) containing Cd^{2+} (140 mg L^{-1}) at a speed of 130 rpm at 298 K over a pH range of 2-8. FAAS was used to determine the Cd^{2+} from the supernatant.

The effects of contact time and temperature on Cd^{2+} adsorption from HGW were investigated using a fixed amount of HEC-Suc-Na (20 mg). The mixture was stirred over a time range of 5-150 min and temperature range of 298-343 K in HGW (100 mL) containing Cd^{2+} (140 mg L^{-1}) at a speed of 130 rpm. The percentage metal ions uptake was assessed by using AAS. The effect of initial concentration on sorption was evaluated by stirring sorbent (20 mg) in HGW (100 mL) containing Cd^{2+} (140, 170, 200, 230 and 260 mg L^{-1}) for 30 min at 130 rpm. The equilibrium concentrations of metal ion were analyzed by AAS. The adsorption capacity and % Cd^{2+} uptake was determined utilizing the following relations:

$$q_e = \frac{C_i - C_f}{m} \times V \tag{1}$$

$$Percentage\,uptake = \frac{C_i - C_e}{C_i} \times 100 \qquad (2)$$

where C_e and C_i are the equilibrium and initial concentrations of Cd^{2+} in mg L^{-1}, respectively, q_e is the equilibrium adsorption capacity in mg g^{-1}, V is the volume of the solution in L and m is the mass of sorbent in grams.

Statistical analysis

The isotherm data were fitted to various models by non-linear regression analysis using the STATISTICA software package (release 6) for Windows. The significance of the data fit by various models was evaluated by the t-test.

Regeneration of sorbent

The sorbent HEC-Suc-Na was easily regenerated using saturated aqueous NaCl solution. The regenerated sorbent was thoroughly washed with deionized water, then air-dried. The absence of the NaCl in the sorbent was verified by the negative $AgNO_3$ test. The regenerated sorbent was reused over three cycles for Cd^{2+} uptake.

Thermodynamics determination

The effect of temperature on Cd^{2+} uptake was used to estimate different thermodynamic parameters such as change in free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) by using the following relations:

$$\Delta G° = -RT\ln K_c \qquad (3)$$

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (4)$$

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (5)$$

where C_e is the equilibrium Cd concentration and C_{ads} is the amount of Cd^{2+} adsorbed. A plot of $\ln K$ against $1/T$ (K^{-1}) gives $\Delta S°$ as slope and $\Delta H°$ as intercept.

RESULTS AND DISCUSSION
Kinetic study of Cd^{2+} removal by HEC-Suc-Na
Effect of contact time

The effect of contact time showed that more than 90% Cd was removed within the first 30 min from the HGW solution by HEC-Suc-Na (Fig. 1). The presence of several sodic-succinate functionalities was the main reason for this initial prompt phase. When adsorption equilibrium time was reached, almost all vacant sites were engaged by Cd^{2+}, which caused a decrease in the rate of adsorption after 30 min.

Kinetic modeling

In order to evaluate the mechanism that controls the sorption phenomenon, sorption experimental data were fit to various kinetic models. It is well established that the sorption mechanism depends on the physical and chemical characteristics of the sorbent and also on the mass transfer process. The pseudo-first, pseudo-second order and the Weber-Morris intraparticle diffusion models were applied to the data obtained from the contact time experiments in order to establish the kinetics of sorption. The linear form of the pseudo-first order model is described by the following relation:

$$log\,(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \qquad (6)$$

It has been found that the pseudo-first order equation is applicable to a limited range of sorption processes only. So, the experimental data obtained from the initial rapid phase of sorption was chosen to fit the pseudo-first order kinetic equation. The time range for the initial rapid phase was 5-60 min, so this time range was chosen for Cd uptake from HGW solution to fit the pseudo-first order kinetic equation. Figure 2 shows the plots of $log(q_e - q_t)$ against t for Cd uptake from HGW solutions. The values of k_1 and q_e are obtained from the slope and intercept of the straight line, respectively. The values of k_1, q_e and R^2 are listed in Table 1. The low value of the correlation coefficients, around 0.86, and the deviation of calculated q_e value from the experimental value suggest the inadequacy of the pseudo-first order model to fit the experimental data, even for the initial phase of the sorption process. The intraparticle diffusion equation is described as:

$$q_t = k_2 t^{1/2} + k_d \qquad (7)$$

This equation may be applied to determine the intraparticle diffusion rate constant, k_2, and the boundary resistance, k_d. The plots of q_t versus $t^{1/2}$ for the Weber-Morris intraparticle diffusion model are shown in Figure 3. From the figure, it is noted that the sorption kinetic data does not fit well to this kinetic model. The pseudo-second order model provided the best fit to the Cd uptake data obtained from the contact time experiments.[25] The linear form of the pseudo-second order model is described by the following relation:

$$\frac{t}{q_t} = \frac{1}{k_3 q_e^2} + \frac{t}{q_e} \qquad (8)$$

where q_t and q_e are the amounts of Cd sorbed at time t and equilibrium, respectively, k_3 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}). Plotting t/q_t versus t gives the best fit pseudo-

second order kinetic model as evident from the high correlation coefficients (Fig. 4). The q_e value calculated from the plot agrees well with the experimental values (Table 1). Thus, it can be confirmed that the adsorption of Cd on HEC-Suc-Na followed the pseudo-second-order kinetic model. Moreover, it can be concluded that the rate-limiting step is chemisorption, which involves the exchange of electrons between Cd and the adsorbent HEC-Suc-Na.

Effect of pH on Cd uptake

The effect of pH on the removal of Cd^{2+} from HGW solution by HEC-Suc-Na was investigated to identify the pH at which maximum adsorption takes place. It was evident from the plot (Fig. 5) that there was a low uptake of Cd^{2+} at lower pH, which can be attributed due to protonation of HEC-Suc-Na to form carboxylic acid and the unavailability of Na functionalities to exchange with Cd^{2+}. Cd uptake increased abruptly as the pH was increased from 4 onward. The maximum removal was witnessed at pH 6 from HGW solution, which favored an enhanced ion exchange mechanism at higher pH values.
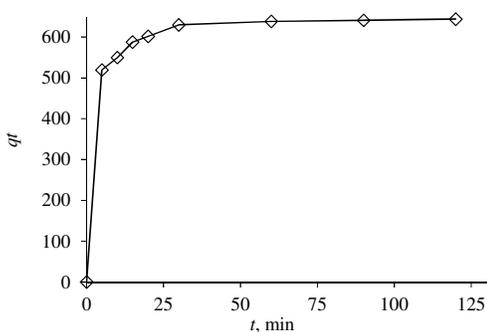

Figure 1: Plot of Cd uptake from HGW on HEC-Suc-Na as a function of contact time
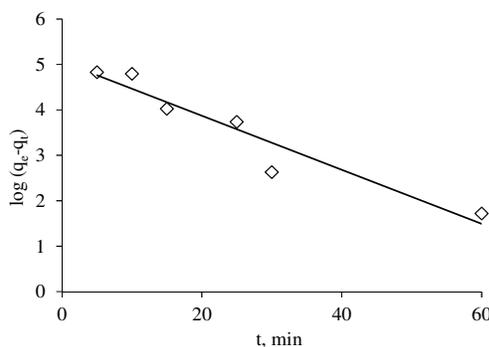

Figure 2: Fitting of pseudo-first order model for Cd uptake from HGW on HEC-Suc-Na
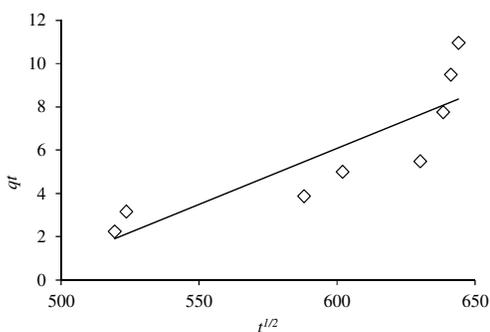

Figure 3: Fitting of intra-particle diffusion model for Cd uptake from HGW on HEC-Suc-Na
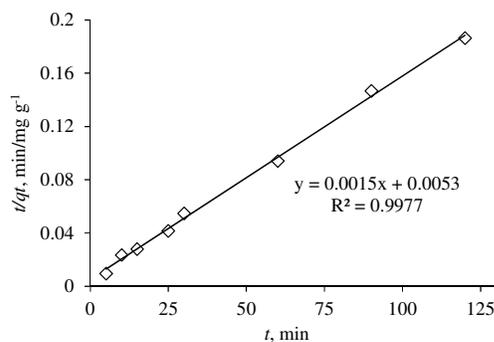

Figure 4: Fitting of pseudo-second order model for Cd uptake from HGW on HEC-Suc-Na

Table 1
Values of q_e, k, k_1 and R^2 calculated from pseudo-first and pseudo-second order kinetic models for Cd^{2+} removal from HGW using HEC-Suc-Na

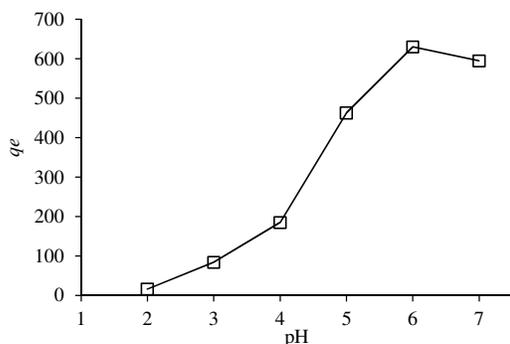| Solution	Experimental	Pseudo-second order			Pseudo-first order		
	q_e(mg g^{-1})	q_e(mg g^{-1})	k_1	R^2	q_e(mg g^{-1})	k_3	R^2
HGW	630.0	666.66	0.00080	0.9997	8.993	0.025	0.9175

Figure 5: Effect of pH on Cd uptake from HGW by HEC-Suc-Na
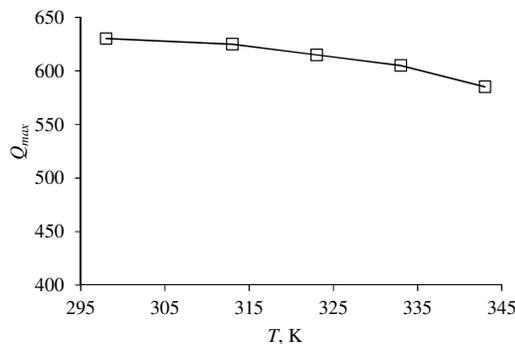

Figure 6: Effect of temperature on % Cd uptake from HGW by HEC-Suc-Na

Effect of temperature

The sorption of Cd decreased by 9% as the temperature increased from 298 to 338 K (Fig. 6). This was due to the fact that at lower temperatures, the Cd ions present in the solution were less mobile and could interact more with the exchange sites. Thus, there was an augmented ion exchange at lower temperature. As the temperature was increased, the ions became highly mobile and there was less attraction between the adsorbent and the adsorbate, resulting in diminished ion exchange.

Sorption isotherm

The equilibrium sorption isotherm describes the interactive behavior between the sorbate and the sorbent. The main parameter to design a sorption system is the sorption capacity of a sorbent. Sorption isotherms also predict the value of sorption capacity. The experimental data obtained for the sorption of Cd^{2+} ions from HGW by the sorbent HEC-Suc-Na was subjected to the Freundlich and Langmuir isotherms. The linear form of the Freundlich isotherm is described as:

$$logq_e = logk_F + \frac{1}{n}logC_e \qquad (9)$$

A straight line with a low correlation coefficient was obtained by plotting values of $logq_e$ against $logC_e$ (Fig. 7). The values of k_F and n are obtained by the slope and intercept of the straight line. The values of R^2, k_F and n obtained from the plot are presented in Table 2. The adsorption isotherm data were best fitted to the Langmuir model. It assumes that the adsorbed ions form a monolayer on the adsorbent surface, as all adsorbent sites are energetically identical and there is no attraction between the adsorbed ions. The linearized form of the Langmuir model is represented as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max} \times b} \qquad (10)$$

where q_e (mg g^{-1}) is the amount of a metal adsorbed, C_e (mg L^{-1}) is the equilibrium Cd concentration, Q_{max} (mg g^{-1}) is the maximum sorption capacity when a complete monolayer is formed on the adsorbent surface and b is the Langmuir constant. The values of C_e/q_e were plotted against C_e. A straight line with high correlation coefficients was obtained, which shows that the sorption data best fitted to the Langmuir model (Fig. 8). The slope and intercept of the straight line give the values of Q_{max} and b. The maximum adsorption capacity of Cd^{2+} from HGW solution was found to be 666.66 mg g^{-1}. The high value of Q$_{max}$ is due to the larger concentration of succinate moieties on the sorbent HEC-Suc-Na (Table 2). A literature review reflected that HEC-Suc-Na appeared as reasonably superior to other reported polysaccharide sorbents (Table 3).

The t-test results showed that the Langmuir model described the isotherm data at 95% confidence level.

Ion exchange mechanism

The involvement of the ion exchange mechanism was evidenced from the fact that HEC-Suc showed a low Cd uptake (11.2%), while HEC-Suc-Na showed a reasonably high Cd uptake (90.02%) from HGW due to the exchange of Cd^{2+} with Na ions present in the sodic form of the sorbent (Fig. 9). It is also worth mentioning that such a high Cd uptake was due to the high degree of substitution (2.84) of succinate groups onto HEC that resulted in the high concentration of Na ions, which, in turn, augmented the ion exchange phenomenon during the rapid initial phase of adsorption.

Table 2
Frendlich and Langmuir parameters for Cd^{2+} removal from HGW sorption using HEC-Suc-Na

Experimental	Parameters	HGW
	q_e(mg g^{-1})	630
Langmuir parameters	Q_{max}(mg g^{-1})	666.66
	Q_{max}(mmol g^{-1})	5.9444
	b (mg L^{-1})	0.1095
	b (mmol L^{-1})	12.279
	R^2	0.9995
	R_L	0.0612
Freundlich parameters	n	158.73
	k_F	640.212
	R^2	0.0055

Table 3
Comparison of HEC-Suc-Na with other reported polysaccharide sorbents for Cd^{2+} removal

| Sorbent (treatment)	Sorption capacity (mg g^{-1})
Bagasse pith (SO$_2$ and H$_2$S, heat)[26]	149.9
Sugarcane bagasse (1,3-diisopropilcarbodiimide, triethylenetetramine)[27]	313
Polymer-modified magnetic nanoparticles[28]	29.6
Filter aid cellulose (succinic anhydride, sodic)[24]	185.6
Mercerized cellulose[29]	87
Poly(vinyl alcohol)/chitosan[30]	126.6
Mercerized cellulose (succinic anhydride)[31]	256.4
Kapok (DTPA)[32]	163.7
Carboxylated cellulose nanocrystals[18]	344.8
Hydroxyethylcellulose (succinic anhydride, sodic)	666.6 from HGW Present work (highest)
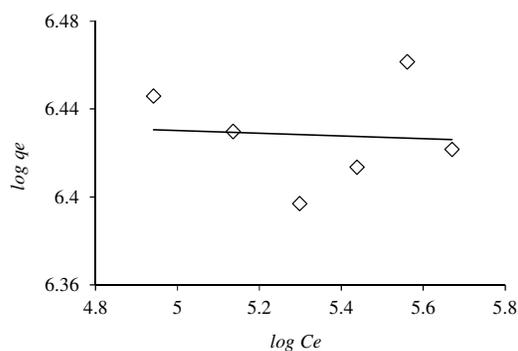
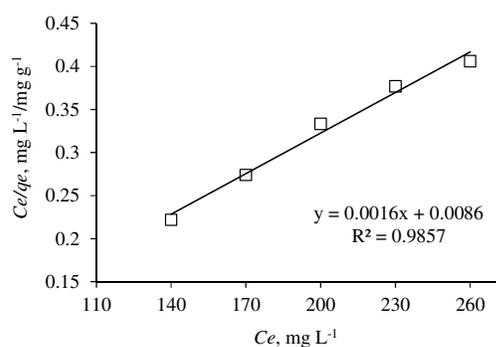Figure 7: Freundlich sorption isotherm for Cd uptake from HGW by HEC-Suc-Na sorbent

Figure 8: Langmuir sorption isotherm for Cd uptake from HGW by HEC-Suc-Na sorbent
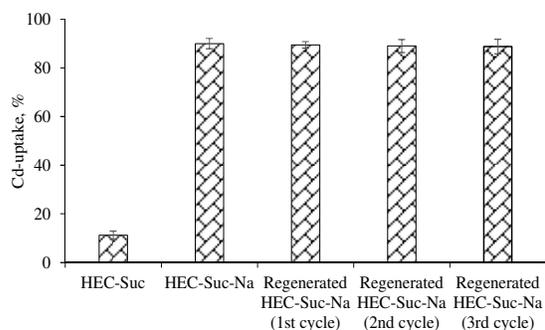
y = 0.0016x + 0.0086
R² = 0.9857

Figure 9: Percentage Cd uptake by acidic (HEC-Suc), sodic (HEC-Suc-Na) and regenerated sodic forms (three cycles) from HGW by sorbent HEC-Suc-Na
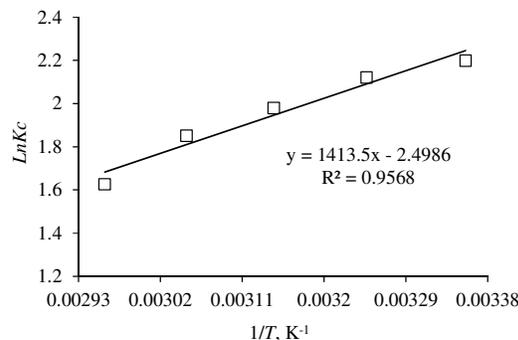

Figure 10: Effect of temperature on equilibrium constant for Cd uptake from HGW by HEC-Suc-Na

Table 4
Thermodynamics parameters for Cd^{2+} sorption using HEC-Suc-Na

Solution	$\Delta S°$ (J/mol/K)	$\Delta H°$ (kJ/mol)	R^2	$\Delta G°$ (kJ/mol)
HGW	-20.77	-11.75	0.9568	-5.44

Regeneration studies

The sorbent was regenerated using green conditions, *i.e.*, by treating the sorbent with brine. This resulted in desorption of the sorbed Cd ions. This regenerated HEC-Suc-Na was again used for Cd uptake from HGW solution. There was a negligible decrease in the adsorption capacity of Cd^{2+} from the HGW solution after regeneration. This process was repeated over three cycles and the total decrease in the adsorption capacity after three cycles was found to be of 1.22%. This result has suggested the potential for manifold use of the sorbent before it needs to be replaced (see Fig. 9).

Thermodynamics determination

The effect of temperature on the adsorption of Cd^{2+} from the HGW solution was used to estimate the values of $\Delta G°$, $\Delta S°$ and $\Delta H°$. A plot of *lnK* against $1/T$ (K^{-1}) gives $\Delta S°$ as slope and $\Delta H°$ as intercept (Fig. 10). The negative values of $\Delta G°$ and $\Delta H°$ were indicative of spontaneous and exothermic nature of sorption. The negative value of $\Delta S°$ revealed a decrease in randomness at the adsorbent-adsorbate interface during the sorption (Table 4).

CONCLUSION

Succinylated hydroxyethylcellulose in its sodic form was explored for the sorption of Cd^{2+} from spiked high-hardness groundwater (HGW). The benign super-sorbent showed maximum sorption capacity for Cd uptake (666.66 mg g^{-1}) from HGW. More than 90% Cd removal achieved within 30 min indicated an augmented ion exchange mechanism. The estimation of the thermodynamics parameter showed that Cd adsorption is spontaneous and exothermic. The sorbent showed high selectivity for Cd removal over background ions naturally present in HGW (Ca^{2+} and Mg^{2+}). The sorbent was efficiently regenerated by using brine and was reused with no significant decrease in the sorption capacity after three cycles. Therefore, it can be established that HEC-Suc-Na is a highly efficient, regenerable and reusable sorbent for Cd uptake from HGW.

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