CELLULOSE CHEMISTRY AND TECHNOLOGY

CHEMICALLY MODIFIED GLUCURONOXYLAN: A NOVEL MATERIAL FOR HEAVY METAL ION REMOVAL FROM AQUEOUS AND SPIKED HIGH HARDNESS GROUNDWATER

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Glucuroxylan (GX) was isolated from *Mimosa pudica* seeds. Then, a novel material – sodium salt of GX succinate (Na-GXS) – was prepared and evaluated for Cd removal from distilled water (DW) and spiked high hardness groundwater (GW). The chemical structure and charge on the surface of Na-GXS (sorbent) was characterized by FTIR spectroscopy and zero point charge, respectively. Adsorption of Cd(II) onto Na-GXS was investigated with respect to pH, adsorption time, initial Cd(II) concentration and temperature. The pseudo-second-order kinetic model and Langmuir isothermal model were better fitted to the kinetics and adsorption isothermal data, respectively, for both DW and GW. The values of thermodynamic parameters, such as $\Delta S°$, $\Delta G°$ and $\Delta H°$, were determined for both DW and GW, indicating that the removal of Cd(II) was spontaneous, favorable and an exothermic process in nature. Na-GXS showed selective removal for Cd(II) from GW in the presence of naturally occurring Ca(II) and Mg(II) ions in GW. Regeneration studies were also carried out.

Keywords: cadmium removal, polysaccharides, *Mimosa pudica* hydrogel, succinylation, regeneration

INTRODUCTION

Both the aquatic environment and aquatic life are seriously affected by heavy metals. Cadmium, being one of the "big three" toxic metals, is released into the environment by power stations, heating systems, electroplating, Ni–Cd batteries, incineration of municipal waste, fertilizers and so on.[1-4]

According to WHO and EPA, the permissible limit for Cd(II) in drinking water is 3.0-5.0 mg L^{-1}.[5] A short-term exposure of humans to cadmium causes pulmonary irritation, while a long-term inhalation or oral exposure to cadmium causes accumulation of the metal in kidneys, which leads to a reduced glomerular filtration rate, a kidney disease – proteinuria – and kidney stone formation. Chronic inhalation or oral exposure to cadmium causes damage to liver, lungs, blood, kidney, bones, nervous and immune system.[5-12] Therefore, there is dire need to control water contamination with heavy metals, so that the ecosystem can be sheltered. Nowadays, modified polysaccharides are being used as supersorbents for the sorption of heavy metal ions preferably because they are commercially available, biocompatible and thermally stable materials.[13-15]

In spite of the low cost and availability of agricultural waste and plant materials, it is difficult to identify which functional group is responsible for the uptake of heavy metal ions from wastewater. In addition, the sorption capacity of such natural materials (*i.e.*, mostly cellulosic materials) is not up to the mark. Therefore, there is utmost desire to prepare more efficient sorbents by the modification of natural polysaccharides. Polysaccharides contain many hydroxyl groups that can be modified with anhydrides of carboxylic acids.[16,17] The resultant carboxylated polysaccharides can adsorb heavy metals from solutions.[18] Amino and ester derivatives of cellulosic materials have been utilized for the adsorption of metals.[19-21]

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Succinylation is the most common modification of polysaccharides resulting in high sorption capacity of polysaccharides after their treatment with alkali to get their sodic form. Succinylated polysaccharides have gained more attention for the removal of metal ions due to their low cost, versatile composition, defined functional groups and environment-friendly nature.[22-25] Hydrogels have not been used for heavy metal ion uptake so far, to the best of our knowledge.

Among polysaccharides, recent research trends have shown that naturally occurring cross-linked polysaccharides, such as arabinoxylan and glucuronoxylan, could be a material of choice for heavy metal ion uptake after their succinylation.[26] Due to natural cross-linking, such materials may not dissolve in water after succinylation and salt formation. Therefore, we introduce here glucuronoxylan as a material for Cd(II) uptake after its succinylation, followed by its sodium salt formation. Glucuronoxylan is obtained as mucilage from *Mimosa pudica* seeds[27] upon soaking in water. *M. pudica* hydrogel (MPH, *i.e.*, glucuronoxylan) will be modified by succinylation (GXS), followed by its treatment with $NaHCO_3$ to form sodium salt of *M. pudica* succinate (Na-GXS). The study aims to evaluate Na-GXS for Cd(II) uptake from distilled water (DW) and spiked high hardness groundwater (GW) solution. The present work also deals with kinetic, isothermal and regeneration studies of Cd(II) uptake from DW and GW solution.

EXPERIMENTAL

Materials

M. pudica seeds were purchased from a local market of Sargodha, Pakistan. Ethanol, *n*-hexane, NaCl and HCl were purchased from Riedel-de-Haën, Germany. Analytical grade NaOH (Merck) was standardized with oxalic acid (Merck) before further use. Succinic anhydride, *N*,*N*-dimethylacetamide (DMAc) and 4-dimethylaminopyridine (DMAP) were obtained from Sigma-Aldrich, St. Louis, MO, USA. $(CdNO_3)_2.2H_2O$ and HNO_3 (> 98%) were procured from Panreac, Spain. Deionized water was used throughout this study. All other reagents and solvents used were of analytical grade.

Measurements

Fourier transform infrared (FTIR) spectra of the samples were recorded on an IR-Prestige-21 (Shimadzu, Japan) spectrometer, using KBr pellets (dried for 30 min at 60 °C before analysis). The pH of different solutions used during the study was measured on an Omega 300 pH meter (Crison Instruments, S.A., Spain). The adsorption of Cd(II) by Na-GXS was studied using a flame atomic absorption spectrophotometer (FAAS) AA 6300 (Shimadzu, Japan), furnished with air-acetylene supply at 228.8 nm.

Isolation of *M. pudica* hydrogel (MPH) and synthesis of MPH succinate (GXS)

M. pudica seeds were soaked in water for 12 h, followed by 30 min warming at 50 °C. Muslin cotton cloth was used to separate the hydrogel extruded by the seeds. The hydrogel was washed thoroughly with non-polar solvent, *n*-hexane, to get rid of fatty substances. The hydrogel was dried at 50 °C, passed through a 60 mesh sieve after grinding and then stored in a vacuum oven. MPH (2.0 g) was suspended in *N*,*N*-dimethylacetamide (DMAc) and stirred for 30 min at 80 °C under nitrogen inert atmosphere. Succinic anhydride (7.4 g) was added to this suspension and stirred at 80 °C for 6 h. The resulting GXS was precipitated with ethanol (250 mL). The precipitates were washed thrice with ethanol (100 mL) and ground to powder after drying in a vacuum desiccator.

Yield: 3.05 g (84%); DS = 2.19/anhydroglucose repeating unit.

FTIR = 1746 cm^{-1} ($C=O_{Ester}$), 2939 cm^{-1} (C-H stretch), 1441 cm^{-1} (CH_2 bending), 1043 cm^{-1} (C-O-C stretch), 3409 cm^{-1} (O-H stretch).

Synthesis of Na-GXS

The dried GXS was stirred with a saturated solution of $NaHCO_3$ for 2 h, to prepare Na-GXS. The precipitates were filtered and washed with distilled water until the pH of the solution became neutral.

FTIR = 1744 cm^{-1} ($C=O_{Ester}$), 2937 cm^{-1} (C-H stretch), 1442 cm^{-1} (CH_2 bending), 1050 cm^{-1} (C-O-C stretch), 3406 cm^{-1} (O-H stretch).

Calculation of GXS yield

Equation 1 was used to calculate the theoretical yield of the products:

$$Theoretical\ yeild = m_{GX} + (\frac{m_{GXS}}{M_{GXS}} \times DS \times M_{Suc}) \qquad (1)$$

where m_{GX} is the mass of the GX used, m_{GXS} is the mass of the GXS obtained, M_{GXS} is molar mass of GXS, M_{Suc} is molecular mass of the succinate portion and DS is the degree of substitution.

Determination of degree of substitution (DS) by acid base titration

DS was calculated by acid base titration. For this purpose, GXS (100 mg) was stirred in 0.02 M NaHCO3 solution (100 mL) for 2 h at room temperature. After filtering this solution, a known volume of the NaHCO3 solution was titrated against 0.02 M HCl. Methyl orange was used as indicator. Equations 2 and 3 were used to calculate the DS of free carboxylic acid moieties of GXS from the volume of HCl used to neutralize the NaHCO3 solution:

$$n_{suc} = V_{NaHCO_3} \times M_{NaHCO_3} - V_{HCl} \times M_{HCl} \qquad (2)$$

$$DS = \frac{276.14 \times n_{Suc}}{m_{GXS} - 100 \times n_{Suc}} \qquad (3)$$

where m_{GXS} is the mass of conjugate GXS; n_{Suc} is the number of moles of carboxylic acid moieties onto GXS.

Determination of the zero point charge pH (pH_{ZPC})

Na-GXS was studied for determining the pH of zero point charge (pH_{zpc}), using the solid addition method.[25] For this purpose, solutions of Na-GXS (20 mg) and $NaNO_3$ (50 mL) were stirred gently at 150 rpm for 2 h. After this, the adjustment of the initial pH values (pH_i) in the range of 2-10 was carried out by adding either 0.1 M HNO_3 or 0.1 M NaOH. The final pH values (pH_f) were noted after decanting the supernatant. The difference between the initial and final pH values ($pH_i - pH_f$), plotted against pH_i and pH_{zpc}, was the point where the resultant curve intersects the x-axis.

Analysis of groundwater

Accurately weighed sorbent (Na-GXS) was stirred with a Cd(II) solution in a 250 mL stoppered conical flask, using a shaking thermostat machine. The supernatant layer was evaluated for Cd(II) concentration, using FAAS at 228.8 nm. Equations 4 and 5 were used to calculate the sorption capacity and the percentage uptake of heavy metals by Na-GXS, respectively:

$$q_e = \frac{C_i - C_e}{m} \times V \qquad (4)$$

$$Percentage\,uptake = \frac{C_i - C_e}{C_i} \times 100 \qquad (5)$$

where q_e (mg g^{-1}), Ci, Ce, V (L) and m (g) represent equilibrium adsorption capacity, initial and equilibrium metal ion concentrations (mg L^{-1}), volume of solution used for adsorption studies, and mass of adsorbent used, respectively.

Effect of initial metal ion concentration

The various dosages of Cd(II) ions (20, 40, 60, 80, 100, 120 and 140 mg L^{-1}) were investigated against the optimized concentration of sorbent using FAAS to find maximum sorption. For this purpose, the sorbent (40 mg) was stirred with different solutions of Cd(II) ions (100 mL) for 30 min at 130 rpm and 298 K.

Effect of sorbent dosage

The uptake of the optimized concentration (60 mg) of Cd(II) ions was determined with various dosages of sorbent (30-100 mg) to get the maximum sorption efficiency with the minimum dose. The optimum concentration of the sorbent was determined by FAAS, after stirring with the optimum concentration of Cd(II) ions (30 mg L^{-1}) for 30 min at 130 rpm and 298 K.

Effect of pH on removal of metal ions

After optimizing the amounts of the sorbent and Cd(II) ions, the solution pH was also optimized to control the extent of ionization and the surface charge of the sorbent. For this purpose, the optimum amounts of the sorbent and Cd(II) ions were stirred at 130 rpm for 30 min. The supernatant was decanted to determine maximum absorption by the sorbent (Na-GXS) in the pH range of 2-7, using FAAS.

Effect of contact time

The contact time of the sorbent with Cd(II) ions was determined by stirring the optimized concentrations of Cd(II) (60 mg L^{-1}) and sorbent (40 mg) in the range of 5-120 min at 130 rpm and 298 K. The equilibrium concentration of Cd(II) in the solution was determined by noting the absorbance using FAAS.

Effect of temperature on metal ion sorption

The effect of temperature on the uptake of metal ions was investigated under optimum conditions of pH and sorbent amount (40 mg). To do so, the sorbent (40 mg) was stirred with the optimum concentration of Cd(II) ions (60 mg L^{-1}) in the temperature range of 298-343 K for 30 min at 130 rpm.

Sorption and desorption (regenerability)

The water purification process was made more cost-effective by regenerating and reprocessing the sorbent. To achieve this, cadmium ions adsorbed by the sorbent were desorbed by treating it with a saturated solution of NaCl (brine) and the left over brine was precipitated with a silver nitrate solution. This regenerated sorbent was dried after centrifugation and was again employed for cadmium ion uptake and the concentration was determined by measuring the absorbance using FAAS. The sorption-desorption cycle was carried out five times.

RESULTS AND DISCUSSION

Synthesis of GXS and Na-GXS

The esterification of MPH was carried out with succinic anhydride under nitrogen inert atmosphere at 80 °C for 24 h, using the catalyst 4-dimethylaminopyridine (DMAP) under homogeneous reaction conditions. The resulting product was precipitated and washed with ethanol. The GXS was further treated with a saturated solution of $NaHCO_3$ at 25 °C for 2 h to get the sodic form of GXS (Na-GXS). Figure 1 outlines the synthesis of GXS and Na-GXS. This Na-GXS can be used as a potential candidate for the sorption of cadmium ions from DW and GW.

FTIR spectroscopy

Successful synthesis of GXS was confirmed by the presence of an ester carbonyl peak at 1746 cm^{-1} in the FTIR spectrum obtained by forming KBr discs of GXS. In the sodium salt of GXS, a distinct carboxylate anion peak was observed at 1553 cm^{-1}. The overlay FTIR spectra of MPH, GXS and Na-GXS (Fig. 2) showed that other important peaks are not affected by the desired chemical changes.

Determination of zero point charge pH (pH_{ZPC})

The pH_{ZPC} for Na-GXS was found to be 4.5 (Fig. 3), indicating the weakly acidic nature of the sorbent, owing to the presence of carboxylic acid groups. Furthermore, the sorption is more favorable beyond pH 4.8, because the sorbent carries negative charge after ionization of carboxylic acid groups.

Sorption of Cd(II) using Na-GXS as sorbent

Effect of initial metal concentration

The sorption capacity of the sorbent (Na-GXS) increases with an increase in the initial concentration of metal ions up to a certain extent, after which it becomes constant, because all exchangeable sites on the surface of the sorbent are occupied and it becomes saturated (Fig. 4a). In the present investigation, the sorption of Cd(II) ions from DW and GW solutions was examined in the concentration range of 20-140 mg L^{-1} and it was found that the sorbent sorbed Cd(II) ions up to 100 mg L^{-1} concentration for DW and GW solutions. Afterwards, the sorption remains constant because all the available sites on the surface of the sorbent were engaged by metal ions. All the experiments and analyses were performed in triplicate and average values are reported.

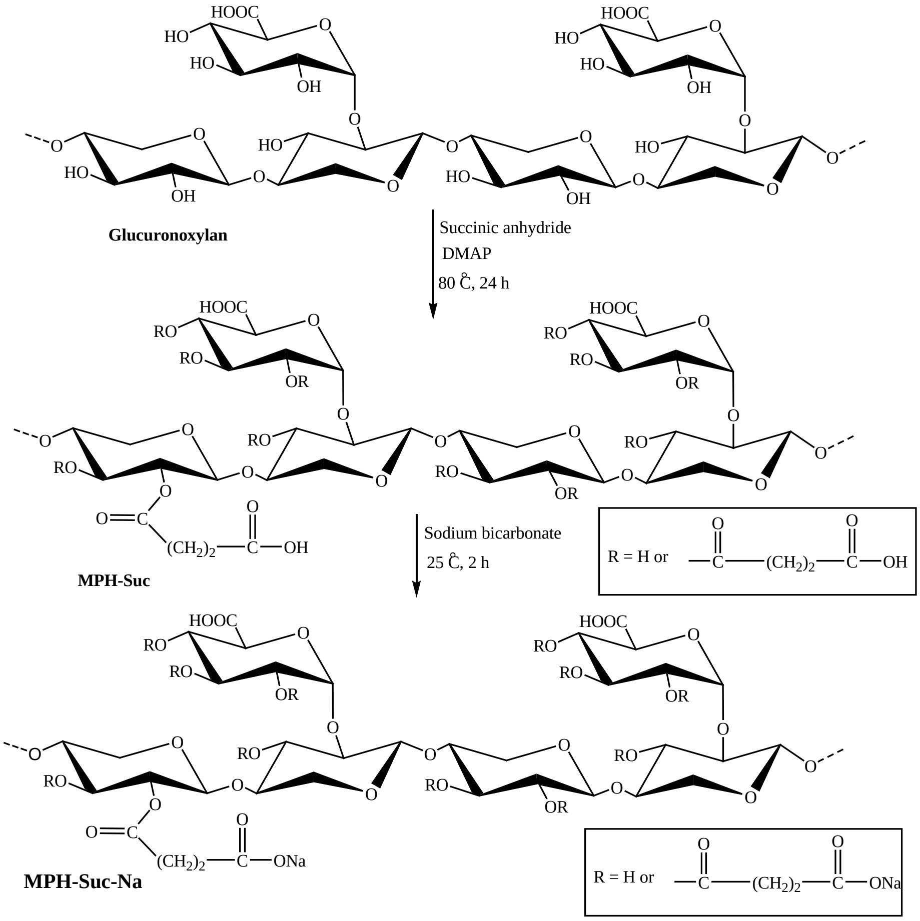

Figure 1: Synthesis of GXS and Na-GXS under homogenous reaction conditions

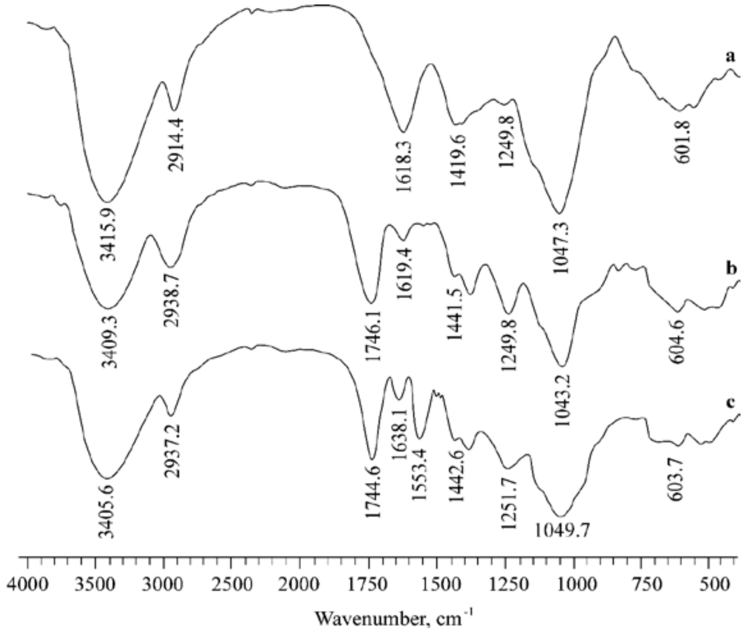

Figure 2: FTIR spectra of a) MPH (reproduced from Muhammad *et al.*[28] with kind permission from Chemical Society of Pakistan); b) GXS and c) Na-GXS exhibiting successful succinylation

Effect of sorbent dosage

The effect of Na-GXS sorbent dosage on the sorption capacity of Cd(II) ions from DW and GW solutions was studied in the range from 30 to 100 mg. With an increase in the amount of the sorbent, the uptake of Cd(II) ions increased because of the increment in exchangeable sites. Beyond the optimum sorbent amount, the uptake of Cd(II) ions was diminished. This is because Cd(II) ions to be exchanged with sodium ions of the sorbent are no more available in the solution at higher concentrations of the sorbent. The removal of Cd(II) ions was investigated more in DW than in GW, owing to the occupation of some of the exchangeable sites by alkaline earth metal ions (IIA elements) in the GW solution, along with Cd(II) ions (Fig. 4b). The optimum amount of sorbent for Cd(II) ion uptake was found to be 40 mg for both DW and GW, which was used for further studies.

Effect of pH on Cd uptake

The effect of pH in the range of 2.0-7.0 on sorption efficiency, using the optimum amounts of sorbent (40 mg) and Cd(II) ions (60 mg L^{-1}), was examined with the optimum metal ion concentration in DW and GW solutions. Below pH 4.9, the sorption of Cd(II) is low because of protonation of the carboxylic acid groups and the decrease in exchangeable sites on the surface of the sorbent. Above pH 4.9, the protonation of the carboxylic acid groups decreases and the number of exchangeable sites increases along with sorption capacity. Furthermore, in acidic media, higher concentration of H+ ions competes with Cd(II) ions for active sites. The sorption efficiency of Na-GXS was found maximum at pH 6.0 for DW and GW (Fig. 4c).

Effect of contact time

The contact time is another important parameter in the sorption of heavy metal ions by different sorbents. We studied Cd(II) ion sorption from DW and GW in a time range of 5-120 min (Fig. 4d). The sorbent removes more than 90% Cd(II) from DW and GW solutions within 5 and 15 min contact time, respectively. This initial abrupt rate of Cd(II) removal is due to the availability of excess active exchangeable groups on the surface of Na-GXS. The removal of Cd(II) ions decreases over time because of a reduction in exchangeable sites. The uptake of Cd(II) ions stops after 15 and 30 min for DW and GW solutions, respectively, because the active sites are no more available at equilibrium.

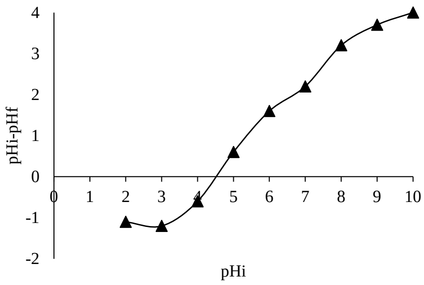

Figure 3: Determination of zero point charge pH (pH_{ZPC}) of Na-GXS

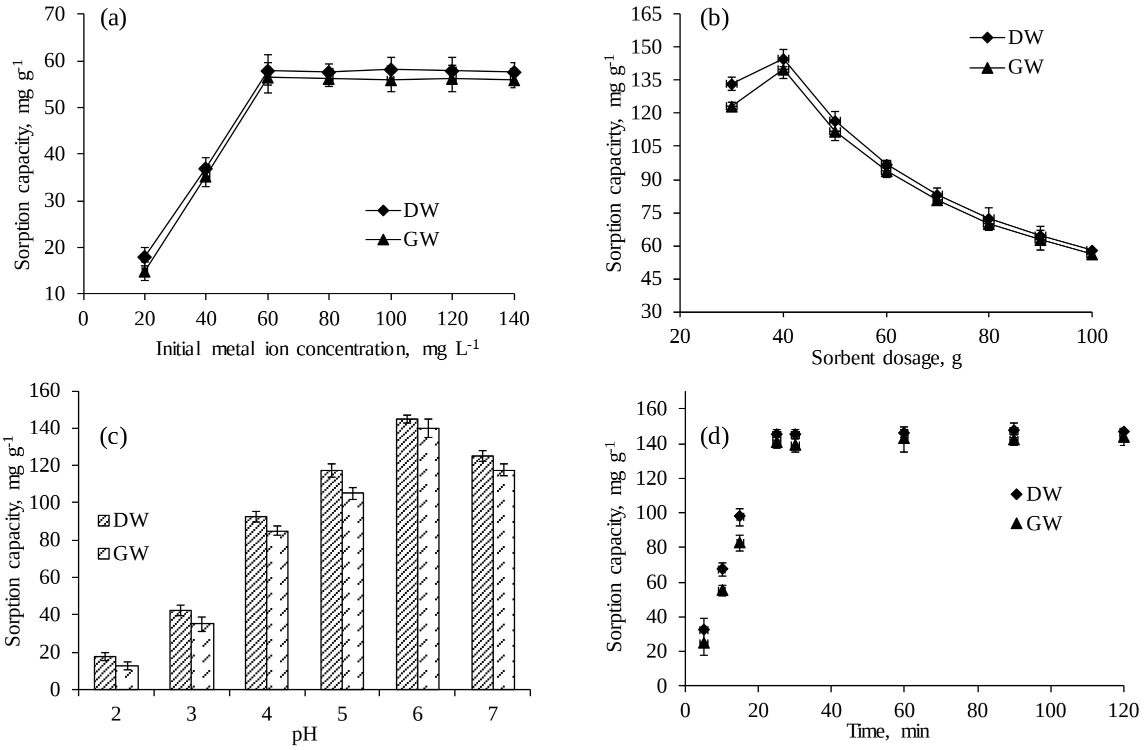

Figure 4: Effect of initial metal ion concentration (a), sorbent dosage (b), pH (c) and contact time (d) on sorption capacity of Na-GXS for Cd(II) ions from DW and GW

Kinetic modeling

The data obtained from the contact time experiments were fitted to the pseudo-first and pseudo-second order kinetic models to determine the likely mechanism of metal removal. The pseudo-first order kinetic model is given as (Eq. 6):

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

where q_e (mg g^{-1}), q_t (mg g^{-1}) and k_1 are the equilibrium sorption capacity, sorption capacity at time t (min) and rate constant for the pseudo-first order reaction, respectively. The graph between $\log(q_e - q_t)$ and t will be a straight line if the metal uptake by the sorbent follows pseudo-first order kinetics. Although the values of the correlation coefficients are high (above 0.90), the q_e values obtained from this plot are not in agreement with the experimental values. It can be concluded that the sorption process did not follow pseudo-first order kinetics (Fig. 5a).

The experimental data of contact time were fitted to the pseudo-second order model, which is given as (Eq. 7):

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e} \qquad (7)$$

where k is the rate constant for the pseudo-second order kinetic model. The straight line between t/q_t and t gave higher values of the correlation coefficients than for the pseudo-first order kinetics (Fig. 5b, Table 1). The intercept and slope of the straight line give the values of k and q_e, respectively. The calculated and experimental values of q_e also revealed that the sorption process followed the pseudo-second order kinetic model, which further supported ion exchange sorption.

Sorption isotherm

Sorption isotherm explains how sorbed molecules are distributed between the sorbate and the sorbent at equilibrium. The sorption isothermal data were fitted to the Freundlich and Langmuir isotherms. According to the Freundlich isotherm, the liquid phase is adsorbed on the solid surface in multilayers. The linear form of the Freundlich isotherm is given by Equation 8:

$$log q_e = log k_F + \frac{1}{n} log C_e \qquad (8)$$

where k_F and n are Frendlich parameters. This isotherm is only applicable if a straight line is obtained between $log\ q_e$ and $log\ C_e$ (Fig. 5c). Table 1 shows the values of R^2, k_F and n calculated from the Freundlich isotherm. The low values of the regression coefficient for the Frendlich model are informative of the inadequacy of this model. So, the Langmuir model was selected to fit the experimental data, according to which sorbed ions form a monolayer. The linear form of the Langmuir model is given as (Eq. 9):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} \times b} \qquad (9)$$

where Q_{max} (mg g^{-1}) and b are maximum sorption capacity and Langmuir constant, respectively.

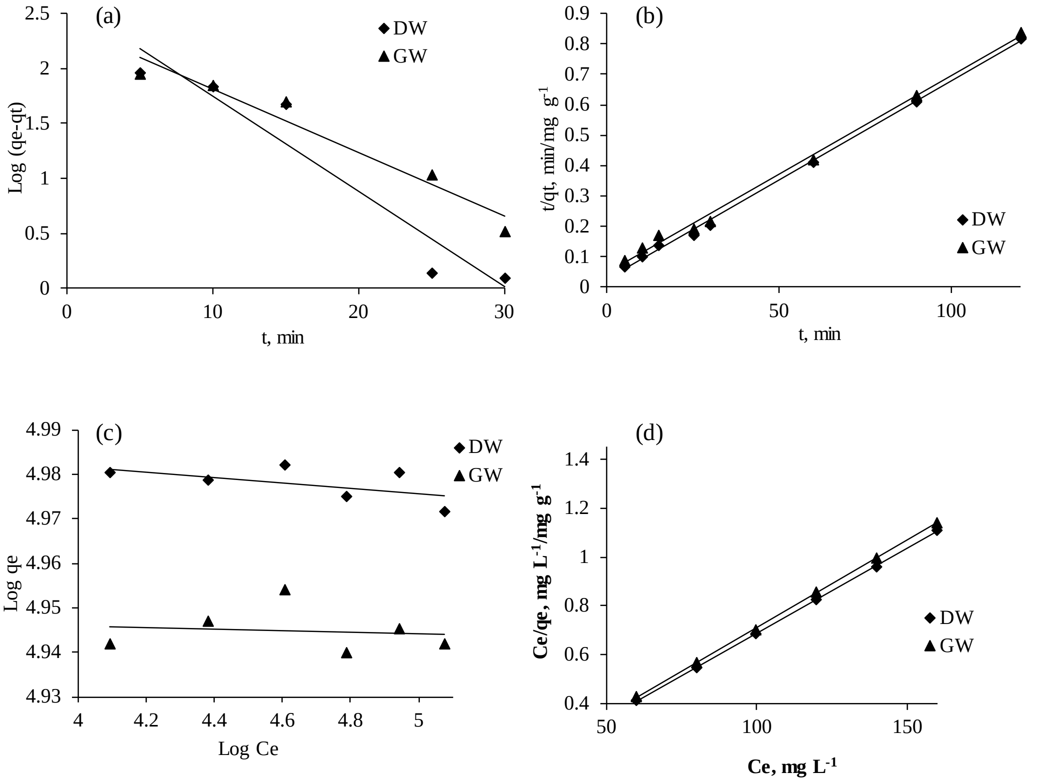

Figure 5: Pseudo-first order (a), pseudo-second order (b), Freundlich sorption isotherms (c) and Langmuir sorption isotherms (d) for Cd(II) removal from DW and GW by Na-GXS

Table 1
Freundlich, Langmuir, pseudo-first order, pseudo-second order, ion exchange model and thermodynamic parameters for Cd(II) removal from DW and GW using Na-GXS

Experimental parameters		DW	GW
Langmuir parameters	q_e (mg g^{-1})	145.5	140.6
	Q_{max} (mg g^{-1})	144.9	138.9
	Q_{max} (mmol g^{-1})	1.290	1.238
	b (mg L^{-1})	1.230	1.947
	R^2	0.9999	0.9998
Freundlich parameters	R_L	0.0133	0.0089
	n	166.6	588.2
	k_F	119.4	113.2
	R^2	0.3228	0.0147
Pseudo-second order	q_e (mg g^{-1})	15.38	15.62
	k	0.1541	0.0855
	R^2	0.9979	0.9952
Pseudo-first order	q_e (mg g^{-1})	8.750	10.93
	k_1	0.0878	0.0577
	R^2	0.9188	0.9456
Ion exchange parameters	S (min^{-1})	0.0806	0.0548
	R^2	0.9997	0.9970
Thermodynamic parameters	$\Delta S°$ (J mol^{-1}K^{-1})	-95.27	-61.87
	$\Delta H°$ (kJ mol^{-1})	-36.93	-24.09
	$\Delta G°$ (kJ mol^{-1})	-8.730	-6.530
	R^2	0.9744	0.9444

Straight lines with higher values of the correlation coefficients are obtained by plotting C_e/q_e against C_e. It means that sorption follows the Langmuir model (Fig. 5d). The values of b and Q_{max} are obtained by the intercept and slope of the straight lines, respectively. The value of Q_{max} is high, which shows that Na-GXS contains a greater number of succinate moieties. The Q_{max} values for Cd(II) was 145.5 mg g^{-1} from DW and 138.9 mg g^{-1} from GW.

The separation factor ($R_{L)}$ is given as (Eq. 10):

$$R_L = \frac{1}{1+bC_i} \tag{10}$$

where C_i (mg L^{-1}) is the initial concentration of metal ions. The values of the separation factor (R_L) between 0 and 1 for both DW and GW indicate that the adsorption is feasible (Table 1).

Ion exchange mechanism

The removal of Cd(II) ions from DW and GW solutions follows the ion exchange mechanism. This can be witnessed by the fact that the acidic form of the sorbent (GXS), which has no sodium ions for exchange with Cd(II) ions, has low values of Cd(II) removal (14 and 11.3% from DW and GW solutions, respectively). However, the sorption of Cd(II) ions by Na-GXS was calculated to be 97 and 94% from DW and GW solutions, respectively, because it contains a large number of sodium ions to be exchanged with Cd(II) (Fig. 6a). The greater removal of Cd(II) ions from the solution is attributed to the greater degree of substitution (2.19) with succinate groups on the polymer backbone, which in turn provides higher concentration of sodium ions, resulting in greater ion exchange. Furthermore, the high Cd(II) uptake during the initial rapid phase is also evidence of the involvement of the ion exchange mechanism.

The data obtained in the contact time experiment were also fitted to the ion exchange model[29] given by the relation (Eq. 11):

$$\log(1-F) = -\frac{S}{2.303}t \tag{11}$$

where $F = q_t/q_e$. and S (min^{-1}) is a constant. *log(1-F)* was plotted against *t.* Straight lines with high values of R^2 were obtained, which evidenced the involvement of the ion exchange mechanism (Fig. 7a, Table 1).

Sorption and desorption (regenerability)

The Cd(II) ions sorbed on Na-GXS can be easily and quickly desorbed by stirring the sorbent with brine (an ecofriendly kind of desorption). After regeneration, the sorbent was again used for

Cd(II) uptake from DW and GW (at pH = 6.0 and Cd(II) concentration = 60 mg L^{-1} for both DW and GW solutions). It was observed that the sorption capacity of Na-GXS is not significantly affected for both DW and GW solutions after regeneration. The regenerated sorbent was washed with deionized water after each sorption–desorption cycle. Regeneration studies were carried out five times for both DW and GW solutions (Fig. 6 (a-b)). The decrease in the sorption capacity of the sorbent after five cycles was found to be of 12.0 and 13.7 mg g^{-1} from DW and GW solutions, respectively (in terms of percentage, 7 and 9% decrease for DW and GW solutions, respectively). Each cycle was carried out three times.

Effect of temperature

A decrease in cadmium uptake with the increase in temperature from 298 to 338 K confirmed that the sorption process is exothermic. The reduction in cadmium ion removal was explored to be 15.5 and 22.2% for DW and GW solutions, respectively (Fig. 7b). Moreover, the increment in temperature enhanced the movement of ions and lessened the attraction between the adsorbent and the adsorbate. All the experiments and analyses were performed in triplicate and mean values were calculated.

Determination of thermodynamic parameters

The data obtained with regard to the effect of temperature on sorption were used to estimate the thermodynamic parameters, such as the free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$), which predict whether the sorption process is feasible and spontaneous or not. The following relations were used to determine these parameters (Eqs. 12-14):

$$K_c = \frac{C_{ads}}{C_e} \tag{12}$$

$$\Delta G° = -RTlnK_c \tag{13}$$

$$lnK_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{14}$$

where C_{ads} (mg L^{-1}) and C_e (mg L^{-1}) are the amount of metal adsorbed and equilibrium concentration of metal ion, respectively and K_c is the sorption equilibrium constant.

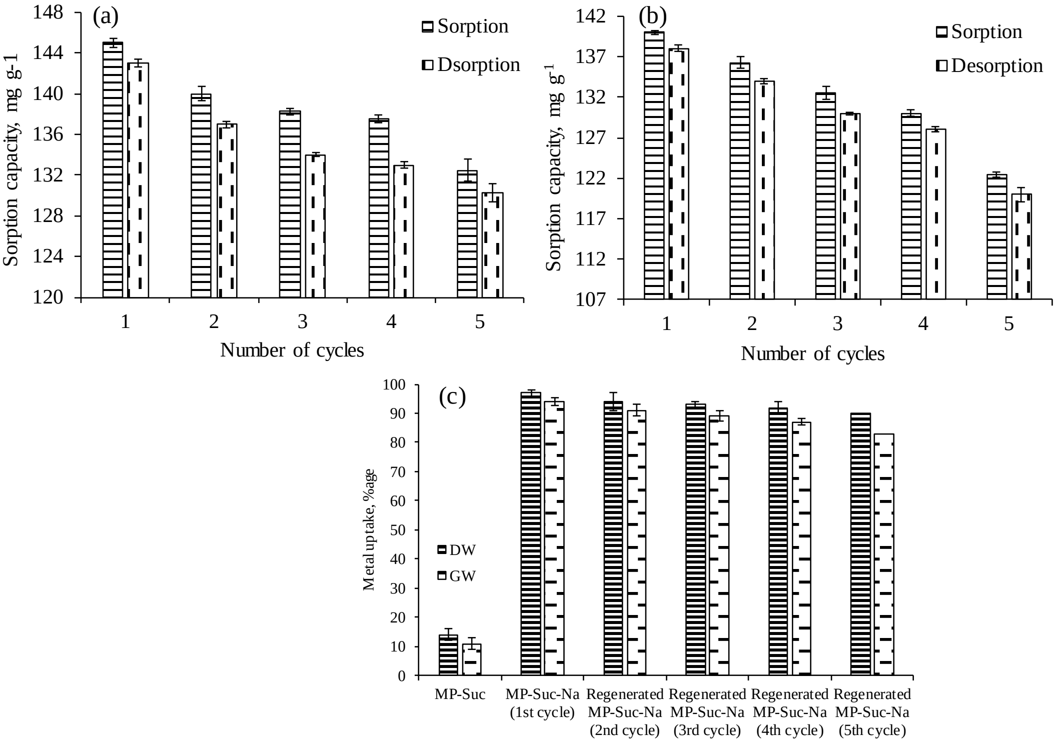

Figure 6: Adsorption-desorption values for Cd(II) from DW (a), GW (b) and percentage metal-uptake by the acidic (GXS), sodic form of the sorbent (Na-GXS, 1st cycle) and regenerated Na-GXS (2nd-5th cycles) from both DW and GW

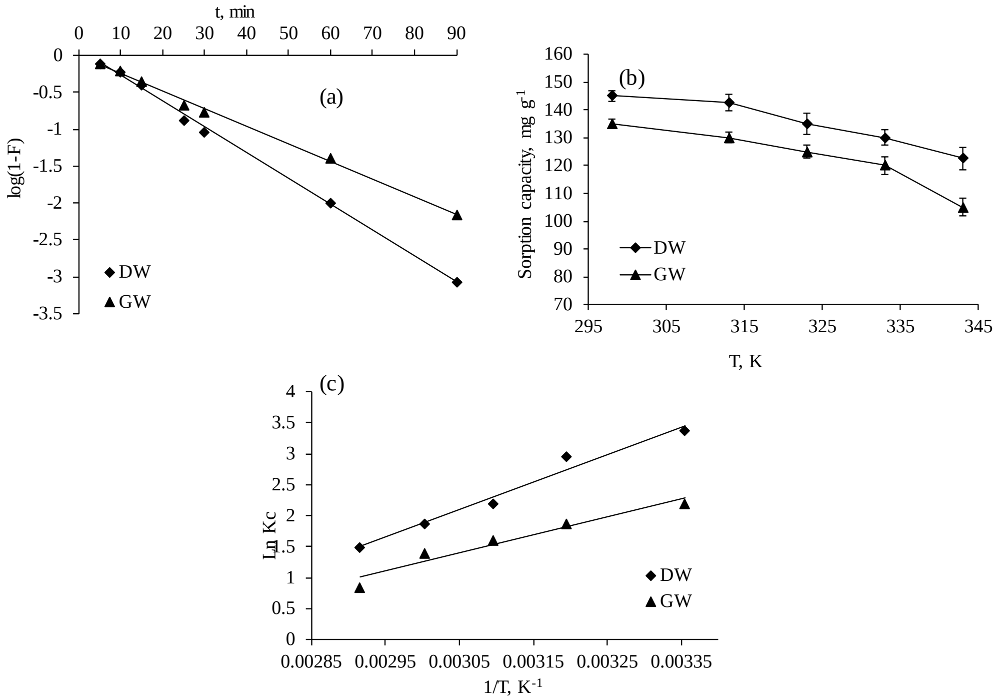

Figure 7: Ion exchange model (a), effect of temperature on sorption capacity (b) and equilibrium constant (c) for Cd uptake from DW and GW by Na-GXS

The value of $\Delta G°$ was calculated by using Equation 9, while the other two thermodynamic parameters, $\Delta S°$ and $\Delta H°$, for the removal of Cd(II) ions from DW and GW solutions were calculated by plotting a graph between lnK_c and $1/T\ (K^{-1})$. The slope and intercept of the straight line give $\Delta S°$ and $\Delta H°$ values, respectively (Eq. 13, Fig. 7c). The negative values of $\Delta G°$, $\Delta H°$ and $\Delta S°$ confirm that the sorption process was exothermic, spontaneous and there was a decrease in the disorder of the ions at the sorbent-sorbate interface during the process of sorption, respectively (Table 1). Table 2 shows the sorption capacity of different sorbents for Cd(II) removal. The Na-GXS has a prominent position among chemically modified polysaccharide-based sorbents.

Table 2
Comparison of sorption capacity values of Na-GXS for Cd(II) removal from DW and GW solutions with other reported sorbents

Sorbent (treatment)	Sorption capacity (mg g^{-1})
Spent grain (modified with sodium hydroxide, pH 5.3-5.6, 298 K, 2 h)[30]	17.3
Sugar beet pulp[31]	24.4
Filter aid cellulose (modified with succinic anhydride, sodic)[24]	185.2 from DW 178.2 from GW
Poly(vinyl alcohol)/chitosan[32]	126.6
Chitosan-stabilized nano zero-valent iron[33]	124.74
Pullulan succinate-Na[24]	476.2 from DW
Hydroxyethylcellulose-succinate-Na[25]	666.6 from GW
Sodium salt of glucuronoxylan succinate (Na-GXS)	144.9 from DW 138.9 from GW

CONCLUSION

Na-GXS demonstrated a potential for selective removal of Cd(II) ions from spiked high hardness groundwater containing naturally occurring Ca(II) and Mg(II) ions. The maximum sorption capacity of Na-GXS for Cd(II) removal from DW and GW, as calculated by the Langmuir model, was found to be 144.9 and 138.9 mg L^{-1}, respectively. The maximum removal of Cd(II) was obtained at a pH of 6 from both DW and GW. The ion exchange model was thought to be responsible for Cd(II) removal from DW and GW because the acidic form of the sorbent (GXS) showed negligible metal uptake, as compared to the sodic from (Na-GXS), which offered Na(I) ions for exchange with Cd(II). Moreover, Na-GXS was easily recovered using green conditions and its sorption capacity was found to be about 91 and 89% of the initial sorption capacity for DW and GW, respectively, after being used five times. The present study and the literature review have revealed that thorough and advanced characterization of MP seed mucilage is required to get a deeper insight into its chemical nature.

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