Succinate-bonded pullulan: An efficient and reusable super-sorbent for cadmium-uptake from spiked high-hardness groundwater

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ABSTRACT

Chemically modified pullulan was evaluated for its sorption efficiency and selectivity to remove cadmium (Cd) from spiked high-hardness groundwater (GW). Pullulan esterified with succinic anhydride using dimethylaminopyridine showed a fairly high degree of substitution value as confirmed by ^{1}H NMR spectroscopy. Pullulan succinate (Pull-Suc) was converted into the sodium salt (Pull-Suc-Na). The effect of contact time (5–200 min) and pH (2–8) on Cd-uptake by the sorbent (Pull-Suc-Na) was investigated. The sorbent showed more than 90% Cd-removal in first 15 min from distilled water (DW) and GW solution, respectively. Comparison of Pull-Suc-Na with other polysaccharidal sorbents suggested its high efficiency (DW 476.2 mg/g and GW 454.5 mg/g) and selectivity for the removal of Cd by an ion exchange mechanism, which is further supported by the negative Gibbs free energy values calculated from Langmuir isotherms. A Langmuir isotherm kinetic model provided the best fit for the sorption of Cd using Pull-Suc-Na. The sorbent showed a negligible decrease in Cd-uptake over three regeneration cycles. The thermal stability testing of the sorbents indicated that Pull-Suc-Na (sorbent) is more stable than Pull-Suc.

Introduction

Cadmium (Cd) is a highly toxic environmental pollutant present in ground water (GW) as a result of waste disposal from industries such as mining, metallurgy, metal finishing, electronics, smelting, alloy manufacturing, plastics, fertilizers, pesticides, textile operations, pigments and nickel –cadmium (Ni–Cd) batteries (Nguyen et al., 2013; Yan et al., 2015; Duan et al., 2014; Liu et al., 2013). The non-biodegradability of Cd may result in its accumulation within living tissues through the food chain (Zhang et al., 2013a). Decrease in activity of metallo-enzymes due to replacement of Zn ion by Cd ion, kidney dysfunction, multiple bone fractures, cancer at multiple sites, lung cancer (Khan et al., 2013; Davis et al., 2006), prostate carcinogenesis (Zeng et al., 2004), elevation in blood pressure levels (Tellez-Plaza et al., 2008) and weight loss (Sud et al., 2008) are some major problems caused by increased levels of Cd in the human body.

Effective techniques for the removal of heavy metal ions from contaminated GW (Wang and Ren, 2014) include ion exchange (Wang and Fthenakis, 2005), adsorption by activated charcoal (Nadeem et al., 2009), binding and chelating with some natural (Zhang et al., 2013b; Tonietto et al., 2014; Wang and Chen, 2014; Shi et al., 2013) or synthetic polymers (Wei et

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al., 2015; Masoumi and Ghaemy, 2014), precipitation (Lin et al., 2005) and solvent extraction (Jia et al., 2004).

Being renewable and abundant, some low-cost sorbents mainly consisting of cellulosic materials such as agricultural waste (Won et al., 2014; Garg et al., 2008), fruit peels and plant barks (Prapagdee et al., 2014), carboxylated cellulose nanocrystals (Yu et al., 2013), have metal binding capacity and find application in removal of heavy metal ions. However, agricultural waste materials contain different types of functionalities; so that it cannot be established which type of functionality is responsible for metal uptake. Moreover, the sorption capacity of agriculture waste is also not appreciable. Therefore, there is an utmost need to introduce more efficient and selective sorbents with a single kind of functional group to obtain a defined and higher sorption capacity.

Naturally-occurring renewable biopolymers, *e.g.*, cellulose, pullulan and dextran, have hydroxyl groups that can be modified by esterification (Hussain, 2010) with carboxylic acid anhydrides (Hussain et al., 2010a, 2010b). The resulting carboxylate groups grafted onto polysaccharides reportedly have a tendency to exchange cations from aqueous solution (De Melo et al., 2009). Therefore, by converting the cellulosic/ polysaccharidal materials into sodium salts, particularly the succinate derivatives, the tendency for the selective removal of Cd increases many-fold, even in the presence of divalent cations generally present in water (De Melo et al., 2009; Belhalfaoui et al., 2009).

Our objective was to synthesize a novel super-sorbent of a commercially available polysaccharide, *i.e.*, pullulan, after its modification. An aim was to evaluate and compare modified pullulan sorbents in terms of their Cd-removal capacity from distilled water (DW) and GW. The present investigation also evaluated the reproducibility of the performance of regenerated sorbent. Besides sorption studies, comparative thermal studies of acidic and sodic forms of the sorbent were carried out.

1. Materials and methods

1.1. Materials

Pullulan (molecular weight 100,000) used in the current study was provided by Fluka and dried under vacuum at 110°C for 2 hr prior to use. GW was collected from the city outskirts of Sargodha (a city having water with high hardness and high ionic strength), Pakistan. The chemical characteristics of the GW (pH 7.2; total hardness 1510 mg/L (as $CaCO_3$); Mg^{2+} hardness 1163.5 mg/L; Ca^{2+} hardness 346.5 mg/L; Cl^{-1} 1544 mg/L) were determined using known analytical techniques. All reagents and solvents used were of analytical grade.

1.2. Sample analysis

Fourier transform infrared spectroscopy (FT-IR, KBr, 4000–400 cm^{-1}) spectra were measured on an IR Prestige-21 instrument (Shimadzu, Japan). Proton nuclear magnetic resonance (^{1}H NMR spectra δ, ppm) of the products were acquired on a Bruker 400 MHz machine in deuterated dimethyl sulfoxide (DMSO-d_6) at 40°C.

Thermogravimetric (TG) and derivative TG (DTG) analyses were recorded on thermal analyzer (SDT Q 600, TA Instruments, USA) for pullulan succinate (Pull-Suc) and sodium salt (Pull-Suc-Na). Thermal analyses were recorded at the onset of significant weight loss from heated samples. Samples were measured under nitrogen with a temperature increase of 10°C/min from ambient to 1000°C.

1.3. Synthesis of Pull-Suc conjugate and Pull-Suc-Na

An optically clear solution of pullulan (10.0 g, 61.6 mmol) was prepared in dimethylacetamide (DMAc, 30 mL) at 80°C under stirring for 1.0 hr. Succinic anhydride (37.0 g, 370 mmol) was added, followed by the addition of dimethylaminopyridine (DMAP, 500 mg) as a catalyst, and the reaction mixture was kept under stirring at 80°C for 24 hr. The product (Pull-Suc) was precipitated in ethanol (500 mL) and washed with ethanol (250 mL) three times to remove the unreacted reagents. The colorless precipitates were dried under vacuum at 50°C overnight.

Yield: 22.8 g (82%), degree of substitution (DS) = 2.84/ Anhydroglucose repeating unit as calculated by ^{1}H NMR spectroscopy by comparing the signal intensities. FT-IR (KBr): 3395 (O–H), 2910 (C–H), 1719 (C=O$_{Ester}$), 1026 (C–O–C) cm^{-1}. ^{1}H NMR (DMSO-d_6, δ ppm): 2.37 (H-7), 2.77 (H-8), 3.14–4.75 (pullulan repeating unit-Hs).

The Pull-Suc-Na was prepared by alkaline treatment of Pull-Suc with saturated NaHCO$_3$ solution. The suspension was stirred at room temperature for 2.0 hr and then filtered. The solid was repeatedly washed with distilled water until neutral pH.

FT-IR (KBr): 3427 (O–H), 2912 (C–H), 1728 (C=O$_{Ester}$), 1560 (COO$^-$), 1022 (C–O–C) cm^{-1}.

1.4. Calculation of DS

DS was calculated by stirring Pull-Suc (100 mg) in 0.02 mol/L NaHCO$_3$ solution (100 mL) for 2 h at room temperature. After filtration, a known volume of the NaHCO$_3$ solution was titrated against 0.02 mol/L HCl using methyl orange as an indicator. From the volume of HCl used, the DS of free carboxylic acid moieties was calculated using the following relations (Eqs. (1) and (2));

$$n_{suc} = V_{NaHCO_3} \times M_{NaHCO_3} - V_{HCl} \times M_{HCl} \qquad (1)$$

where, n_{suc} is the number of moles of free carboxylic acid moieties; V_{NaHCO_3} is the volume of NaHCO$_3$ titrated against V_{HCl}; M_{NaHCO_3} is the molarity of NaHCO$_3$; M_{HCl} is the molarity of HCl.

$$DS = \frac{162.14 \times n_{suc}}{m_{pull\text{-}suc} - 100 \times n_{suc}} \qquad (2)$$

where, 162.14 (g/mol) is the molar mass of an anhydroglucose unit; 100 g/mol is the net increase in the mass of an anhydroglucose unit for each substituted succinyl moiety; n_{suc} is number of moles of free carboxylic acid moieties; $m_{pull\text{-}suc}$ is the mass in g of Pull-Suc analyzed.

The DS of the Pull-Suc was also calculated using ^{1}H NMR spectral analysis as described in references (Goodlett et al., 1971; Hussain et al., 2015).

1.5. Calculation of yield of Pull-Suc

The formula used to calculate the theoretical yield of the products is as Eq. (3):

$$\text{Theoretical yeild} = m_{\text{pull-suc}} + \left(\frac{m_{\text{pull-suc}}}{M_{\text{pull-suc}}} \times \text{DS} \times M_{\text{suc}} \right) \qquad (3)$$

where, $m_{\text{pull-suc}}$ (g) is the mass of Pull-Suc; $M_{\text{pull-suc}}$ (g/mol) is the molecular mass of conjugate, DS is the degree of substitution, and M_{suc} (g/mol) is the molecular mass of succinate.

1.6. Determination of the zero point charge pH (pH$_{ZPC}$)

The pH corresponding to the point of zero charge (ZPC) for the Pull-Suc-Na was determined by the solid addition method (Kumar et al., 2008). Pull-Suc-Na (20 mg) was placed in NaNO$_3$ solutions (50 mL), with initial pH (pH$_i$) values adjusted between 2 and 10 by adding either 0.1 mol/L HNO$_3$ or 0.1 mol/L NaOH, and shaken for 2 h at 150 r/min at 298 K. The final pH (pH$_f$) values of the supernatant liquid were noted.

1.7. Cd-removal using Pull-Suc-Na

1.7.1. Kinetic study
The amount of sorbent was optimized by adding 10, 20, 40, 60, 80 and 100 mg of the sorbent to Cd^{+2} (100 mg/L) solutions and stirring at 298 K for 30 min at 130 r/min in both DW and GW. The results indicated that the sorption capacity of the 20 mg sorbent dose appeared maximum for both DW and GW solutions. Therefore, the kinetic study was conducted on the percentage Cd-uptake by Pull-Suc-Na over a range of 5-200 min by stirring the optimized sorbent dose (20 mg) in DW and GW (100 mL each) containing Cd (100 mg/L) at a speed of 130 r/min at 298 K. The supernatant layer was collected and Cd concentration was determined at 228.8 nm wavelength using a flame (air-acetylene) atomic absorption spectrophotometer (FAAS, AA 6300, Shimadzu, Japan). The difference between the initial and final concentrations of the Cd solutions was taken as a measure of sorbed amounts of Cd.

1.7.2. Effect of pH on Cd-removal
The effect of pH was investigated over a range of 2–8 by stirring sorbent Pull-Suc-Na (20 mg) in DW and GW (100 mL each) containing Cd (100 mg/L) for 30 min at a speed of 130 r/min.

1.7.3. Sorption isotherms and Gibbs free energy
The sorption isotherms were established by stirring the sorbent (20 mg) in DW and GW (100 mL each) Cd solutions (100–300 mg/L) for 30 min at 100 r/min.

Gibbs free energy can be calculated using the following Eq. (4):

$$\Delta G^{\text{Å}} = -RT \times \ln K \qquad (4)$$

where, R is the gas constant, T (K) is the temperature, K (L/mol) is the equilibrium constant, which can be related to the molar mass of adsorbed metal (Gurgel and Gil, 2009) as follows:

$$K \approx b M_A \qquad (5)$$

where, b (L/g) is the Langmuir constant and M_A (g/mol) is the molar mass of metal studied.

1.7.4. Regeneration test
Saturated NaCl solutions were used to carry out the regeneration of the sorbent Pull-Suc-Na. For this purpose, sorbent was first stirred for 30 min in DW (100 mL) containing Cd (100 mg/L). The mixture was then centrifuged and Cd-uptake was determined by FAAS. The recovered material was suspended in brine solution (100 mL) after being thoroughly washed with DW and air-dried. The mixture was allowed to stand overnight, then centrifuged and washed with DW until the wash water gave a negative AgNO$_3$ test. The regenerated Pull-Suc-Na was used to determine Cd-uptake over three cycles.

1.7.5. Thermal analysis of sorbents
The initial, maximum and final thermal decomposition temperatures (Tdi, Tdm and Tdf) were noted from TG and derivative TG (DTG) curves. The thermal data were analyzed by Universal Analysis 2000 v 4.2E and MS Excel® 2010 software.

2. Results and discussion

2.1. Characterization of Pull-Suc and Pull-Suc-Na sorbents

FT-IR (KBr) spectra of Pull-Suc and Pull-Suc-Na are cumulatively shown in Fig. 1 to illustrate the desired modifications. The FT-IR spectrum of Pull-Suc revealed the success of the succinylation reaction by the appearance of a distinct ester carbonyl signal at 1719 cm^{-1}, which was moved to higher wavenumber at 1728 cm^{-1} after its salt formation. The characteristic carboxylate anion absorption in the spectrum of Pull-Suc-Na at 1560 cm^{-1} indicated the sodium salt formation. All other vital polymer backbone signals of the pullulan polymer were also present in the spectra of Pull-Suc and Pull-Suc-Na.
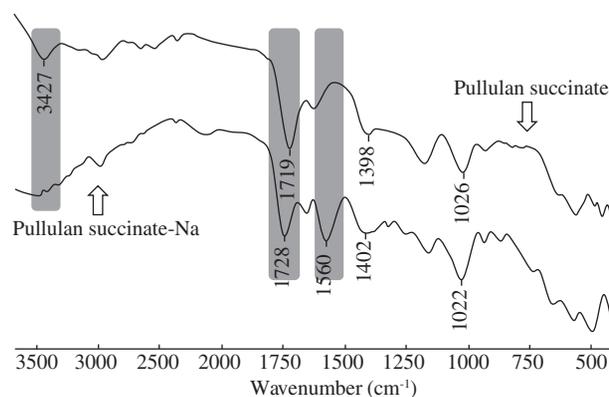
Fig. 1 – Fourier transform infrared spectroscopy (FT-IR) (KBr) spectra of Pull-Suc and Pull-Suc-Na and ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of Pull-Suc.
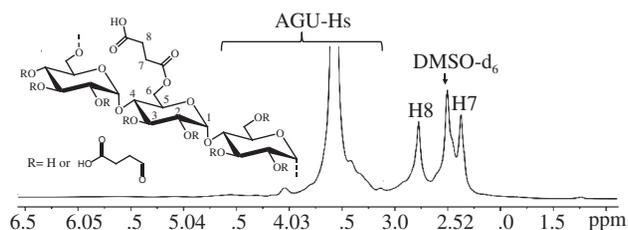
Fig. 2 – Fabrication of homogeneous synthesis of pullulan succinate (Pull-Suc) and its conversion to pullulan succinate sodium salt (Pull-Suc-Na).
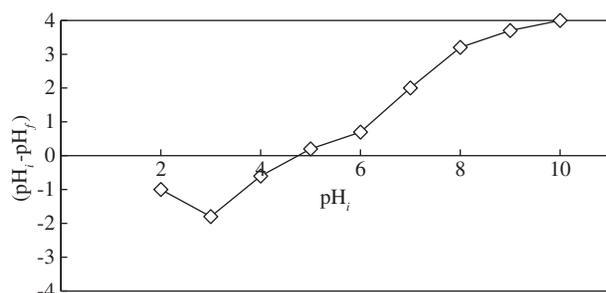
^{1}H NMR spectroscopy was carried out to check the success of the esterification reaction and purity of the sorbent before modification to its sodic form. A typical ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of Pull-Suc conjugates is shown in Fig. 2. The success of esterification was confirmed by the appearance of the methylene (–CH$_2$) protons of succinic acid in Pull-Suc at two different δ values, i.e., δ 2.37 and 2.77 ppm (H-7 and H-8, respectively). The signal of H-7 was observed upfield, indicating the presence of the ester group in the neighborhood, while the signal of H-8 shifted downfield due to the neighboring carboxylic group. Pullulan backbone protons appeared at δ 3.14–4.75 ppm. Thus, the ^{1}H NMR spectrum confirmed the purity of the Pull-Suc conjugates.

Experiments on the pH variation in the solutions of different pHs on the addition of sorbent dose indicated pH$_{ZPC}$ equal to 4.9 for Pull-Suc-Na (Fig. 3). The pH$_{ZPC}$ also suggested the presence of carboxylic acid groups, indicating the weak acid character of the material. It can be inferred from the value of pH$_{ZPC}$ that the sorption of Cd will be greatly favorable from pH 4.9 onward.

2.2. Kinetic study of cadmium-removal on Pull-Suc-Na

2.2.1. Effect of contact time

The effect of contact time on Cd-uptake by newly synthesized Pull-Suc-Na sorbent shows that more than 94% and 90% Cd is removed within the first 15 min from DW and GW solution, respectively (Fig. 4a). This suggests an ion exchange mechanism for Cd ion removal. Our assumption is supported by two arguments: the presence of several reactive sites in the form of Na succinate functionalities, and the absence of a slope

decrease between the fast initial step and the equilibrium plateau, which rules out intraparticulate diffusion.

2.2.2. Kinetic modeling

Pseudo-second order model (Ho and McKay, 1999) was used to determine the sorption rate law and is described by the following differential equation:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{6}$$

where, q_e (mg/g) and q_t (mg/g) are the amounts of metal sorbed at equilibrium and time t, and k (g/(mg·min)) is the rate constant.

Integration and rearrangement of the above equation gives the following relation:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{t}{q_e}. \tag{7}$$

Plotting t/q_t versus t shows that the pseudo-second order kinetic model gives the best fit, as evident from the straight

Fig. 3 – Zero point charge pH (pH$_{ZPC}$) of Pull-Suc-Na.
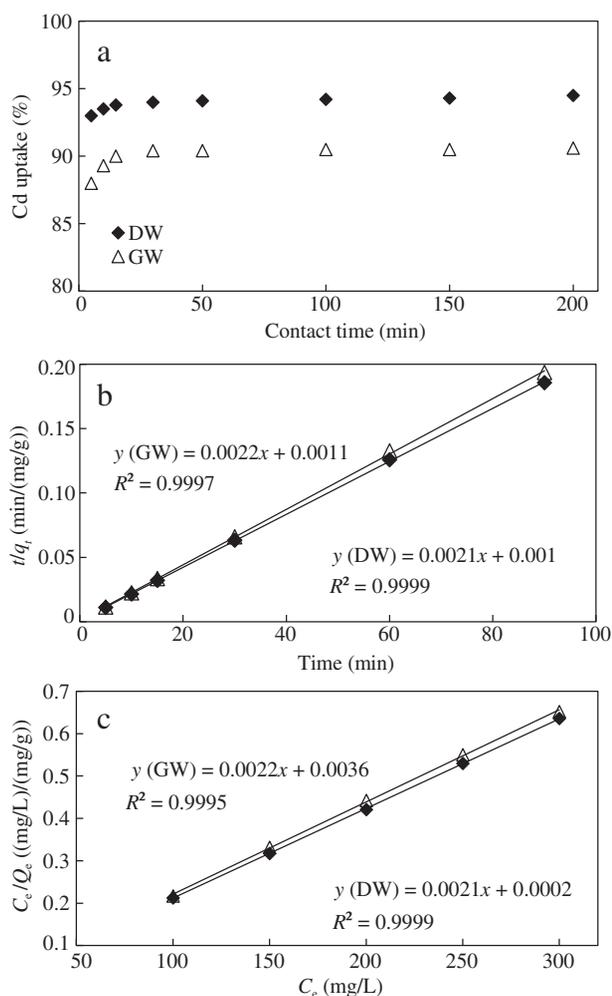
Fig. 4 – Plots of Cd-uptake by Pull-Suc-Na sorbent from DW and GW solution: (a) as a function of contact time, (b) fitting of pseudo-second order model and (c) Langmuir sorption isotherms. DW: distilled water; GW: groundwater.

line (Fig. 4b). This result further supports the high sorption rate of Cd from both DW and GW as ascertained from contact time experiments.

2.2.3. Sorption isotherm and Gibbs free energy

The sorption data were plotted according to the most commonly used models, *e.g.*, the Langmuir isotherm model, which provided the best fit for the sorption of Cd. The Langmuir isotherm model is described by the following equation:

$$q_e = \frac{Q_{max} b C_e}{1 + b C_e}. \tag{8}$$

Rearrangement of the above equation gives the following relation:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{Q_{max} \times b} \tag{9}$$

where, C_e (mg/L) is the Cd-concentration at equilibrium, q_e (mg/g) is the Cd-removal/g of the sorbent, Q_{max} (mg/g) is the maximum sorption capacity/g of sorbent and b (L/mg) is the Langmuir constant.

Langmuir plots (C_e/q_e *versus* C_e) were straight lines and adequately fit the sorption data attained from both DW and GW solutions (Fig. 4c). These results revealed the high efficiency of the sorbent to remove Cd both from DW (476.2 mg/g) and GW (454.5 mg/g). Pull-Suc-Na, like other polysaccharidal sorbents, showed high efficiency and selectivity for Cd ion removal over alkaline earth metal cations (Ca^{2+} and Mg^{2+}) naturally present in GW, and could also displace them from sorption sites on the surface of succinate linkers.

It is important to mention the ranking of the present super-sorbent with other already known polysaccharidal sorbents. Comparison with literature data showed that Pull-Suc-Na sorbent ranks the highest amongst polysaccharidal sorbents for Cd-uptake as reflected in Table 1.

Gibbs free energy values were calculated from the Langmuir isotherms, and the results are summarized in Table 2. The negative values of ΔG^0 indicated the feasibility and spontaneity of chemisorption.

2.2.4. Effect of pH on Cd-uptake

The effect of pH on Cd-uptake by the pristine sorbent, *i.e.*, Pull-Suc-Na, was investigated. It is evident from the plot (Fig. 5) that the removal of Cd is negligible at low pH. This is because protonation of Pull-Suc-Na triggered the formation of Pull-Suc, which has been reported to have a low ion exchange capacity. It is also obvious from the graph that Cd-uptake increases sharply with increase in pH from 4 to 8, with maximum values observed at pH 7 for DW as well as GW. Higher pH (6–8) favors the augmented ion exchange mechanism.

2.2.5. Ion exchange mechanism

The sodic form of the sorbent (Pull-Suc-Na) showed high Cd-uptake (94%) due to an ion exchange mechanism, whereas the acidic form of the sorbent (Pull-Suc) did not show significant Cd-uptake (13.2%) under similar conditions, thereby excluding the possibility of an adsorption mechanism.

The results revealed that presence of Na ions in the sorbent (Pull-Suc-Na) augmented the Cd-uptake substantially.

Table 1 – Comparison of Pull-Suc-Na with other reported polysaccharidal sorbents for Cd-removal.

Sorbent (treatment)	Sorption capacity (mg/g)	References
Bagasse pith (200 and 400°C under steam with SO_2 and H_2S)	149.9	Krishnan and Anirudhan, 2003
Corncob (modified with citric acid and nitric acid pH 6.0, 298 K, 5 days)	32.3 and 19.3, respectively	Leyva-Ramos et al., 2005
Jackfruit peel (H_2SO_4 at 160°C)	52	Inbaraj and Sulochana, 2004
Sugarcane bagasse (modified with succinic anhydride)	196	Karnitz et al., 2007
Filter aid cellulose (modified with succinic anhydride, sodic)	178.6 from GW	Belhalfaoui et al., 2009
Spent green (modified with sodium hydroxide, pH 5.3–5.6, 298 K, 2 hr)	17.3	Low et al., 2000
Mercerized cellulose (modified with succinic anhydride, 10 min)	250	Gurgel et al., 2008
Mercerized sugarcane bagasse (functionalized with ethylenetetramine, 20 min)	86 and 106.4	Gurgel and Gil, 2009
Pullulan succinate sodium (pH 7.0, 298 K, 30 min)	454.5 from GW / 476.2 from DW	Present work / Present work

Pull-Suc-Na: pullulan succinate sodium salt; DW: distilled water; GW: groundwater.

Additionally, it is noteworthy that the designed pristine sorbent Pull-Suc-Na has a high degree of substitution (2.84) of succinate groups, hence a high concentration of Na ions was available to trigger the rapid ion exchange mechanism even at the start of the sorption process (within 15 min). Moreover, the absence of a slope decrease between the fast initial step and the equilibrium plateau ruled out the possibility of intraparticulate diffusion as well.

2.2.6. Regenerability

The super-sorbent Pull-Suc-Na was regenerated using mild and green conditions. The sorbed Cd can be readily desorbed by treating the sorbent (Pull-Suc-Na) with a saturated solution of NaCl (Belhalfaoui et al., 2009). The procedure permits desorption of almost all Cd ions from the sorbent, with negligible decrease in its Cd ion removal efficiency after regeneration (Fig. 6). This negligible decrease (2.34%) in Cd-removal efficiency after three cycles shows the reusability potential of Pull-Suc-Na.

Table 2 – Langmuir parameters for Cd^{2+} sorption and Gibbs free energy.

Solution	Q_{max} (mg/g)	Q_{max} (mmol/g)	b (L/mg)	R^2	ΔG^0 (kJ/mol)
DW	476.2	4.23	10.4	0.9999	−34.62
GW	454.5	4.04	0.611	0.9995	−27.59

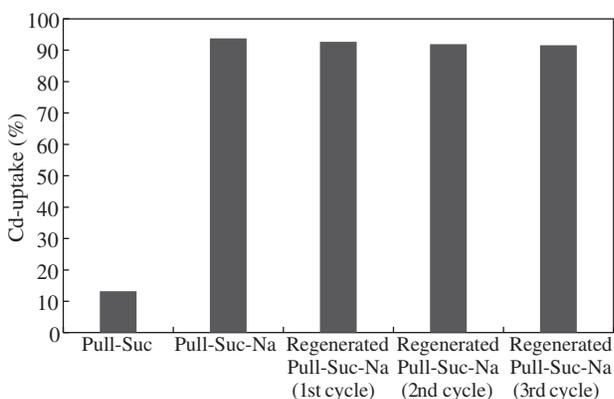DW: distilled water; GW: groundwater; Qmax: maximum adsorption capacity; b: Langmuir constant.
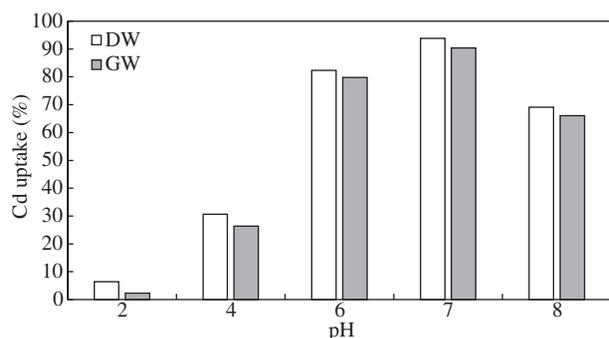
Fig. 5 – Effect of pH on Cd-uptake from DW and GW by Pull-Suc-Na.

Fig. 7 – Overlay of thermogravimetric (TG) curves of Pull-Suc and Pull-Suc-Na, indicating thermal stability imparted in sodic form of sorbent throughout the degradation profile.
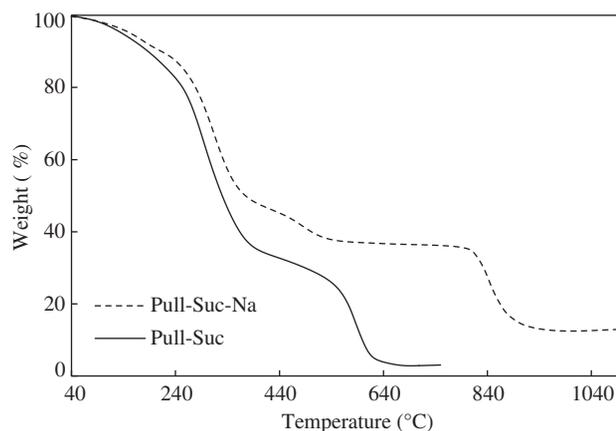
2.3. Thermal analysis of sorbent

Data on the thermal stability of Pull-Suc-Na (sorbent) is essential to obtain information about storage, handling (Giron, 2002) and prediction of the performance parameters of the material (Neto et al., 2010; Stulzer et al., 2008). Therefore, thermal analyses of Pull-Suc and its sodic form Pull-Suc-Na (sorbent) were recorded for comparison. Fig. 7 shows an overlay of the TG curves of Pull-Suc-Na and Pull-Suc. The thermal decomposition temperatures Tdi, Tdm and Tdf were obtained for each degradation step from TG and associated DTG curves (Table 3). A two step degradation profile was observed from the degradation data of Pull-Suc and Pull-Suc-Na.

The degradation maximum (Tdm) of the first degradation step of Pull-Suc-Na appeared at 313.75°C, which is about 24°C higher than the Tdm of Pull-Suc. Likewise, Tdi of the second degradation step of Pull-Suc-Na was almost 97°C higher than for the precursor (Pull-Suc). A second degradation step, with weight loss of 21.97%, was observed in the sodic form of the sorbent Pull-Suc-Na starting at 795.40°C and ending at Tdf 920.08°C, with Tdm 840.16°C.

It is obvious from the thermal data of major degradation steps that Tdi, Tdm and Tdf of Pull-Suc-Na are significantly higher than those of Pull-Suc. It is therefore inferred that the sorbent has extraordinary thermal stability in its sodic form, i.e., Pull-Suc-Na, which can be observed throughout the TG curve. This increased thermal stability could be beneficial in order to increase the shelf-life of the sorbent, indicating its potential for viable commercial applications.

3. Conclusions

A convenient chemical modification of pullulan to Pull-Suc-Na via the formation of Pull-Suc was developed. Sorption data and kinetics showed the high efficiency of the benign Pull-Suc-Na sorbent for Cd-uptake from both distilled water and a spiked high-hardness ground water solution. Cd-uptake followed an ion exchange mechanism rather than adsorption. Furthermore, the presence of a single kind of functionality, i.e., Na-succinate on the pullulan backbone, makes it a superior sorbent compared to unmodifiable/less modifiable multi-functionalized agricultural waste materials. In summary, it can be stated that Pull-Suc-Na is a highly efficient, regenerable and reusable sorbent with high selectivity for Cd-uptake in the presence of other divalent metal ions generally present in water.

Fig. 6 – Percentage Cd-uptake by the acidic (Pull-Suc), sodic (Pull-Suc-Na) and regenerated sodic forms (three cycles) of the sorbent Pull-Suc-Na.

Table 3 – Thermal decomposition data of Pull-Suc and Pull-Suc-Na sorbent.						
Sample	Step	Tdi (°C)	Tdm (°C)	Tdf (°C)	Weight loss (%) at Tdf	Char yield (wt.%)
Pull–Suc	I	111.84	290.15	404.53	62.54	2.85 at 694.37°C
	II	506.83	589.94	624.04	29.97	
Pull–Suc–Na	I	209.32	313.75	395.80	52.24	12.58 at 973.77°C
	II	795.40	840.16	920.08	21.97	
Pull-Suc: pullulan succinate; Pull-Suc-Na: pulluan succinate sodium salt.						

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