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Evaluation of chemically modified polysaccharide pullulan as an efficient and regenerable supersorbent for heavy metal ions uptake from single and multiple metal ion systems

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ABSTRACT

Pullulan succinate (Pull-Suc) was synthesized by esterification of pullulan with succinic anhydride and converted into its sodic form (Pull-Suc-Na) by treating with saturated $NaHCO_3$ solution. These acidic (Pull-Suc) and sodic forms (Pull-Suc-Na) of the sorbent were characterized by solid-state CP/MAS ^{13}C NMR and scanning electron microscopy–energy dispersive X-ray spectroscopy (SEM–EDS) techniques. SEM analysis showed that surface of the sorbent was rough and rigid. The Pull-Suc-Na was used to sorb Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) ions from aqueous solution using batch methodology. Sorption data were fitted to various kinetic and isothermal model. Pseudo-second-order kinetic model and Langmuir isotherm model fitted well to the experimental data. Ion-exchange model was applied to verify the involvement of ion-exchange mechanism during initial rapid phase of sorption. Langmuir isotherm model was used to find maximum sorption capacities of Pull-Suc-Na for Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) which were found to be 714.28, 588.2, 416.6, 357.1 and 250 mg g^{-1}, respectively. Competitive removal of a metal ion from binary, tertiary and mixture of five metal ions was studied to check the potential of sorbent for wastewater treatment procedures. Thermodynamic parameters determination showed that sorption process was spontaneous and exothermic in nature. The sorbent was regenerated using green conditions, that is, by treating with brine. The sorbent showed negligible decrease in sorption capacity after five sorption–desorption cycles.

Keywords: Competitive sorption; Heavy metal ions; Regeneration; Succinylated pullulan

1. Introduction

The last century witnessed an accelerated emergence of water pollution sources both naturally and due to human activities. The exponential population, continuous development of industries and use of modern technologies provide excessive exoneration of pollutants to the environment. The presence of various hazardous pollutants especially heavy metal ions in the receiving sinks like rivers, lakes, seas, etc. is of major concern because of their toxicity, non-biodegradability and bioaccumulation [1,2].

The assimilation of heavy metals (copper, nickel, cadmium, chromium, arsenic, lead, mercury, etc.) in water is directly linked to human and cause diseases like cancer, diarrhea, gastrointestinal disorders, mental disorders, etc. [3,4]. Trace quantity of some metals is required by the human, but

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their large persistent dosages are not metabolized by the body and produce toxicity due to accumulation in the soft tissues [5].

To eradicate such contaminants present in wastewater need recuperative techniques such as solvent extraction [6], filtration [7], adsorption [8], ion exchange [9], precipitation [10], biological treatment [11] and destructive techniques such as ozonation, oxidation, etc. [12]. However, most of these methods especially chemical methods were found to be less efficient, expensive, time consuming and may produce harmful by-products [13]. Use of ion-exchange method for the decontamination of wastewater from heavy metals provided remarkable results because it is rapid, reversible and selective [14–18]. During ion exchange, solution containing heavy metal ions is contacted with essentially insoluble porous solid matrix and heavy metal ions present in solution are exchanged with ions held in solid.

Biopolymers find application in almost every field life such as electronic, photonics, aerospace, food, medicine, pharmaceutics, etc. [19]. Biopolymer such as cellulose is the main part of renewable and abundant sorbents such as agricultural waste (fruit peels) and plant barks, which being low cost are highly beneficial in mitigating pollution problem [20,21]. Various biopolymers are extensively employed for the purification of water bearing heavy metal ions. These biopolymers when used as such, that is, in unmodified form were found less efficient for the removal of heavy metals form aqueous solution. Last decade witnessed that sorption capacity of biopolymers can be increased many times after its chemical modification to a suitable functional group [22,23]. One of these chemical modifications include esterification of polysaccharides with succinic anhydride to give succinylated product. This succinylated product is then converted into its sodium salt which allows the exchange of these sodium ions with heavy metal ions present in aqueous solution [24,25].

Pullulan is a biopolymer having hydroxyl groups like cellulose which are available for chemical modification. In the present study, these hydroxyl groups of pullulan were esterified with succinic anhydride to form pullulan succinate (Pull-Suc). The Pull-Suc was converted into sodic form (Pull-Suc-Na) by treating with saturated solution of $NaHCO_3$. The Pull-Suc-Na so obtained was used to treat water containing heavy metal ions such as Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II). Effects of various parameters such as sorbent dosage, pH, temperature and contact time on sorption capacity of the sorbent for these heavy metal ions is also the aim of this study. The present work is also aimed to fit various kinetic and isothermal models to the experimental sorption data. Estimation of thermodynamic parameters, regeneration of the sorbent and competitive uptake of various metal ions is also the aims of the present work.

2. Experimental setup

2.1. Reagent and materials

Pullulan (molecular weight 100,000) used in the current study was provided by Sigma-Aldrich (St Louis, MO, USA) and dried under vacuum at 110°C for 2 h prior to use. All reagents and solvents used were of analytical grade.

2.2. Synthesis and characterization of Pull-Suc and Pull-Suc-Na

Pull-Suc and its sodium salt (Pull-Suc-Na) were synthesized by a reported method [24]. These were characterized by solid-state CP/MAS ^{13}C NMR and SEM–EDS.

2.3. Sorption studies

Stock solutions (1,000 ppm) of heavy metal ions, that is, Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) were prepared by dissolving their salt in deionized water. Furthermore a series of metal ion solutions of required concentration were prepared by diluting the stock solution. Sorption experiments were carried out by stirring optimized amount of sorbent (Pull-Suc-Na) with these metal ions solution in a stoppered conical flask (250 mL) in shaking thermostat machine (Orbital Shaking Incubator, PA-42/250R, PAMICO Equipments, Faisalabad, Pakistan) at a fixed temperature for desired time. 0.1 M HNO_3 and 0.1 M NaOH solution was used to carry out pH studies. The initial and final metal ion concentrations were measured by flame atomic absorption spectrophotometer (FAAS; AA 6300, Shimadzu, Japan) using air-acetylene flame at 283.3, 357.9, 240.7, 324.5 and 232 nm for Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II), respectively. Triplicate evaluation was done.

Percentage metal removal and sorption capacity are determined by Eqs. (1) and (2):

$$\text{Percentage uptake} = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

$$q_e = \frac{C_i - C_e}{w} \times V \tag{2}$$

where C_i is initial concentration of metal ion in mg L^{-1}, C_e is equilibrium metal ion concentrations in mg L^{-1}, w is the mass of adsorbent used in g, q_e is the equilibrium adsorption capacity in mg g^{-1} and V is the volume of the solution in L.

To establish the mechanism of removal of metal uptake, acidic form of the sorbent (Pull-Suc) was also stirred with solution of all the five metal ions, that is, Pb(II) (130 mg L^{-1}), Cu(II) (70 mg L^{-1}), Cr(VI) (120 mg L^{-1}), Ni(II) (50 mg L^{-1}) and Co(II) (80 mg L^{-1}) one by one at pH optimized for above experiments for 30 min at 298 K.

Competitive adsorption of binary mixtures [(i) Ni(II) and Cr(VI), (ii) Ni(II) and Cu(VI), (iii) Cu(II) and Pb(II)], tertiary mixtures [Ni(II), Cu(II), Cr(VI) and Ni(II), Cu(II), Cr(VI)] and mixture of all the five metal ions [Ni(II), Cu(II), Co(II), Pb(II) and Cr(VI)] by Pull-Suc-Na was studied at optimal conditions.

3. Results and discussion

3.1. Synthesis and characterization of Pull-Suc and Pull-Suc-Na

3.1.1. Synthesis of Pull-Suc and Pull-Suc-Na

Pull-Suc was synthesized by esterification of pullulan with succinic anhydride using dimethylaminopyridine as catalyst by a reported method [24]. Acid–base titration was used to find out degree of substitution (DS) of Pull-Suc. DS of Pull-Suc was very high (DS 2.84). The Pull-Suc was then treated with saturated $NaHCO_3$ solution to get its sodic form, that is, Pull-Suc-Na. Successful succinylation of pullulan was evidenced by appearance of distinct ester carbonyl signals at 1,728 cm^{-1}

in the Fourier transform infrared spectroscopy spectrum of Pull-Suc. Formation of sodium salt of Pull-Suc was confirmed by appearance of characteristic carboxylate anion peak at 1,560 cm^{-1} in the spectrum of Pull-Suc-Na. To monitor surface charge of Pull-Suc-Na, pH$_{ZPC}$ (pH corresponding to the point of zero charge) was calculated. The pH$_{ZPC}$ value for Pull-Suc-Na was found to be 4.9. Determination of pH$_{ZPC}$ for any sorbent is an important parameter to study sorption behavior of the sorbent. At pH > pH$_{ZPC}$, surface of the sorbent becomes negatively charged which favors metal uptake [25]. Fig. 1 is the schematic illustration of fabrication of Pull-Suc and Pull-Suc-Na.

3.1.2. Solid-state CP/MAS ^{13}C NMR spectroscopic analysis

Fig. 2 shows the solid-state CP/MAS ^{13}C NMR spectrum of the sorbent Pull-Suc-Na. Successful esterification and sodium salt formation were witnessed by appearance of carbonyl of ester and carboxylate sodium signals at about 176.40 and 181.29 ppm, respectively. Pullulan backbone signals and signal of CH$_2$ of succinyl moieties were observed at 55.0–90.11 and 32.21 ppm, respectively. The C1 of pullulan was assigned to signals at 98.53–103.26 ppm.

3.1.3. SEM–EDS analyses

Figs. 3(c)–(g) show the surface morphology of the Pull-Suc, Pull-Suc-Na, Pull-Suc-Cr, Pull-Suc-Co, Pull-Suc-Ni, Pull-Suc-Pb and Pull-Suc-Cu. SEM analyses showed that the surface was rough and inhomogeneous. The presence of Na ions and Cr(VI), Co(II), Ni(II), Pb(II) and Cu(II) before and after metal uptake on the surface of the sorbent, respectively, was confirmed by EDS analyses (Figs. 3(j)–(n)).

3.2. Sorption studies

This Pull-Suc-Na was then used to sorb Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) from aqueous solution. Different

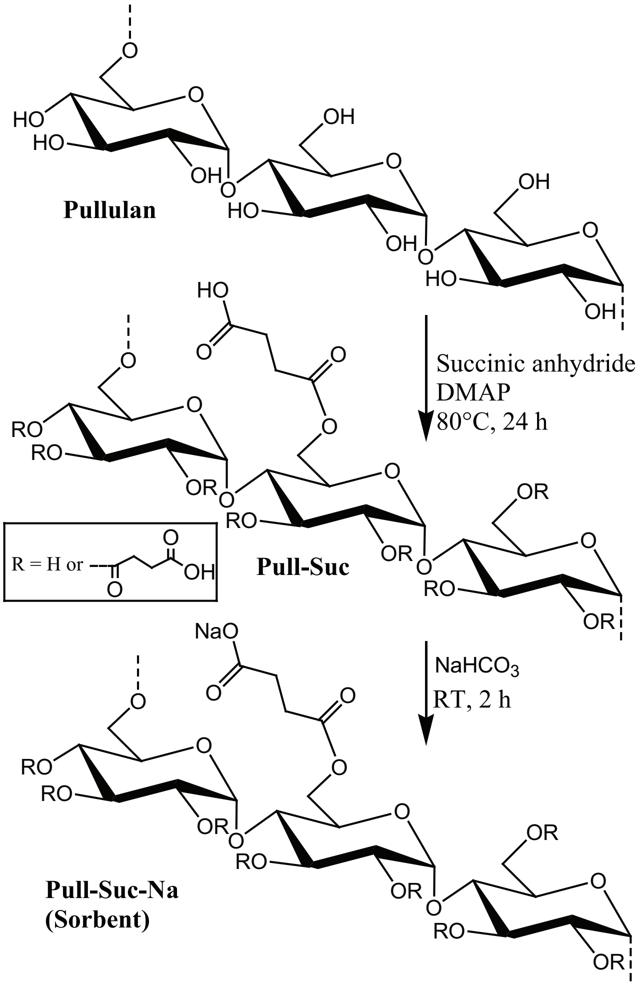

Fig. 1. Synthesis of Pull-Suc and Pull-Suc-Na.

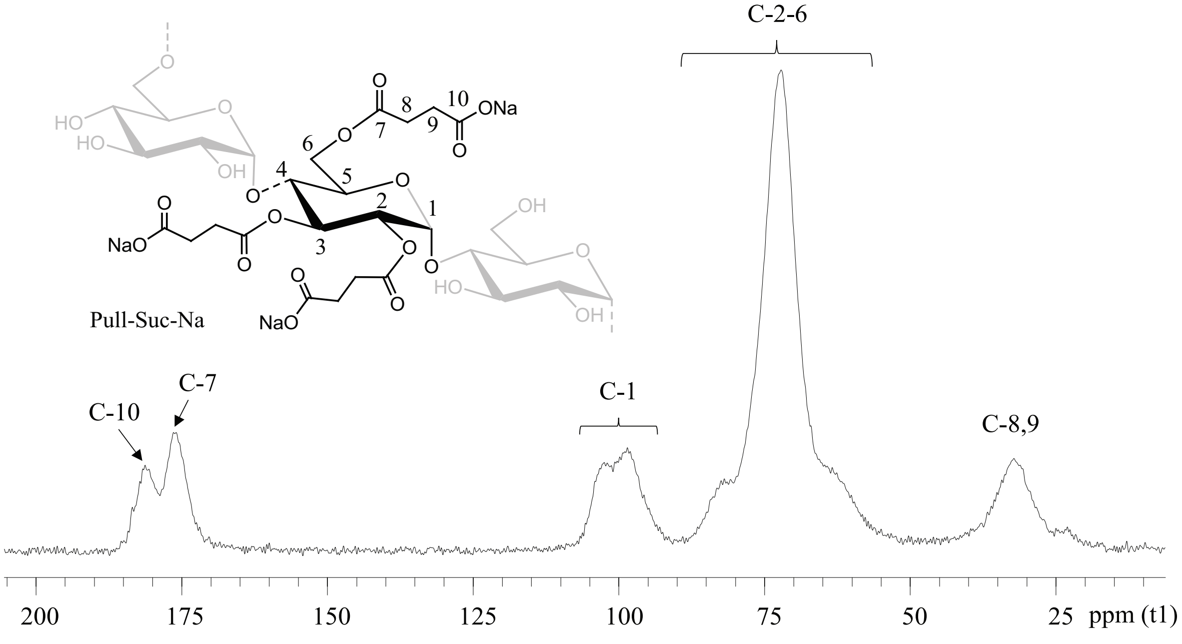

Fig. 2. The solid-state CP/MAS ^{13}C NMR spectrum of Pull-Suc-Na.

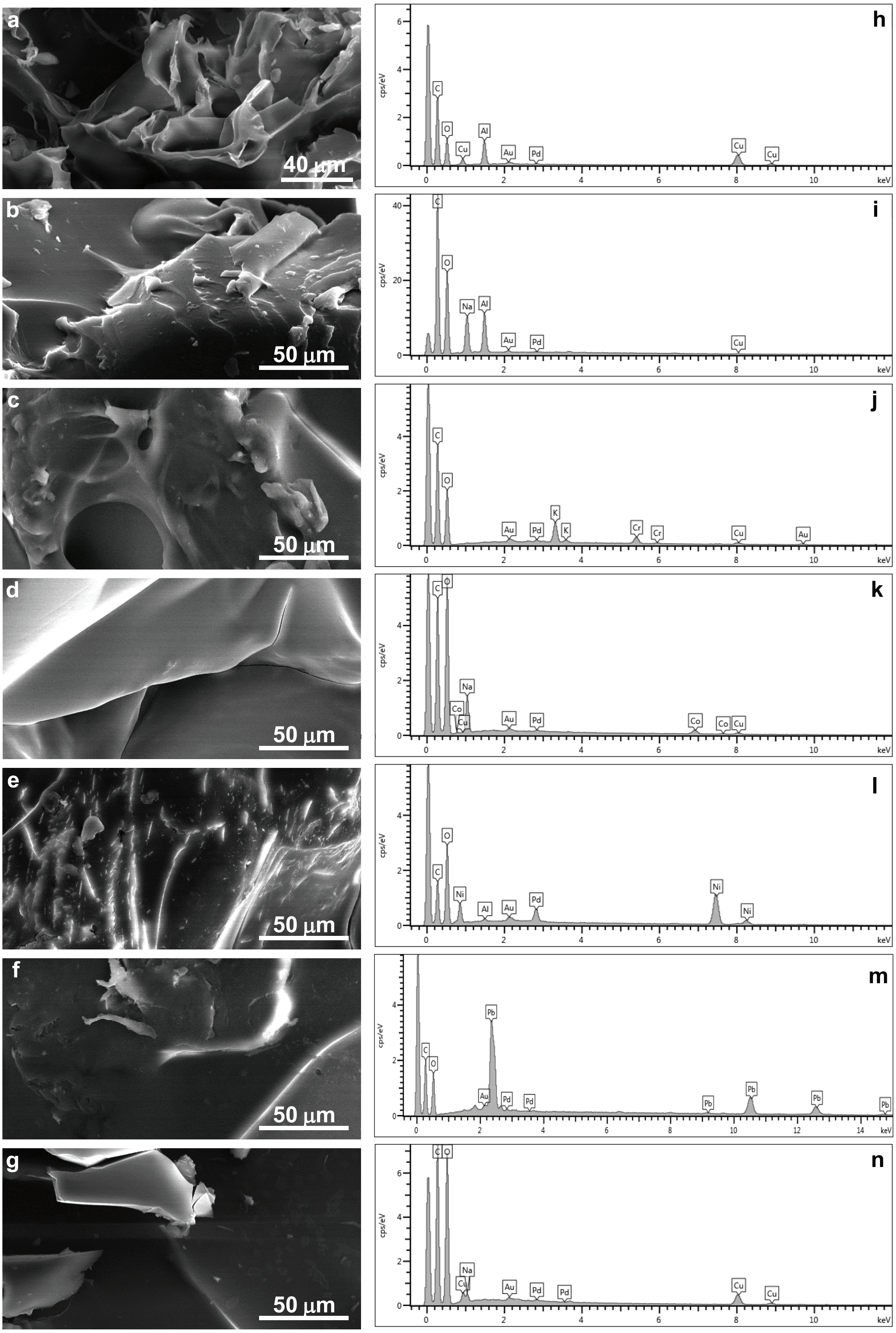

Fig. 3. SEM (a)–(g) images and EDS (h)–(n) spectra of Pull-Suc, Pull-Suc-Na, Pull-Suc-Cr(VI), Pull-Suc-Co(II), Pull-Suc-Ni(II), Pull-Suc-Pb(II) and Pull-Suc-Cu(II), respectively.

parameters were optimized. Sorption data were subjected to isotherm and kinetic analysis.

3.2.1. Effect of initial metal concentration

To study the effect of initial metal ion concentration, sorbent (20 mg) was stirred with metal ion solution (100 mL) in concentration range Pb(II) (70–250 mg L^{-1}), Cr(VI) (60–240 mg L^{-1}), Co(II) (30–200 mg L^{-1}), Cu(II) (30–190 mg L^{-1}) and Ni(II) (30–170 mg L^{-1}) for 30 min at 298 K at a speed of 130 rpm. Fig. 4(a) shows that metal ions uptake increases with increase in initial metal ions concentration in the solution. This increase in metal uptake with increase in concentration might be due to an increase in the mass transfer driving force, that is, concentration gradient. Low values of sorption capacities at lower concentrations of metal ions might be due to the reason that large number of exchange sites is available but metal ions are fewer. It is also evident from plot that the saturated sorption capacities are reached at 130, 120, 80, 70 and 50 mg L^{-1} for Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II), respectively (see Fig. 4(a)).

3.2.2. Effect of sorbent dosage

Amount of sorbent was optimized by stirring the sorbent (10–80 mg) with metal ion solution (100 mL) containing Pb(II) (130 mg L^{-1}), Cu(II) (70 mg L^{-1}), Cr(VI) (120 mg L^{-1}), Ni(II) (50 mg L^{-1}) and Co(II) (80 mg L^{-1}) for 30 min at a speed of 130 rpm at 298 K. It is evident from Fig. 4(b) that sorption capacities first increase with increase in sorbent dosage and after an optimum sorbent dosage it starts decreasing. This decrease in sorption capacity (mg g^{-1}) after an optimum sorbent dosage was attributed to the fact that exchange sites are available on the surface of the sorbent but there are no metal ions present in the solution to exchange with these sites. Sorbent dosage of 20 mg provided maximum sorption capacity for all the five metal ions under equilibrium conditions. Therefore, Pull-Suc-Na can be suggested as a more economical design for the removal of heavy metal ions.

3.2.3. Effect of pH on metal uptake

Effect of pH was studied in the range 2–7 under optimal conditions, that is, sorbent dosage (20 mg), metal ion concentration Pb(II) (130 mg L^{-1}), Cu(II) (70 mg L^{-1}), Cr(VI) (120 mg L^{-1}), Ni(II) (50 mg L^{-1}) and Co(II) (80 mg L^{-1}), time 30 min and temperature 298 K. Fig. 5(a) shows that there is negligible metal uptake at low pH which increases with increase in pH. The low metal sorption at low pH might be due to protonation of Pull-Suc-Na which results in the formation of Pull-Suc which has low metal uptake capability due to unavailability of the negative charge density. A sharp increase in the sorption occurred in the pH range 4.0–7.0 and it was maximum at pH 6.0, 6.0, 5.0, 5.0 and 5.5 for Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II), respectively. This increase in metal removal at higher pH can be explained on the basis that at higher pH the Pull-Suc becomes deprotonated and metal binding capacity of the sorbent increases. Moreover at pH > 4.9 which is pH_{ZPC} for Pull-Suc-Na, there becomes

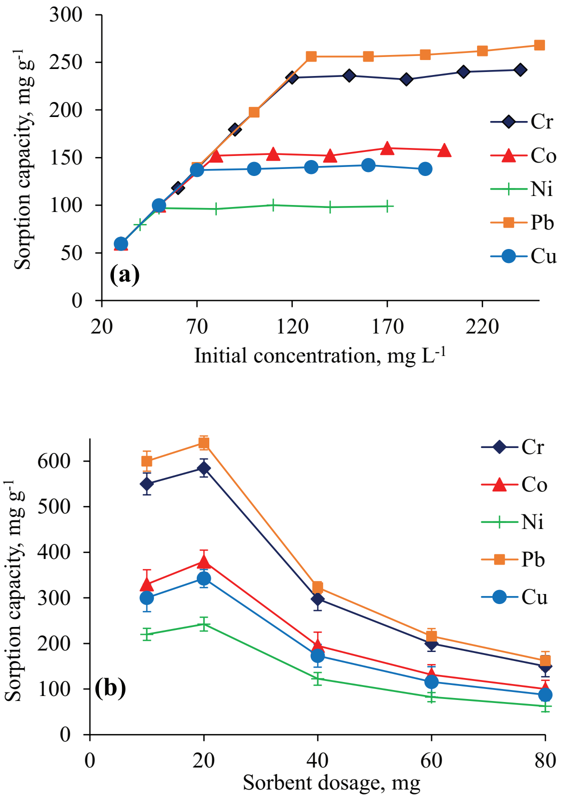

Fig. 4. Effect of initial metal ions concentration (a) and sorbent dose (b) on sorption capacity of Pull-Suc-Na.

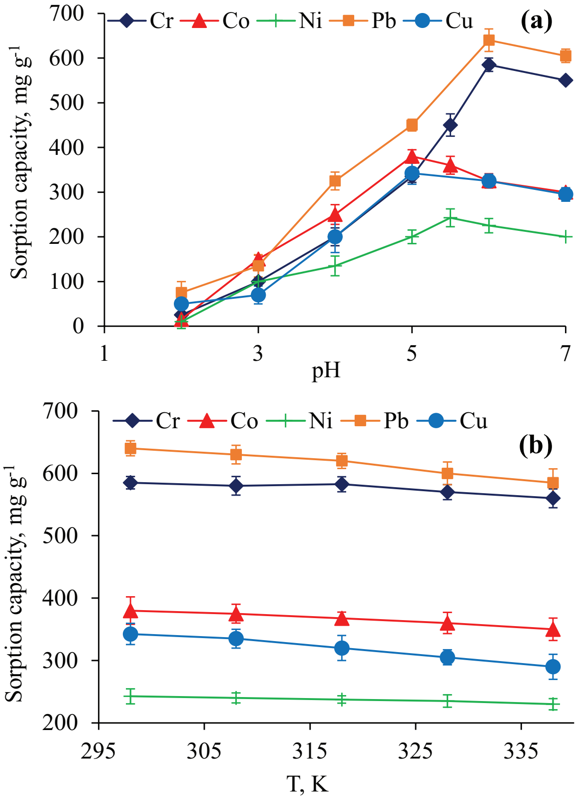

Fig. 5. Effect of pH (a) and temperature (b) on sorption capacity of the sorbent.

a negative charge on the surface of the sorbent which facilitates metal ions uptake. Metals showed a trend of declining sorption when the pH was increased beyond certain limit due to precipitation of insoluble metal hydroxides. These results reported in the present study were in conformity with earlier studies.

3.2.4. Effect of temperature

Temperature was varied in the range 298–338 K in order to study the effect of temperature on sorption capacity of the sorbent while all other parameters were kept constant. Fig. 5(b) showed decrease in sorption capacity values with increase in temperature for all the five metal ions. The reason behind might be that at lower temperatures metal ions present in the solution could interact more with the binding sites and as temperature is increased mobility of ions increases causing less attraction between sorbent and sorbate. Moreover, this decrease in sorption capacity at increased temperatures was indicative of exothermic behavior of the sorption process.

3.2.5. Effect of contact time

Effect of contact time was studied by stirring optimized amount of the sorbent (20 mg) with solution containing optimized concentration of all metal ions at optimum pH over a time range of 5–120 min at a speed of 130 rpm and 298 K. The experimental results reveal that the uptake of metal was faster at initial stages of contact and it became less as the equilibrium was attained. This was due to the presence of large number of vacant sites for metal uptake during earlier stages and remaining vacant sites were difficult to be occupied at later stages of adsorption, might be due to repulsive forces between the metal ions on the adsorbent and aqueous solution. It is evident from Fig. 6(a) that about 95% Pb(II) and Cr(VI) are removed within first 15 min and more than 95% Co(II), Cu(II) and Ni(II) within the first 30 min. Sorption equilibrium was achieved within first 15 min for Pb(II) and Cr(VI) and within the first 30 min for Co(II), Cu(II) and Ni(II). At equilibrium almost all vacant sites are engaged. Such rapid sorption process was interrelated with the characteristics of the sorbent and its physicochemical interactions with the metal ions. Figure clarifies that the contact time of 15 and 30 min was sufficient for the maximum metal ions uptake. However, to ensure complete saturation of sorbent, the contact time was extended.

3.2.6. Kinetic modeling

The prediction of rate of sorption gives significant information for designing batch sorption systems for the uptake of metal ions. Information about the kinetics for the metal ions uptake is required for selecting optimized operating conditions for full-scale batch process. Hence, the kinetics of the sorption process was analyzed using both pseudo-first-order and pseudo-second-order models. Linear form of pseudo-first-order kinetic model is given as:

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

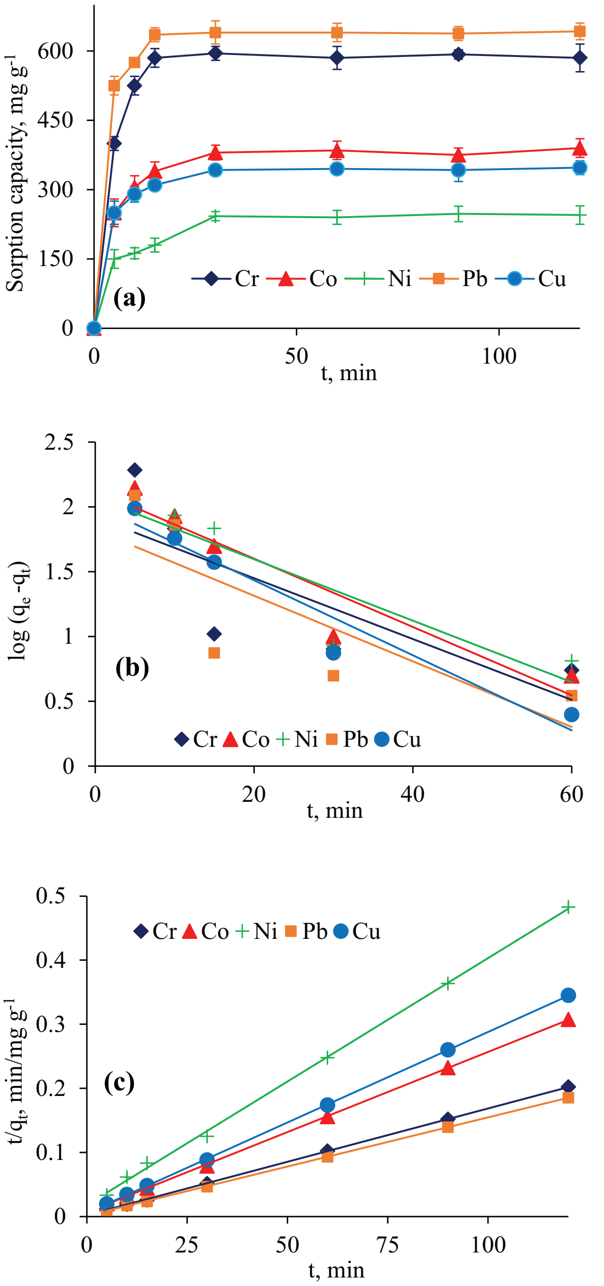

Fig. 6. Plot of sorption efficiency of Pull-Suc-Na as a function of contact time (a), fitting of pseudo-first-order model (b) and pseudo-second-order model (c).

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the equilibrium sorption capacity and sorption capacity at time t (min), respectively, and k_1 is the rate constant for pseudo-first-order reaction. This model fits well to the data for initial stage of sorption, so the time range chosen was 5–60 min. Plot of $\log(q_e - q_t)$ against t gives a straight line slope and intercept of which gives values of rate constant (k_1) and q_e, respectively (Fig. 6(b)). Deviation of experimental values of sorption capacity from q_e values calculated from pseudo-first-order kinetic model and less values of linear regression correlation coefficients (<0.99; Table 1) showed that the Lagergren pseudo-first-order kinetic plot did not fit well to the sorption data for each metal ion. Therefore, the kinetic data were applied to pseudo-second-order kinetic model linear form of which is given as:

$$\frac{t}{q_t} = \frac{1}{kq_e^{\,2}} + \frac{t}{q_e} \tag{4}$$

where k is rate constant for pseudo-second-order kinetic model. Plotting t/q_t against t gives a straight line. Slope and intercept of this straight line give values q_e and k, respectively. The calculated values of q_e were in agreement with experimental values of sorption capacities. The higher linear regression correlation coefficients values were found for pseudo-second-order kinetic model (>0.99; Table 1). Both these facts show that pseudo-second-order kinetic plot fitted well to the sorption data for all the five metal ions (Fig. 6(c)). Hence, it is concluded that this model could be applied to predict the sorption kinetics of these metal ion on Pull-Suc-Na very well and it is predicted that rate determining step followed chemisorption mechanism.

3.2.7. Sorption isotherm

The distribution of sorbed molecules between the sorbate (liquid phase) and the sorbent (solid phase) at the equilibrium stage is governed by the sorption isotherm. The experimental data obtained for the sorption of Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) was fitted to Freundlich and Langmuir isotherm. Linear form of Freundlich isotherm is given as:

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \tag{5}$$

where k_F and n are Freundlich parameters. While fitting the data to Freundlich isotherm, the values of $\log q_e$ were plotted against $\log C_e$. Values of Freundlich isotherm parameters (k_F, R^2 and n) are summarized in Table 2. Linearized plot obtained from the Freundlich isotherm offered low values of R^2 which shows inadequacy of this model (Fig. 7(a)). Therefore, the data were analyzed with Langmuir isotherm model linear form of which is given as:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} \times b} \tag{6}$$

where $Q_{\max}$ (mg g^{-1}) and b are maximum sorption capacity and Langmuir constant, respectively. When values of C_e/q_e were plotted against C_e, straight lines were obtained giving high values for correlation coefficients. Whereas the values of $Q_{\max}$ and b were calculated from slope and intercept of these linear lines, respectively (Table 2). Therefore, the Langmuir model provided better fit to the experimental data (Fig. 7(b)). Values of maximum sorption capacities obtained from Langmuir isotherm model were 714.28, 588.2, 416.6, 357.1 and 250 mg g^{-1} for Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II), respectively, were in good agreement of experimental values of sorption capacities. Dimensionless constant separation factor (R_L) tells that whether a sorption process is favorable or unfavorable and is given by the following relation:

Table 1
Pseudo-first-order and pseudo-second-order parameters for the sorption of Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) using Pull-Suc-Na

	Experimental	Pseudo-second-order			Pseudo-first-order		
Solution	q_e (mg g^{-1})	q_e (mg g^{-1})	k	R^2	q_e (mg g^{-1})	k_1	R^2
Pb(II)	640.0	666.67	0.00173	0.9999	66.06	0.05827	0.6264
Cr(VI)	585.0	588.24	0.00126	0.9998	83.06	0.05412	0.6062
Co(II)	380.0	400.0	0.00098	0.9998	134.0	0.06080	0.8925
Cu(II)	342.5	357.14	0.00148	0.9999	103.2	0.06656	0.9410
Ni(II)	243.0	256.41	0.00084	0.9990	117.3	0.05458	0.8224

Table 2
Freundlich and Langmuir parameters for Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) removal from aqueous solution using Pull-Suc-Na

Experimental	Parameters	Pb(II)	Cr(VI)	Co(II)	Cu(II)	Ni(II)
Langmuir parameters	q_e (mg g^{-1})	640.0	585	380	342.5	243
	$Q_{\max}$ (mg g^{-1})	714.2	588.2	416.60	357.15	250.0
	$Q_{\max}$ (mmol g^{-1})	3.451	11.31	7.0622	5.6243	4.260
	b (mg L^{-1})	0.062	0.472	0.1326	0.7778	0.510
	b (mmol L^{-1})	12.88	24.56	7.8230	49.389	30.05
	R^2	0.9978	0.9935	0.9973	0.9984	0.9993
Freundlich parameters	R_L	0.110	0.110	0.0861	0.0006	0.0007
	n	13.96	97.087	20.33	49.50	49.02
	k_F	447.8	561.8	304.9	315.3	222.9
	R^2	0.7715	0.0166	0.5827	0.3076	0.3723

$$R_L = \frac{1}{1+bC_i} \tag{7}$$

where b and C_i (mg L^{-1}) are Langmuir constant and initial concentration of metal ions, respectively. If value of R_L is greater than 1 then it predicts unfavorable sorption while value of R_L between 0 and 1 predicts favorable sorption. Table 2 shows that values of R_L are between 0 and 1 for all the five metal ions indicating favorable adsorption.

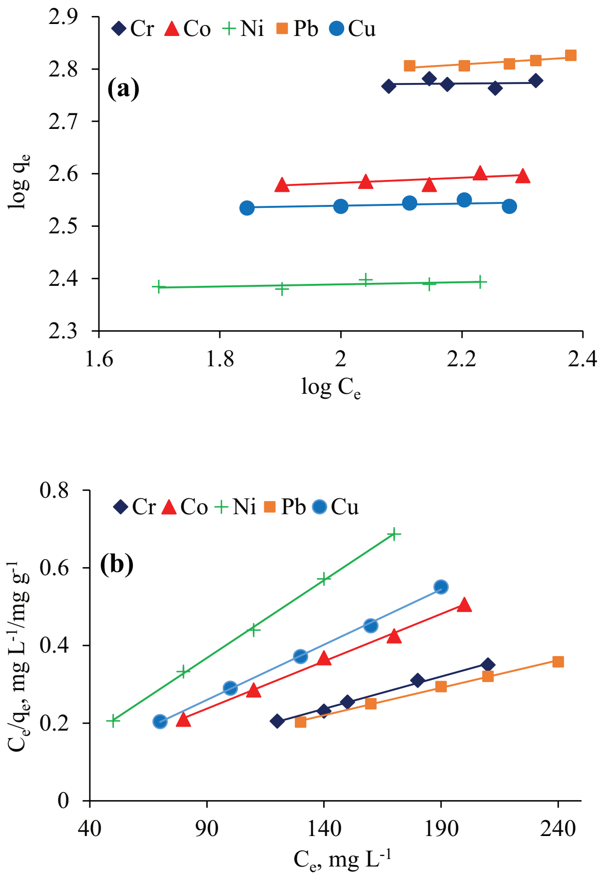

Fig. 7. Freundlich sorption isotherms (a) and Langmuir sorption isotherms (b) for heavy metal ions removal from aqueous solution by Pull-Suc-Na sorbent.

Table 3 shows the sorption capacity values of some known polysaccharidal sorbents for the removal of Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) from aqueous solution. Comparison suggests that our sorbent has prominent position among these sorbents.

3.2.8. Sorption and desorption (regenerability)

Regenerability and reusability studies were carried out by stirring sorbent (20 mg) with optimum concentration of each metal ion at optimum pH for 30 min. Metal uptake was determined by FAAS after separation of the sorbent from metal solution by centrifugation and filtration. The separated sorbent was then stirred with brine solution overnight to desorb the sorbed metal ion and washed with deionized water until negative $AgNO_3$ test [24]. This regenerated sorbent was used again for metal sorption. These sorption and regeneration studies were repeated over five successive cycles. After each sorption–desorption cycle, concentration of sorbed and desorbed metal ion was calculated (Figs. 8(a)–(e)). Decrease in values of sorption capacities for Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) were 23.4, 26.35, 11.7, 16.2 and 19 mg g^{-1}, respectively, after five cycles. Fig. 7(f) shows that total decrease in percentage uptake for Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) was 3.5%, 3.1%, 1.8%, 2.4% and 2.6%, respectively, after five cycles. The presence of electrostatic force of attraction between the sorbent and the metal ion act as a hindrance for complete desorption of sorbed metal ion from sorbent surface. Minimum loss in sorption capacity of sorbent for each sorption–desorption cycle suggested its repeated use.

3.2.9. Ion-exchange mechanism

The ion-exchange mechanism during sorption process was verified by investigating the potential of both Pull-Suc and Pull-Suc-Na toward metal uptake. It was noted that Pull-Suc-Na showed reasonably high uptake capacity for

Table 3
Comparison of the sorbent (Pull-Suc-Na) with other reported polysaccharidal sorbents for the heavy metal ions removal

Sorbent (treatment)	Metal ion	Sorption capacity (mg g^{-1})
Modified cashew nut shell [26]	Cu(II), Ni(II)	406.6, 456.3
Multiwall carbon nanotubes [27]	Pb(II)	104.2
Modified wheat straw [28]	Cu(II)	397
Chitosan (epichlorohydrin and triethylenetetramine) [29]	Pb(II)	559.4
Polyethylene-*g*-poly(acrylic acid)-*co*-starch/organo-montmorillonite hydrogel composite [30]	Pb(II)	430
Brown seaweed (*Sargassum wightii*) [31]	Co(II)	20.63
Chitosan/graphene oxide [32]	Pb(II), Cu(II), Cr(VI)	461.3, 423.8, 310.4
Cellulosic okra fibers (acrylonitrile/methacrylic acid) [33]	Pb(II), Cu(II)	268.32, 76.82
Poly(itaconic acid) grafted cross-linked starch nanoparticles (PIACS) [34]	Pb(II)	1,320
Pullulan (succinic anhydride and sodic)	Pb(II), Cr(VI), Cu(II), Co(II), Ni(II)	714.28, 588.2, 416.6, 357.1, 250 Present work

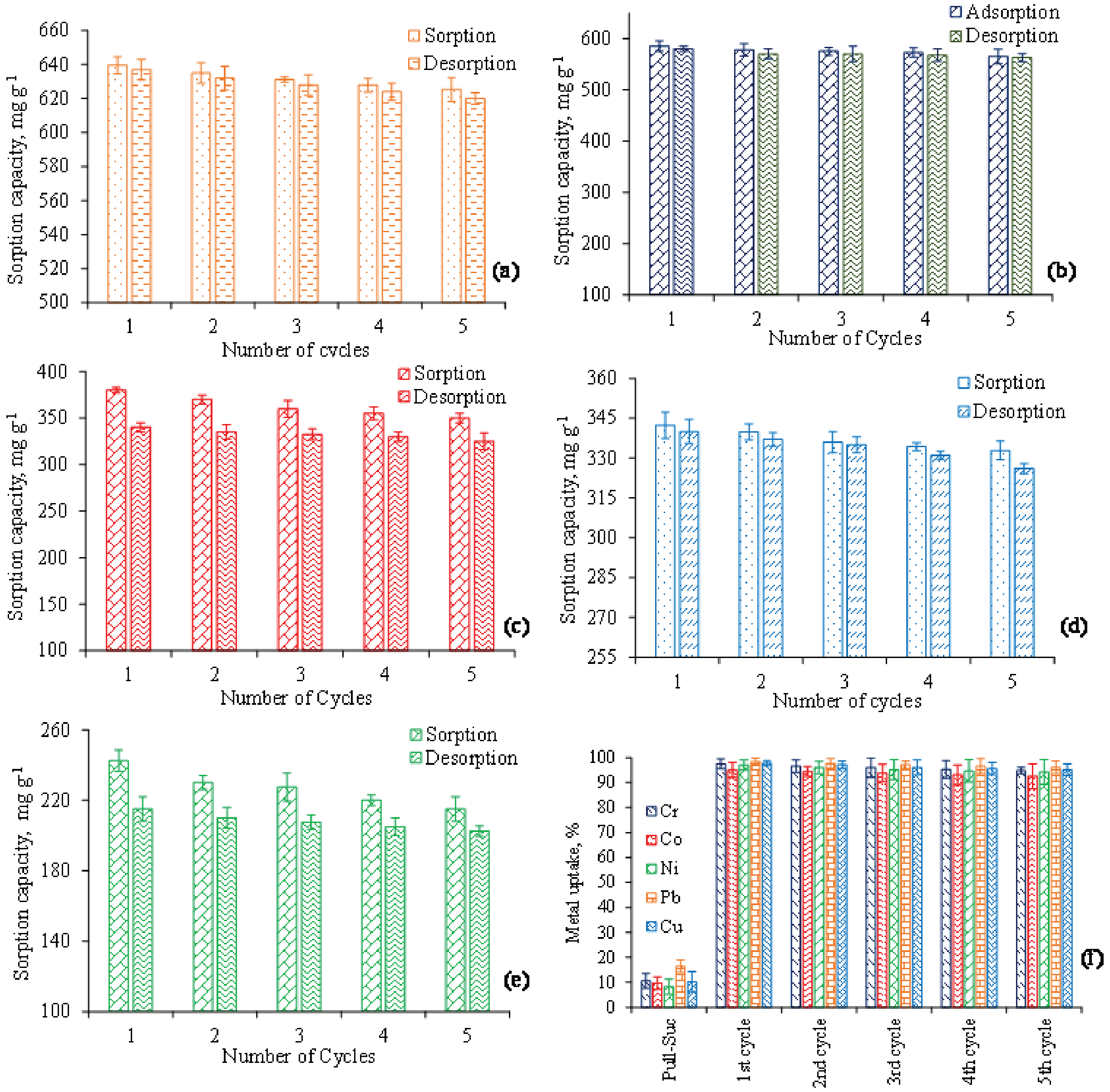

Fig. 8. Adsorption and desorption (a)–(e) values for Pb(II), Cr(VI), Co(II), Cu(II) and Ni (II) ions by Pull-Suc-Na from aqueous solution, respectively, (f) percentage metal uptake by the acidic (Pull-Suc), sodic form of sorbent Pull-Suc-Na (first–fifth cycles) after five cycles of regeneration.

Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) was 98.3%, 98.8%, 96.1%, 95.4% and 97%, respectively. The protic form of the sorbent showed less removal of Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) was 17.3%, 16.4%, 11.7%, 11.7% and 9.2%, respectively. This can be explained in terms of an ion exchange that occurred between metal ions and Na^+ present in the sodic form of the sorbent (Fig. 8(f)). Greater the DS of succinate moieties (2.84) in Pull-Suc, there is higher concentration of H^+ in it. Conversion of this acidic form into sodic form delivers higher concentration of Na^+ in Pull-Suc-Na giving plenty of binding sites for the metal ions. The high values of percentage sorption suggested the use Pull-Suc-Na as an effective sorbent. Furthermore fitting of pseudo-second-order kinetic model and Langmuir isotherm model to the experimental data is also an evidence that metal uptake by Pull-Suc-Na took place through chemisorption process, that is, through ion exchange.

Boyd et al. [35] derived a rate equation which explains uptake of a metal ion from aqueous solution through ion-exchange mechanism which is given as (Eq. (15)):

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

where S (min^{-1}) is a constant and $F = q_t/q_e$. Values of $\log(1-F)$ are plotted against t. Straight lines of high values of correlation coefficient are obtained which evidenced involvement of ion-exchange mechanism (Fig. 9(a) and Table 4).

3.2.10. Thermodynamic parameters determination

Data obtained from effect of temperature on sorption studies were used to estimate thermodynamic parameters such as change in 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. Following relations were used to determine these parameters:

$$K_c = \frac{C_{\text{ads}}}{C_e} \tag{9}$$

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. The Gibbs free energy ($\Delta G°$) changes for Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) uptake by Pull-Suc-Na were determined by using the equilibrium constants evaluated from Langmuir isotherm model by following Eq. (4):

$$\Delta G° = -RT\ln K_c \tag{10}$$

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{11}$$

Plot of $\ln K_c$ against $1/T$ (K^{-1}) gives a straight line (Fig. 9(b)). Slope and intercept of this straight line gives values of $\varDelta S°$ (J mol^{-1} K^{-1}) and $\varDelta H°$ (kJ mol^{-1}), respectively. Entropy and enthalpy changes were found negative for sorption of all the five metal ions by Pull-Suc-Na showing a decrease in randomness at solid–liquid interface and exothermic nature of sorption, respectively. The negative values of $\Delta G°$ (kJ mol^{-1}) calculated by Eq. (4) confirmed the feasibility and spontaneity of the sorption of Pb(II), Cr(VI), Co(II), Cu(II) and Ni(II) by Pull-Suc-Na. Values of thermodynamic parameters are summarized in Table 5. Some other researchers also reported similar results [36].

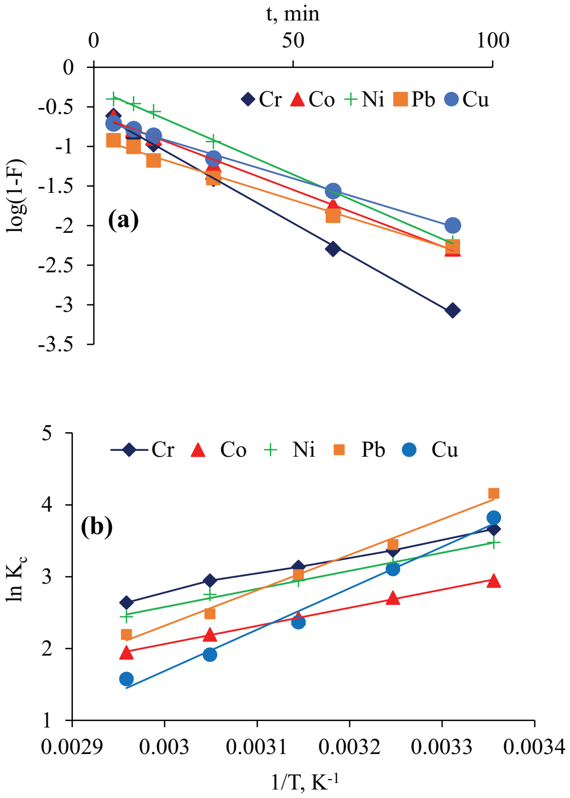

Fig. 9. Ion-exchange model (a) and effect of temperature on equilibrium constant for heavy metal ion removal from aqueous solution by the sorbent (b).

Table 4
Parameters for ion-exchange model

Solution	*S* (min^{-1})	R^2
Pb(II)	0.06579	0.9973
Cr(VI)	0.04418	0.994
Co(II)	0.05043	0.9989
Cu(II)	0.03731	0.9915
Ni(II)	0.03517	0.9975

3.2.11. Competitive adsorption of multimetal ions system by Pull-Suc-Na

3.2.11.1. Competitive adsorption from binary system by Pull-Suc-Na Competitive metal uptake from binary solution (100 mL each) containing (i) Ni(II) (50 mg L^{-1}) and Cr(VI) (120 mg L^{-1}), (ii) Ni(II) (50 mg L^{-1}) and Cu(VI) (70 mg L^{-1}), (iii) Cu(II) (70 mg L^{-1}) and Pb(II) (130 mg L^{-1}) was studied by stirring Pull-Suc-Na (20 mg) with these binary solution one by one at 298 K for 30 min. The pH of all the binary solutions was kept 6 because all the five metal ions have maximum metal uptake around this pH in single metal system. FAAS was used to determine the uptake of one metal ion in the presence of other metal ion. This competitive metal uptake from binary mixture was designed so that systems containing multiple heavy metal ions can be treated (electroplating effluent, galvanic wastewater, etc.). The effect of uptake of one metal ion in the presence of other metal ion is given by ratio of sorption capacity for a metal ion along with other ion (q^{mix}) to the sorption capacity of that metal ion when present alone ($q°$) in the aqueous system [37]. If $q^{\text{mix}}/q° > 1$, then sorption capacity of one metal ion increases in the presence other metal ion. Values of $q^{\text{mix}}/q° < 1$ for a metal ion show decrease in the sorption capacity of this ion in the presence

Table 5
Thermodynamic parameters for the heavy metal ions removal from aqueous solution by the sorbent (Pull-Suc-Na)

Metal	$\Delta S°$ (J mol^{-1} K^{-1})	$\varDelta H°$ (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})	R^2
Pb(II)	–104.01	–41.094	–4.15	0.9889
Cr(VI)	–39.007	–20.691	–3.70	0.9937
Co(II)	–45.819	–20.991	–2.90	0.9983
Cu(II)	–129.45	–47.835	–3.82	0.9850
Ni(II)	–41.179	–20.875	–3.48	0.9936

Table 6
Sorption capacity values of Pull-Suc-Na for removal of heavy metal ion from single metal system and binary system

Metal ion	System	q_e (mg g^{-1})	$q^{mix}/q°$
Ni(II)	Ni(II) alone	256.4	
Cr(VI)	Cr(II) alone	588.2	
Ni(II)	Ni(II) + Cr(VI)	80.3	1.2893
Cr(VI)	Ni(II) + Cr(VI)	250.3	0.5620
Ni(II)	Ni(II) alone	256.4	
Cu(II)	Cu(II) alone	357.14	
Ni(II)	Ni(II) + Cu(II)	122.3	0.7862
Cu(II)	Ni(II) + Cu(II)	79.3	0.5644
Ni(II)	Ni(II) alone	256.4	
Cd(II)	Cd(II) alone	476.19	
Ni(II)	Ni(II) + Cd(II)	95.3	0.9383
Cd(II)	Ni(II) + Cd(II)	145.3	0.5052
Cu(II)	Cu(II) alone	357.14	
Pb(II)	Pb(II) alone	666.6	
Cu(II)	Cu(II) + Pb(II)	43.2	0.9674
Pb(II)	Cu(II) + Pb(II)	302.3	0.5183

of other ion. Table 6 showed that sorption capacity value of a metal ion become less in binary system as compared with removal of a single metal ion from a solution containing only single metal ion. This is attributed to the fact that in a single metal assembly there is no competition between different metal ions for exchange of sites on the sorbent surface. The results showed that Cr(VI), Ni(II) and Pb(II) have higher sorption capacity values over their competing ions Ni(II), Cu(II) and Cu(II) for mixtures (i), (ii) and (iii), respectively. This is attributed to the greater ion-exchange potential of Cr(VI), Ni(II) and Pb(II) over Ni(II), Cu(II) and Cu(II), respectively. The value of $q^{mix}/q°$ was found to be less than unity for all binary systems except Pb(II) + Cu(II) showing decrease in sorption capacity of each ion in the presence of each other. The value of $q^{mix}/q° > 1$ for Pb(II) + Cu(II) binary exhibits increase in sorption capacity of Cu(II) in the presence of Pb(II). The favored sorption of one metal ion over the other from a binary system is attributed to the difference in their redox potentials.

3.2.11.2. Competitive adsorption from a tertiary mixture and mixture of five metal ions by Pull-Suc-Na Large amounts of Ni(II), Cu(II) and Cr(VI); and Co(II), Cr(II) and Ni(II) are present in galvanic wastewater and synthetic nuclear power plant coolant water, respectively. In order to test the efficiency of sorbent materials for removal of heavy metal ions from galvanic wastewater [38] and synthetic nuclear power plant coolant water [39], competitive adsorption of a metal ion from tertiary mixture [(i) Ni(II), Cu(II) and Cr(VI), (ii) Co(II), Cr(II) and Ni(II)] and mixture of five metal ions [Pb(II), Cr(VI), Ni(II), Co(VI) and Cu(VI)] by Pull-Suc-Na was studied. For this purpose a solution (100 mL each) containing (i) Ni(II) (50 mg L^{-1}) + Cu(II) (70 mg L^{-1}) + Cr(VI) (120 mg L^{-1}), (ii) Ni(II) (50 mg L^{-1}) + Co(II) (80 mg L^{-1}) + Cr(VI) (120 mg L^{-1}) and (iii) Pb(II) (130 mg L^{-1}) + Cr(VI) (120 mg L^{-1}) + Co(VI) (80 mg L^{-1}) + Cu(VI) (70 mg L^{-1}) + Ni(II) (50 mg L^{-1}) was agitated with Pull-Suc-Na (20 mg) at 298 K and pH 6 for 30 min.

It was noticed that sorption capacity values for Cr(VI), Ni(II) and Cu(II) were 192.5, 73.3 and 55.2 mg g^{-1}, respectively, from mixture (i), sorption capacity values for Cr(VI), Ni(II) and Co(II) were found to be 185.3, 50.2 and 35.2 mg g^{-1}, respectively, from mixture (ii) and sorption capacity values for Pb(II), Cr(VI), Ni(II), Co(VI) and Cu(VI) were 94, 75.64, 62.1, 47.6, 32.3 and 20.7 mg g^{-1}, respectively. Preferentially removal of Cr(VI) over Ni(II) and Cu(II) and Ni(II) and Co(II) from mixture (i) and (ii), respectively, revealed that Pull-Suc-Na has high affinity for Cr(VI) ions.

4. Conclusion

Sodic form of succinylated pullulan appeared supersorbent for the sorption of heavy metal ions from aqueous solution. Fitting of pseudo-second-order kinetic model, Langmuir isotherm model, ion-exchange model and low values of sorption capacities of acidic form of sorbent (Pull-Suc) suggested the involvement of ion-exchange mechanism. The negative values of thermodynamics parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) indicated feasibility, spontaneity and exothermic nature of sorption. Negligible decrease in sorption capacity values for all the five metal ions after five sorption–desorption cycles suggested repeated use of Pull-Suc-Na. Results of competitive sorption show that Pull-Suc-Na can be a choice for industrial wastewater treatment procedures and can be a potential and selective sorbent for removal of heavy metal ions from nuclear power plant coolant water, galvanic wastewater, etc.

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