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Removal of Cr(III) and Ni(II) from aqueous solution using a mixed cellulose ether-ester hydroxyethylcellulose adipate

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ABSTRACT

The HEC-Adip-Na sorbent has been synthesized by the esterification reaction between hydroxyethylcellulose (HEC) and adipic anhydride followed by saponification with $NaHCO_3$ for the removal of Cr(III) and Ni(II) from aqueous solution. Surface charge on the sorbent was evaluated by zero-point charge pH analysis and was found to be 5.0 which indicated the presence of negative charge on its surface. The sorption experiments were conducted in batches and found that the uptake of targeted metal ions was predominantly dependent on pH, sorbent dose, metal ions concentration, contact time, and temperature. The sorption isotherm indicated that sorption has occurred through the exchange of ions *via* chemisorption and maximum sorption capacity (Q_{max}) was 156 mg/g for Cr(III) and 79 mg/g for Ni(II) according to Langmuir isotherm. Uptake-kinetics revealed that the sorption rate was too rapid and achieved equilibrium within the first 30 min. Thermodynamic studies suggested the spontaneous and exothermic nature of the sorption. Moreover, HEC-Adip-Na was appeared as generable. Conclusively, HEC-Adip-Na is a material of superb choice for the purification of water.

Keywords: Chemisorption; Esterification; Hydroxyethylcellulose; Ion-exchange; Sorption–desorption

1. Introduction

Water pollution caused by heavy metals has been spreading continuously throughout the globe due to the industrial revolution, urbanization, human activities, etc., thus disordering the heath structure of living organisms [1–3]. Among the heavy metals, trivalent chromium, that is, Cr(III) and divalent nickel, that is, Ni(II) have much commercial utilization particularly in the preparation of corrosion-free alloys and precursors of batteries. Besides, their applications have also been found in the preparation of commercial and household articles [4,5]. To make it possible for the safe use of both of these heavy metals and their compounds, the World Health Organization (WHO) set a standard for their maximum limit in drinking water (0.06 mg/L Cr(III) and 0.02 mg/L Ni(II)) [6]. Beyond this limit both of these heavy metals are hazardous to living species. Hence, the controlled use of Cr(III) and Ni(II) should be necessary to maintain balanced health.

Literature indicates several methods for the removal of Cr(III), Ni(II), and their derivatives from contaminated water. Such methods include coagulation–flocculation, membrane filtration, solvent extraction, centrifugation, reverse

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osmosis, electrochemical processes, etc. [7–12]. But, these all methods are not economical and may contain other hazards coming from synthetic sorbents. Therefore, from the economical point of view and high enrichment efficiency of the process, the adsorption followed by ion-exchange has been proved as one of the most promising methods of water purification [13–17]. Hence, keeping in view the worth of methodology, cost-effectiveness, health benefits, recontaminations, and efficiency of sorbents, it is therefore needed to develop more efficient sorbents with fewer hazards to the health and generable nature [18].

Hydroxyethylcellulose (HEC) is a water–soluble derivative of cellulose. It is extensively used as a stabilizer for soaps, thickeners in industrial products, binders, and pharmaceutical excipients [19]. Due to its non-ionic, hydrophilic, and biocompatible nature, it has been utilized as admirable material to design prodrugs [20,21]. Literature revealed that HEC can be chemically modified with succinic anhydride and becomes water-insoluble. Therefore, chemically modified HEC as HEC-succinate sodium salt and HEC-adipate sodium salt (HEC-Adip-Na) appeared as supersorbents and efficient material in a couple of studies to remove cadmium from aqueous solutions [22,23].

Herein this study, we are aimed to explore the performance of HEC-Adip-Na to remove Cr(III) and Ni(II) from aqueous solution as a function of pH, sorbent dose, initial concentration of metal ions, time of contact, and temperature. It was also aimed to establish the mechanism, uptake-kinetics, and thermodynamics of sorption. The studies regarding the generable nature of HEC-Adip-Na are also aimed. Furthermore, a comparative study has also been conducted for HEC-Adip and HEC-Adip-Na to the established ion-exchange mechanism.

2. Materials and methods

2.1. Materials

Hydroxyethylcellulose (Natrosol, HE10K, Belgium) was procured from the local market. Adipic anhydride was of Sigma-Aldrich, USA. *N,N*-dimethylacetamide, 4-dimethylaminopyridine, NaOH, HCl, HNO_3, $NaHCO_3$ were obtained from Alfa-Aesar, Germany. Other reagents and chemicals were of Riedel-de-Haën, Germany. Deionized water (DW) was used to wash the glassware and to execute sorption experiments in batches.

2.2. Instrumentation and measurements

The charge on the surface of HEC-Adip-Na was determined by measuring zero-point charge pH (pH_{ZPC}) using the already reported solvent pH drift method as opted by others [24,25]. To measure the concentration of tested metal ions adsorbed by HEC-Adip-Na and the remaining concentration of metal ions in the aqueous solution was determined using flame atomic absorption spectrometer (FAAS) (AA 6300, Shimadzu, Japan) equipped air-acetylene flame.

2.3. Synthesis of sorbent

HEC was dried in a vacuum oven at 110°C for 5 h to remove moisture contents present in it. The dried HEC was converted into a biosorbent, that is, HEC-Adip-Na in two steps.

In the first step, HEC (10 g, 36 mmol) was dispersed in a solvent *N,N*-dimethylacetamide (DMAc, 80 mL) for 120 min at 80°C under stirring at 200 rpm. To the resulting clear solution, adipic anhydride (AAn, 59.6 g, 216 mmol) was mixed in the solution by parts and the reaction was continued for a further 22 h under similar heating temperature (80°C) and stirring rate (200 rpm). A catalytic amount of 4-dimethylaminopyridine (DMAP, 100 mg) was also added to the reaction mixture. The material of the flask was taken out, cooled at 298 K, and precipitated in diethyl ether (250 mL). The precipitates were filtered and washed again with diethyl ether to reduce the unreacted fractions of adipic acid or adipic anhydride (if any). This material was then dried in a vacuum oven at 50°C for 24 h.

In the second-step, a saturated aq. $NaHCO_3$ was prepared by dissolving 10 g of $NaHCO_3$ in 100 mL of DW at 298 K temperature and 150 rpm stirring rate for 2 h. The solution was then filtered and clear filtrate was obtained. To the filtrate, the dried HEC-Adip (2.0 g) was added and stirred again at 150 rpm at 298 K for 3 h. After that, the material (HEC-Adip-Na) was allowed to settle down, filtered, dried in an oven at 50°C for 24 h, and stored in an-air tight container for further use in the sorption experimentations.

2.4. Determination of degree of substitution

The degree of substitution (DS) was determined by mixing the sorbent HEC-Adip (0.1 g) in 100 mL of aqueous saturated solution of $NaHCO_3$ (0.02 M). The reaction mixture was homogenized by gentle mixing and shaking for 120 min at 150 rpm and then filtered at room temperature. A definite volume (10 mL) of the filtrate was titrated against a standard solution (100 mL) of HCl (0.02 M). The end point of titration was located using methyl orange indicator (2 drops). The net volume of HCl (V_{HCl}) at which solution of $NaHCO_3$ neutralized (V_{NaHCO3}) was determined and applied in the following equations [Eqs. (1) and (2)] to calculate DS [26].

$$n_{Adip} = V_{NaHCO_3} \times M_{NaHCO_3} - V_{HCl} \times M_{HCl} \tag{1}$$

$$DS = \frac{276.14 \times n_{Adip}}{m_{HEC-Adip} - 100 \times n_{Adip}} \tag{2}$$

The terms n_{Adip} and $m_{HEC-Adip}$ involved in the above-mentioned relations denoted the number of moles of adipic acid moieties attached to HEC-Adip and mass (g) of sorbent HEC-Adip, respectively. The quantities 276.14 and 100 simultaneously represented the molar mass (g/mol) of the repeating unit of HEC and increment added to the mass of HEC after each substitution of adipate group.

2.5. Calculation of yield

Theoretical yield of the acidic form of sorbent HEC-Adip produced as a result of esterification reaction between HEC and adipic anhydride was measured using Eq. (3).

$$\text{Theorectical Yield} = W_{\text{HEC}} + \left[\frac{W_{\text{HEC-Adip}}}{W_{\text{HEC-Adip}}} \times \text{DS} \times M_{\text{Adip}} \right] \quad (3)$$

where W_{HEC} (g) is the mass of biopolymer HEC used to do reaction, $W_{\text{HEC-Adip}}$ (g) is the mass of sorbent HEC-Adip obtained as a result of the reaction, $M_{\text{HEC-Adip}}$ (g/mol) and M_{Adip} (g/mol) are the molar masses of HEC-Adip and adipic anhydride, respectively.

2.6. Sorption experiments

Sorption studies were carried out to obtain optimized sorption conditions at which sorbent (HEC-Adip-Na) can effectively remove highest fractions of Cr(III) and Ni(II) ion from aqueous solution. For this purpose, experiments were performed in batches and the influence of various factors, including the effect of pH 1–7, effect of initial concentration of metal ions (Cr(III) ranging from 40 to 160 mg/L and Ni(II) ranging from 20 to 140 mg/L), sorbent dosage (30 to 100 mg), contact time between sorbent and sorbate (5–120 min), and temperature (298 K–338 K) were studied. Before studying the effect of these factors on sorption potential of HEC-Adip-Na, standard aqueous solutions (1,000 mg/L, 500 mL) were prepared by gentle mixing of analytical reagents $CrCl_3{\cdot}6H_2O$ (1.5228 g) and $NiCl_2{\cdot}6H_2O$ (2.025 g) in DW (500 mL) separately. To ensure homogeneous mixing, solutions were stirred at 200 rmp for 60 min and then filtered. Dilutions were performed where needed. Standard acidic (1.0 M HCl) and basic (1.0 M NaOH) solutions were prepared and used to set the pH of all the tested Cr(III) and Ni(II) solutions in a pre-defined range. An optimum amount (50 mg) of sorbent HEC-Adip-Na was added in conical flasks containing 50 mL of Cr(III) and Ni(II) based aqueous solutions and then put in a shaking incubator (JSSI-100C, JS Research Inc. Republic of Korea) for proper mixing. Solutions were then stirred for 30 min at 298 K at 200 rpm and filtered. Filtrate of Cr(III) and Ni(II) based aqueous solutions were centrifuged and analyzed by FAAS at 357.9 and 232 nm wavelengths, simultaneously to determine the concentration of both the metals loaded onto HEC-Adip-Na and left behind in aqueous solution in terms of equilibrium sorption capacity (q_e) and percentage metal uptake (%). q_e was calculated by subtracting the residual concentration of metal ions (C_e, mg/L) from their initial concentration (C_i, mg/L) and then multiplied with the total volume of solution (V, L) followed by dividing onto the mass of sorbent taken (mg) [Eqs. (4) and (5)]:

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

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

The sorption data obtained from the effect of initial concentration of metal ions was used to establish the sorption isotherm and the sorption data obtained from the effect of contact time was used to study the uptake kinetics and ion-exchange mechanism. Moreover, the sorption data obtained from the effect of temperature was used to study the thermodynamics of sorption process.

2.7. Regeneration studies

Tests were conducted to regenerate HEC-Adip-Na over five repeated cycles. HEC-Adip-Na was first suspended in aqueous solutions of Cr(III) and Ni(II) by keeping sorbent-water ratio 50 mg/100 mL. The pH of solutions was maintained at 6.0 and 5.5 for uptake of Cr(III) and Ni(II), respectively. Solutions were shaken for 30 min at 298 K temperature and 200 rpm stirring speed. After that, the solutions were filtered and the filtrate was centrifuged before measuring the concentration of targeted metal ions on FAAS. The solid sorbent material was carefully separated, washed with DW, air-dried, and tuned with a saturated aqueous solution of sodium chloride (100 mL). The mixture of HEC-Adip-Na and brine was stirred overnight and filtered again. The resulting solid residue, that is, regenerated sorbent was allowed to wash in DW until the effect of silver nitrate should neutralize. After drying, the solutions of regenerated material were prepared again using the alike protocol and run on FAAS. This process was continued to achieve five regenerated cycles.

Acidic form of sorbent, that is, HEC-Adip was also utilized to check its efficiency for Cr(III) and Ni(II) uptake from aqueous solutions and to compare percentage removal efficiency with sodium derivative. Experiments were performed under similar conditions as described earlier. Moreover, for statistical validity by *t*-test, experimentations were carried out in replicates and concurrent values were plotted and presented herein.

3. Results and discussion

3.1. Synthesis of sorbent

HEC was treated with adipic anhydride in the presence of a base DMAP and a stable ester derivative of it, that is, HEC-Adip was synthesized. The DMAP is an effective catalyst because it catalyzes more than 80% of the –OH group of HEC with adipic anhydride that can be witnessed from the high yield of HEC-Adip (84.5%) and DS (2.0) of adipate moieties on to the HEC (Table 1). The esterification reaction between HEC and adipic anhydride increased the number of free terminal COOH groups. Such groups are responsible for the enhancement of sorption sites on HEC. HEC-Adip was further treated with a saturated solution of $NaHCO_3$. As a result, the free COOH groups of HEC-Adip

Table 1
Reaction conditions, yield of HEC-Adip, and DS of adipate moieties on to HEC

Molar ratio[a]	1:6
Temperature, time	80°C, 24 h
Yield of HEC-Adip	84.5%
DS of adipate moieties on to HEC	2.0

[a]HEC: adipic anhydride (using DMAP as a catalyst).

were deprotonated and HEC-Adip was converted to its sodic derivative, that is, HEC-Adip-Na. The detailed mechanism is descripted in Fig. 1.

Moreover, the solubility tests of HEC-Adip and HEC-Adip-Na were performed in DW and organic solvents, such as ethanol, methanol, etc. It was found that the sorbent HEC-Adip-Na and its acidic forms were insoluble in water, methanol, and alcohol because of lengthening of alkyl chain after esterification. Due to this insoluble nature of HEC-Adip-Na, it can be used as a sorbent for the uptake Cr(III) and Ni(II) from an aqueous solution.

3.2. Determination of point of zero-charge pH

The zero-point charge pH (pH_{ZPC}) of HEC-Adip-Na was determined to examine the nature of charge present on its surface. The pH_{ZPC} appeared 5.0 as revealed from the intersecting point of the plot between initial pH (pHi) and difference of initial and final pH (pHi-pHf) (Fig. 2a). The shifting of pH_{ZPC} towards lower pH (acidic pH) is due to the introduction of week carboxylic acidic (COOH) groups of adipic anhydride on the surface of HEC-Adip-Na. This value indicated that the sorbent (HEC-Adip-Na) surface bear positive charge when $pH < pH_{ZPC}$, that is, $pH < 5.0$, negative charge when $pH > pH_{ZPC}$, that is, $pH > 5.0$, and no charge when $pH = pH_{ZPC}$, that is, $pH = 5.0$. In such cases where $pH > pH_{ZPC}$, the sorbent possess greater affinity to uptake positively charged metal ions from aqueous solution because of having negative charge on its surface [27].

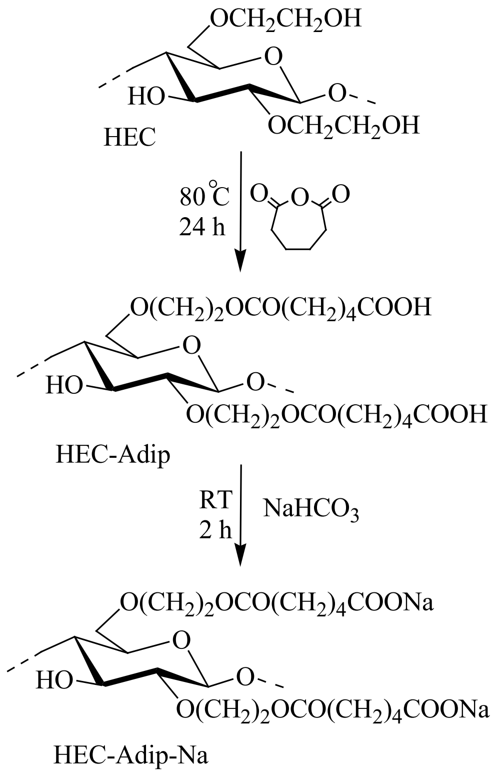

Fig. 1. Schematic diagram for the synthesis of HEC-Adip and HEC-Adip-Na.

Moreover, the Henderson–Hasselbalch equation [Eq. (6)] also helps to describe the pH_{ZPC} of sorbent HEC-Adip-Na.

$$\mathrm{pH} = \mathrm{pKa} + \log\frac{\left[\mathrm{HEC-Adip}\right]}{\left[\mathrm{HEC-COOH}\right]}\times 100 \tag{6}$$

where [HEC-Adip$^-$] represented the salt of HEC, that is, HEC-Adip-Na and [HEC–COOH] stands for the acidic derivative of HEC, that is, HEC-Adip. Once, [HEC-Adip$^-$] will become equal to [HEC–COOH] then pH is also equal to pKa and it is only possible when half of the weak acidic moieties are completely disintegrated. Thus the pH_{ZPC} of HEC-Adip can also be designated as its pKa. In a case where pH > pKa, COOH groups dissociate up to great extent. Consequently, pH became more acidic and the sorbent surface bears negative charges which might promote uptake of Cr(III) and Ni(II) onto HEC-Adip-Na. The converse is also true in a case where pH < pKa. Therefore, it is necessary to evaluate the effect of pH on the sorption potential of HEC-Adip-Na.

3.3. Sorption experiments

3.3.1. Effect of pH

At different pHs of aqueous solutions, the sorbent behaves differently to interact with heavy metal ions. Therefore, the effect of pH was studied to monitor the aptitude of HEC-Adip-Na towards Cr(III) and Ni(II) uptake within pH range 2–7. It was observed that both the metals adsorbed on HEC-Adip-Na more quickly at acid pH, that is, up to or less than pH 6.0. However, the rate of sorption was too slow up to pH 3.0 and then increased significantly up to pH 6.0 for Cr(III) and 5.5 for Ni(II). After that pHs, there happened to decrease in removal of said metal ions as evidenced from Fig. 2b. This might be because at lower pH the presence of a large number of protons H(I) in aqueous solutions protonated the sodic functionality of HEC-Adip-Na due to the exchange of H(I) ions with Na(I) ions and re-converted it to the COOH groups, that is, an acidic conjugate of sorbent (HEC-Adip) which has low sorption affinity due to fewer number of exchangeable sites while at higher pHs, that is, basic pH, the COOH groups of HEC-Adip deprotonated to HEC-Adip-Na and favor the sorption of the metal ion. On the other hand, as the pH_{ZPC} of this novel sorbent was found to be 5.0, therefore at $pH > pH_{ZPC}$ it bears negative charges on its surface and offers more attraction for positively charged metal ions [28]. The value of optimum pH for Cr(III) was found to be 6.0 and for Ni(II) was 5.5.

3.3.2. Effect of initial concentration

The effect of the initial concentration of Cr(III) and Ni(II) ions was studied to determine the sorption potential of HEC-Adip-Na. Sorption capacities (q_e, mg/g) were plotted against initial metal ion concentration (C_i, mg/L) (Fig. 3a). From the graph, it is obvious that in the beginning, HEC-Adip-Na remove more and more metal ions from aqueous solutions as their concentration increases from 40–80 mg/L for Cr(III) and 20–40 mg/L for Ni(II). However, at 80 mg/L of Cr(III) and 40 mg/L of Ni(II) concentration, sorption equilibrium was established (Fig. 3a). The reason underlying

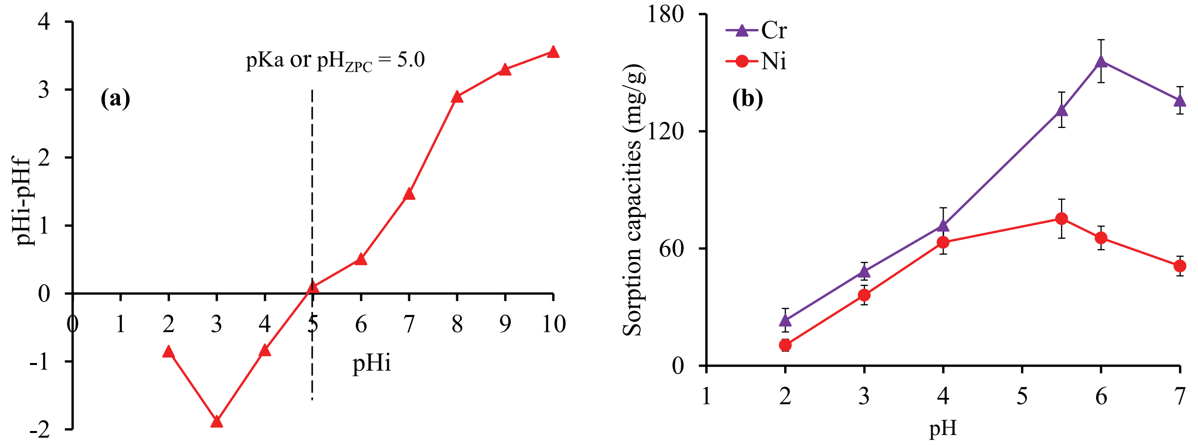

Fig. 2. Zero point charge pH (pH$_{ZPC}$) analysis of HEC-Adip-Na (a) and the effect of pH (2–7), (b) on sorption capacity of HEC-Suc-Na for the uptake of Cr(III) and Ni(II) from aqueous solution (optimized sorption conditions for Cr(III): pH = 6.0, initial concentration of metal ions = 80 mg/L, sorbent dose = 50 mg, contact time = 30 min, temperature = 298 K; optimized sorption conditions for Ni(II): pH = 5.5, initial concentration of metal ions = 40 mg/L, sorbent dose = 50 mg, contact time = 30 min, temperature = 298 K).

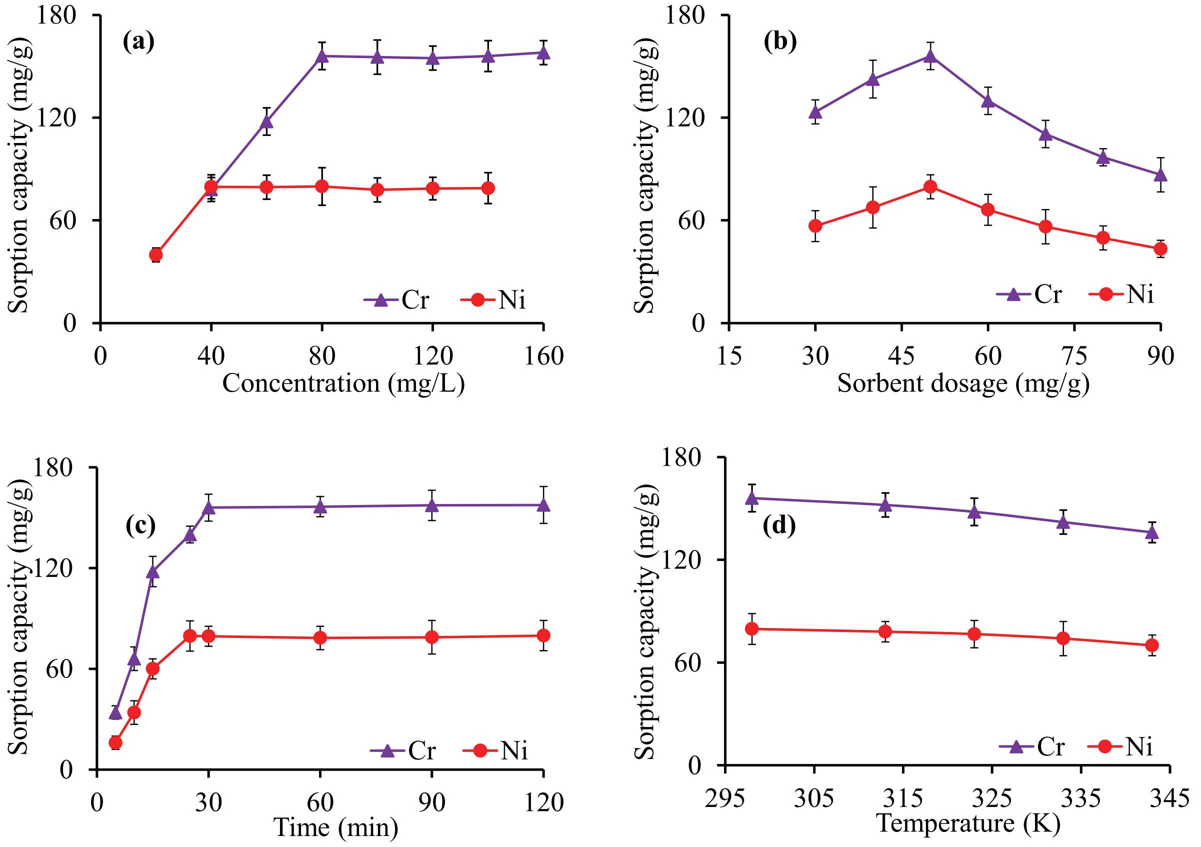

Fig. 3. Effect of initial concentration of metal ions (a), sorbent dosage (b), contact time (c), and temperature (d) on the ability of HEC-Adip-Na to uptake Cr(III) and Ni(II) from aqueous solution (optimized sorption conditions for Cr(III): pH = 6.0, initial concentration of metal ions = 80 mg/L, sorbent dose = 50 mg, contact time = 30 min, temperature = 298 K; optimized sorption conditions for Ni(II): pH = 5.5, initial concentration of metal ions = 40 mg/L, sorbent dose = 50 mg, contact time = 30 min, temperature = 298 K).

this trend is that at the beginning of the sorption process, all the surface sites of sorbent were naked and available to sorbed metal ions, thus more uptake took place at the beginning. However, with the increase in the concentration of metal ions in aqueous solution the sorbent surface sites were occupied by these metal ions and very minute fractions of active sites were left behind for the attachment of more metal ions. Hence, the rate of sorption became persistent [18].

3.3.3. Effect of sorbent dosage

Different amounts of sorbent in aqueous solutions affect greatly the process of sorption by affecting the surface area of sorbent. Hence, we investigated the effect of sorbent dosage on removal of Cr(III) and Ni(II) by experimenting with 30, 40, 50, 60, 70, 80, 90, and 100 mg of HEC-Adip-Na. Plot between sorption capacities (q_e, mg/g) and sorbent dosage (mg) (Fig. 3b) indicated as the sorbent dose increases from 30–50 mg, both Cr(III) and Ni(II) were removed rapidly and at 50 mg of HEC-Adip-Na highest fractions of these metals were loaded on it while after 50 mg, the uptake has been decreased significantly. The increase in sorption capacities is due to the increase in surface area. Whereas, after an optimum level, that is, 50 mg of sorbent, the decrease in sorption capacities might occur due to the saturation of metallic fragments on the sorbent surface which consequently lowered the number of exchangeable sites on the surface of the sorbent [29,30].

3.3.4. Effect of contact time

For the determination of equilibrium time at which sorbent can remove the highest amount of metal ions from aqueous environment the sorption capacities were examined as a function of contact time. For this purpose, sorption experiments were performed by changing the time of contact between sorbent and sorbate from 5–120 min, and the rest of the conditions were maintained at the pre-optimized level. It was also observed that at the start of the sorption process the rate of metal sorption was fast which is due to the greater number of adipate functionality conjugated with sodium present on the surface of HEC-Adip-Na. Thus, due to the greater number of adipate moieties, the chances of exchange of Cr(III) and Ni(II) ions with Na(I) ions becomes greater which is the reason for more uptake of metal ions. Though after achieving an optimum level the steepness of curves became nearly parallel to the time axis which indicated that the maximum amount of Cr(III) and Ni(II) has been removed by HEC-Adip-Na from the aqueous solution within the first 30 min of the sorption process (Fig. 3c).

3.3.5. Effect of temperature

The mode and thermodynamics of Cr(III) and Ni(II) sorption on HEC-Adip-Na, that is, either spontaneous or non-spontaneous, exothermic or endothermic were investigated using a temperature range of 298–338 K with a pH value of 6.0 for Cr(III) and 5.5 for Ni(II), sorbent dosage 50 mg, concentration 80 mg/L of Cr(III) and 40 mg/L of Ni(II) for 30 min. Obtained results (Fig. 3d) pointed out that temperature has a negative effect on sorption capacities, that is, by increasing temperature from 298 to 338 K, the sorption capacities decreases for both the tested metals. At 298 K maximum metals were sorbed. Hence, this temperature was selected to perform all other sorption experiments in batches. The reason for such a decrease in sorption capacity with an increase in temperature might be due to the lowering of sorbent-sorbate forces of interactions which results due to increase in the mobility of metal ions of sorbate by increasing temperature. Such lowering of sorbent–sorbate forces of interactions may damaging the surface of sorbent at high temperature and tends to start desorption due to which the sorption capacity of metal ions decreased.

3.4. Isothermal modeling

Sorption isotherms are very crucial to establish because they help in describing the distribution of sorbate between two immiscible phases, that is, liquid (sorbate) and solid (sorbent), optimizing the conditions for sorption process at equilibrium, correlating sorption maxima obtained experimentally and theoretically, and to illustrate the physical or chemical nature of sorption. Therefore, sorption data acquired from the effect of initial metal ion concentration was fitted to Freundlich and Langmuir isotherms. Both of these two isotherms are applied to heterogeneous systems and proved to be very useful while describing the aforesaid features of any sorption process [23,24]. The linearized form of both of the isotherms is presented in the following equations [Eqs. (7) and (8)].

$$\log q_e = \log k_F + \frac{1}{n}\log C_e \tag{7}$$

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

where the parameters q_e (mg/g), C_e (mg/L), and $Q_{\max}$ (mg/g) denoted the amounts of Cr(III) and Ni(II) sorbed on HEC-Adip-Na at equilibrium, amounts of Cr(III) and Ni(II) left behind in the aqueous solutions, and sorption maxima acquired from Langmuir isotherm, respectively. k_F and n are dimensionless constants associated with Freundlich isotherm while b is a constant associated with Langmuir isotherm that is measured in mg/L. Once the sorption data fitted to these isotherms by plotting logq_e vs. logC_e log and C_e/q_e vs. C_e, straight lines with slope and intercepts were obtained (Fig. 4a and b). From the slope and intercepts, the values of different parameters associated with linearized forms of isotherms were calculated and tabulated (Table 2). Low values of the regression coefficient (R^2) were obtained from the Freundlich plot whereas the very high value of R^2 (>0.99) was obtained from Langmuir plots for both the metals. Moreover, the values of sorption maxima calculated from Freundlich isotherm have deviated from experimental sorption capacities while sorption maxima calculated from Langmuir isotherm were found much closed to experimental ones. These findings witnessed the best fit of the Langmuir model to sorption data. Hence, both Cr(III) and Ni(II) got adsorb on HEC-Adip-Na via chemisorption through the formation of monolayers.

The feasibility of the sorption process was also predicted by computing the values of separation factors, that is, R_L. For such calculations, we use isothermal sorption data obtained from Langmuir isotherm. Generally, for $R_L = 0$, $R_L = 1$, $R_L > 1$, and $0 < R_L < 1$ the mode of sorption process should be reversible, linear, unfavorable, and favorable. In our study, we found R_L by putting the values of C_i (80 mg/L for Cr(III) and 40 mg/L for Ni(II)) and b (1.085 mg/L for Cr(III)

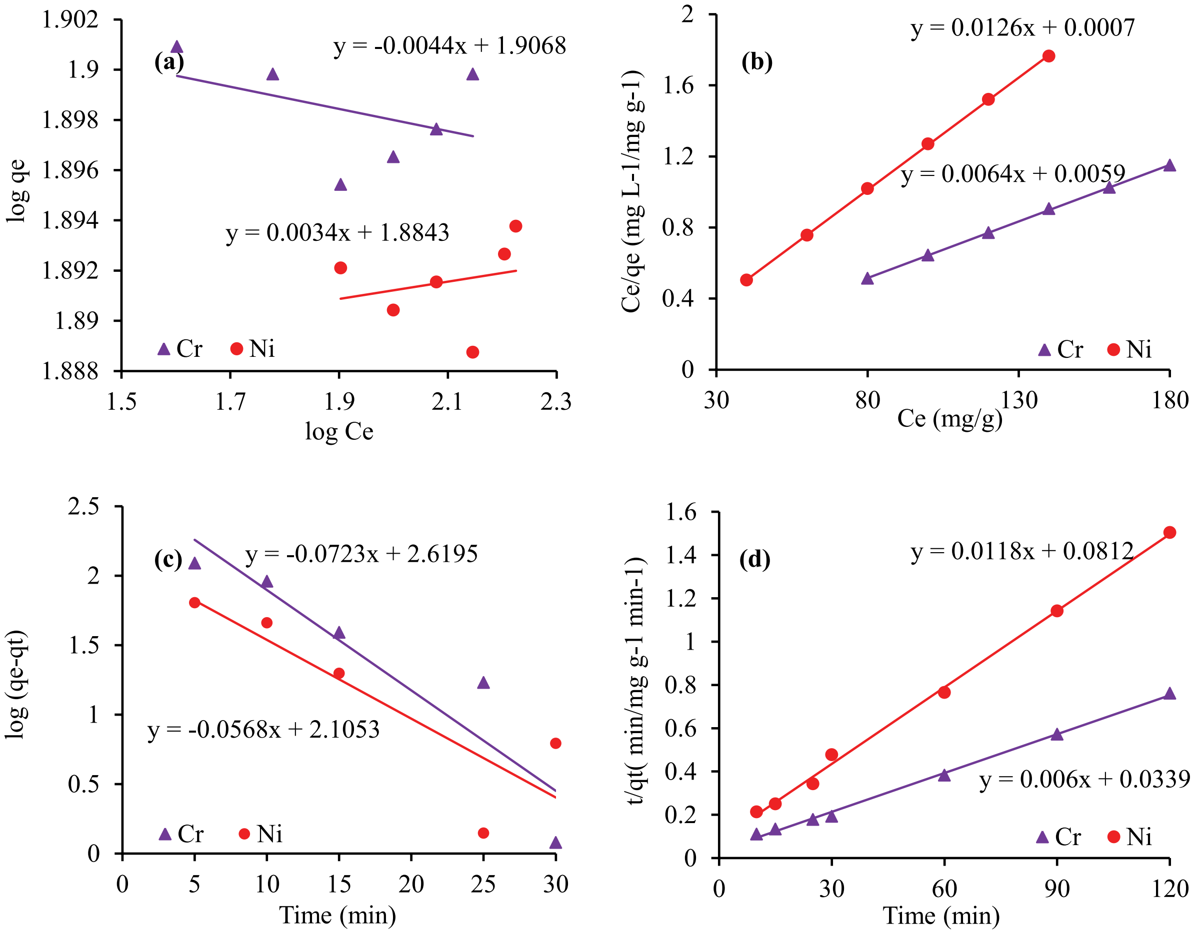

Fig. 4. Fitting of Freundlich (a), Langmuir (b), pseudo-first-order (c), and pseudo-second-order (d) models for sorption of Cr(III) and Ni(II) on HEC-Suc-Na from aqueous solutions (optimized sorption conditions for Cr(III): pH = 6.0, initial concentration of metal ions = 80 mg/L, sorbent dose = 50 mg, contact time = 30 min, temperature = 298 K; optimized sorption conditions for Ni(II): pH = 5.5, initial concentration of metal ions = 40 mg/L, sorbent dose = 50 mg, contact time = 30 min, temperature = 298 K).

and 0.180 mg/L for Ni(II)) in Eq. (9). R_L values lies in between 0 and 1, that is, $0 < R_L < 1$ (0.012 for Cr(III) and 0.122 for Ni(II)) (Table 2). Hence, suggested the feasibility of Cr(III) and Ni(II) sorption on HEC-Adip-Na [31].

$$R_L = \frac{1}{1 + bC_i} \tag{9}$$

3.5. Kinetic modeling

Before designing a water purification system, one should have an idea about the mechanism of the sorption process. Therefore, uptake-kinetics was established to know about the involvement of physical or chemical mechanism of sorption in the rate-determining step. Sorption data obtained from contact time experiments were fitted to linearized forms of pseudo-first-order and the pseudo-second-order kinetic models [Eqs. (10) and (11)] [32,33]:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \tag{10}$$

$$\frac{t}{q_t} = \left(\frac{1}{kq_e^2} + \frac{t}{q_e}\right) \tag{11}$$

where q_e (mg/g) and q_t (mg/g) were denoted the amounts of Cr(III) and Ni(II) adsorbed on HEC-Adip-Na at equilibrium and at any time t (min) while k_1 (g/mg·min) and k (g/mg·min) are the rate constants associated with pseudo-first-order and the pseudo-second-order kinetic models, respectively. Plot between $\log(q_e - q_t)$ vs. t and t/q_t vs. t gave straight lines with slope and intercept (Fig. 4c and d). From the slope of pseudo-first-order plots, the values of k_1 were calculated and from the intercept, the values of q_e were calculated and compared with experimental sorption capacity. Similarly, from the slope of pseudo-second-order plots, the values of q_e were obtained in mg/g and from the intercepts, the values of k were obtained. The high values of R^2 (>0.99) and closeness between experimental and theoretical sorption capacities acquired from both the models indicate that the sorption data fitted well to the pseudo-second-order kinetic model and suggested the involvement of chemical sorption in the rate-determining step (Table 2). It means that the valence force involved in the sorption process through the exchange or sharing of electrons between metal ions, that is, Cr(III) and Ni(II) and sorbent, that is, HEC-Adip-Na. Hence the mechanism is due ion-exchange mechanism involving chemisorption. Furthermore, the sorbent has sodium ions, so as far as the Cr(III) and Ni(II) ion containing solution come in contact with it, maximum fractions of metal ions get adsorbed on the surface of sorbent and equilibrium achieved within short interval of time, that is, 30 min.

Table 2
Sorption data for experimental value of sorption capacity (q_e, mg/g), Freundlich, Langmuir, pseudo-first-order, pseudo-second-order models, Boyd's parameters for ion-exchange mechanism, and the thermodynamic parameters for Cr(III) and Ni(II) uptake by sorbent HEC-Adip-Na

Models	Parameters	Cr(III)	Ni(II)
Experimental	q_e (mg/g)	156.000	79.800
Freundlich parameters	N	–227.270	294.118
	k_F	80.686	76.610
	R^2	0.171	0.059
Langmuir parameters	Q_{max} (mg/g)	156.250	79.365
	b (mg/L)	1.085	0.180
	R^2	0.999	0.999
	R_L	0.012	0.122
Pseudo-first-order	q_e (mg/g)	416.389	127.438
	k_1 (g/mg·min)	0.167	0.131
	R^2	0.866	0.756
Pseudo-second-order	q_e (mg/g)	166.670	84.746
	k_2 (g/mg·min)	0.001	0.002
	R^2	0.997	0.997
Ion-exchange model	S (min^{-1})	0.102	0.117
	R^2	0.975	0.941
Thermodynamic parameters	$\Delta S°$ (J/mol·K)	–92.951	–165.116
	$\Delta H°$ (kJ/mol)	–36.771	–61.869
	$\Delta G°$ (kJ/mol)	–9.730	–13.130
	R^2	0.998	0.973

3.6. Ion-exchange mechanism

The sorption mechanism was established by comparing the net removal of Cr(III) and Ni(II) in percentage (%) using acidic (HEC-Adip) and sodic (HEC-Adip-Na) sorbents. HEC-Adip removed only 17% Cr(III) and 7% Ni(II) from aqueous solutions while HEC-Adip-Na removed more than 90% of both the metals even after five replicates (Fig. 5b). This trend was due to the absence of exchangeable sites on the surface of HEC-Adip and the presence of Na(I) ions on the surface of HEC-Adip-Na that can exchange with Cr(III) and Ni(II). Moreover, an exceptionally high degree of substitutions (DS = 2.0) of adipate moieties onto HEC also evidenced the presence of Na(I) ions in the saturation on the surface of HEC-Adip-Na that are radially available to exchange with Cr(III) and Ni(II) ions. Additionally, the fitting of adsorption data to the Langmuir isothermal and pseudo-second-order kinetic models also witnessed the involvement of the ion-exchange mechanism during the removal of Cr(III) and Ni(II) ions [34].

Moreover, the Boyd et al. [35] equations of the form [Eqs. (12) and (13)] was applied to explain the ion-exchange mechanism.

$$\log\left(1-F\right)=-\frac{S}{2.303}t \tag{12}$$

$$F=\frac{q_t}{q_e} \tag{13}$$

where S (min^{-1}) represent the Boyd constant for sorption phenomenon. The straight lines plot between the values of log(1–F) and t was obtained for both Cr(III) and Ni(II)

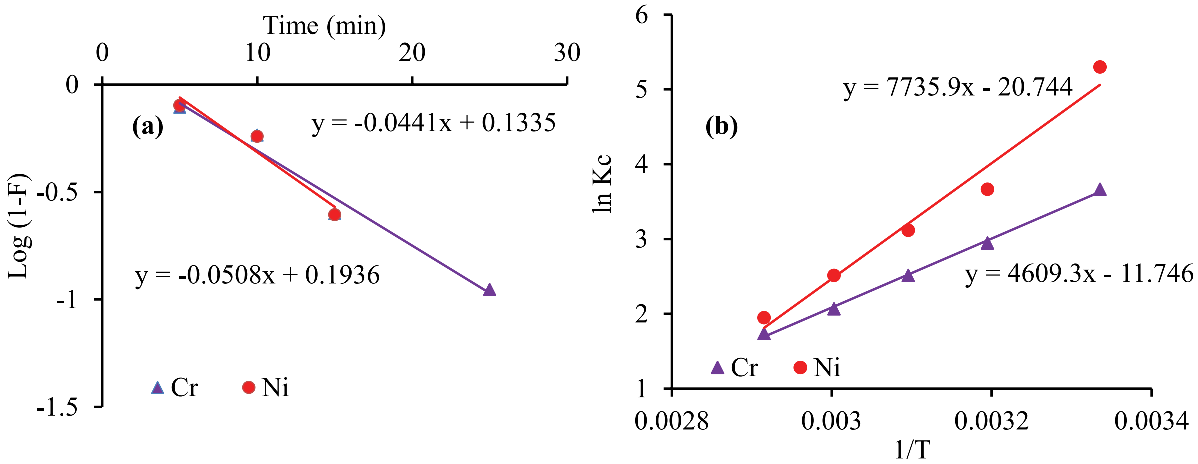

Fig. 5. Boyd's plot for ion-exchange mechanism (a) and effect of temperature to study the sorption thermodynamics (b) (optimized sorption conditions for Cr(III): pH = 6.0, initial concentration of metal ions = 80 mg/L, sorbent dose = 50 mg, contact time = 30 min, temperature = 298 K; optimized sorption conditions for Ni(II): pH = 5.5, initial concentration of metal ions = 40 mg/L, sorbent dose = 50 mg, contact time = 30 min, temperature = 298 K).

(Fig. 5a). The high values of R^2 for both the metals evidenced about the involvement of ion-exchange mechanism during sorption (Table 2).

3.7. Sorption thermodynamic

The values of thermodynamic triplets, that is, change in standard free energy ($\Delta G°$), entropy ($\Delta S°$) and enthalpy ($\Delta H°$) were calculated to know about the spontaneous or non-spontaneous, exothermic or endothermic nature of Cr(III) and Ni(II) removal by HEC-Adip-Na from aqueous solutions. The sorption data resulting from the effect of temperature was put into Vant's Hoff thermodynamic equation as presented in a set of following equations [Eqs. (14)–(16)].

$$K_C = \frac{C_{\text{ads}}}{C_e} \tag{14}$$

$$\ln K_C = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{15}$$

$$\Delta G° = -RT \ln K_C \tag{16}$$

where C_{ads} (mg/L) and C_e (mg/L) are the amounts of Cr(III) and Ni(II) removed by HEC-Adip-Na from aqueous solutions, the amounts of Cr(III) and Ni(II) retained in the aqueous solution. T is the absolute temperature and R and K_c are constants representing ideal gas constant and equilibrium constant, respectively. A plot between lnK_c along the dependent axis (Y-axis) and $1/T$ (K^{-1}) along the independent axis (X-axis) gave straight lines (Fig. 5b). From the slope of straight lines, the values of $\Delta H°$ were calculated and appeared as negative while from the intercepts of straight lines the values of $\Delta S°$ were calculated which were also appeared as negative. Likely, the values of $\Delta G°$ obtained as negative after putting the values of constants K_c, R, and absolute temperature in K (Table 2). These negative values recommended the spontaneous and exothermic nature of Cr(III) and Ni(II) sorption studies by HEC-Adip-Na.

3.8. Regeneration tests

As regenerated ion-exchangers are safe to probe them for the purification of contaminated water, therefore, regeneration tests (sorption-desorption) tests were conducted to estimate the reproducibility of HEC-Adip-Na using brine. Findings presented in Fig. 6a and b indicated that only

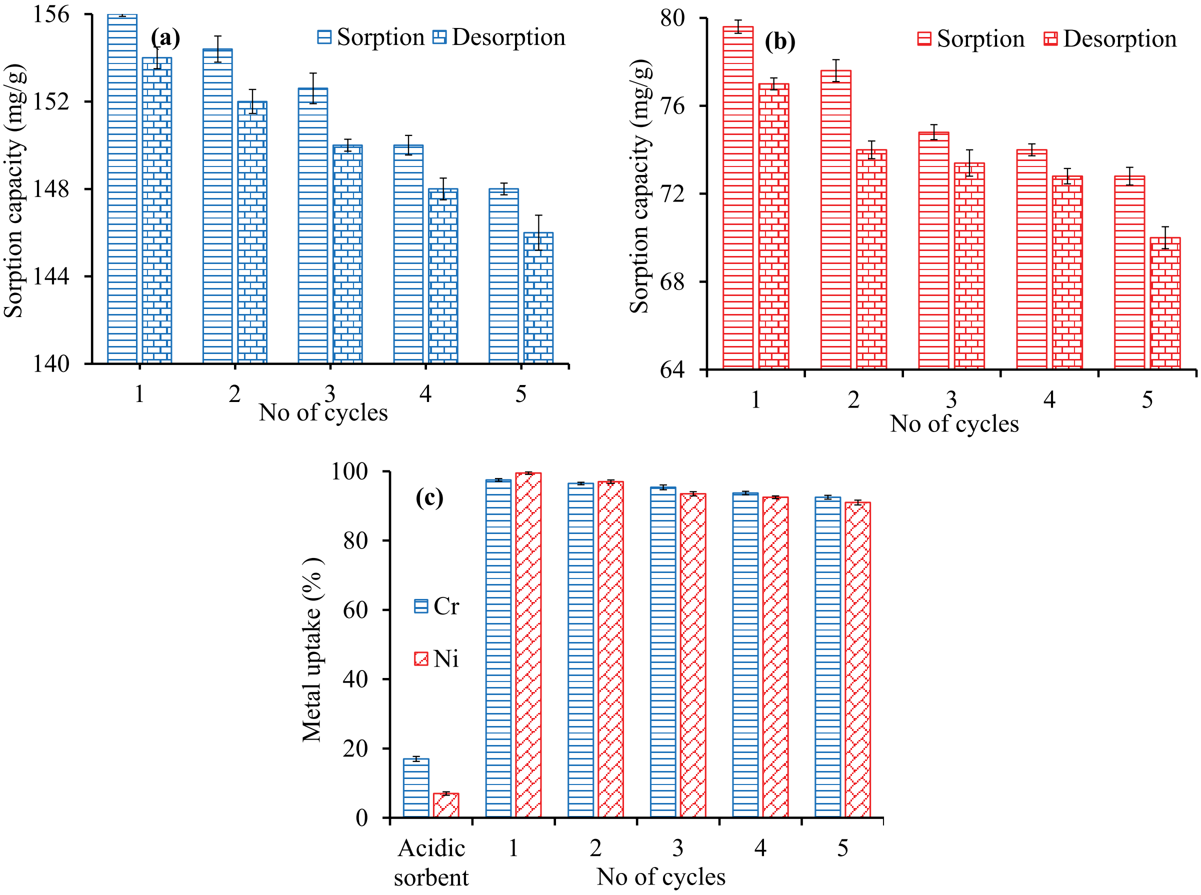

Fig. 6. Plot for sorption–desorption values for Cr(III) (a), Ni(II) (b) ion, and percentage metal removal (c) by the HEC-Adip and HEC-Adip-Na (optimized sorption conditions for Cr(III): pH = 6.0, initial concentration of metal ions = 80 mg/L, sorbent dose = 50 mg/g, contact time = 30 min, temperature = 298 K; optimized sorption conditions for Ni(II): pH = 5.5, initial concentration of metal ions = 40 mg/L, sorbent dose = 50 mg/g, contact time = 30 min, temperature = 298 K).

Table 3
Comparison of sorption maxima of HEC-Adip-Na with other low-cost modified and un-modified reported sorbents for Cr(III) and Ni(II) uptake

Sorbent (treatment)	Target metal	Sorption capacity (mg/g)
Diatomite-treated with microemulsion [36]	Cr(III)	11.55
Cellulose beads (1) acrylonitrile [37]	Cr(III)	73.50
Chemically modified corncob waste [38]	Cr(III)	84.60
Fenton-modified dried biomass of *Hydrilla verticillata* [39]	Cr(III)	107.40
Moringa oleifera bark [40]	Ni(II)	30.38
Modified chitosan [41]	Ni(II)	32.40
Gracilaria caudate [42]	Ni(II)	45.00
Gum kondagogu [43]	Ni(II)	50.50
Enteromorpha prolifera [44]	Ni(II)	65.36
Modified HEC	Cr(III)	156.25
	Ni(II)	79.37
		Present study (highest)

10.0 and 9.6 mg/g of sorption capacities were decreased, respectively for Cr(III) and Ni(II) after five repetitive cycles of sorption–desorption. Fig. 6c also revealed the removal efficiency in percentage and it is obvious that only a 5.0% decrease in sorption capacity was found in a case of Cr(III) and 8.5% in a case of Ni(II) that also witnessed the regenerable nature of HEC-Adip-Na.

3.9. Comparison of sorption capacities with already reported sorbents

In comparison with other commercial and natural chemically modified biomaterials, we came to know that our developed sorbent, that is, HEC-Adip-Na has a superior position. Thus, it can occupy a decent place in the list of ion-exchanger in the substantial market of water purification (Table 3).

The values of sorption capacities ($Q_{\max}$ in mg/g) of all the sorbent coated in Table 3 were calculated by Langmuir isothermal model.

4. Conclusion

A supersorbent based on HEC and adipic anhydride (HEC-Adip-Na) was synthesized and used for Cr(III) and Ni(II) uptake from aqueous solutions. Maximum removal of 156 mg/g for Cr(III) and 79 mg/g for Ni(II) was occurred at pH 6.0 for Cr(III) and 5.5 for Ni(II), sorbent dose 50 mg, initial concentration of metal ions (80 mg/L Cr(III) and 40 mg/L Ni(VI)), contact time 30 min, and temperature 298 K. The order of sorption of both the metals on HEC-Adip-Na was found to be Cr(III) > Ni(II) as expressed from Langmuir isotherm. Uptake-kinetics and negligible removal of metals by HEC-Adip (17% for Cr(III) and 7% for Ni(II)) compared to HEC-Adip-Na (97.5% for Cr(III) and 99% for Ni(II)) revealed the involvement of the ion-exchange mechanism. Thermodynamic data evidenced the spontaneous and exothermic nature of sorption. Moreover, HEC-Adip-Na was fully regenerated without any significant decrease in sorption maxima even after five regenerated cycles. Morally, HEC-Adip-Na can be used as a safe and excellent sorbent for water desalination.

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