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Application of Cellulose-Clay Composite Biosorbent toward the Effective Adsorption and Removal of Chromium from Industrial Wastewater

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ABSTRACT: Biopolymer composites are known for their utility in diverse applications. In this paper, we report an effective methodology for the detoxification of chromium using cellulose-montmorillonite composite material as the adsorbent. The interaction of surfactant modified sodium montmorillonite (NaMMT) with cellulose biopolymer is followed by the subsequent adsorption of Cr(VI) from aqueous solution as bichromate anion onto the surface of the biocomposite material. The composite adsorbent was characterized comprehensively using Fourier transform infrared spectroscopy (FT-IR), Energy dispersive X-ray spectrometry (EDX), X-ray diffraction (XRD) and Branauer-Emmett-Teller (BET) isotherm studies. The material exhibited a maximum adsorption capacity of 22.2 mg g^{-1} in accordance with the Langmuir isotherm model. The mesoporous nature of the material was ascertained from the nitrogen adsorption isotherm study and the adsorption process was in accordance with second order kinetics. The spontaneity of the adsorption process could be confirmed from the study of the adsorption thermodynamics. The composite material could be regenerated using sodium hydroxide as the eluent. The adsorbent could be reused with quantitative recovery for 10 adsorption—desorption cycles. An aqueous phase feed volume of 400 mL could be quantitatively treated by column method at 100 mg L^{-1} concentration of Cr(VI) with a preconcentration factor of 50. The applicability of the method is demonstrated in the quantitative removal of total chromium from a chrome tannery effluent sample.

1. INTRODUCTION

The impact of heavy metal pollution has led to the search for biodegradable and cost-effective adsorbent materials in order to alleviate the associated hazards caused to the environment. Chromium is not an exception and is known to be carcinogenic in the +6 oxidation state. Cr(III) is relatively less toxic and is known for its importance in the glucose metabolism.[1] Nevertheless, the presence of manganese oxides in the soil can oxidize the chromium in +3 oxidation state to the +6 state.[2] The wastewater from the tanneries contain chromium[3] and hence it is of paramount importance to address the removal of total chromium present in these effluents. Solid phase extraction is an effective methodology for heavy metal adsorption.[4] Macrocyclic crown ether and layered double hydroxides are known for their secondary host guest interaction in the recognition of metals, such as cobalt, nickel, and zinc.[5] Adsorbents, such as agricultural waste biomass,[6] synthetic polymeric resins,[7,8] and alumina[9] are well-known for the adsorption of chromium. The removal of chromium from aqueous solution using polyaniline—polyethylene glycol composite has been investigated in terms of adsorption capacity and other parameters.[10] Natural materials which are cost-effective and biodegradable are also known for their efficacy in wastewater treatment.[11−13] Chitosan-based composite biosorbents[14,15] are known for their good adsorption capacity toward chromium. Renewable polymers such as cross-linked starch have been reported for the effective adsorption of chromium.[16] Bentonite based organoclays have also been utilized for the remediation of chromium.[17] The work presented in this paper deals with the application of cellulose-clay composite material as an effective adsorbent for the removal of chromium. Cellulose, a natural biopolymer

is a polysaccharide with about 1500 β-glucose units and the chains are held together by intermolecular hydrogen bonding.[18] The hydroxyl groups in the cellulose macromolecule play a vital role in the adsorption of metal ions. Natural cellulose fibers possess a porous structure with 10−30 nm width of the micro fibrils and show an excellent interaction with noble metal nanoparticles.[19] Polymeric composites are known for their excellent properties[20] and the biodegradable nanocomposites prepared in conjunction with layered silicates (clays) possess excellent mechanical strength, flame retardancy, etc.[21] The cellulose-montmorillonite composite material prepared from *N*-methyl morpholine oxide is known for its good morphological and thermal properties.[22] A systematic survey of the literature indicates that organophilic NaMMT clay (surfactant modified)—cellulose composite has not been explored for the adsorption of chromium. Montmorillonite is a 2:1 smectite type layered silicate with good surface area and interlammellar spacing.[23] Montmorillonite clays are naturally hydrophilic which makes them inadequately suited to interact with most polymer matrices. The organophilic clays ensure better compatibility with the biopolymer and is intended to separate the silicate layers for the effective interaction with cellulose.[24] The sodium ions in the clay can be exchanged with organo ammonium cations and to the best of our knowledge, there is no literature evidence on the application of cellulose-sodium montmorillonite clay composite for the detoxification of chromium

from wastewater. Herein, we present an interesting interaction between surfactant modified sodium montmorillonite (NaMMT) and cellulose biopolymer followed by its application toward the adsorption and remediation of chromium from chrome tannery wastewater sample.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Reagents. Analytical grade reagents were used for the adsorption studies. The aqueous solutions were prepared in Milli Q water. A 1000 mg L^{-1} stock solution of Cr(VI) was prepared using potassium dichromate (Merck, India). A working solution of 20 mg L^{-1} Cr(VI) for the batch adsorption study was prepared by appropriate dilution. Cellulose was procured from Himedia, India and montmorillonite was obtained from Sigma Aldrich. Cetyltrimethylammoniumbromide (CTABr) was obtained from Sisco Research Laboratories, India. Acetone, sulfuric acid, ascorbic acid, and sodium hydroxide were procured from Merck, India.

2.2. Instrumentation. The cellulose-clay composite material was characterized using various physicochemical characterization techniques. The FT-IR samples were prepared by mixing 0.01 g of the material with 0.1 g of spectroscopy grade KBr. The FTIR spectra were recorded using a Jasco-4200 FT-IR spectrometer in the range 400 to 4000 cm^{-1}. The surface area, pore size, and pore volume measurements were done using a Micromeritics Porosimeter model ASAP 2020 analyzer at an outgassing temperature of 200 °C for 12 h. The XRD measurements were taken using a Panalytical X-ray spectrometer at a scan rate of 0.5° min^{-1} using Cu Kα radiation and a secondary beam graphite monochromator. The EDX spectrum was recorded with a Hitachi S-3000H analyzer the pH adjustments were done with sulfuric acid and sodium hydroxide using an Elico LI-127 pH meter (Elico, India). The concentration of chromium was measured by the standard diphenylcarbazide method at 540 nm using a Jasco V-650 UV−visible spectrophotometer.

2.3. Preparation of Cellulose−NaMMT Composite Adsorbent. The NaMMT clay was prepared from montmorillonite as described earlier in literature.[25] A 0.001 mol L^{-1} CTABr solution was prepared by appropriate dilution with Milli Q water. Six grams of the sodium form of the clay was suspended in 20 mL of acetone. A 100 mL volume of 0.001 mol L^{-1} cetyltrimethylammonium bromide was added to the clay suspension. The selection of an appropriate solvent for effective swelling and dispersion of clay is an important aspect to be considered.[26,27] The contents were stirred magnetically for 8 h. The mixture was centrifuged and the centrifugate was discarded. The solid material was washed with water until it was free from bromide (confirmed through the AgNO$_3$ test) and then dried overnight at 80 °C. Three grams of cellulose powder was taken and added slowly to the prepared organophilic NaMMT (as a suspension in 20 mL of acetone), and the resulting mixture was stirred for 12 h at a temperature of 60 °C. The resulting composite adsorbent was washed with Millipore water and dried in a hot air oven for 6 h and used for further studies.

2.4. Batch Adsorption Study. The batch adsorption studies were conducted by equilibrating 0.5 g of the adsorbent material with 25 mL of 20 mg L^{-1} chromium(VI) solution at pH 5.0 in an orbital incubator shaker (Biotechnics, India) for varying time intervals, and the concentration of chromium in the solution phase was estimated by the standard spectrophotometric method.[28] The amount of chromium adsorbed (mg g^{-1}) at equilibrium (q_e)
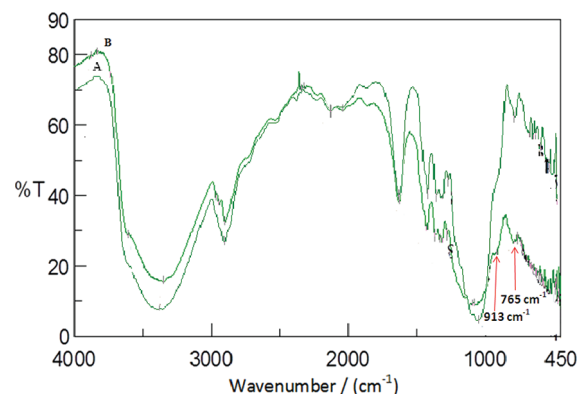

Figure 1. FT-IR spectrum of cellulose-clay composite adsorbent (A) and the adsorbed chromium (B).

was calculated using the expression

$$q_e = \frac{(C_o - C_e) \times V}{W} \tag{1}$$

where C_o and C_e are the initial and final liquid phase concentrations (mg L^{-1}) of chromium(VI), V is the volume of aqueous solution (L), and W is the weight of the adsorbent (g) used for the adsorption study. The percentage of chromium adsorbed increased with time and reached its maximum (99.5 ± 0.4% with three replicate measurements) at 40 min, signifying the saturation of the adsorption sites.

3. RESULTS AND DISCUSSION

3.1. FT-IR Characterization and Mechanism of Biopolymer− Clay−Chromium Interaction. The FT-IR spectrum (Figure 1) showed characteristic bands corresponding to the various functional groups in cellulose[29] and NaMMT. A strong band at 3379 cm^{-1} is ascribed to O−H stretching and that at 2902 cm^{-1} is attributed to the C−H stretching in cellulose. The band at 1635 cm^{-1} could be ascribed to the H−OH bonding in water. A strong peak at 1063 cm^{-1} arises from the C−O−C pyranose ring skeletal vibration. The peaks characteristic of NaMMT were observed at 794 (Si−O stretching of quartz and silica), 694 (Si−O deformation), 611 (Al−O and Si−O out of plane vibration), 543 (Al−O−Si deformation), 489 (Si−O−Fe deformation), and 470 cm^{-1} (Mg−O deformation), respectively.[30,31] There exists an interesting molecular interaction between the surfactant modified NaMMT and the cellulose biopolymer. The central point to take cognizance is that the hydroxyl groups in the biopolymer play a pivotal role in this interaction. The quaternary ammonium cation present in CTABr interacts with the cellulose hydroxyl group in the form of a weak electrostatic attraction. There are considerable amendments in the spectral features after the adsorption of hexavalent chromium and the change is more obvious in the O−H region of the FT-IR spectrum. Hexavalent chromium exists primarily as bichromate ion (HCrO$_4^-$) and dichromate (Cr$_2$O$_7^{2-}$) in acidic medium.[32] The bichromate anion is the prime species in weakly acidic medium. The cellulose-clay composite material is now involved in the ensuing interaction with chromium(VI) as bichromate anion. The bichromate ion forms an ion-pair with the positively charged nitrogen of the surfactant molecule and this interaction is more pronounced than the interaction that exists between the quaternary ammonium cation and the hydroxyl

groups of the biopolymer. This fact is also substantiated through the appearance of characteristic Cr=O and Cr—O peaks at 913 and 765 cm^{-1}, respectively.[33] We have also demonstrated the operation of a similar mechanism in our earlier study involving the interaction of ionic liquid in a cellulose matrix.[34] Hydrogen bonding interaction is also probable between the hydroxyl protons in cellulose and the oxygen atoms in the bichromate anion. The conceptual graphic illustration of the mechanism involved in the interaction between chromium and the biopolymer—clay adsorbent surface is shown in Figure 2. Furthermore, it is also probable that the silanol groups in clay could be protonated as SiOH^{2+} in acidic medium[35] and this would further reinforce the interaction of bichromate anion with the positively charged composite adsorbent surface.
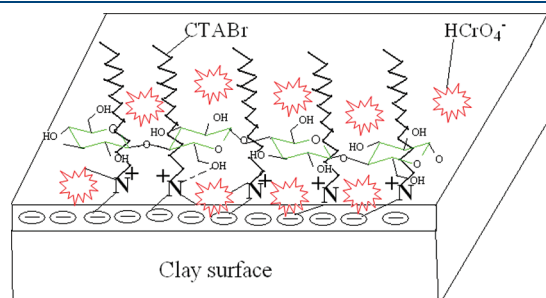

Figure 2. Conceptual illustration showing the interaction of bichromate ion with the biopolymer—clay adsorbent surface.
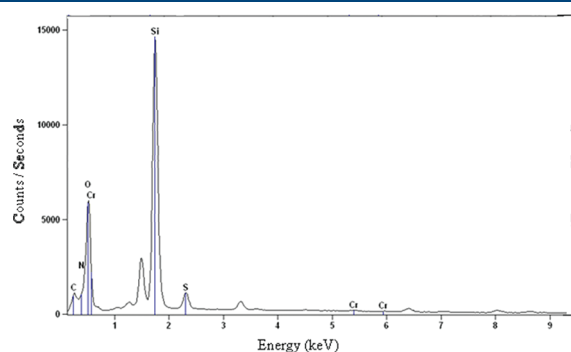

Figure 3. EDX spectrum of the adsorbed Cr(VI) on the adsorbent material.

3.2. Energy Dispersive X-ray Spectrum (EDX) and Powder X-ray Diffraction (XRD) Analysis of the Cellulose-Clay Composite Material. The adsorption of chromium on the surface of the cellulose-clay composite was authenticated from the EDX spectrum (Figure 3), which shows the presence of adsorbed chromium along with the other major elemental peaks, such as C, N, O, S, and Si, respectively. The peak for silicon is ascribed to the Si—O present in montmorillonite and the sulfur peak could originate from the sulfuric acid medium[8] used for maintaining the pH of the medium. Depending on the amount of the added clay, the silicate layers would be either dispersed or exfoliated in the composite.[24] The XRD pattern of the composite material shows sharp and pointed diffraction peaks (Figure 4a) at 2θ values corresponding to 6.25°, 8.8°, 18.14°, 20.73°, and 22.79°, which indicates the crystalline nature of the polymeric composite with certain degree of exfoliation.[36] The noteworthy sharp peaks also signifies the ordered distribution of clay layers in the biopolymer composite. The surface modification of the clays makes them more organophilic and this provides an enhanced interaction with the biopolymer cellulose resulting in a fine dispersion in the matrix. Interestingly, the crystalline nature of the composite is not disturbed after the adsorption of chromium and the new sharp peaks obtained at 2θ values corresponding to 39° and 42.47° are attributed to the adsorption of chromium (Figure 4b), which concurs with the reported values in literature.[37]

3.3. Nitrogen Adsorption Isotherm Study, Pore Size Distribution. The BET surface area of the material obtained from N$_2$ adsorption isotherm was found to be 87.09 m^2 g^{-1}. The shape of the isotherm indicates the mesoporous nature of the cellulose-clay composite material.[38,39] The Barrett—Joyner—Halenda (BJH) pore size distribution curve (Figure 5a) for the composite adsorbent material provides a pore size of 1.8 nm at a maximum pore volume of 0.31 cm^3 g^{-1}. The adsorption hysteresis relates to the Type IV isotherm (Figure 5b). The mesoporous nature of the cellulose-clay composite, nano pore size, and the good surface area is an indication of effective adsorption of chromium on the polymeric adsorbent.

3.4. Optimization of pH. The optimization of pH is a significant factor in the adsorption study. Hexavalent chromium can exist in various forms such as HCrO$_4^-$, CrO$_4^{2-}$, and Cr$_2$O$_7^{2-}$ depending on the pH and concentration of the aqueous phase.[40] In the pH range 3.8—5.5, Cr(VI) exists in solution primarily as bichromate (HCrO$_4^-$) anion, whereas the dichromate (Cr$_2$O$_7^{2-}$) anion predominates at lower pH values. The favorable pH for the
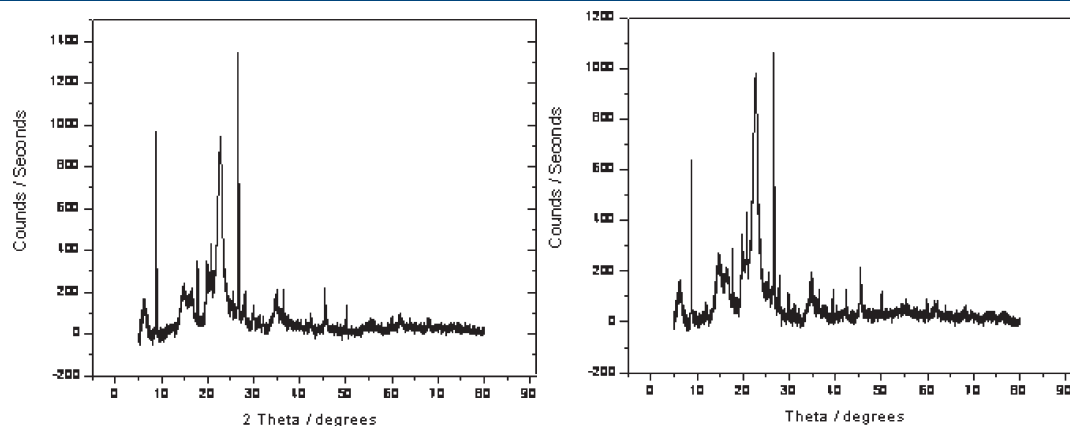

Figure 4. XRD pattern (a) cellulose-clay composite adsorbent and (b) after chromium(VI) adsorption on the adsorbent.
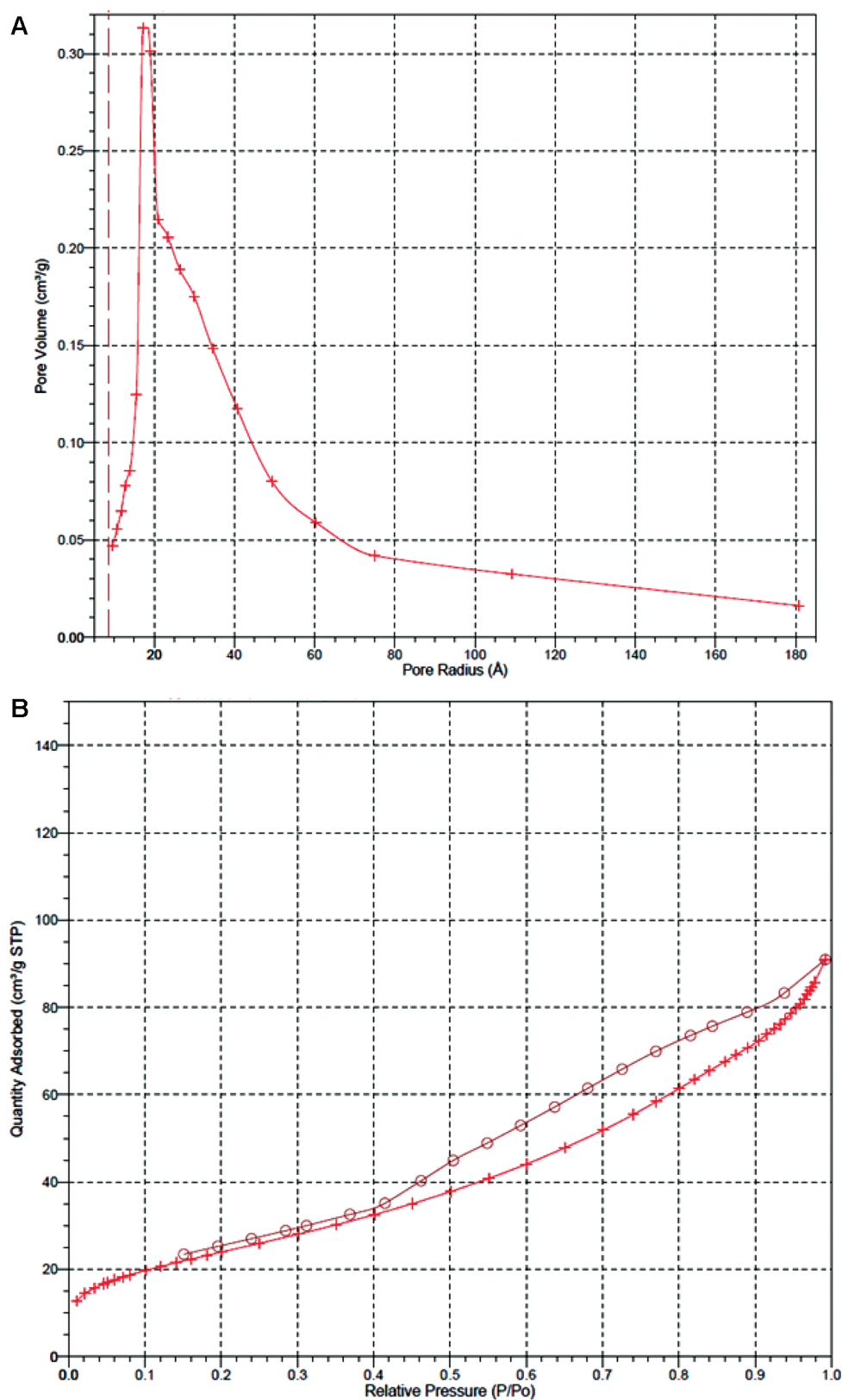
Figure 5. (a) BJH pore distribution curve and (b) nitrogen adsorption and desorption isotherm.

adsorption of Cr(VI) was observed in weakly acidic medium (3.8–5.5). In weakly acidic medium, the bichromate ion forms an ion-pair with the positively charged biopolymer composite surface as evidenced by the FT-IR study. The hard acid soft base (HSAB) principle is a very useful model to explain a variety of complexation reactions. According to Pearson's classification,[41]

chromium is categorized as a hard acid and nitrogen is classified as a hard base. Hence, we can expect good interaction between the positively charged nitrogen and negatively charged bichromate anion. In the case of hard acids such as chromium, the energy difference between the acceptor and donor orbital level is quite large and hence the bonding is strongly electrostatic in nature.[42] Beyond pH 5.5, there is a decrease in the percentage adsorption of chromium. This could be attributed to the deprotonation of the surface hydroxyl groups in the biopolymer composite, which causes the decrease in adsorption.[35] Similarly, at higher pH the competition of the hydroxide anion with the bichromate anion for the effective adsorption sites could also lead to a reduction in the percentage adsorption of chromium.[8] Three replicate measurements yielded a maximum adsorption of 99.6 ± 0.2% at the optimized pH, and it is the $HCrO_4^-$ species which is associated as an ion pair with the biopolymer-organophilic clay adsorbent followed by the hydrogen bonding interaction with the hydroxyl groups of cellulose.

3.5. Amount of Adsorbent. The amount of adsorbent used in the batch study was varied in the range 0.1−1.0 g. The percentage adsorption was found to be maximum (99.5 ± 0.3%) with three replicate measurements when the amount of adsorbent was in the range 0.5−0.6 g in 25 mL sample volume. The initial increase in adsorption is attributed to the strong electrostatic attraction between the bichromate anion and the biopolymer clay adsorbent. Beyond 0.6 g, there was no appreciable increase in the percentage adsorption, which indicates the saturation of the active adsorption sites in the biopolymer composite.

3.6. Adsorption Isotherm Studies. *3.6.1. Langmuir Adsorption Isotherm.* Langmuir isotherm model is commonly used to describe the relationship between the equilibrium concentration of the adsorbate and the amount adsorbed on the surface of the adsorbent. This isotherm is essentially based on three assumptions:[43] (a) Adsorption is essentially monolayer coverage. (b) All the sites are equivalent with surface uniformity. (c) There is negligible interaction between the adsorbed molecules and the ability of a molecule to adsorb at a particular site is independent of the occupancy of the adjacent sites. The assumptions b and c imply that ΔH_{ads} is identical for all sites and is independent of the degree of surface coverage. The surface interaction of chromium with the composite adsorbent can be represented as

$$X + S \rightleftharpoons XS \tag{2}$$

where X and S represent the chromium and the biopolymer clay composite surface and XS refers to the chromium adsorbed on the adsorbent.

The Langmuir isotherm model is utilized to calculate the maximum adsorption capacity, which is a measure of amount of the metal ion adsorbed per unit weight of the adsorbent. The maximum adsorption capacity was obtained by fitting the experimental data to Langmuir isotherm model,[44] which assumes monolayer adsorption. The linearized form of Langmuir equation can be expressed as

$$\frac{C_e}{q_e} = \frac{1}{q_o b} + \frac{C_e}{q_o} \tag{3}$$

where C_e is the equilibrium concentration of the metal ion in mg L^{-1}, q_e is the amount of Cr(VI) adsorbed at equilibrium in mg g^{-1}, q_o is the maximum adsorption capacity in mg g^{-1}, and b is a constant (L mg^{-1}) related to the energy of adsorption. The maximum adsorption capacity, q_o and the constant b are obtained

from the slope and intercept of the plot of C_e/q_e against C_e (Figure 6a). The values indicate good affinity of the bichromate anion toward the composite adsorbent material. The regression coefficient obtained from this plot was found to be 0.99 and the respective isotherm parameters are given in Table 1. The applicability of this isotherm model is evident from the good correlation obtained through the above plot. The favorable nature of adsorption can be expressed in terms of a dimensionless parameter R_L, which is given by the following equation

$$R_L = \frac{1}{1 + bC_o} \tag{4}$$

where C_o is the initial concentration of chromium(VI) in mg L^{-1} and b is the Langmuir constant (L mg^{-1}). An R_L value of zero indicates irreversible adsorption while values greater than 1 indicate unfavorable adsorption. It has been well established in many adsorption systems that the value of R_L in the range 0 to 1 serves as an index to constructive adsorption.[45] The value of R_L for the adsorption of chromium on the cellulose-clay composite material was found to be 0.3178 and this indicates the effectiveness of interaction between $HCrO_4^-$ and the adsorbent surface under the optimized experimental conditions.

3.6.2. Freundlich Isotherm. The Freundlich isotherm[46] is yet another useful model to study the adsorption from dilute solutions. The adsorption on inequivalent adsorption sites is well described by this empirical isotherm. The Freundlich equation takes into account the logarithmic decrease in the energy of adsorption with increasing surface coverage and this is attributed to the surface heterogeneity. The linearized form of this isotherm can be expressed as

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

where C_e is the equilibrium concentration of the metal ion in mg L^{-1}, q_e is the amount of chromium(VI) adsorbed at equilibrium in mg g^{-1}, and K_F and n are the Freundlich constants, which indicate the adsorption capacity and the adsorption intensity, respectively. The values of K_F and n were obtained from the slope and intercept of the logarithmic plot of q_e vs C_e (Figure 6b) and the results are presented in Table 1. The plot is linear with a regression coefficient of 0.99. The Freundlich constant n lies between 1 and 10 for a favorable adsorption process, and a larger value of n implies effective interaction between adsorbent and the adsorbate.[47]

3.7. Dubinin−Radushkevich Isotherm. The Dubinin−Radushkevich isotherm (D−R) is analogous to the Langmuir isotherm but it does not assume a homogeneous surface or a steady adsorption potential.[48] The D−R isotherm helps in calculating the adsorption energy and the nature of the adsorption mechanism involved in the interaction between chromium and the adsorbent surface. The linearized D−R isotherm equation can be written as

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{6}$$

where q_e is the amount of chromium(VI) adsorbed at equilibrium per unit weight of adsorbent (mg g^{-1}), q_m is the maximum adsorption capacity, β is a constant related to the adsorption energy, and ε is the Polanyi potential expressed as

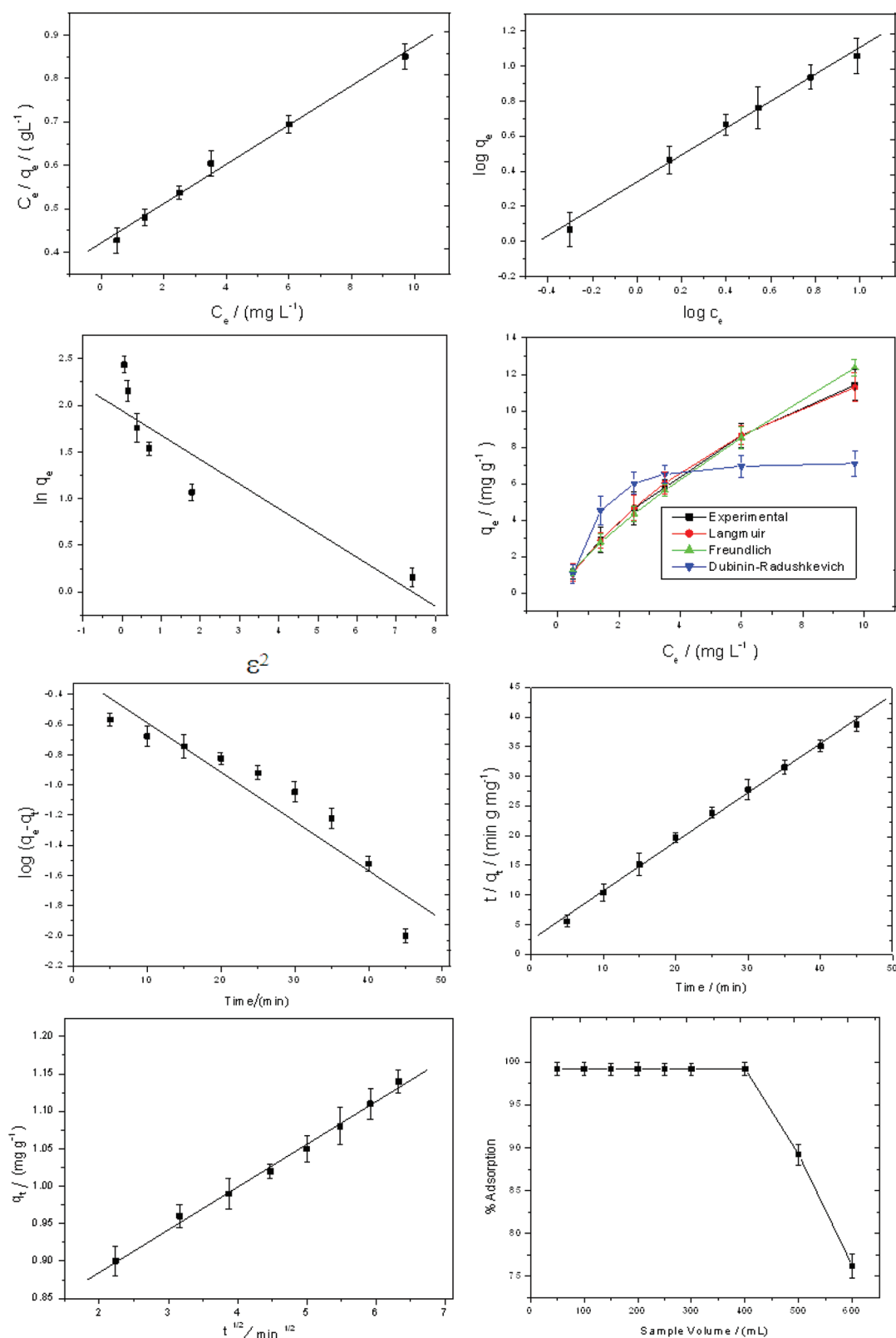$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{7}$$

Figure 6. (a) Langmuir isotherm, (b) Freundlich isotherm, (c) Dubinin−Radushkevich isotherm, (d) plot of q_e vs C_e, (e) pseudo-first-order kinetic plot, (f) pseudo-second-order kinetic plot, (g) plot of q_t versus square root of time, and (h) effect of sample volume.

where R is the gas constant $(J\ mol^{-1}\ K^{-1})$, C_e is the equilibrium concentration of chromium $(mg\ L^{-1})$, and T is the temperature (Kelvin). The values of β and q_m were obtained from the slope and intercept of the plot of $\ln q_e$ versus ε^2 (Figure 6c), and the results are presented in Table 1. The regression coefficient value was found to be 0.83. The adsorption energy, E can also be

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dx.doi.org/10.1021/ie201349h |*Ind. Eng. Chem. Res.* 2012, 51, 58–69

Table 1. Adsorption Isotherm Parameters

Langmuir					Freundlich				Dubinin–Radushkevich				
q_o (mg g^{-1})	b (L mg^{-1})	R_L	r^2	χ^2	K_F (mg$^{1-1/n}$ g^{-1} L$^{1/n}$)	n	r^2	χ^2	q_m (mg g^{-1})	β (mol^2 kJ^{-2})	E (kJ mol^{-1})	r^2	χ^2
22.2	0.1073	0.3178	0.99	0.0133	2.1458	1.2975	0.99	0.1064	7.22	0.263	1.379	0.83	0.7821

Table 2. Kinetic Parameters and Intraparticle Rate Constant for Chromium(VI) Adsorption

first-order rate constant k_1/(min^{-1})	R_1^2	χ^2	second-order rate constant k_2/(g mg^{-1} min^{-1})	R_2^2	χ^2	intraparticle rate constant k_{int}/(mg g^{-1} min$^{-1/2}$)
0.0723	0.88	0.2623	0.2817	0.99	0.0013	0.0575

expressed as $-(2\beta)^{-0.5}$, and the positive value of E indicates an endothermic adsorption. The adsorption energy was found to be 1.379 kJ mol^{-1} and this indicates that the electrostatic interaction between the bichromate anion and polymeric adsorbent is endothermic and higher temperatures favor the adsorption process.

3.8. Chi Square Test for the Adsorption Isotherms. The values of the regression coefficient above 0.9 indicate that the experimental data could fit into Langmuir and Freundlich isotherm models. Hence, the chi square test[49] was adopted in order to find the suitability of an isotherm that fits best with the experimental data. The chi-square test is essentially the sum of the squares of the differences between the experimental and calculated data (obtained from the respective isotherm models) with each squared difference divided by the corresponding data obtained by calculation. The chi square test can be expressed mathematically as

$$\chi^2 = \Sigma(q_{eexp} - q_{ecal})^2/q_{ecal} \tag{8}$$

where q_{ecal} (mg g^{-1}) is the amount of chromium(VI) adsorbed at equilibrium obtained by calculating from the respective isotherm models and q_{eexp} (mg g^{-1}) is the value obtained experimentally The value of χ^2 would be of a smaller magnitude if the data obtained from a particular isotherm model is in close concurrence with the experimental values.[50]

The results from Table 1 indicate lower χ^2 values for Langmuir isotherm model showing that the experimental data correlates well with the Langmuir isotherm. This was also further verified from the respective isotherm data plots of q_e against C_e. The L-shaped adsorption isotherms are in accordance with the classification of Giles,[51] which indicates a good correlation to the Langmuir type isotherm as shown in Figure 6d. The initial increase is attributed to the effective interaction between the bichromate anion and the adsorbent and the plateau signifies the saturation of the adsorption sites.

3.9. Kinetics of Adsorption. The kinetic parameters were evaluated using the well-known first-order and pseudo-second-order models. The pseudo-first-order[52] and the second-order rate equations[53] can be expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{9}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

where q_e and q_t refers to the amount of chromium absorbed at equilibrium and time t with the first- and second-order rate constants k_1 and k_2, respectively. The slope and intercept obtained from the plots of $\log(q_e - q_t)$ and t/q_t against t (Figure 6e and 6f)

gives the respective kinetic parameters. The adsorption data is in good concurrence with the pseudo-second-order model because of the higher regression coefficient (Table 2). The q_e values obtained experimentally and from the second-order kinetic model were found to be 1.16 and 1.21 mg g^{-1}, respectively. The close correlation between the experimental and calculated values authenticates the applicability of second-order kinetic model in the adsorption of chromium. The overall rate of adsorption of chromium on the biopolymer–clay adsorbent could be influenced by the following three steps:[54] (a) film or surface diffusion, where the Cr(VI) is transported from the bulk solution to the external surface of the adsorbent, (b) intraparticle or pore diffusion, where the adsorbate molecules move into the interior of the adsorbent particles, and (c) adsorption of chromium ion on the interior sites of the adsorbent. Since, the adsorption step happens quite rapidly it is assumed that it does not bear significant influence on the adsorption kinetics. Hence, the overall rate of adsorption could be controlled by surface or intraparticle diffusion. The Weber–Morris[55] intraparticle diffusion model has often been used to determine whether intraparticle diffusion is the rate-determining step. According to this model, a plot of q_t versus $t^{0.5}$ should be linear if intraparticle diffusion is involved in the adsorption process and if the plot passes through the origin then intraparticle diffusion is the only rate-limiting step. This plot is linear and the slope gives the intraparticle rate constant k_{int} and the nonzero intercept (Figure 6g) points to the fact that diffusion is not the only phenomenon that controls the adsorption of the metal ion on the cellulose-clay composite material.[56] Furthermore, the hysteresis between the nitrogen adsorption and desorption isotherms (Figure 5b) also indicate that intra particle diffusion is not the only rate controlling mechanism[57] operating in the adsorption of chromium on the polymeric adsorbent.

3.10. Thermodynamics of Adsorption. The adsorption thermodynamics was studied at varying temperatures and the respective thermodynamic parameters, such as the free energy, enthalpy, and entropy changes, were obtained from the following equations[58]

$$\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{11}$$

$$\Delta G^0 = -RT \ln K \tag{12}$$

where ΔH^0 and ΔS^0 are enthalpy and entropy changes, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is the absolute temperature (Kelvin). The equilibrium constant K is obtained from the ratio of concentration of Cr(VI) adsorbed on the composite material to that in the solution. The values of ΔH^0

Table 3. Thermodynamic Parameters for the Adsorption of Chromium(VI)

temperature (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta S°/$(J mol^{-1} K^{-1})	$\Delta H°$ (kJ mol^{-1})
298	−3.434	313.02	90.07
308	−6.455		
318	−9.685		

Table 4. Optimization of Bed Height and Flow Rate in Column Studies

S. No	initial concentration (mg L^{-1})	bed height (cm)	flow rate (mL min^{-1})	adsorption (%)
1.	50	3	5	94.3 ± 0.3
		5	5	99.5 ± 0.2
		8	5	99.5 ± 0.3
2.	50	5	2	99.5 ± 0.4
		5	5	99.5 ± 0.3
		5	10	97.0 ± 0.2

and ΔS^0 were calculated from the slope and intercept of the Van't Hoff plot of ln K against $1/T$ and eq 12 was used to calculate the Gibb's free energy (ΔG^0). The spontaneity of adsorption process is ascertained from the equilibrium constant K and the Gibb's free energy values. The results are presented in Table 3 and the negative free energy value implies a spontaneous adsorption process.[59] The magnitude of ΔH^0 gives information about the adsorption mechanism and for physical adsorption, ΔH^0 is generally less than 80 kJ mol^{-1} while for chemical adsorption the value lies in the range 80 and 400 kJ mol^{-1}.[60,61] The equilibrium constant increases with temperature and this is reflected in the free energy values obtained at higher temperatures. Higher temperatures favor the adsorption process as evident from these values. The entropy of adsorption was found to be positive and this is indicative of increased randomness at the adsorbent-solution interface. The positive value of enthalpy change indicates the endothermic reaction between the adsorbent and the adsorbate. The energy is manifested in weakening the interaction between N$^+$ in CTABr and the hydroxyl groups of cellulose and strengthening the subsequent electrostatic interaction between the positively charged nitrogen and the bichromate anion respectively. These data demonstrate the effectiveness of the cellulose-clay composite material as an useful adsorbent for chromium-(VI). When the clay matrix is dispersed in the solvent medium, the molecules tend to be disordered in order to accommodate the cellulose polymeric chains. The process involves a gain in the translational entropy resulting in the separation of the clay layers.[62] This leads to a positive entropy change during the adsorption process. This fact can be further substantiated by considering the free energy changes associated with cellulose, NaMMT and chromium. The change in the free energy can be expressed as the difference in the enthalpy and the entropy changes of the respective components as follows:

$$\Delta G_{cellulose} = \Delta H_{cellulose} - T\Delta S_{cellulose} \quad (13)$$

$$\Delta G_{NaMMT} = \Delta H_{NaMMT} - T\Delta S_{NaMMT} \quad (14)$$

$$\Delta G_{Cr} = \Delta H_{Cr} - T\Delta S_{Cr} \quad (15)$$

$$\Delta G_{adsorption} = \Delta H_{adsorption} - T\Delta S_{adsorption} \quad (16)$$

$$\Delta G_{adsorption} = \Delta H_{adsorption} - T(\Delta S_{cellulose} + \Delta S_{NaMMT} + \Delta S_{Cr}) \quad (17)$$

The interaction of hard cation (N$^+$) with the negatively charged bichromate oxoanion is characterized by a positive value of enthalpy and entropy. The overall entropy contribution arises from the individual entropy changes associated with the biopolymer, clay and cellulose. Hence, the summation ($\Delta S_{cellulose}$ + ΔS_{NaMMT} + ΔS_{Cr}) becomes largely positive reflecting the increased randomness at the adsorbent-solution interface. Furthermore,

the fact that $T\Delta S > \Delta H$ shows that the physicochemical adsorption process is entropically driven rather than the enthalpy effect. The large entropy and the positive enthalpy contribution ($\Delta H > 0$) is attributed to the decrease in the hydration of the ions.[60] The positive entropy change is related to the release of the water molecules leading to an increase in the total degrees of freedom attributed to the effective interaction between the bichromate anion and the polymeric adsorbent. The energy of activation (E_a) at various temperatures can be calculated using the relation $E_a = \Delta H°_{ads} + RT$ for adsorption from solutions.[63] The average energy of activation was found to be 92.63 kJ mol^{-1} and the positive value of E_a indicates the endothermic nature of adsorption.

3.11. Column Study. After optimizing the parameters in batch study, the applicability of the composite adsorbent material was examined for the detoxification of chromium from a larger sample volume. A glass column 2.5 cm in diameter and 30 cm in length was used for the column adsorption study; 3.5 g of the adsorbent material was packed in the glass column to a height of 5 cm. A known volume (250 mL) of 100 mg L^{-1} Cr(VI) was transferred to the column at a flow rate of 6 mL min^{-1}. Cr(VI) was effectively adsorbed on the column at pH 4.0, and this was ascertained spectrophotometrically from the concentration of chromium in the solution phase.

3.12. Effect of Sample Volume. The effect of sample volume for the adsorption of chromium(VI) on the biopolymer clay composite adsorbent was investigated in the range (100−600) mL maintaining an overall concentration of 100 mg L^{-1}. As can be seen from Figure 6h, it is evident that the adsorption of chromium is quantitative until a 400 mL of sample volume with a preconcentration factor of 50. The amount of the adsorbent, bed height, and diameter of the column play a pivotal role in the performance of the column.[8] On loading the column with a higher aqueous sample volume, the degree of swelling in the biopolymer clay composite adsorbent increases and results in the expansion of the adsorbent bed. This would create some voids in the column by disturbing the effective packing and hence the adsorption of chromium decreases beyond a 400 mL sample volume.

3.13. Optimum Flow Rate and Bed Height of the Column. The flow rate and bed height are two vital parameters which affect the percentage adsorption of chromium. The interaction of bichromate with the biopolymer adsorbent depends on the contact or residence time of the adsorbate with the adsorbent. The results presented in Table 4 indicate an optimum flow rate of 5 mL min^{-1} and a bed height greater than 3 cm ensures quantitative adsorption of chromium(VI) from aqueous solution. At low flow rates, there exists an effective contact between the bichromate anion and the adsorbent. Similarly, a low bed height also results in lesser adsorption of chromium since the amount of the adsorbent used in the packing of the column is insufficient for the complete
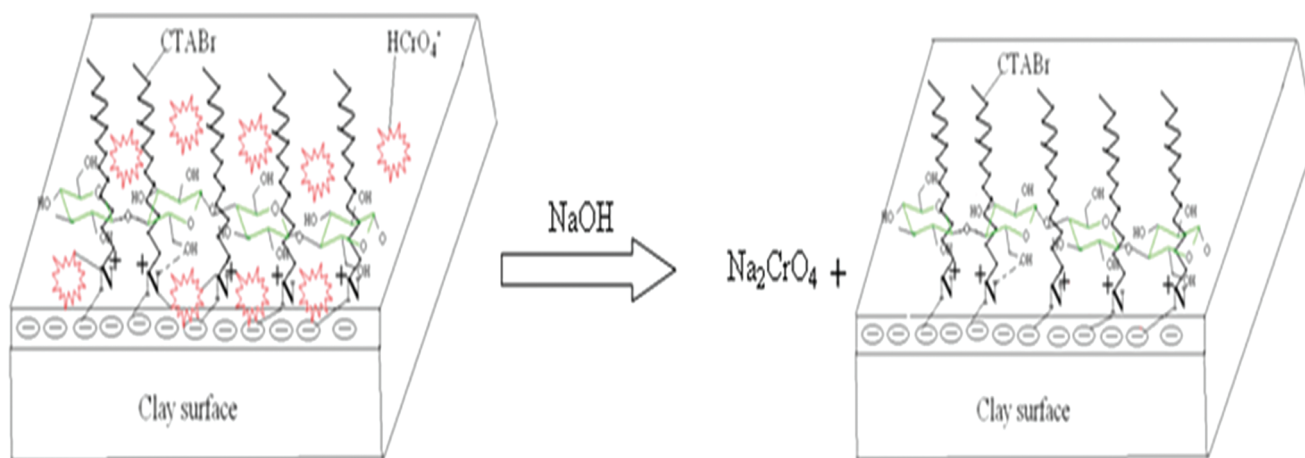
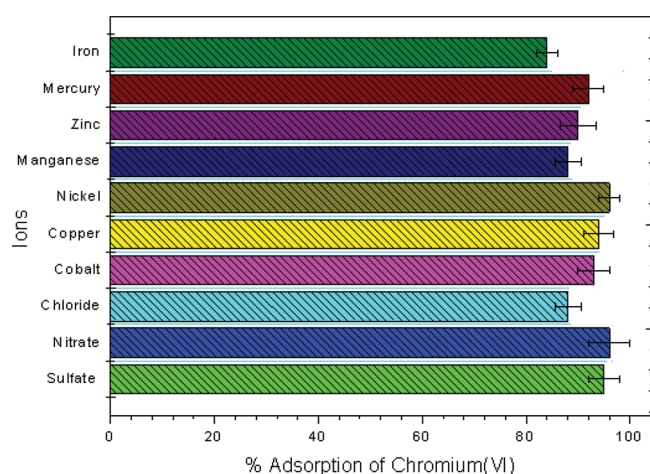**Figure 7.** Conceptual illustration showing the regeneration of the adsorbent.

Figure 8. Effect of diverse ions.

Table 5. Characteristics of Chrome Tan Waste Liquor

constituents	concentration ($mg\ L^{-1}$)
total dissolved solids	1270
zinc	5.2
copper	3.5
iron	7.2
manganese	1.0
nickel	1.1
chloride	1520
cadmium	0.5
sulfate	840
lead	1.2
carbonate	17.0
nitrate	560
phosphate	320
total chromium	190

retention of chromium. A flow rate of 5 mL min^{-1} was maintained for maximum column efficiency and effective retention of chromium. At higher flow rates, there was a decrease in the column adsorption efficiency and this could be ascribed to the lesser contact time between the sample and the biopolymer—clay composite adsorbent.

3.14. Regeneration and Reusability of the Biopolymer Clay Composite Adsorbent. The regeneration of adsorbent is important from a greener perspective and hence it is imperative to look for effective and nontoxic eluents for the quantitative recovery of chromium. Considering the above aspect, reagents, such as sodium hydroxide, as well as reducing agents like sodium sulfite and ascorbic acid, were examined for effective desorption. These reagents have also proved their efficacy in some of our earlier studies[8,64−66] pertaining to the removal of chromium. Ascorbic acid was quite effective in reducing Cr(VI) to the less toxic Cr(III). Nevertheless, the recovery was only 85% with 15 mL of the eluent and a larger volume (2×10 mL) of the reagent was required for quantitative desorption of chromium as Cr(III). The overall mechanism of this reduction is well established and is recognized to proceed through a Cr(IV) intermediate.[67] In the proposed methodology, we found that with three replicate measurements, an 8 mL volume of 3 mol L^{-1} sodium hydroxide

was effective in the quantitative elution (99 ± 0.3%) of chromium(VI) as sodium chromate in the eluate (Figure 7). The adsorbent could be reused for 10 adsorption—desorption cycles with good efficiency. Beyond 10 cycles, the repeated use of acidic and alkaline medium for the adsorption and desorption of chromium(VI) decreased the performance efficiency of the column. This could be attributed to the decrease in the effective interaction between the adsorbent and the adsorbate due to the nonavailability of active sites for adsorption.

3.15. Interference of Diverse Ions. To apply the solid phase extraction methodology to real effluent samples, it is essential to study the interfering effect of diverse ions that are usually associated with these effluents. The effect of diverse ions were studied at 50 mg L^{-1} Cr(VI) concentration, maintaining a sample volume of 250 mL. Ions such as Ca^{2+} and Mg^{2+} did not cause any interference up to 800 mg L^{-1} level. Lower concentrations of anions (<500 mg L^{-1}), such as chloride, nitrate, and sulfate, did not affect the quantitative adsorption of chromium. However, considerable interference was observed because of the cations, such as Co^{2+}, Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+}, and Hg^{2+}, at 600 mg L^{-1} level in the presence of 750 mg L^{-1} chloride. The results presented in the bar diagram (Figure 8) illustrates the above fact, and this could be attributed to the order of stability of the chloro

Table 6. Comparison with Similar Clay-Based Adsorbents in Terms of the Adsorption Capacity

Sl. No	nature of the adsorbent	adsorption capacity (mg g^{-1})	ref
1	chitosan-NaMMT (unmodified clay)	9.36	69
2	HDTMA modified montmorillonite clay	7.28	70
4	Fe (II)-stevensite	2.54	71
5	hydroxyaluminum modified montmorillonite clay	11.97	72
6	acid activated kaolinite	13.9	73
7	cellulose-NaMMT composite	22.2	present work

complexes of these metal ions. The stability of the high spin complex chloro-anions[68] follows the order $Ni^{2+} < Mn^{2+} < Co^{2+} < Cu^{2+} < Fe^{3+} < Zn^{2+}$. Iron in the +2 oxidation state could act as a reducing agent and interferes by reducing the Cr(VI) to Cr(III). The negatively charged high spin metal complexes could contend with the bichromate anion for the active sites in the biopolymer-composite adsorbent, thereby, leading to a decrease in the percentage adsorption of chromium. A similar phenomena arising from the competing nature of the halocomplexes has also been observed in our earlier studies pertaining to the removal of chromium.[8] Anions, such as chloride, nitrate, and sulfate, could also directly compete with the bichromate anion for the effective adsorption sites at higher concentrations (>500 mg L^{-1}) causing a reduction in the percentage adsorption of chromium.

3.16. Application to a Real Industrial Effluent. The performance of the composite material was investigated for the detoxification of chromium from a chrome tannery leather effluent. The chrome tan waste liquor at the time of collection was green in color with a pH value of 6.5, and it is the basic chromium sulfate, which is used in tanning of the leather. The distinct characteristics of the effluent sample procured from a leather tannery unit are given in Table 5. Prior to the adsorption, it is essential to destroy the organic components present in the sample, and this was achieved by treatment with nitric acid-sulfuric acid mixture. The Cr(III) present in the sample is oxidized to the +6 oxidation state using hydrogen peroxide in alkaline medium.[8,66] A 100 mL volume of the concentrated effluent sample was diluted to 500 mL, and a known volume of the diluted effluent (300 mL) was passed through the glass column packed with the adsorbent by maintaining the optimum pH required for the adsorption of Cr(VI). Five replicate measurements ensured effective adsorption of chromium (97.5 ± 0.25%), and this was confirmed through the spectrophotometric determination of chromium in the treated effluent. In the diluted effluent sample, anions such as chloride, nitrate, sulfate and commonly present cations such as calcium, magnesium, zinc, copper, etc., did not cause any appreciable reduction in the removal efficiency of chromium. After the effective adsorption and removal of chromium from the effluent sample, the regeneration of the column was also effective with sodium hydroxide as the eluent.

3.17. Comparison with Similar Clay-Based Solid-Phase Adsorbents. The effectiveness of biopolymer−clay adsorbent was compared in terms of the adsorption capacity with some of the clay-based adsorbents recently reported in literature. The results are given in Table 6, and it is evident that the surfactant modified biopolymer clay adsorbent shows a reasonably good adsorption capacity for chromium.

4. CONCLUSIONS

In conclusion, the interaction between the cellulose and NaMMT has demonstrated the potential application of a biopolymer composite material for the effective adsorption of chromium. The biopolymer composite exhibits an adsorption capacity of 22.2 mg g^{-1} and the experimental data showed a good fit to the Langmuir adsorption isotherm model. The spontaneity of adsorption was ascertained from the thermodynamic properties and the experimental data showed excellent adherence to second order kinetics. The mesoporous nature of the material was established from the nitrogen adsorption isotherm study and there is no significant change in the crystalline nature of the composite adsorbent after the adsorption of chromium. A sample volume of 400 mL could be quantitatively treated by column method at 100 mg L^{-1} concentration of Cr(VI) with a pre-concentration factor of 50. The efficiency of the method is well illustrated in terms of regeneration of the composite material in a facile manner. The adsorbent could be reused with quantitative recovery for 10 cycles, and its applicability to detoxify chromium from wastewater has shown good prospects in addressing the global environmental concern for heavy metal pollution.

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