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Microwave assisted preparation and characterization of biopolymer-clay composite material and its application for chromium detoxification from industrial effluent

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ABSTRACT

The microwave assisted preparation and characterization of chitosan-surfactant modified NaMMT clay composite material is discussed, followed by its interesting application to detoxify heavy metal chromium. Cr(VI) could be effectively adsorbed in a weakly acidic medium (pH 5) from a large sample volume. The composite material before and after the adsorption of chromium was scrupulously characterized using FT-IR, SEM, XRD and EDX techniques. The XRD study revealed the crystalline nature of the composite material with sharp and symmetric peaks. The bichromate ion forms an ion-pair with the protonated amine group in chitosan and this is reflected in the appearance of a Cr=O peak at 916 cm^{-1} in IR study. The surface hydroxyl groups in clay can be protonated and this could also serve as a source of electrostatic interaction with the bichromate oxyanion. The material exhibited a superior adsorption capacity of 133 mg g^{-1} and the adsorption data fitted well with Langmuir and Freundlich isotherm models. The composite adsorbent material exhibits a pore size of 3.5 nm at maximum pore volume of 0.16 cm^3g^{-1}. The BET surface area of the material obtained from N_2 adsorption was found to be 52 m^2g^{-1}. The experimental data also showed a good correspondence to the pseudo second order kinetics and the sorption thermodynamics correlated to the endothermic nature of the adsorption. The adsorbent could be regenerated using ascorbic acid or sodium sulfite which is indicative of the greener aspect in the methodology. Copyright © 2011 VBRI press.

Keywords: Chitosan; surfactant modified montmorillonite; microwave assisted method; chromium(VI); regeneration.

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Introduction

The environmental impact of heavy metals such as chromium emanating from industrial units is an important problem to be addressed [**1**]. Chromium in the +6 oxidation state is a known carcinogen, while the +3 oxidation state is vital for glucose metabolism [**2**]. Hence, there is an increasing need to develop biodegradable and efficient sorbent materials for effective detoxification of chromium from a large sample volume. Solid phase extraction is one of the best techniques suited for heavy metal adsorption [**3, 4**]. Potato starch-silica nanobiocomposite is known for its excellent adsorption for heavy metal cadmium from aqueous solution [**4**]. In this context, biopolymers deserve special mention for their potential application in waste water treatment [**5**]. Cellulose modified with beta cyclodextrin and quaternary ammonium groups has been recently reported for the effective adsorption of chromium [**6**]. Polymer-clay composites have also found interesting and flexible applications ranging from packaging to drug delivery [**7**]. Poly (etheretherketone) clay composites are known for their high performance characteristics [**8**]. Some interesting mechanical properties and morphological characteristics of silicone/montmorillonite nanocomposites prepared by in-situ intercalative polymerization have been reported [**9**]. Chitosan is an interesting gluosamine biopolymer with free amino groups available for interaction with metals [**10**]. The composite chitosan-clay hybrid material offers more exciting properties in its application as electrochemical sensor for various oxyanions [**11**]. The mechanism involves the intercalation of chitosan as a bilayer in the clay matrix [**12**]. Carboxymethyl chitosan is known for its interesting application in drug delivery [**13**]. Chitosan-alumina composite material has been utilized for the removal of arsenate [**14**] and chromium [**15**] respectively. Xanthated chitosan has also proved to be an effective sorbent for chromium [**16**]. The interaction of chromate with surfactant modified NaMMT has been studied [**17**]. It is worth mentioning here that conventionally prepared chitosan-NaMMT (unmodified clay) has been tested in preliminary batch study for the adsorption of chromium [**18, 19**]. However, with a view to enhance the adsorption capacity and to detoxify chromium from real industrial effluents, an unconventional methodology is proposed using surfactant modified NaMMT clay material and chitosan. Surfactant modification of clays is essential for effective compatibility between the hydrophilic clay and the biopolymer [**7**]. Upon treatment with long chain quaternary ammonium cations, the clays acquire organophilic character. CTABr is an excellent choice for such surface modification, where the alkyl ammonium cation replaces the Na^+ in the clay matrix [**20**]. The various methods by which the biopolymer clay composites can be prepared are (a) melt intercalation (b) direct insertion of polymer in the host layer lattice [**21**]. Microwave assisted or dielectric heating is known for its increased efficiency and compact time for the preparation of polymer composites. A novel composite material prepared by microwave assisted reaction of sucrose with layered silicates is known for their potential sensor applications [**22**]. The microwave assisted graft copolymerization of sunn hemp fibers chemically modified with ethyl acrylate and binary monomers are known for their improved mechanical and thermal stability [**23**]. Chitosan grafted styrene prepared by microwave irradiation has been reported for very effective removal of chromium(VI) with an excellent adsorption capacity of 529 mg g^{-1} in accordance with the Langmuir isotherm model [**24**].

To the best of our knowledge, there is no literature report on the application of microwave assisted preparation of chitosan-clay (surfactant modified) composite material for the removal of chromium from a large volume of real effluents. In the present work, we propose the microwave assisted preparation and characterization of surfactant modified NaMMT-chitosan composite material followed by its application to detoxify chromium from a large sample volume.

Experimental

Reagents

Analytical grade reagents were used throughout. The aqueous solutions were prepared using MilliQ water (Elix 3). 0.2828 g of potassium dichromate (Merck, India) was diluted to 100 mL to give 1000 mg L^{-1} Cr(VI). A working solution of 70 mg L^{-1} Cr(VI) was prepared by appropriate dilution. Chitosan and montmorillonite clay were procured from Sigma Aldrich. Cetyltrimethylammoniumbromide (CTABr) was purchased from Sisco Research Laboratories, India, and a 0.01 mol L^{-1} solution was prepared by appropriate dilution with water. The pH of the medium was adjusted using sulfuric acid and sodium hydroxide (Merck, India) respectively. Ascorbic acid and sodium sulfite (Merck, India) of the required concentration were prepared by appropriate dilution. Methanol (Merck, India) was used as such without further purification.

Instrumentation

Characterization of the composite material: The composite material was characterized using FT-IR, XRD, SEM, EDX and BET surface area studies. The FT-IR study was performed using a Jasco- 4200 FT-IR spectrometer. XRD measurements were taken with Panalytical diffractometer using Cu Kα (40 kV, 35mA) radiation and a secondary beam graphite monochromator. The spectra were recorded in the 2θ range 5 to 55 degrees. Leica Stereoscan 440 Scanning electron microscope was used for recording the

SEM images of the composite material. The energy dispersive X ray spectrum was recorded with Hitachi S-3000H analyzer. BET surface area, pore size and pore volume measurements were performed using a Micromeritics Porosimeter model ASAP2020 analyzer.

Analysis of chromium: The batch adsorption study was performed using Orbital incubator shaker supplied by Biotechnics, India. Elico LI-127 model pH meter (Elico, India) was used for pH measurements. The concentration of chromium was determined spectrophotometrically by the standard diphenyl carbazide method using Jasco V-650 UV-Visible spectrophotometer.

Preparation of surfactant modified sodium montmorillonite (NaMMT)

The MMT clay (6 g approx) was mixed with 200 mL of 1.0 mol L^{-1} NaCl and the mixture was stirred magnetically for 18 h [**25**]. The resulting suspension was centrifuged and the supernatant discarded. The clay suspension was washed several times with Milli-Q water until no precipitate was observed in the filtrate with $AgNO_3$. This ensures the removal of chloride ions completely. The prepared NaMMT was dried and a small quantity of methanol (5 mL) was added so as to craft the clay less sticky and adaptable [**17**]. The sodium form of the clay was stirred magnetically with 100 mL of 0.01 mol L^{-1} CTABr for 6 h. The mixture was centrifuged and the solid was washed with water and tested with $AgNO_3$ for the absence of bromide in the solution phase.

Microwave assisted preparation of the composite material

About 3 g of chitosan was dissolved in 10 mL of 1 % v/v acetic acid and the pH was adjusted to 5.0 with NaOH solution. 6 g of the surfactant modified NaMMT clay material was dispersed in 10 mL of methanol and the chitosan solution was slowly added to the clay suspension and stirred magnetically for about 5 min to ensure homogeneity. The mixture was then irradiated under microwave conditions for 30 min with 1 min time interval. Every minute, a small quantity of methanol was added, made as a paste and further irradiated with MW. This process was continued for 30 min and the prepared composite material was dried in hot air oven at 120 ^{o}C for 6 h. The composite material was then characterized by various analytical techniques and used subsequently for the adsorption of chromium.

Batch adsorption studies

The batch adsorption was studied by equilibrating 0.5 g of the composite material in a conical flask containing 70 mg L^{-1} Cr(VI). The pH of the medium was maintained at 5.0 and the reaction mixture was equilibrated in orbital incubator shaker at room temperature at 150 rpm at various time intervals and the amount of chromium(VI) adsorbed (q_t) can be expressed as:

$$q_t = \frac{(C_o - C_t) \times V}{W} \qquad (1)$$

where C_o and C_t are the initial and final aqueous phase concentrations of the chromium(VI) in mg L^{-1} , V is the volume of the solution (L) and W is the weight of the adsorbent (g). The amount of Cr(VI) adsorbed on the composite material was calculated by measuring the concentration of chromium left in the aqueous solution spectrophotometrically after complexation with diphenyl carbazide in acidic medium.

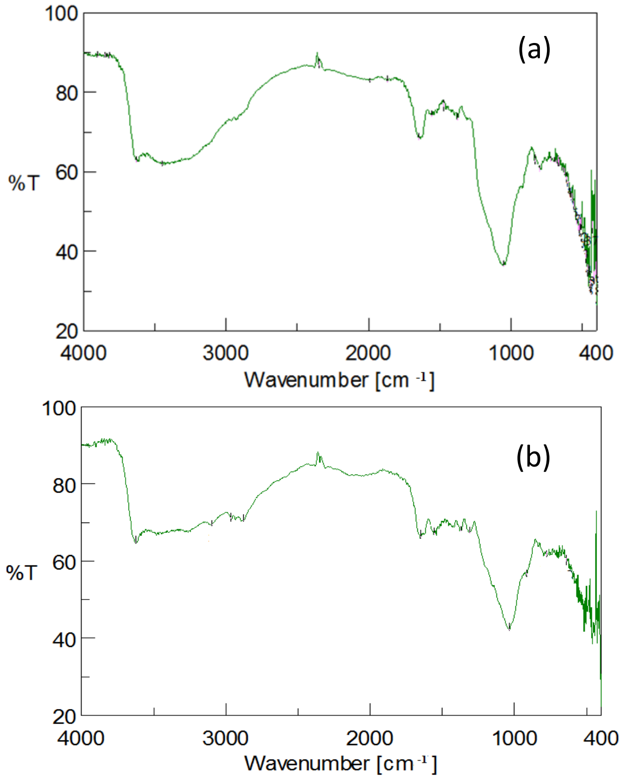

Fig. 1. FT-IR spectrum of the (a) composite adsorbent, and (b) obtained after chromium(VI) adsorption.

Results and discussion

Characterization of the chitosan-clay composite by FT-IR spectroscopy

The infra red spectrum of the Chitosan-NaMMT (**Fig. 1a, b**) shows the combination of characteristic absorptions due to chitosan and the clay material as reported earlier in literature [**12, 26, 27**]. The FT-IR spectrum shows the following characteristic bands: 3627 cm^{-1}(O-H stretching), 3445 cm^{-1} (Hydrogen bonded water), 1645 cm^{-1} (O-H deformation). The band corresponding to 1867 cm^{-1} could be ascribed to the ν_{CO} stretching frequency of acetate ions associated with chitosan [**12**]. In addition, distinct bands are observed at 833 cm^{-1} (Al-Fe-OH deformation) 800 cm^{-1}(Si-O stretching) 694 cm^{-1} (Si-O deformation) 613 cm^{-1} (Al-O and Si-O out of plane) 577 cm^{-1}(Al-O-Si deformation), 1472 (N–H bending), 1377 cm^{-1} (C-H bending) and 1051 cm^{-1} (C–O stretching) respectively. There is a considerable modification in the spectral features after the adsorption of chromium(VI), Hexavalent chromium exists principally as bichromate ion ($HCrO_4^-$) in weakly acidic medium [**28**]. The vibrational bands at 1557 cm^{-1} corresponding to N-H deformation mode in chitosan are shifted towards lower frequency with also considerable reduction in the peak intensity after the adsorption of chromium. This indicates that the free amino group in chitosan plays an important role in the mechanism [**12**]. The primary amine group is protonated and the NH_3^+ cation is electrostatically bound to $HCrO_4^-$ in acidic medium. This fact is also confirmed through the characteristic Cr=O peak at 916 cm^{-1} [**29-31**].

Optimization of pH and mechanism of adsorption

The optimisation of pH is an important factor in sorption studies. The optimum pH for the adsorption of Cr(VI) was found to be in the range 4-5 which corresponds to a weakly acidic medium. As mentioned earlier, in weakly acidic medium the bichromate ion forms an ion-pair with the protonated amine group in chitosan and this has also been substantiated by the IR study. It is also possible that in acidic medium, the surface hydroxyl groups in clay can be protonated and this could also serve as a source of electrostatic interaction with the bichromate oxyanion. Beyond pH 5 the percentage adsorption decreases and at alkaline pH there is a considerable decrease in the adsorption of chromium. This could be attributed to the deprotonation of the surface hydroxyl groups [**32**] in the composite material which causes the decrease in adsorption.

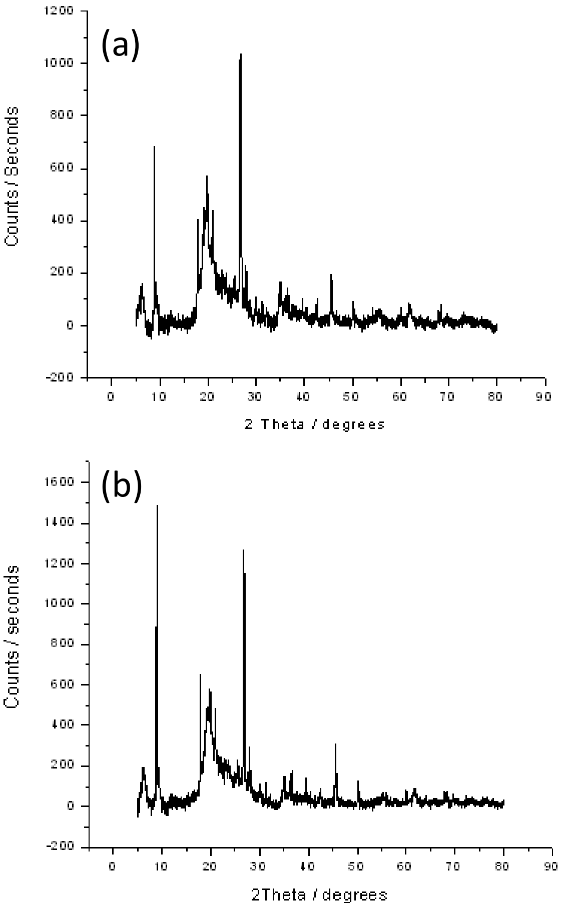

Fig. 2. Powder XRD pattern of the (a) composite adsorbent, and (b) obtained after chromium(VI) adsorption.

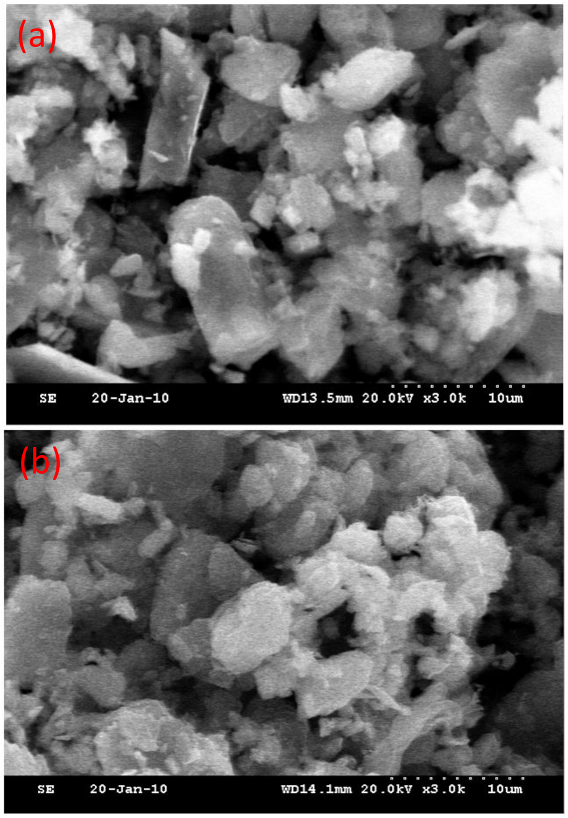

Fig. 3. SEM image of the (a) composite adsorbent, and (b) obtained after chromium(VI) adsorption.

Effect of amount of adsorbent

The amount of the composite adsorbent was varied from 0.2 g to 1.0 g with a constant initial concentration of 70 mg L^{-1} and agitation time of 40 min. The extent of adsorption (%) enhanced with increase in the amount of adsorbent. The availability of increasing number of active adsorption sites ensured the enhanced uptake of chromium(VI). This is a common phenomenon in adsorption, when the number of active sites or the effective surface area is increased. The quantitative adsorption efficiency (>99 %) was attained with 0.5 g of the composite adsorbent material. However, beyond 0.5 g the % adsorption is constant, due to the saturation of effective adsorption sites for the retention of Cr(VI).

Powder XRD, SEM and EDX analysis of the composite material

The wide angle X ray diffraction (WAXRD) of the composite material shows sharp and symmetric diffraction peaks (**Fig. 2a, b**) at 2θ values corresponding to 8.84^0, 17.88^0, 19.70^0, 26.92^0 which is indicative of the crystalline and exfoliated nature of the material. Considerable degree of exfoliation is known in polar polymers [**33**]. The SEM images (**Fig. 3a, b**) also show good difference in the surface morphology after the adsorption of chromium with the appearance of glossy particles on the surface of the adsorbent. The intercalative or exfoliated nature of the polymer composite depends on the amount of the added clay. When the amount of added clay is less, the silicate layers would be dispersed or exfoliated in the polymeric matrix [**34**]. The organophilicity of the clays leads to a better interaction with the biopolymer chitosan, resulting in a good dispersion and tendency to exfoliate in the matrix. The significant sharp peaks at higher 2θ values indicate a relatively more ordered distribution of clay layers in the biopolymer composite. At lower angles ($<10^0$) peak sharpening is slightly reduced and this could reflect a less ordered morphology [**33**]. After the adsorption of chromium, the crystallinity of the composite material is retained with the appearance of a new sharp peak at 2θ value corresponding to 35.20^0 which is characteristic of chromium adsorption and this is in close agreement with the earlier reported value in literature [**35**]. The adsorption of chromium on the surface of the composite material was confirmed from the energy dispersive X ray spectrum (**Fig. 4**) which shows the presence of chromium (observed in the range 5-6 keV) with the other elemental constituents.

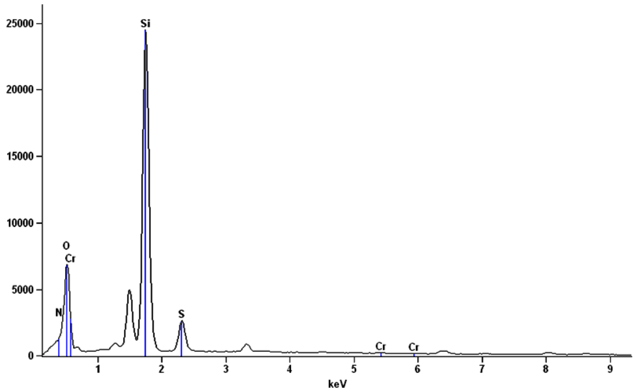

Fig. 4. Energy dispersive X ray spectrum of the adsorbed Cr(VI) on the composite material

Adsorption hysteresis

The adsorption hysteresis can be classified as Type IV isotherm with an inflexion at P/Po= 0.4 (**Fig. 5a**). The shape of the isotherm indicates the mesoporosity in the composite material [**36**]. The Barret-Joyner-Halenda (BJH) pore size distribution curve (**Fig. 5b**) for the composite adsorbent material gives a pore size of 3.5 nm at maximum pore volume of 0.16 $cm^3 g^{-1}$. The BET surface area of the material obtained from N_2 adsorption was found to be 52 m^2 g^{-1}. The effective surface area, mesoporous nature of the composite material and the nano pore size reflect the effectiveness in the adsorption of chromium.

Adsorption isotherm

The experimental data were fitted into the Langmuir and Freundlich isotherm models [**37, 38**]. The Langmuir model assumes monolayer adsorption and the maximum adsorption capacity was obtained from the expression

$$q_e = \frac{q_o b\, C_e}{1+bC_e} \qquad (2)$$

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 (L mg^{-1}) is the Langmuir constant.

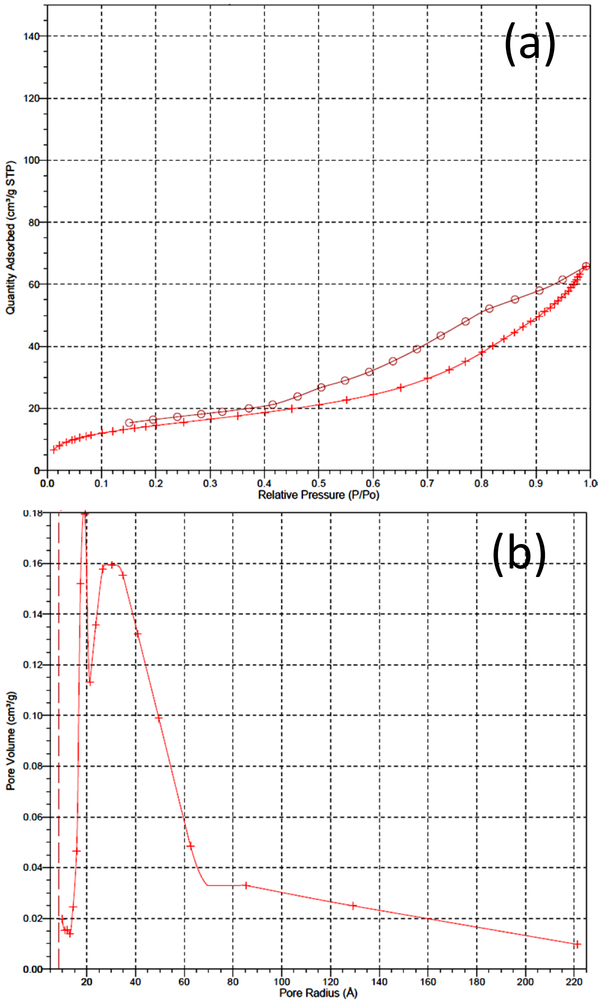

Fig. 5. (a) Nitrogen adsorption and desorption isotherm, and (b) BJH pore distribution curve.

The maximum adsorption capacity, q_o and the constant b obtained from the slope and intercept of the plot of C_e/q_e against C_e (**Fig. 6a**) were found to be 133 mg g^{-1} and 0.0884 L mg^{-1} respectively. The Langmuir isotherm model also provides another vital parameter, R_L, a dimensionless constant expressed as $1/(1 + b.C_0)$. It is known in many adsorption systems that the value of R_L in the range 0 to 1 signifies favorable adsorption [**39**]. In the present investigation, the value of R_L for the adsorption of chromium on the composite material was found to be 0.1391 and this indicates effective adsorption under the optimized experimental conditions. The well known Freundlich isotherm expression for adsorption from aqueous solution is represented as

$$q_e = K_F.C_e^{1/n} \qquad (3)$$

where C_e is the equilibrium concentration of the metal ion in mg L^{-1} q_e is the amount adsorbed in mg g^{-1}, K_F and n are the Freundlich constants which indicate the adsorption capacity and the adsorption intensity respectively. The constants K_F and n were found to be 11.51 $mg^{1-1/n}$ g^{-1} $L^{1/n}$ and 1.4355 obtained from the slope and intercept of the plot of log q_e against log C_e (**Fig. 6b**). The regression coefficients obtained from the Langmiuir and Freundlich plots were found to be 0.99 and 0.98 respectively and this indicates the applicability of both these isotherm models to the experimental data.

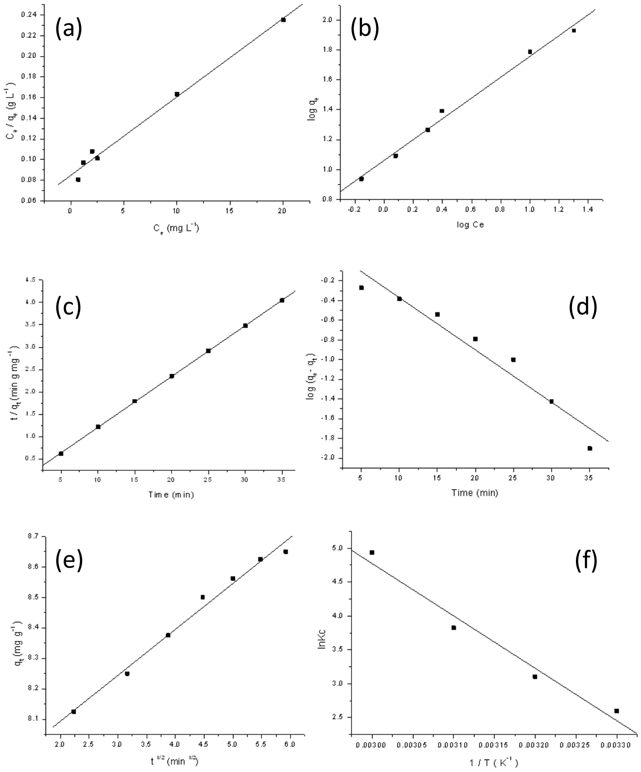

Fig. 6. (a) Langmuir isotherm, (b) Freundlich isotherm, (c) Pseudo second order kinetic plot, (d) Pseudo first order kinetic plot, (e) Plot of q_t versus square root of time, and (f) Van't Hoff plot showing the variation of $\ln K_c$ against reciprocal of temperature.

Kinetics of adsorption

The rate of adsorption increased with time and reached its maximum at 40 min. The first order and pseudo second order models were used to fit the experimentally obtained adsorption data. The first order [40] and the pseudo-second order rate equations [41] can be expressed as follows.

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \qquad (4)$$

The plot of t/q_t versus t (**Fig. 6c**) and log (q_e –q_t) versus t (**Fig. 6d**) gives the kinetic parameters. The adsorption data was well in agreement with the pseudo second order model in view of the higher regression coefficients (**Table 1**). Moreover, the q_e value obtained from the second order model and the $q_e$value obtained experimentally were found to be 8.779 mg g^{-1} and 8.125 mg g^{-1}, respectively. The close agreement between the experimental and calculated values further confirms the applicability of the second order kinetics. A plot of q_t against the square root of time gives a straight line with a definite intercept (**Fig. 6e**). This plot is linear and the slope gives the intraparticle rate constant k_{int} [**42**]. The nonzero intercept indicates that diffusion is not the only process that controls the adsorption of the metal ion on the composite material. Boundary layer control could also reflect on the adsorption process. This fact is consistent with the literature reports on similar phenomena observed in various other adsorbent-adsorbate interactions [**43**].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

Table 1. Kinetic parameters for the sorption of chromium (VI) on the composite material.

q_e (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	Regression coefficient	k_1 (min^{-1})	Regression coefficient	k_{int} (mg.g^{-1} min $^{-1/2}$)
8.779	0.1968	0.99	0.1222	0.94	0.1509

Sorption thermodynamics

The free energy, enthalpy and entropy change associated with the adsorption process was obtained from the sorption thermodynamics at different temperatures. The change in Gibb's free energy which reflects the spontaneity of the adsorption is related to the equilibrium constant by the well-known expression [**44**].

$$\Delta G^0 = -RT\ln K_c \qquad (6)$$

The equilibrium constant (K_c) is obtained from the ratio of the concentration of the adsorbed chromium in the composite material to the concentration left in solution. The well known Van't Hoff equation [**44**] also relates the equilibrium constant with enthalpy and entropy changes as a function of temperature. The equilibrium constant values were obtained at various temperatures and a plot of $\ln K_c$ against 1/T (**Fig. 6f**) gives the corresponding thermodynamic parameters. The free energy values were found to be ascendingly negative with rise in temperature. The negative free energy is a good indication of spontaneous adsorption. The enthalpy change (ΔH^0) was found to be positive which indicates the endothermic nature of adsorption (**Table 2**). The endothermic nature of adsorption has also been reported earlier for chromium adsorption using kaolinte clay in the absence of biopolymer [**45**]. The entropy of adsorption (ΔS^0) was also found to be positive and this is indicative of increased randomness at the adsorbent-solution interface. These facts demonstrate the efficacy of the composite material as an useful material for chromium(VI) adsorption.

Scale up to a larger sample volume

The above mentioned study of various optimized parameters has demonstrated the applicability of the material for detoxification of chromium from a larger sample volume. The polymeric composite was packed in a small glass column upto a height of 4 cm. A known volume of 150 mg L^{-1} Cr(VI) was transferred into the column at a flow rate of 4 mL min^{-1}. Cr(VI) was effectively retained on the column at pH 5.0 and this was confirmed by measuring the concentration of chromium spectrophotometrically in the solution phase. A maximum breakthrough volume of 500 mL could be achieved by this column study at 150 mg L^{-1} concentration of Cr(VI).

Table 2. Thermodynamic data for the adsorption of chromium (VI) on the composite material.

Temperature (K)	Conc. (mg L^{-1})	Equilibrium constant (K)	Free energy change (ΔG^0 k $Jmol^{-1}$)	Entropy change (ΔS^0J $mol^{-1}K^{-1}$)	Enthalpy change (ΔH^0k J mol^{-1})
300	70	22.33	-7.74	276.09	76
310	70	45.66	-9.84		
320	70	139	-13.12		

Table 3. Comparison of the adsorption capacity of the composite material with other sorbents.

Sl. No	Adsorbent	Method of preparation	Max adsorption capacity (mg g^{-1})	References
1	Surfactant modified Na MMT	Conventional	41.42	[**17**]
2	Chitosan-Na MMT (unmodified clay)	Conventional	9.36	[**18**]
3	Chitosan -Na MMT (unmodified clay)	Conventional	41.67	[**19**]
4	Cross-linked chitosan .	Conventional	50	[**48**]
5	Chitosan- surfactant modified Na MMT	Microwave assisted	133	Present work

Regeneration of the composite material

The regeneration of the composite material is an important fact that needs to be considered in the adsorption process. Since, Cr(VI) is toxic and carcinogenic, it is advisable to convert the chromium in +6 oxidation state to the less toxic +3 state. The adsorbed Cr(VI) could be effectively reduced with 0.1 mol L^{-1} sodium sulfite as well as 0.2 mol L^{-1} ascorbic acid respectively. These well-known reducing agents [**46, 47**] were found to be equally effective in the reduction of Cr(VI) with >99 % efficiency thereby regenerating the sorbent.

Application to a real industrial effluent

The performance of the composite material was tested for chromium detoxification from a leather tannery effluent. The effluent sample which contains Cr(III) as its major constituent(in addition to the organic matter) was oxidized to the +6 oxidation state using hydrogen peroxide in alkaline medium [**47**]. The organic constituents were decomposed initially by boiling the sample with nitric acid-sulfuric acid mixture. A known volume of the effluent (300 mL) was passed through the glass column containing the composite material at pH 5.0. The composite material could retain chromium quantitatively and the regeneration of the column was also equally effective.

Evaluation of performance efficiency of the composite sorbent

The effectiveness of this composite material for chromium removal is well illustrated by the adsorption capacity. The sorption capacity of the biopolymer composite was compared with other similar materials prepared by conventional method. As can be seen from the comparison data (**Table 3**), the composite chitosan material prepared under microwave conditions shows a higher adsorption capacity and is of admirable utility in the treatment of real industrial effluents containing chromium.

Conclusion

In conclusion, the chitosan-NaMMT clay composite prepared under microwave conditions has proved to very effective in the adsorption and removal of chromium from a large sample volume. The biopolymer composite exhibits an adsorption capacity of 133 mg g^{-1} and interestingly the crystallinity of the composite material was retained after adsorption of chromium. The mesoporous nature and the nano pore size prove to be a value addition for the retention of chromium. The study of the sorption thermodynamics indicates spontaneity and the endothermic nature of adsorption. The material could also be regenerated by using simple reducing agents, thereby making the process eco-friendly and benign.

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References

1. Cavaco, S.A.; Fernandes, S.; Quina, M.M; Ferreira, L.M. *J. Hazard. Mater.* **2007,** *144*, 634.
   DOI: 10.1016/j.jhazmat.2007.01.087
2. Rajesh, N.; Deepthi, B.; Archana, S. *J. Hazard. Mater*. **2007,** *144,* 464.
   DOI:10.1016/j.jhazmat.2006.10.059
3. Gupta, V.K.; Shrivastava, A.K.; Jain, N. *Water Res.* **2001,** *35,* 4079.
   DOI: 10.1016/S0043-1354(01)00138-5
4. Singh, V.; Singh, S.K.; Pandey, S.; Sanghi, R. *Adv. Mat. Lett.* **2010,** *1,* 40.
   DOI: 10.5185/amlett.2010.4107
5. Crini, G. *Prog. Polym. Sci.* **2005,** *30,* 38.
   DOI: 10.1016/j.progpolymsci.2004.11.002
6. Zhou, Y.; Jin, Q.; Zhu, T.; Akama, Y. *J. Hazard. Mater.* **2011,** *187,* 303.
   DOI: 10.1016/j.jhazmat.2011.01.025
7. Zeng, Q. H.; Yu, A. B.; Lu, G. Q.; Paul. D. R. *J. Nanosci. Nanotechnol*. **2005**, *5,* 1574.
   DOI: 10.1166/jnn.2005.411
8. Goyal. R.K.; Sahu, J.N. *Adv. Mat. Lett.* **2010,** *1,* 205.
   DOI: 10.5185/amlett.2010.8151
9. Yuan, X.; Tian, Z. *Adv. Mat. Lett.* **2010,** *1,* 135**.**
   DOI: 10.5185/amlett.2010.4119
10. Wanngah, W.S.; Teong, L.C.; Hanafiah, M.A.K.M. *Carbohydr. Polym.* **2011,** *83,*1446.
    DOI: 10.1016/j.carbpol.2010.11.004
11. Darder, M.; Colilla, M.; Ruiz-Hitzky. E. *Appl. Clay Sci.* **2005,** *28,*199.
    DOI: 10.1016/j.clay.2004.02.009
12. Darder, M.; Colilla, M.; Ruiz-Hitzky. E. *Chem. Mater.* **2003,** *15,* 3774.
    DOI: 10.1021/cm0343047

13. Mouryaa, V.K.; Inamdara, N. N.; Tiwari, A. *Adv. Mat. Lett.* **2010,** *1,* 11.

    DOI: 10.5185/amlett.2010.3108
14. Chauhan, V. S.; Yunus, M.; Sankararamakrishnan, N**.** *Adv. Mat. Lett.* **2010,** *3,* 225.

    DOI: 10.5185/amlett.2010.613
15. Boddu, V.; Abburi, K.; Talbott, J. L.; Smith, E. *Environ. Sci. Technol.* **2003**, *37,* 4449.

    DOI: 10.1021/es021013a
16. Chauhan, D.; Sankararamakrishnan, N. *J. Hazard. Mater.* **2011,** *185,* 55.

    DOI: 10.1016/j.jhazmat.2010.08.120
17. Krishna, B.S.; Murthy, D.S.R.; Jai Prakash, B.S. *J. Colloid Interface Sci.* **2000,** *229,* 230.

    DOI: 10.1006/jcis.2000.7015
18. Jong-Hyok An, J.; Dultz, S. *Clays Clay Miner.* **2008,** *56,* 549.

    DOI: 10.1346/CCMN.2008.0560508
19. Fan, D.; Zhu, X.; Xu, M.; Yan, J. *J. Biol. Sci.* **2006**, *6,* 941.

    DOI: 10.3923/jbs.2006.941.945
20. Wenhua, L.; Guangjie, Z. *Forestry Studies in China*. **2004,** *6,* 54.

    DOI: 10.1007/s11632-004-0010-8
21. Pomogailo, A.D. *J. Polym. Sci.* **2006,** *48,* 85.

    DOI:10.1134/S181123820601005X
22. Darder M.; Ruiz-Hitzky, E. *J. Mater. Chem.* **2005,** *15,* 3913.

    DOI: 10.1039/B505958E
23. Kalia, S.; Kumar, A.; Kaith, B.S. *Adv. Mat. Lett.* **2011,** *2,* 17.

    DOI: 10.5185/amlett.2010.6130
24. Sharma, A. K.; Mishra, A. K. *Adv. Mat. Lett*. **2010,** *1,* 59.

    DOI: 10.5185/amlett.2010.4120
25. Boufatit, M.; Ait-Ama. H. Desalination **2007,** *206,* 300.

    DOI: 10.1016/j.desal.2006.04.058
26. Monvisade, P.; Siriphannon, P. *Appl Clay Sci.* **2009,** *42,* 427.

    DOI: 10.1016/j.clay.2008.04.013
27. Katti, K.S.; Sikdar, D.; Katti, D.R.; Ghosh, P.; Verma, D. *Polymer.* **2006,** *47,* 403.

    DOI: 10.1016/j.polymer.2005.11.055
28. Venkateswaran, P.; Palanivelu, K. *Sep. Purif. Technol.* **2004,** *40,* 279.

    DOI:10.1016/j.seppur.2004.03.005
29. Hoffmann, M. M.; Darab, J. G.; Fulton, J. L. *J. Phys. Chem. A* **2001,** *105,*1772.

    DOI: 10.1021/jp0027041
30. Shahawi, M.S.E.; Hassan, S.S.M.; Othman, A.M.; Zyada, M.A.; Sonbathi,M.A.E. *Anal. Chim. Acta,* **2005,** *534,* 319.

    DOI: 10.1016/j.aca.2004.11.085
31. Harrison, P.G.; Lloyd, N.C.; Daniel, W.; Bailey, C.; Azelee, W. *Chem. Mater.* **1999,** *11,* 896.

    DOI: 10.1021/cm980347p
32. Hu, Q. H.; Qiao, S. Z.; Haghseresht, F.; Wilson, M. A.; Lu, G. Q. *Ind. Eng. Chem. Res.* **2006**,*45*,733.

    DOI: 10.1021/ie050889y
33. Ghosh, A. K.; Woo, E. M. *J. Mater. Chem.* **2004,** *14,* 3034.

    DOI: 10.1039/B407660E
34. Tronto, J.; Perotti, G. F.; Parrira, D. F.; Constantuno, V. R. L.; Lugao, A. B. *Proceedings of Polymer Processing Society 23rd annual meeting, Brazil,* **2003.**

    URL: http://www.poly-eng.uakron.edu/pps/pps-newsletter-april07.pdf
35. Lin, C. K.; Chen, J. N.; Lin, C. C. *J. Hazard. Mater.* **1997**, *56,* 21.

    DOI: 10.1016/S0304-3894(97)00032-0
36. Cai, G.B.; Zhao, G.Z.; Wang, X.K.; Yu, S.H.; *J. Phys. Chem. C* **2010,** *114,* 12948.

    DOI: 10.1021/jp103464p
37. Langmuir, I. *J. Am. Chem. Soc.* **1916,** *40,* 1361.

    DOI: 10.1021/ja02242a004
38. Skopp, J. *J. Chem. Educ.* **2009,** *86,* 1341.

    DOI: 10.1021/ed086p1341
39. Mohan, D.; Pittman Jr, C. U.; Bricka, M.; Smith, F.; Yancey, B.; Mohammad, J.; Steele, P. H.; Franco, M. F. A.; Serrano, V. G.; Gong, H. *J. Colloid Interface Sci.* **2007,** *310,* 57.

    DOI: 10.1016/j.jcis.2007.01.020
40. Rudzinski, W.; Plazinsk, W. *Langmuir* **2008,** 24, 5393.

    DOI: 10.1021/la800044
41. Ho, Y. S.; Mckay, G. *Process. Biochem.* **1999,** *34,* 451.

    DOI: 10.1016/S0032-9592(98)00112-5
42. Plazinski, W.; Rudzinsk,W. *J. Phys. Chem. C* 2009, 113, 12495.

    DOI: 10.1021/jp902914z
43. Bulut, E.; Ozacar, M.; Sengil, I.A. *Microporous Mesoporous Mater.* **2008,** *115,* 234.

    DOI: 10.1016/j.micromeso.2008.01.039
44. Atkins, P.; Paula, J. D. *Elements of Physical Chemistry* 4 th Ed. Oxford University Press, New York, **2005**, pp 161-171.

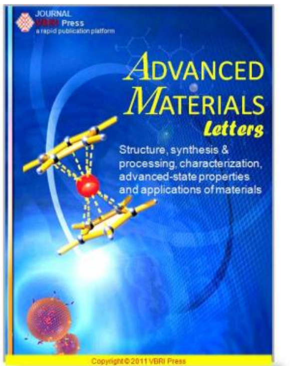
    ISBN: 9780195672527
45. Bhattacharyya, K. G.; Gupta, S. S. *Ind. Eng. Chem. Res*. **2006,** *45,* 7232.

    DOI: 10.1021/ie060586j
46. Kalidhasan S.; Rajesh, N. *J. Hazard. Mater.* **2009**, *170,* 1079.

    DOI: 10.1016/j.jhazmat.2009.05.071
47. Kalidhasan, S. Sricharan, S.; Ganesh, M.; Rajesh, N. *J. Chem. Eng. Data.* **2010,** *55,* 5627.

    DOI: 10.1021/je100518w
48. Schmuhl, R.; Krieg, H. M.; Keizer, K. *Water SA* **2001**, *27,* 1.

    Water SAISSN: 0378-4738



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