

Effective detoxification of hexavalent chromium using sulfate-crosslinked chitosan

Shashikant Kahu, D. Saravanan and Ravin Jugade

ABSTRACT

A sulfate-crosslinked chitosan (SCC) was prepared for effective detoxification of hexavalent chromium (Cr(VI)) from effluents. SCC was characterized using Fourier transform infrared, X-ray diffraction, scanning electron microscopy and energy dispersive X-ray studies. The maximum adsorption of Cr(VI) was observed at pH 6.0 with adsorption capacity of 157 mg/g in accordance with the Langmuir adsorption isotherm model. The adsorption process was found to follow the pseudo-second-order rate kinetics. From the study of various thermodynamic parameters (Gibbs energy, entropy and enthalpy changes), the adsorption capacity was found to decrease with increase in temperature. Column studies were carried out to obtain a breakthrough point of the adsorbent. The adsorbent was regenerated using sodium hydroxide with no change in the adsorption efficiency for up to 10 cycles. Effect of diverse ions on adsorption efficiency was studied and SCC was applied for Cr(VI) removal in synthetic effluents.

Key words | chitosan, chromium detoxification, SCC

Shashikant Kahu
Ravin Jugade (corresponding author)
Department of Chemistry,
R.T.M. Nagpur University,
Nagpur 440033,
India
E-mail: ravinj2001@yahoo.co.in

D. Saravanan
Department of Chemistry,
National College,
Tiruchirappalli 620001,
India

INTRODUCTION

Hexavalent chromium, Cr(VI), is a potent ecotoxicant as it is a carcinogen. Thus, there is a need to develop newer and more environmentally friendly techniques for the detoxification of Cr(VI). The effluents from tannery, electroplating, mining and dyeing industries contain two major species of chromium, which are Cr(III) and Cr(VI). Out of these, Cr(VI) is a potential carcinogen causing damage to DNA (Owlad *et al.* 2009), while Cr(III) is biologically essential in mammals for metabolic processes (Mertz 1976). The maximum permissible limit recommended by the World Health Organization for Cr(VI) in drinking water is 0.05 mg/L.

In the present study a chitosan, a linear polysaccharide of β -1,4-*O*-glycosyl-linked glucosamine, has been chemically modified and effectively used for the detoxification of Cr(VI). Chitosan is obtained by deacetylation of chitin, which is a major component of crustacean shells and fungal biomass. Chitosan proves to have wide applications in various fields (Ravi Kumar 2000). Since chitosan has biological origin, it shows interesting properties such as biocompatibility and biodegradability, and its degradation products are non-toxic (Crini 2005). Because of chemical stability, high reactivity, excellent chelation behavior and high selectivity toward heavy metals, chitosan is used as a

toxic metal scavenger (Alves & Mano 2008; Mourya & Inamdar 2008). Owing to the presence of the large number of free $-NH_2$ groups, metal cations can be removed in near neutral solutions (Benavente *et al.* 2011), and when the $-NH_2$ group is protonated it adsorbs anions by ion exchange (Boddu *et al.* 2003; Singh & Singh 2012).

Chitosan obtained from chitin is in the form of flakes or powder and so it has limited utility for adsorption of toxic elements. One of the important properties of chitosan is that it is insoluble in sulfuric acid. Since it has free amino groups, it is expected to react with sulfuric acid by forming the corresponding salt. Salts of chitosan with HCl and acetic acid are water soluble and form a gel. However, sulfate, being divalent, crosslinks the protonated chitosan chains, forming sulfate-crosslinked chitosan (SCC). Such cross-linking in chitosan has been reported by Mayyas (2012) who has prepared SCC for medicinal applications by treating chitosan hydrochloride gel with sodium sulfate. However, the synthesis method requires a long time, and applications of the product have not been fully exploited in wastewater treatment. Lasko *et al.* (2004) have used sulfuric acid pretreated chitosan for removal of Cr(VI). Since they did not wash the material prior to use for extraction of Cr(VI), it resulted in

decrease in pH, reducing adsorption capacities to just 60 mg/g. A critical review of various synthesis methods of sulfated chitin and chitosan with their applications has been reported (Jayakumar *et al.* 2007). However, applicability of SCC for extraction of Cr(VI) has never been exploited. In the present study, we report the preparation and characterization of SCC and its applicability in the removal of Cr(VI) by batch and column adsorption. The thermodynamics and kinetics parameters of adsorption have also been investigated.

METHODS

Materials

Chitosan with 85% degree of deacetylation was supplied by Uniloid Bio-Chemicals India Limited, Hyderabad (India). Diphenyl carbazide, sulfuric acid, sodium hydroxide and potassium dichromate were purchased from Merck, India, and were used without further purification. All the aqueous solutions were prepared using double distilled water.

Preparation of sulfate-crosslinked chitosan

About 5 g chitosan powder was taken in a round bottom flask. To it, 100 mL of 4% v/v sulfuric acid solution was added and stirred using a magnetic stirrer for 1 hour at room temperature (298 K). The reaction mixture was filtered and the residue was washed with double distilled water. The washings were tested for complete removal of sulfate ions to give a solid residue of SCC. The residue was dried at 60 °C in a hot air oven for 1 hour. The crosslinking phenomenon can be schematically represented as in Figure 1.

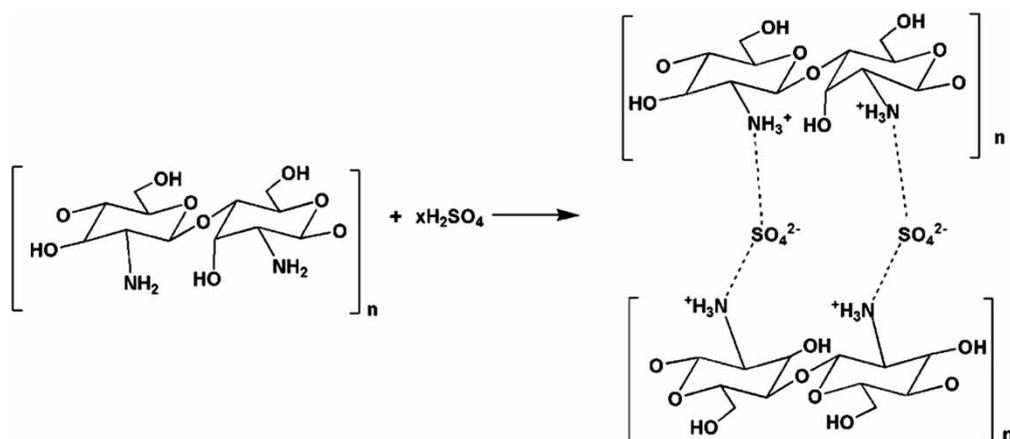


Figure 1 | Synthesis of SCC.

Characterization

The Fourier transform infrared (FT-IR) spectrum was recorded using a Shimadzu FT-IR 8101A spectrometer in the range 500–4,000 cm^{-1} to obtain structural information of SCC. The X-ray diffraction (XRD) measurements were taken by an X-ray diffractometer system, XPERT-PRO Analytical, using $\text{Cu-K}\alpha$ radiation. The surface morphology of the SCC was studied with the aid of the fully integrated computer-controlled digital scanning electron microscope (SEM) model TESCAN VEGA 3 SBH for high vacuum operation. Elemental spectra of adsorbent before and after the adsorption of Cr(VI) were recorded using an energy dispersive X-ray (EDX) analyser, Oxford INCA Energy 250 EDS System, during SEM observations, which helps for qualitative detection and localization of elements.

Batch adsorption experiments

Fifty millilitres of Cr(VI) solution with concentrations between 50 and 800 mg/L at pH 6.0 were equilibrated with 400 mg of SCC in stoppered conical flasks. The flasks were stirred using a magnetic stirrer at 298 K for 45 min. The amount of Cr(VI) adsorbed (mg/g) at equilibrium (q_e) can be given by

$$q_e = \frac{C_0 - C_e}{W} \times V \quad (1)$$

where C_0 and C_e are the initial and equilibrium liquid phase concentrations (mg/L) of Cr(VI) respectively, V is the volume of aqueous solution (L) and W is the weight (g) of the SCC used in the batch adsorption study. All the adsorption experiments were performed with three replicates to obtain reliable results.

Column studies

After optimizing the parameters in batch study, the applicability of the SCC was examined for the detoxification of Cr(VI) for a larger sample volume. A glass column 1 cm in diameter and 30 cm in length was used for the column adsorption study. Then 1.0 g of SCC was packed in the glass column to a height of 6 cm and Cr(VI) solution was introduced at a flow rate of 5 mL/min at pH 6.0. The eluent was analyzed spectrophotometrically for the concentration of chromium in solution phase.

Regeneration of SCC

The adsorbent regeneration is important from an environmental perspective. Considering this aspect, reagents such as sodium hydroxide and sulfuric acid were examined for effective desorption. The best results were obtained with 10% (w/v) NaOH solution. Five grams of SCC with adsorbed Cr(VI) was placed in a round-bottomed flask; 50 mL of 10% NaOH solution was added to it and boiled for 15 min. The reaction mixture was cooled, filtered and then washed with distilled water to give back the chitosan. It was sulfate-crosslinked as explained previously. The SCC was examined for 10 adsorption-desorption cycles.

Analysis

The concentration of Cr(VI) in the solution phase was determined by a Spectronic 20D+ spectrophotometer at various stages of the adsorption process by the standard diphenylcarbazide method (Mendham et al. 2002) at 540 nm using 1 cm matched quartz cuvettes. The pH measurements were done using an Equiptronics model EQ-615 pH meter and the pH was adjusted using dilute H₂SO₄ and NaOH solutions. After adsorption of Cr(VI) on SCC, the sample solution was filtered and the filtrate was treated with diphenylcarbazide, developing a pink color. The absorbance was recorded and quantitation was done from the calibration curve.

RESULTS AND DISCUSSION

Characterization of sulfate-crosslinked chitosan

The SCC was characterized thoroughly using various techniques: FT-IR, XRD, SEM and elemental analysis by EDX. These studies clearly indicate sulfate-crosslinking in

chitosan and adsorption of Cr(VI) during extraction. The FT-IR spectral analysis of chitosan and SCC showed characteristic broad peaks corresponding to O—H and N—H stretching vibrations in the regions 3,300 and 3,500 cm⁻¹, N—H bending vibration around 1,585 cm⁻¹, C—N bending vibration at 1,375 cm⁻¹ and C—H and C—O stretching bands around 2,880 and 1,070 cm⁻¹ (Figure 2). After treatment with sulfuric acid, the characteristic peak due to the sulfate group appeared at around 620 and 1,110 cm⁻¹ (Mayyas 2012).

The adsorbent was also characterized by XRD. The patterns of chitosan, SCC and with adsorbed Cr(VI) are depicted in Figure 2. Characteristic peaks of chitosan were observed at $2\theta = 10.4288$ and 19.6908° and, after reaction with sulfuric acid, the previous peaks disappeared and new peaks corresponding to $2\theta = 11.5519$ and 18.2605° were observed, which clearly indicates the formation of SCC. After adsorption, an additional peak was observed at $2\theta = 26.7227^\circ$ which is of Cr(VI) in accordance with the reported value (Omotoso et al. 1995; Srinivasa Rao et al. 2007).

SEM micrographs of the chitosan, SCC and with adsorbed Cr(VI) were recorded (Figure 2). It can be seen from the SEM micrograph of the raw chitosan that particles were mostly irregular in shape and had loose surfaces, while, in the SEM micrograph of SCC, particles showed regular arrangement. The presence of shiny and bright spots in the SEM images highlights the electrostatic affinity between the SCC and Cr(VI). This testifies to the fact that chromium is indeed adsorbed on the adsorbent surface by interacting with the protonated amine groups in the biopolymer matrix.

The EDX spectrum of chitosan clearly indicates elemental constituents such as carbon, oxygen and nitrogen. After the reaction of chitosan with sulfuric acid, there occurs a peak of sulfur in the EDX spectrum of SCC along with the other elements. Peaks due to chromium are clearly visible after adsorption of chromium on SCC. The K_α and K_β peaks of chromium could be clearly seen in the EDX spectrum (Figure 2).

Effect of contact time

The effect of contact time on the adsorption of chromium was studied by varying the contact time in the range 5–75 min with initial Cr(VI) concentration of 50 mg/L at 298 K. It was observed that the rate of adsorption of chromium is higher at the beginning and decreases with increase in time. Equilibrium extraction of $(99.2 \pm 0.3)\%$ Cr(VI) was attained in about 45 min (Figure 3(a)). Therefore, for further studies the contact time was fixed as 45 min.

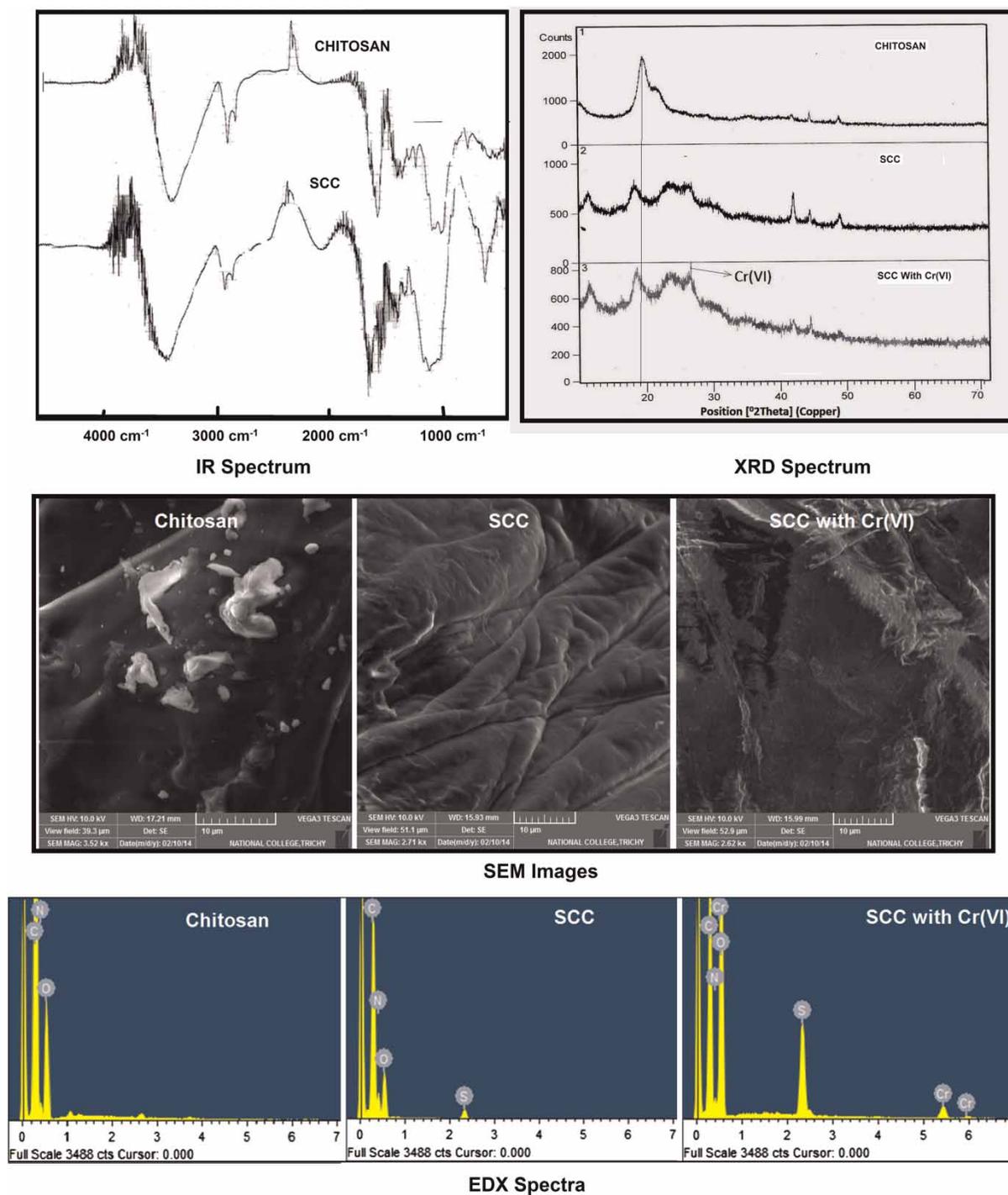


Figure 2 | IR, XRD, SEM and EDX spectra of chitosan, SCC and with adsorbed Cr(VI).

Effect of adsorbent dosage

The effect of the adsorbent dose was studied by varying its amounts from 100 to 600 mg at room temperature (298 K),

fixing the initial Cr(VI) concentration, pH and contact time (Figure 3(b)). It is evident that the adsorption of chromium increases rapidly with increase in the amount of SCC. A steady increase in uptake was observed when the

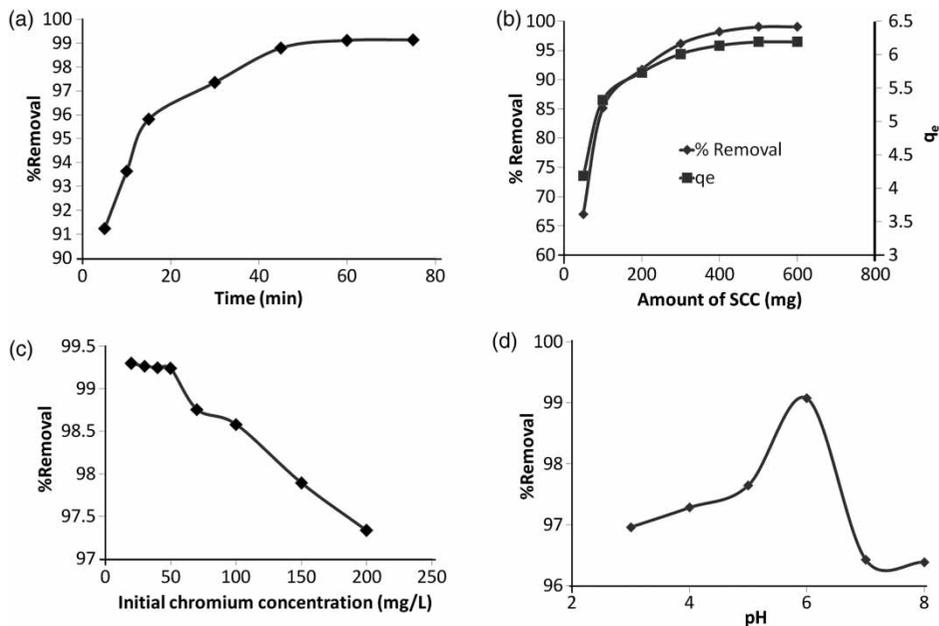


Figure 3 | Effect of (a) contact time, (b) adsorbent dose, (c) initial Cr(VI) concentration and (d) pH on adsorption efficiency.

dose of SCC was increased from 100 to 600 mg. The maximum adsorption occurs at 400 mg dose of SCC.

Effect of initial Cr(VI) concentration

Adsorption experiments were performed at different initial Cr(VI) concentrations ranging from 10 to 300 mg/L with fixed contact time (45 min) and SCC dosage (400 mg). Up to 50 mg/L concentration of Cr(VI), the percent removal was found to be almost steady and then it started decreasing probably due to sorbent saturation (Figure 3(c)). Thus 50 mg/L Cr(VI) solution was used for further adsorption studies.

Effect of pH

In aqueous solution, pH is an important parameter for metal biosorption. Cr(VI) mainly exists as hydrogen chromate (HCrO_4^-), dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and chromate (CrO_4^{2-}) (Cabatingan *et al.* 2001). The pH of the solution was varied from 3.0 to 8.0 at constant initial concentration, contact time and temperature to optimize the pH for maximum removal efficiency. The Cr(VI) removal was found to be maximum at $\text{pH } 6.0 \pm 0.2$ and, at this pH, it exists as chromate (CrO_4^{2-}) ions which get adsorbed (Figure 3(d)). This may be attributed to the existence of CrO_4^{2-} species at this pH, which resembles SO_4^{2-} ion

making the ion, with reference to charge and geometry, exchange feasible. Hence, further studies were carried out at pH 6.0.

Kinetics of adsorption

The uptake of metal ion by the adsorbent depends on the contact time, and in this context the study of the kinetics of adsorption is of considerable significance. The pseudo-first-order and pseudo-second-order kinetic models were utilized to correlate the experimental data. The studies were carried out using 50 mL of 50 mg/L Cr(VI) solution at pH 6.0. It was equilibrated with 400 mg SCC at 298 K for different time intervals.

Pseudo-first-order kinetics

The pseudo-first-order kinetics is given by the following equation (Lagergren 1898):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

where q_e and q_t refer to the amounts of Cr(VI) adsorbed at equilibrium and at time t , respectively, with the first-order rate constant k_1 . The plot of $\log(q_e - q_t)$ against t

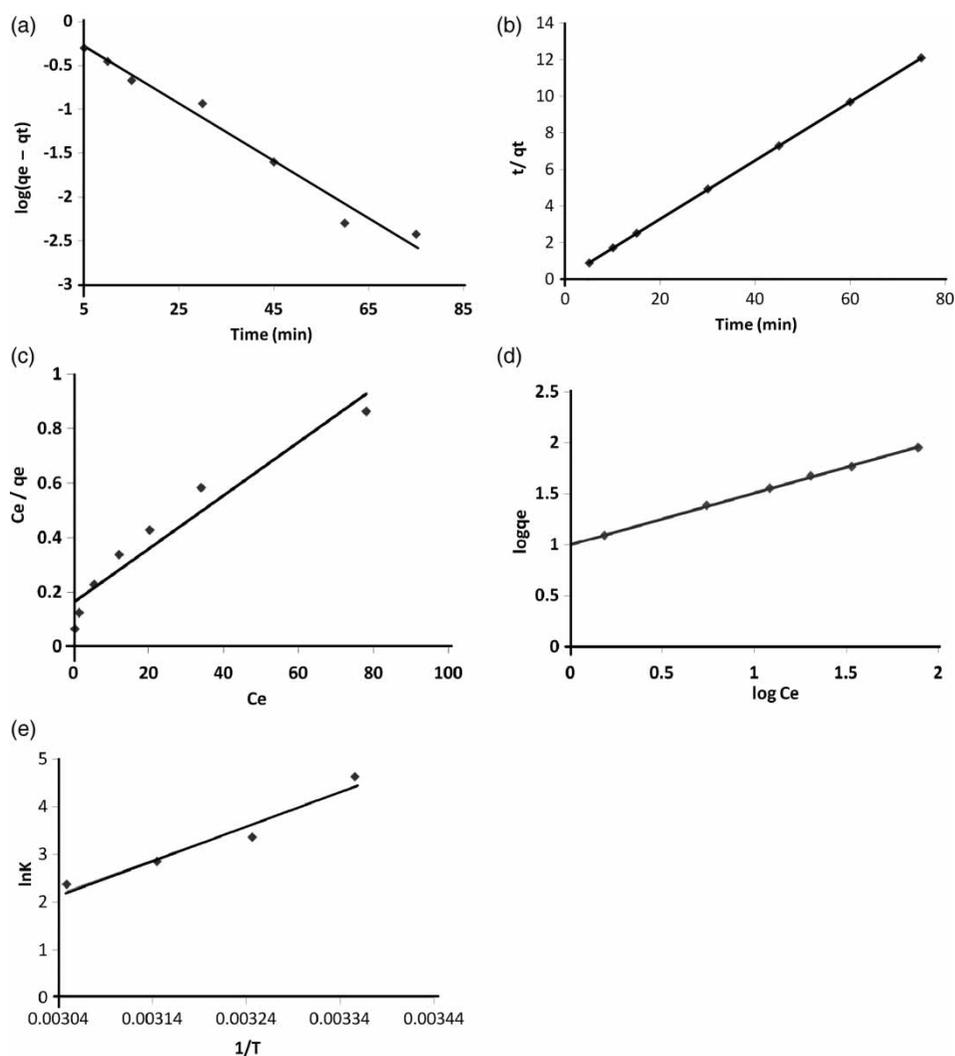


Figure 4 | (a) Pseudo-first-order kinetics, (b) pseudo-second-order kinetics, (c) Langmuir adsorption isotherm, (d) Freundlich adsorption isotherm and (e) effect of temperature on equilibrium constant.

(Figure 4(a)) gives the pseudo-first-order rate constant as 0.00737 1/min with regression coefficient 0.978.

Pseudo-second-order kinetics

The pseudo-second-order equation is given as (Ho & Mckay 1999)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 is the pseudo-second-order rate constant in g/(mg·min). The plot of $\log t/q_t$ against t (Figure 4(b))

gives the pseudo-second-order rate constant as 0.256 g/(mg·min) with regression coefficient 0.999. The q_e values obtained experimentally and from the pseudo-second-order kinetic model were found to be 6.20 and 6.25 mg/g, respectively. The close correlation between the experimental and calculated values proves the applicability of the pseudo-second-order kinetic model in the adsorption of Cr(VI) by SCC (Ho 2006).

Adsorption isotherms

Adsorption isotherms are of prime importance in the design of adsorption systems for understanding the partition of metal ion between the adsorbent and liquid phases. The

studies were carried out using 50 mL of Cr(VI) solutions of varying concentrations from 50 to 800 mg/L at pH 6.0. They were equilibrated with 400 mg SCC at 298 K for 45 min.

Langmuir isotherm

The Langmuir isotherm is a widely used monolayer adsorption model which relates the maximum adsorption capacity (q_0) and the adsorption energy (b) (Langmuir 1918). The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constant by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \quad (4)$$

The maximum adsorption capacity, q_0 , and the constant b were obtained from the slope and intercept of the plot of C_e/q_e against C_e and were found to be 157 mg/g and 0.0391 L/mg with correlation coefficient (r) of 0.96 (Figure 4(c)). A dimensionless parameter R_L relates to the effectiveness of adsorption and is given by the following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

An R_L value in the range 0–1 is an index of the efficient adsorption. The value of R_L for the adsorption of chromium ($C_0 = 50$ mg/L) by SCC was found to be 0.52 and this indicates the effective electrostatic interaction between the SCC and Cr(VI) under the optimized experimental conditions.

Freundlich isotherm

A linearized form of the Freundlich isotherm (Freundlich 1906) for studying the adsorption from aqueous solutions is given as

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (6)$$

where k_F and n are the Freundlich constants that indicate the adsorption capacity and the adsorption intensity, respectively. A favorable adsorption tends to have n between 1 and 10. The logarithmic plot of q_e against C_e gives the constants k_F and n as 9.97 mg/(g·L) and 1.97 with $r = 0.999$ (Figure 4(d)). This value of r clearly shows

that the Freundlich isotherm model is followed, indicating multilayered adsorption over a heterogeneous surface.

Thermodynamics of adsorption

The temperature effect on the adsorption of Cr(VI) was studied in order to obtain relevant thermodynamic parameters at 298, 308, 318 and 328 K. The free energy change of adsorption (ΔG^0) is given by

$$\Delta G^0 = -RT \ln K \quad (7)$$

and the entropy (ΔS^0) and enthalpy (ΔH^0) changes in the adsorption process are related by the van 't Hoff equation (Donia et al. 2006)

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

where R is the gas constant (8.314 J/(mol·K)) and T is absolute temperature (K). The equilibrium constant K has been evaluated from the ratio of concentration of Cr(VI) adsorbed on SCC to that in the solution phase. The slope and intercept of the plot of $\ln K$ against $1/T$ (Figure 4(e)) gives ΔH (−59.39 kJ/mol) and ΔS (−0.162 kJ/mol), respectively. The negative free energy change (−11.11 kJ/mol at 298 K) indicates the spontaneous nature of the adsorption process. Negative enthalpy change indicates the exothermic nature of the adsorption process while negative entropy change indicates the decrease in randomness of Cr(VI) as it passes from solution to adsorbed state.

Evaluation of breakthrough point of column

The effects of the initial Cr(VI) concentrations (100 and 200 mg/L) on the adsorption process in column were studied at a constant flow rate of 5 mL/min and fixed bed height of 6 cm. Effluent solution coming out from the column was collected after every 10 min interval and analyzed spectrophotometrically for Cr(VI) until inlet and outlet concentrations became the same. The breakthrough point for 100 and 200 mg/L Cr(VI) inlet concentrations occurred after 360 min (bed volume 1,800 mL) and 240 min (bed volume 1,200 mL), respectively. These results clearly indicate that larger sample volumes can be treated using the column method compared to batch extraction.

Detoxification of Cr(VI) in synthetic effluents

In order to test the applicability of SCC for detoxifying Cr(VI), two different synthetic effluents were prepared, having similar composition to that of real effluents, and results are depicted in Table 1. More than 98% removal of Cr(VI) was observed in single batch extraction, which may further be improved using multiple extractions. An important observation about SCC is that when the used SCC was kept overnight, the orange-yellow color of Cr(VI) changed to the green color of Cr(III). It clearly indicated that SCC effectively reduces Cr(VI) to the less toxic Cr(III); thus, one can directly dispose of the used SCC (Dambies et al. 2001).

Reusability of SCC

The SCC was regenerated by NaOH treatment as discussed above. The regenerated SCC was tested for adsorption efficiency. The adsorption efficiency was found to be the same as the original SCC.

Comparison with reported crosslinked chitosan adsorbents

The utility of SCC compared with previously reported materials is shown in Table 2. SCC has been found to be a better choice when simplicity of method of preparation as well as adsorption capacity are compared with other materials.

CONCLUSION

The present work gives a simple and very efficient way for detoxification of Cr(VI). The preparation of SCC is very

Table 1 | Application of sulfate-crosslinked chitosan to synthetic effluents

Synthetic effluent	Concentration of ions (mg/L)	% removal of Cr(VI)
1	Cl ⁻ (950), SO ₄ ²⁻ (80), NO ₃ ⁻ (300), PO ₄ ³⁻ (400), F ⁻ (50), Zn ²⁺ (100), Fe ³⁺ (100), Ni ²⁺ (50), Cr ⁶⁺ (50), Ca ²⁺ (200), Mg ²⁺ (200), Cu ²⁺ (50)	98.78 ± 0.3
2	Cl ⁻ (950), SO ₄ ²⁻ (1,640), NO ₃ ⁻ (150), PO ₄ ³⁻ (200), F ⁻ (25), Zn ²⁺ (200), Fe ³⁺ (200), Ni ²⁺ (100), Cr ⁶⁺ (50), Ca ²⁺ (200), Mg ²⁺ (200), Cu ²⁺ (100)	98.92 ± 0.2

Table 2 | Comparison of sulfate-crosslinked chitosan with reported materials

Adsorbent	Adsorption capacity (mg/g)	Reference
Chitosan	2.48	Singh & Singh (2012)
Ethylenediamine-modified crosslinked magnetic chitosan resin	51.81	Hu et al. (2011)
Fe-crosslinked chitosan	295	Zimmermann et al. (2010)
Protonated crosslinked chitosan	189.33	Huang & Yang (2013)
Sulfate-crosslinked chitosan	156.85	This study

simple compared to modifications suggested by various workers. The method is economic and has a 'greener' perspective as the SCC can be reused and also has 100% atom economy. The high adsorption capacity (156.85 mg/g) in relatively little time (45 min) is the most interesting feature of SCC. The Freundlich adsorption isotherm fits well with pseudo-second-order kinetics.

ACKNOWLEDGEMENT

The authors are thankful to University Grants Commission, New Delhi, India, for the start-up grant.

REFERENCES

- Alves, N. M. & Mano, J. F. 2008 Chitosan derivatives obtained by chemical modifications for biomedical and environmental applications. *Int. J. Biol. Macromol.* **43**, 401–414.
- Benavente, M., Moreno, L. & Martinez, J. 2011 Sorption of heavy metals from gold mining wastewater using chitosan. *J. Taiwan Inst. Chem. Eng.* **339**, 1–13.
- Boddu, V. M., Abburi, K., Talbott, J. L. & Smith, E. D. 2003 Removal of hexavalent chromium from wastewater using a new composite chitosan. *Environ. Sci. Technol.* **37**, 4449–4456.
- Cabatingan, L. K., Agapay, R. C., Rakels, J. L., Ottens, M. & van der Wielen, L. A. M. 2001 Potential of biosorption for the recovery of chromate in industrial wastewaters. *Ind. Eng. Chem. Res.* **40**, 2302–2309.
- Crini, G. 2005 Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci.* **30**, 38–70.
- Dambies, L., Guimon, C., Yiacoumi, S. & Guibal, E. 2001 Characterization of metal ion interactions with chitosan by X-ray photoelectron spectroscopy. *Colloids Surf. A: Physicochem. Eng. Aspects* **177**, 203–214.

- Donia, A. M., Atia, A. A., El-Boraey, H. A. & Mabrouk, D. 2006 Uptake studies of copper (II) on glycidyl methacrylate chelating resin containing Fe₂O₃ particles. *Sep. Purif. Technol.* **49**, 64–70.
- Freundlich, H. M. F. 1906 Over the adsorption in solution. *Z. Phys. Chem.* **57**, 385–470.
- Ho, Y. S. 2006 Review of second-order models for adsorption systems. *J. Hazard. Mater.* **136**, 681–689.
- Ho, Y. S. & McKay, G. A. 1999 A multi-stage batch adsorption design with experimental data. *Adsorpt. Sci. Technol.* **17**, 233–243.
- Hu, X. J., Wang, J. S., Liu, Y. G., Li, X., Zeng, G. M., Bao, Z. L., Zeng, X. X., Chen, A. W. & Long, F. 2011 Adsorption of chromium(VI) by ethylenediamine-modified cross-linked magnetic chitosan resin: isotherms, kinetics and thermodynamics. *J. Hazard. Mater.* **185**, 306–314.
- Huang, R. & Yang, B. 2013 Removal of chromium(VI) ions from aqueous solutions with protonated crosslinked chitosan. *J. Appl. Polym. Sci.* **129**, 908–915.
- Jayakumar, R., New, N., Tokura, S. & Tamura, H. 2007 Sulfated chitin and chitosan as novel biomaterials. *Int. J. Biol. Macromol.* **40**, 175–181.
- Lagergren, S. 1898 Zur theorie der sogennanten adsorption geloster stoffe. *Sven. Vetenskapsakad. Handl.* **24**, 1–39.
- Langmuir, I. 1918 The adsorption of gases on plane surface of glass, mica and platinum. *J. Am. Chem. Soc.* **40**, 1361–1403.
- Lasko, C. L., Adams, K. H., DeBenedet, E. M. & West, P. A. 2004 A simple sulphuric acid pretreatment method to improve the adsorption of Cr(VI) by chitosan. *J. Appl. Polym. Sci.* **93**, 2808–2814.
- Mayyas, M. A. 2012 Properties of chitosan nanoparticles formed using sulphate anions as crosslinking bridges. *Am. J. Appl. Sci.* **9**, 1091–1100.
- Mendham, V. J., Denny, R. C., Barnes, J. D. & Thomas, M. J. K. 2002 *Vogel's Textbook of Quantitative Chemical Analysis*, 6th edn. Pearson Education, Singapore.
- Mertz, W. 1976 Chromium and its relation to carbohydrate metabolism. *Med. Clin. N. Am.* **60**, 739–744.
- Mourya, V. K. & Inamdar, N. N. 2008 Review chitosan modifications and applications: opportunities galore. *React. Funct. Polym.* **68**, 1013–1118.
- Omotoso, O. E., Ivey, D. G. & Mikula, R. 1995 Characterization of chromium doped tri-calcium silicate using SEM/EDS, XRD and FT-IR. *J. Hazard. Mater.* **42**, 87–102.
- Owlad, M., Aroua, M. K., Daud, W. A. & Baroutian, S. 2009 Removal of hexavalent chromium contaminated water and wastewater – a review. *Water Air Soil Pollut.* **200**, 59–77.
- Ravi Kumar, M. N. V. 2000 A review of chitin and chitosan applications. *React. Funct. Polym.* **46**, 1–27.
- Singh, D. & Singh, A. 2012 Chitosan for the removal of chromium from waste water. *I. Res. J. Environ. Sci.* **1**, 55–57.
- Srinivasa Rao, P., Sridhar, S., Wey, M. Y. & Krishnaiah, A. 2007 Pervaporative separation of ethylene glycol/water mixtures by using crosslinked chitosan membranes. *Ind. Eng. Chem. Res.* **46**, 2155–2163.
- Zimmermann, A. C., Mecabô, A., Fagundes, T., Rodrigues, C. A., Ana, C. Z., Ariany, M., Tathyane, F. & Clovis, A. R. 2010 Adsorption of Cr(VI) using Fe-crosslinked chitosan complex (Ch-Fe). *J. Hazard. Mater.* **179**, 192–196.

First received 16 July 2014; accepted in revised form 29 October 2014. Available online 11 November 2014