



Adsorption of Chromium (VI) from Aqueous Solution using Crosslinked Chitosan Graft Polyacrylonitrile Copolymer

KEYWORDS

Shankar.P

Part time Research scholar, Department of Chemistry, Sathyabama University, Chennai, India

Gomathi. T

Department of Chemistry, DKM College for Women, Vellore, Tamilnadu, India

Vijayalakshmi. K

Department of Chemistry, DKM College for Women, Vellore, Tamilnadu, India

*** Sudha. P.N.**

ASSOCIATE PROFESSOR, PG & RESEARCH DEPARTMENT OF CHEMISTRY, DKM COLLEGE FOR WOMEN, VELLORE-632 001

*Corresponding Author

ABSTRACT *The present work concerns with the synthesis of chitosan copolymers for removal of chromium ions wastewater. Crosslinked chitosan graft polyacrylonitrile copolymer was prepared, characterized and used as the adsorbent under various experimental parameters such as contact time, adsorbent dose and pH of the solution. The obtained results reveal that the adsorption of metal ion increases with the increase of shaking time and adsorbent dose. A pH 5.0 was found to be an optimum pH for Cr (VI) adsorption. The adsorption kinetics has been explained using Lagergren pseudo-first order and pseudo-second order kinetics model. From the obtained results it was concluded that under optimum conditions, the chitosan grafted poly AN was found as an effective adsorbent for the removal of chromium.*

INTRODUCTION

Heavy metals are often problematic environmental pollutants, with well-known toxic effects on living systems. The discharge of non-biodegradable heavy metals into water stream is hazardous which causes various health problems (GardeaTorresdey et al., 2004). Chromium is the important toxic material which is non-biodegradable. Wastewaters obtained from textile, leather tanning, electroplating, and metal finishing industries contains chromium (Schneider et al., 2007). Chromium generate serious health problems such as epigastric pain, nausea, vomiting, severe diarrhea, corrosion of skin, respiratory tract and lungs carcinoma (Sajidu et al., 2008), when accumulated at higher levels and when concentration reaches 0.1 mg/g body weight, it can ultimately become lethal (Salamatinia et al., 2008). Hence it is important to eliminate trace of chromium from drinking water, or to remove chromium from wastewaters before they are discharged into receiving bodies.

Many removal methods have been proposed for the removal of heavy metals. But biosorption is one of the emerging and attractive technologies. It was a promising method which is more economic with high metal binding capacity. The biopolymer chitosan is one among them, which has the highest sorption capacity for several metal ions (Deshpande, 1986).

To improve chitosan's performance as an adsorbent, certain physical and chemical modifications were done. Chemical modifications lead to the formation of chitosan derivatives. Grafting technique has gained much attention which was extensively studied and reported. The graft copolymerization of chitosan with various vinyl monomers have been conducted with different initiating systems and different mechanisms. Among the many vinyl monomers grafted, acrylonitrile (AN) has been the most frequently used due to its high grafting efficiency and easy to hydrolyze to introduce varied subsequent derivatives (Pourjavadi et al., 2003).

The main objectives of this study was to prepare a new modified synthetic polymer such as the graft copolymer of cross linked chitosan with the acrylonitrile monomer using ceric ammonium nitrate as an initiator for the removal of the heavy

metal ions such as Cr⁶⁺. Batch technique was used to study the sorption of Cr⁶⁺.

Materials and Methods

Materials

Chitosan was kindly gifted by India Sea food, Cochin, Kerala, India. Acrylonitrile, glutaraldehyde, ceric ammonium nitrate and the other chemicals used in the experiments were of analytical grade.

Preparation of crosslinked chitosan copolymer

To 100 ml of chitosan solution 15 ml of glutaraldehyde was added and stirred for 20 minutes using a magnetic stirrer. To this mixture, a solution of 0.1 M ceric ammonium nitrate (CAN) in 10 ml of nitric acid was added followed by a known amount of acrylonitrile drop by drop with continuous stirring with exposure to UV lamp. The temperature of reaction was maintained at 70 °C for 45 minutes. After the process is over, the product was precipitated by using sodium hydroxide solution with vigorous stirring. The precipitate was washed with distilled water several times to remove homopolymer formed and filtered.

Polymer characterization

The prepared crosslinked chitosan-g-acrylonitrile copolymer was characterized by FTIR in a wide range wavelength between 400 cm⁻¹ and 4000 cm⁻¹, and in solid state using KBr pelletisation. A Perkin – Elmer spectrophotometer was used. SEM study of the prepared graft copolymer was done using JSM – 640 Scanning Electron Microscope, JEOL at 20 MA and 15 KV. The dried sample film was cut and was sputter – coated with gold using a microscope sputter coater and viewed through the microscope. Xray diffraction studies were performed using Xray powder diffractometer (XRD – SHI-MADZU XD – D1) using a Ni filtered Cu K Xray radiation.

Experimental process of removal of chromium

The stock solutions of Cr(VI) was prepared to get a concentration of 200mg/L of chromium as potassium dichromate. 1:1 Hydrochloric acid and 2N sodium hydroxide solutions were used for pH adjustment. The exact concentration of

each metal ion solution was calculated on mass basis and expressed in terms of mg L^{-1} . Synthetic solution of Cr(VI) ion taken in stoppered bottles were agitated at 30°C by orbital shaker at fixed speed, 160 rpm for various time intervals. After attaining the equilibrium adsorbent was separated by filtration using Whatman filter paper and aqueous phase concentration of metal was determined with atomic adsorption spectrophotometer.

Results and Discussion

FTIR

Figure-1 shows the FTIR spectrum of the CS-g-PAN (b) and original crosslinked chitosan (a). The broad and strong absorption peak obtained at around 3454 cm^{-1} , 2923 cm^{-1} and the three peaks at range of $1000\text{--}1157\text{ cm}^{-1}$ (C–O stretching) in both spectra (a) and (b) corresponds to the O–H, N–H stretching, C–H stretching and C–O stretching. The above observed peaks were common in spectra due to the crosslinked chitosan backbone. The successful graft copolymerization of cross linked chitosan with AN (Sun et al., 2003) was confirmed from the appearance of strong peak in spectra (b) observed at 2244 cm^{-1} corresponding to the stretching absorption of –CN group.

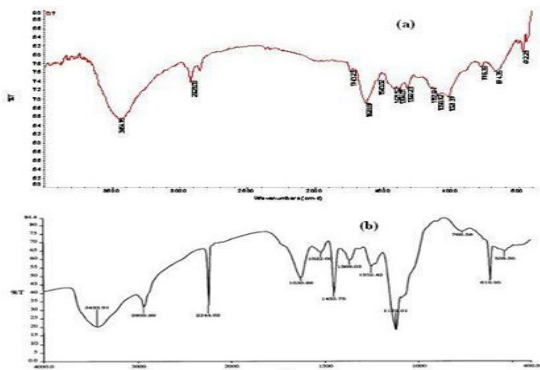


Figure 1: FTIR spectra of (a) crosslinked chitosan; (b) crosslinked CS-g-PAN.

XRD

The XRD pattern of crosslinked chitosan and its graft copolymer was shown in figure-2(a) and 2(b). The crosslinked chitosan shows two diffraction peaks at around $2\theta = 11^\circ$ and 20° . These are characteristics of the hydrated crystalline structure of crosslinked chitosan, while the peak of (b) at around 42° was due to the overlapped diffraction peaks from the AN's crystal.

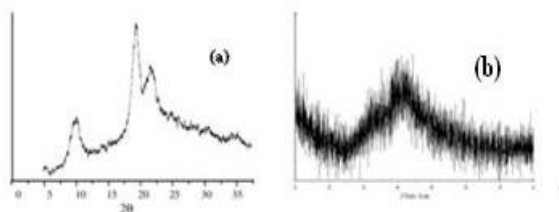


Figure 2: XRD analysis of (a) crosslinked chitosan; (b) crosslinked chitosan-g-acrylonitrile

From the results of XRD spectrum (b), it is evident that the diffraction intensity of the peak obtained at around $2\theta = 20^\circ$ was obviously weakened which indicate that the crystallinity of the crosslinked chitosan was decreased after modification. The above results illustrated that on copolymerization, the crystallinity of crosslinked chitosan was disappeared. This phenomenon was due to the strong interaction (formation of covalent bond) between crosslinked chitosan and acrylonitrile.

Scanning electron Microscopy (SEM)

The scanning electron micrographs of cross linked chitosan and crosslinked chitosan-g-acrylonitrile copolymer was represented in Figure 4(a) and (b), respectively. The SEM image of crosslinked chitosan (a) was smooth and no pores or semi-pores was present on the surface whereas the SEM image of crosslinked chitosan-g-acrylonitrile (b) copolymer showed a rough surface (Thejappa et al., 1982). The graft copolymer shows spherulites like structure which may be due to the strong interactions occurring between crosslinked chitosan and acrylonitrile. This interaction provides the larger surface area for better adsorption.

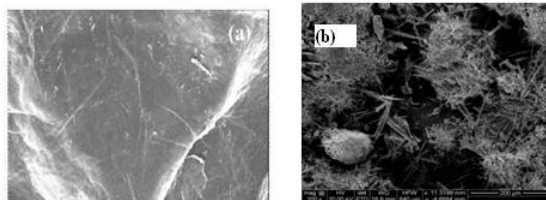


Figure 4: Scanning electron micrographs of (a) crosslinked chitosan; (b) crosslinked chitosan-g-acrylonitrile copolymer.

Factors influencing the adsorption of Cr(VI)

The influences of several operational parameters such as pH, adsorbent dose and contact time were investigated.

Effect of pH

The pH of the solution has a significant impact on the uptake of heavy metals, since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate. In order to establish the effect of pH on the bi-adsorption of chromium (VI) ions, the batch equilibrium studies at different pH values were carried out in the range of 4–8 respectively (Fig.5).

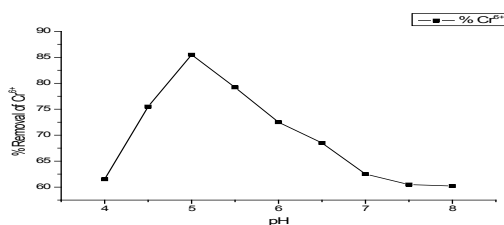


Figure-5 Effect of pH on the removal of chromium(VI)

The maximum percent removal of chromium (VI) ion on the adsorbent was observed at pH 5. It shows significant increase in the metal ion removal with the increase in pH at first and thereafter it shows a decrease on further increase in pH. According to Low et al., little sorption at lower pH could be ascribed to the hydrogen ions competing with metal ions for sorption sites. In addition to this at a higher pH, the chromium ions were precipitated as their hydroxides which decreased the rate of adsorption and subsequently the percent removal of metal ions (Toti et al., 2002).

Effect of adsorbent dose

The dependence of Cr(VI) adsorption was studied by varying the amount of adsorbent from 1 to 6 g, while keeping other parameters (pH, and contact time) constant. From Figure 6, it was observed that with the fixed metal concentration, it can easily be inferred that the percent removal of metal ions increases with increase in adsorbent dose. This initial increase of percent removal of heavy metal ions with increase in adsorbent dose was due to the greater availability of exchangeable sites for the ions (Johan et al., 2011).

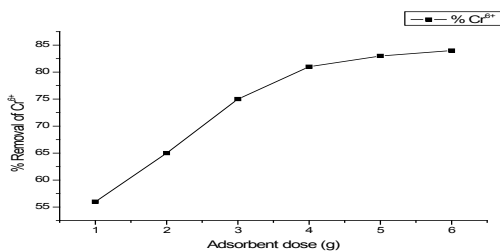


Figure-6- Effect of adsorbent dose on the removal of chromium(VI)

Effect of contact time

The effect of contact time was represented in the figure-7. It shows that the removal of chromium (VI) ion increases with increase in contact time upto 325 mins and remained constant (75.2%) from 325 to 350 mins. This may be due to the availability of larger surface area for the metals. The initial removal occurs immediately as soon as the metal and grafted copolymer came into contact and after some extent further increase in contact time did not increase the uptake which was due to decrease of the easily available active sites for adsorption till the equilibrium is reached.

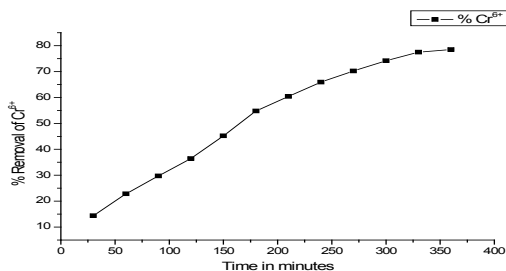


Figure-7 Effect of contact time on the removal of chromium(VI)

Kinetics studies

The linearized form of pseudo-first-order Lagergren equation is given as follows

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303$$

The pseudo-second-order rate equation can be represented as follows

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

where q_e and q_t are the amounts of metal adsorbed (mg/g) at equilibrium and at time t (min), k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) are the adsorption rate constant of pseudo-first-order, pseudo second order adsorption rate, respectively. The linear plots of $\log (q_e - q_t)$ versus t and (t/q_t) versus t are drawn for the pseudo-first-order and the pseudo-second-order models, respectively (Figure-8 and figure-9). The rate constants k_1 and k_2 can be obtained from the plot of experimental data.

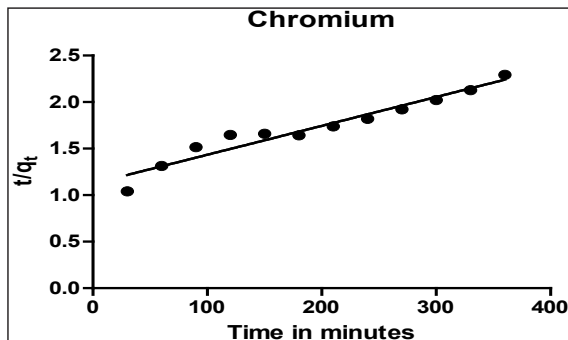


Figure-8

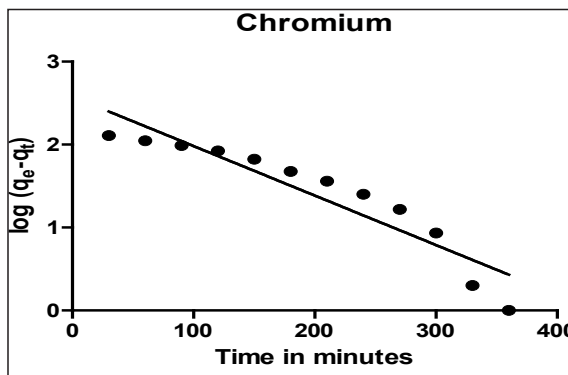


Figure-9

Table-1

Pseudo-first-order kinetic model			Experimental value	Pseudo-second-order kinetic model		
q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	q_e (mg/g)	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
431.99	0.00597	0.8749	138	362.58	0.0031	0.9379

From the table, it was observed that the pseudo-second-order linear plots resulted in higher R^2 values than the pseudo-first-order. The values of q_e (cal) from the pseudo-second-order were close to q_e (exp) than that from the pseudo-first-order. These indicated the better applicability of the pseudo-second-order model when compared to the pseudo first order model.

Freundlich Adsorption Isotherm

The Freundlich equation is mainly used to describe heterogeneous surface energies. The Freundlich isotherm is the most widely used non-linear sorption model (Rengaraj et al., 2003) and its linearised form is.

$$\log Q_e = \log K_F + 1/n \log C_{eq}$$

where

C_{ads} = amount of Cr(VI) adsorbed ($\text{mg} \cdot \text{g}^{-1}$)

C_{eq} = equilibrium concentration in solution ($\text{mg} \cdot \text{dm}^{-3}$)

$1/n$ = Freundlich constant ($\text{mg} \cdot \text{g}^{-1}$)

P = Freundlich constant ($\text{g} \cdot \text{dm}^{-3}$)

A plot of $\log C_{ads}$ vs. $\log C_{eq}$ (Figure-10) yielded a straight line. The linearity of the plot supports the applicability of the Freundlich adsorption isotherm in this study.

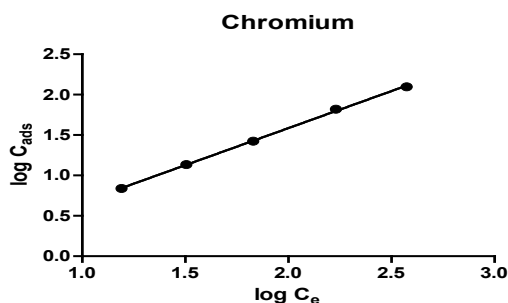


Figure-10

The values of the Freundlich constants of chromium (VI) were represented in the table-2. The obtained R^2 values conclude that the Freundlich model better describes the adsorption process very effectively. Also the n value is in between 1 – 10, which shows the favorability of multilayer adsorption.

Table-2

Freundlich constants		
P (dm ³ /g)	n(dm ³ /mg)	R ²
0.5640	1.091	0.9992

Conclusion

The graft copolymerization of crosslinked chitosan with acrylonitrile has been done in the presence of CAN as redox initiator and by novel technique UV irradiation. The grafting was strongly confirmed by FTIR and XRD. The morphological structure by SEM revealed that copolymer is uniformly formed, which showed that the grafted copolymer has improved porosity and fractured structure, which can be responsible for adsorption of molecules. The results showed that the adsorbent dose, pH and the contact time had a pronounced effect on the removal of Cr (VI) ions from metal solution. The removal follows Freundlich isotherm model and pseudo-second order kinetics.

REFERENCE

- Aggarwal,D, Goyal.M and Bansal.R.C (1999), Adsorption of chromium by activated carbon from aqueous solution, Carbon, 37, 1989–1997.
- Deshpande, M. V. (1986). Enzymatic degradation of chitin and its biological applications”, Journal of Scientific and Industrial Research, 45, 277-281. | • GardeaTorresdey, J. L., de La Rosa, G., & PeraltaVidea, J. R. (2004). Use of phytofiltration technologies in the removal of heavy metals: A review, Pure and Applied Chemistry, 76(4), 801. | • Johan.N.A, Kutty.S.R., Isa.M.H ,Muhamad.N.S , Hashim.H.(2011) Adsorption of Copper by using Microwave Incinerated Rice Husk Ash (MIRHA) International Journal of Civil and Environmental Engineering 33. | • Pourjavadi, A., Mahdavinia, G. R., ZohuriaanMehri M. J., and Omidian, H. (2003). Modified chitosan. I. Optimized cerium ammonium nitrateinduced synthesis of chitosangraftpolyacrylonitrile, Journal of Applied Polymer Science, 88(8), 2048-2054. | • Rengaraj, Cheol Kyun Joo, Younghun Kim, Jongheop Yi (2003) “Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H”, Journal of Hazardous Materials B102 , 257–275. | • Sajidu, S.M.I., Persson, I., Masamba, W.R.L., and Henry, E.M.T., (2008). Mechanisms for biosorption of chromium (III), copper (II) and mercury (II) using water extracts of Moringa oleifera seed powder. Afr. J.Biotech. 7, 800 – 804. | • Salamatinia, B., Kamaruddin, A.H., and Abdullah, A.Z., (2008). Modeling of the continuous copper and zinc removal by sorption on to sodium hydroxide – modified oil palm frond in a fixed bed column. Chem. Eng. J. 145, 259 –266. | • Schneider.R.M, Cavalin.C.F, Baros M.A.S.D and Tavares.C.R.G (2007). Adsorption of cheomium ions in activated carbon ,Chem.Eng.J ,132,355-362 | • Sun.T, P. Xu, Q. Liu, J. Xue, and W. Xie, (2003) European Polymer Journal, 39(1), 189–192. | • Thejappa.N and Pandey.S.N, (1982).J. Appl. Polym. Sci., 21, 2307 | • Toti SU, Aminabhavi TM (2002). Pervaporation separation of waterisopropyl alcohol mixture with bland membranes of sodium alginate and poly (acrylamide)-grafted guar gum J. Appl. Polym. Sci. 85: 2014-2024. |