Removal of Chromium (VI) ions from Aqueous solution onto Chitosan and Cross-linked Chitosan Beads

PS JASSAL*, VP RAUT and NEELAM ANAND
Department of Chemistry, S.G.T.B Khalsa College, University of Delhi, Delhi 110 007, India

The adsorption of Cr (VI) ions onto chitosan and cross-linked chitosan beads has been investigated at different pH values and at different time intervals. Chitosan beads were cross-linked with epicholrohydrin (ECH) in order to obtain sorbent that are insoluble in aqueous, acidic and basic medium, resulting in improvement of swelling behaviour. Batch adsorption experiment were carried out as a function of pH, contact time and concentration of Cr (VI) ions. At lower pH, the adsorption of Cr (VI) on chitosan and cross-linked chitosan beads is more because in the presence of H^+, the amino group of chitosan and cross-linked chitosan behaves as quarternary ammonium ion to attract more and more dichromate ions from the reaction mixture. Adsorption isotherm data could be well interpreted by the Langmuir equation. A dimensionless constant separation factor or equilibrium parameter, R_L values had been calculated and show that there is favourable adsorption of Cr (VI) on chitosan and chitosan-ECH beads.   The experimental data of the adsorption equilibrium from Cr (VI) solution correlated well with the Langmuir isotherm equation. The uptake of Cr (VI) ions on chitosan and chitosan-ECH beads was 52-80% and 48-78% at different time intervals and at pH values of of 4, 3.5, 3, 2.5 and 2 at the initial concentration of potassium dichromate solution of 4.56×10^{-4} M.

Key Words: Chitosan and Cross-linked Chitosan Beads; Chromium (VI); Swelling; Adsorption Isotherm

Introduction

The contamination of water from the disposal of industrial waste often contain considerable amount of heavy metals that would endanger public health and environment if not given adequate treatment. Heavy metals such as Hg, Cr, Ni, Cd, Cu and Zn, which are usually associated with greater degree of toxicity are present in wastewater.

Pollution by chromium is of considerable concern as the metal has found widespread use in electroplating, leather tanning, metal finishing, nuclear power plant, textile industries and chromate preparation. The National Institute for Occupational Safety and Health (NIOSH) recommends that the level of chromium in water should be reduced to 10^{-3} mg/L. The metal is reported to be bio-accumulated into flora and fauna creating ecological problems [1]. The use of chromate and dichromate in metal plating and as corrosion control agents in cooling waters is quite extensive. It is well-known that Cr (VI) is toxic to living systems and the removal of Cr (VI) involves acid catalyzed chemical reduction to Cr^{3+}. The Cr^{3+} is then precipitated as hydroxide at alkaline condition using either caustic or lime [2].

The toxicity of various pollutants to aquatic environment is variable but all of them contaminate on the bottom of water system where they poison or smother the aquatic organism. Most of the industrial effluents are insusceptible to degradation [3]. Heavy metal ions, aromatic compound (including phenolic derivatives and polycyclic aromatic compounds) and dyes are often found in the environment as a result of their wide industrial use. They are common contaminants in wastewater and are known to be toxic or carcinogenic [4].

Cr (III), an essential trace element in human nutrition is associated with glucose metabolism and dietary amount has been reported from 50 to 200mg per day. Dietary deficiency of trivalent chromium causes faulty sugar metabolism. The required Cr (VI) enters the living beings by inhaling air, consuming food or by contaminated water. Short

*Author for Correspondence : E-mail : psj.sgtb57@gmail.com

term exposure due to inhalation at high level can cause several problems like nosebleeds, ulcers, irritation of nasal mucosa, holes in the nasal septum and dermal exposure can also cause skin irritation and allergies. It is also known to cause kidney failure, metabolic acidosis and oral ulcer [5].

Different technologies and processes are currently used such as ion-exchange, activated charcoal, complexation, precipitation and other chemical and electrochemical techniques. Adsorption is widely recognized as an effective, efficient and economic method for water contamination applications, and for separation analytical purposes. Biosorption or sorption to materials of biological origin is recognized as an emerging technique for treatment of wastewater containing heavy metals. Chitosan is a biopolymer which is of interest to researchers concerning the adsorption of metal ions and other impurities [6-7]. A comparison of different adsorbents alongwith adsorption by chitosan based natural polymer is given in Table 1.

Chitosan is a natural product derived from chitin, a polysaccharide found in the exoskeleton of shellfish like shrimp or crab. Chitosan is a linear polysaccharide composed of randomly distributed β-(1-4) linked D-glucosamine and N-acetyl-D-glucosamine units, since the amine group and hydroxyl group on the chitosan chain act as chelation sites for metal ion. The cross-linked chitosan are very stable and maintain their strength even in acidic and basic solutions. These characteristics are very important for an adsorbent so that it can be used in a lower pH environment [14].

Materials and Method

Chitosan, 75% deacetylated, a powdery material, was purchased from Sigma-Aldrich Chemicals (India). 0.1N sodium hydroxide solution was used for solubility and swelling experiment (BDH, ampules). The epichlorohydrin (GR), a Loba chemine product and acetic acid (glacial 99-100%) was from E. Merck chemicals. Anhydrous Sodium tripolyphosphate (A R), CDH and potassium dichromate (GR), E Merck chemicals, products were used. Doubly distilled water was used for the preparation of different solutions. UV-Visible spectra were recorded using a Perkin-Elmer spectrophotometer.

Preparation of Chitosan Beads

5 gm of chitosan powder was dissolved in 200 ml of 0.1N acetic acid and doubly distilled water was added to make 250 ml of solution in a standard flask. Solution was stirred for an overnight. 0.5%, (w/v) sodium tripolyphosphate (STPP) solution was prepared to provide strength to the chitosan gel beads. Taking chitosan solution in a burette and sodium tripolyphosphate solution in a patry dish, chitosan gel coagulated in STPP solution, forming spherical uniform chitosan gel beads. Keep chitosan gel beads in STPP solution for overnight. The wet chitosan beads were extensively rinsed with double distilled water. The washed chitosan beads kept in double distilled water for 24 hours, after that decant off water and finally air dried to remove the water from the pore structure. To ensure the complete removal of water, chitosan and chitosan-ECH beads were air dried till a constant weight is obtained. Here after called chitosan beads [15].

Table 1: Comparison of adsorption by different adsorbents

Adsorbent	Advantages	Disadvantages
Activated carbon [8,9]	Most effective adsorbent with high surface area, adsorbs wide range of pollutants, high capacity and high rate of adsorption. Porous sorbent and effluent obtained is of high quality	Expensive and performance is related with type of carbon used, non-selective and not a good adsorbent for hydrophilic substances, high reactivation cost and ineffective for disperse and vat dyes.
Ion-exchange Resins [10,11]	Wide range of pore structure and excellent selectivity for aromatic solutes, effective sorbent with good surface area and no adsorbent loss on regeneration	Expensive and obtained from petroleum based raw materials, pH dependence and not effective for all dyes and performance is dependent on the type of resin used.
Chitosan based natural polymers [12,13]	Low-cost natural easily-available polysaccharides with outstanding metals and dye removal capacity, high quality treated effluent obtained, easy regeneration and highly cost effective	pH dependence and low affinity for basic dyes, requires chemical modification to improve its performance and sorption is dependent on degree of N-acetylation.

Cross-linked Chitosan Beads with Epichlorohydrin (ECH)

A solution of 0.01M ECH containing 0.06M NaOH was prepared using 250 ml standard flask. Freshly prepared wet chitosan beads were added to this ECH solution to obtain a ratio of 1:1. Chitosan beads in ECH solution were heated to a temperature between 40 to 50^0 C for 2 hours and stirred continuously. Decant off ECH solution, washed intensively with distilled water to remove the traces of unreacted ECH and dried in air. The newly formed chitosan-ECH beads were ground to a constant size, <250mm (using a mesh no. 60) before use [16-18]. The chitosan-ECH beads were confirmed by an FT-IR System 2006 Model Spectrometer (Perkin-Elmer).

Dissolution and Swelling test of Chitosan and Cross-linked Chitosan Beads

Chitosan and cross-linked chitosan beads were tested with regard to their solubility in each of 0.10M acetic acid, distilled water and 0.10M NaOH solution. 0.1 g of chitosan and cross-linked chitosan beads were taken in non woven polypropylene bags for the swelling test by suspending in solution and stirring for 24 h [19-21]. The percentage of swelling of these beads was calculated from the following :

$$\text{Percentage swelling} = (W_S - W)/W \times 100$$

where W_S is the weight of swollen beads and W is the weight of dry beads.

Adsorption Experiment

The stock solution of Cr (VI) containing 353 mg/L of $K_2Cr_2O_7$ was prepared and the standard curve was obtained by plotting absorbance versus concentration. Adsorption was carried out by taking 50 ml of this solution and 0.1g of chitosan or cross-linked chitosan beads in a 100ml beaker. The experiment was carried out using different Buffer solutions to obtain the desired pH. Chitosan or cross-linked chitosan beads were equilibrated at the particular pH for 20 minutes of contact time with continuous stirring. After filtration the concentration of Cr (VI) was measured by recording the absorbance, at λ_{max} of 365nm and then the concentration was calculated using the standard curve. The chromium adsorption was studied in the pH values of 2, 2.5, 3, 3.5 and 4 and at a temperature of 30ºC.

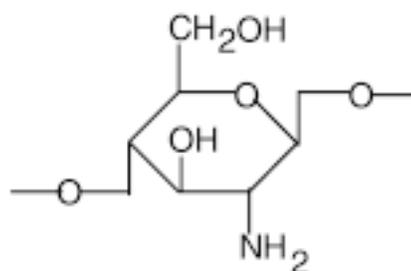The amount of adsorption was calculated based on the difference of Cr (VI) concentration in aqueous
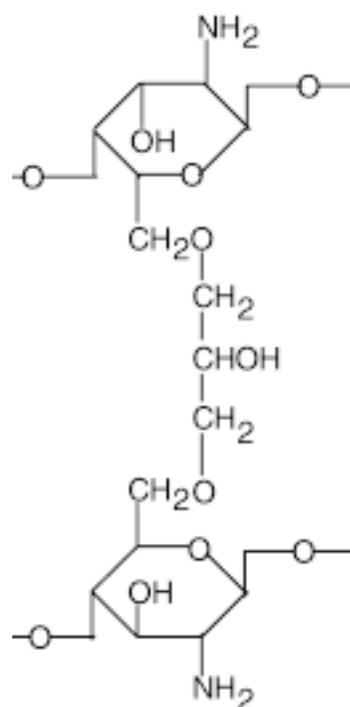

Fig. 1(a): Chitosan unit

Fig. 1(b): Chitosan-ECH unit

solution before and after adsorption. The volume of aqueous solution 50 ml and the weight of beads (0.1g) according to:

$$\text{Adsorption Capacity (X)} = [(C_o - C_e).V]/W]$$

where C_o is the initial concentration of Cr (VI), C_e is the final or equilibrium Cr (VI) concentration, V is the volume of Cr (VI) solution and W is the weight of chitosan or cross-linked chitosan beads [22-24].

Results and Discussion

1) Solubility and Swelling Test

The chitosan beads after cross-linking was found to be insoluble in, acidic and alkaline medium, as well as in distilled water. The chitosan have high hydrophilicity due to the presence of primary amine group which makes chitosan easily soluble in dilute acetic acid or formic acid solution to yield a hydro

gel in water [25]. The swelling of cross-linked chitosan beads should be necessary to reinforce the chemical stability of beads in such acidic solution. The chitosan beads show good swelling result in comparison with cross-linked chitosan beads as given in Table 2.

2) Effect of pH on the Cr (VI) Adsorption by Chitosan and Chitosan-ECH Beads

The effect of pH on the adsorption of Cr(VI) by chitosan and cross-linked chitosan beads was carried out at 30°C and at different pH values. The important parameters for adsorption of metal ions are, the concentration of the counter ions on the functional group of the adsorbent and the degree of ionization of the adsorbate during the reaction. To examine the effect of pH on the chromium adsorption efficiency, the pH was varied from 2 to 4. The reason for this is at low pH the amine group of chitosan is easily protonated and which causes electrostatic repulsion to Cr(VI) ion [26]. Therefore competition existed between proton and Cr(VI) ions for adsorption sites and adsorption capacity was decreased (Table 3). Adsorption increased as pH was lowered from 4 to 2 (Fig. 2) and at the same time Cr (VI) adsorption was higher in the initial stage and after that it was almost stabilized (Fig. 3).

3) Adsorption Isotherm /Langmuir and Freundlich equilibrium Istherms

The Langmuir model assumes that uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions. The experimental equilibrium isotherm for adsorption of Cr (VI) on chitosan and chitosan-ECH can be described with the Langmuir adsorption equation:

$$C_e = [C_e/ X_{max} + 1/ X_{max}]. X$$

Where C_e is the equilibrium or final concentration of concentration of Cr (VI), X is the amount of Cr (VI) adsorbed per unit weight of chitosan or cross-linked chitosan beads at equilibrium concentration (mg/g), X_{max} is the maximum adsorption at monolayer coverage (mg/g) and b is the Langmuir adsorption equilibrium constant (ml/mg) and is a measure of the energy of adsorption. A linearized plot of $(C_o - C_e)/ X_{max}$ versus C_e gives X_{max} and b (Fig. 4).

It shows that Langmuir equation best fits for Cr (VI) adsorption on the chitosan beads under the concentration range studied. The treatment of chitosan beads with cross-linking agent results in the decrease of free amine group, a decrease in the accessibility to the internal site, which lead to the

Table 2: Solubility and swelling behaviour of chitosan and cross-linked chitosan beads (Temperature : 30⁰C; pH : 3.5)

Beads	0.1 N CH₃COOH		Distilled water		0.1 N NaOH	
	Solubility	Swelling (%)	Solubility	Swelling (%)	Solubility	Swelling (%)
Chitosan	Partial soluble	557.2	Insoluble	587.3	Insoluble	198.2
Chitosan-ECH	Insoluble	920.8	Insoluble	441.1	Insoluble	313.5

Table 3: A comparative study of the progress of adsorption of $K_2Cr_2O_7$ on chitosan and chitosan-ECH (Initial $[K_2Cr_2O_7]$ = 4.56×10⁴; Temperature : 30°C; pH : 3.5)

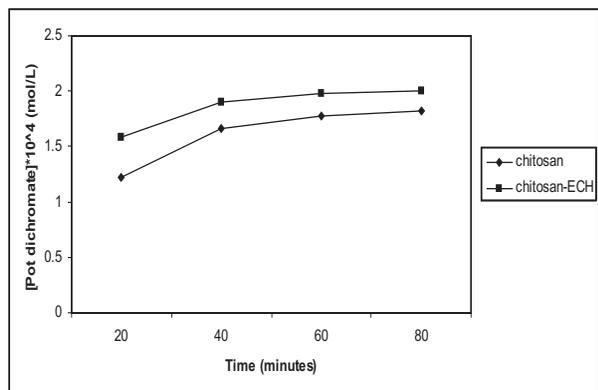| S.No.	Time (min)	$[K_2Cr_2O_7]$ x 10⁴ adsorbed by chitosan beads (mol/L)	Adsorption by Chitosan beads (%)	$[K_2Cr_2O_7]$ x 10⁴ adsorbed by Chitosan-ECH (mol/L)	Adsorption by Chitosan - ECH beads (%)
1	20	1.58	36.7	1.22	28.4
2	40	1.90	44.2	1.70	39.5
3	60	1.98	46.1	1.78	41.4
4	80	2.0	51.2	1.92	44.7

Fig. 2: Plot of the adsorption of K$_2$Cr$_2$O$_7$ on chitosan and chitosan-ECH beads versus time at pH 3.5 and temperature 30^{0}C
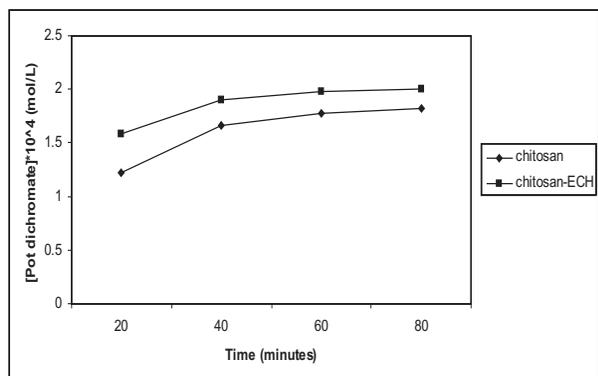

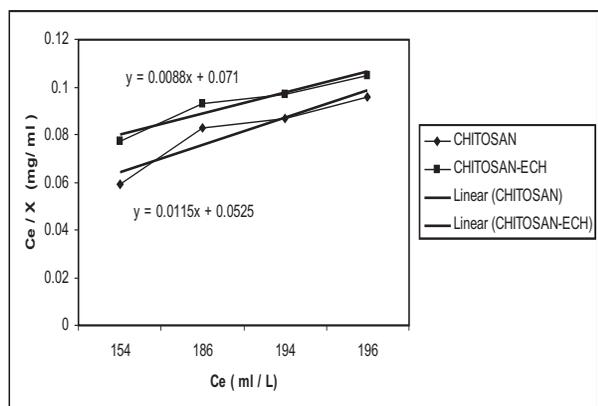**Fig. 3: Dependence of K$_2$Cr$_2$O$_7$ adsorption with pH at 30^{0}C**

Fig. 4: Linearized Langmuir isotherms of Cr(VI) on chitosan and chitosan-ECH

Table 4: Adsorption constants and R$_L$ values calculated from Langmuir equation

Beads	Adsorption constants		R$_L$ values
	X$_{ma}$ (mg/g)	b, (ml/mg)	
Chitosan	86.9	4.5	0.05
Chitosan-ECH	11.3	1.2	0.02

decrease of adsorption performance. The effect of isotherm shape with a view to predicting if an adsorption system is favourable or unfavourable. Langmuir isotherm can be expressed in term of a dimensional constant separation factor or equilibrium parameter, R$_L$ which is defined by

$$R_L = [1/(1+ b.C_o)]$$

Where C$_\ominus$ is the initial Cr (VI) concentration (ppm) and b is Langumir adsorption equilibrium constant (ml mg^{-1}). The R$_L$ values, show (0 < R$_L$ < 1) that favourable adsorption of Cr (VI) on chitosan and chitosan-ECH beads takes place, are given in Table 4 along with the X$_{max}$ and b values. If value of R$_L$ > 1, it shows the unfavourable conditions for adsorption and R$_L$ = 0, is for irreversible adsorption [27].

Conclusion

Environmental requirements in today's society have an increased interest in the industrial use of natural and renewable resources such as chitosan and its derivatives. In particular, the increasing cost of conventional adsorbents undoubtedly make biopolysaccharide materials as one of the most attractive biosorbents for wastewater treatment, for separation processes and also for analytical purposes.

Despite, a lot of the of research work published on natural adsorbents for pollutants uptake from contaminated water, there is yet little literature containing a full study of removal of Cr(VI) by using chitosan and its cross-linked derivatives. In this research paper we have taken into account the different pH values for adsorption of Cr(VI), solubility, swelling and cross-linking behaviour. Chitosan beads show higher adsorption capacity than cross-linked chitosan beads but cross-linked chitosan beads can be used in low pH solution. R$_L$ values obtained show that there is favorable adsorption of Cr(VI) ions on chitosan and chitosan-ECH beads.

Reference

1. Rengaraj S, Yeon HK and Moon HS *Journal of Hazardous Materials* **B87** (2001) 273-287

2. Crini G *Progress in Polymer Science* **30** (2005) 38

3. Shetty R A *Thesis submitted to the faculty of Worcester Polytechnic Institute* May 2006

4. Jassal PS *Proc Indian Natn Sci Acad* **74** No. 2 (2008) 57

5. Moser L *Separation and Purification Technology* **26** (2002) 137

6. Ngah WWS, Endud CS and Mayanar R *Reactive & Functional Polymers* **50** (2002) 181

7. Nomanbhay M and Palanisamy K *Electronic J Biotechnology* Vol **8**(1) (2005) 44

8. Grégorio C *Progress in Polymer Science* **30**(1) (2005) 38

9. McKay G *Chem Eng J* **27** (1983) 187

10. Guibal E, Milot C and Tobin JM *Ind Eng Chem* **37** (1998) 1454

11. Guibal E, Milot C, Eerradosi O, Gauffier C and Domard A *Int J Biol Macromol* **24** (1999) 49

12. Zeng XF and Ruckenstein E *J Membra Sci* **148** (1998) 195

13. Zeng XF and Ruckenstein E *Ind Eng Chem Res* **37** (1998) 159

14. Chiou MS and Li HY *Chemosphere* **50** (2003) 1095

15. Wei YC, Hudson SM, Mayer JM and Kaplan DC *J Polym Sci Part A Polym Chem* **30** (1992) 2187

16. Paulino TA *Journal of Hazardous Materials* **147** (2007) 139

17. Ngah WSW, Endud CS and Mayanar R *Reactive & Functional Polymers* **50** (2002) 181

18. Kozlowski CA, Walkowiak W *Water Res* **36** (2002) 4870

19. Pearce CI, Lloyd JR and Guthrie JT *Dyes Pigments* **58** (2003) 179

20. McMullan G, Meehan C, Conneely A, Kirby N, Robinson T and Nigam P *Appl Microbiol Biotechnol* **56** (2001) 81

21. Fu Y and Viraraghavan T *Bioresour Technol* **79** (2001) 251

22. Jansson-Charrier M, Guibal E, Roussy J, Delanghe B and LeCloirec P *Water Res* **30** (1996) 465

23. Wu FC, Tseng RL and Juang RS *Hazardous Mater* **B3** (2000) 63

24. Guibal E, Jansson-Charier M, Saucedo I and LeCloierc P *Langmuir* **11** (1995) 591

25. Hsien TY and Rorree GL *Ind Eng Chem Res* **36** (1997) 3631

26. Ngah WSW and Isa IM *J Appl. Polym Sci* **67** (1998) 1067

27. Paulino AT, Simionato JI, Garcia JC and Nozaki *J Carbohydr Poly* **64** (2006) 98