



# Studies on the Performance of Protonated cross linked Chitosan Beads (PCCB) for Chromium Removal

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## Abstract

The heavy metals in the soil and ground water have endangered our environment and human body by direct or indirect pathway. Theoretically, the traditional remediation method is physical-chemical processes, which resulted in high capital cost and serious damage in contaminated sites. Currently, bioremediation is a developing biologic process that offers the possibility to destroy various contaminants using natural biological activity. Biopolymers are industrially attractive for a number of reasons; their capability of lowering transition metal-ion concentration to parts per billion concentrations, they are widely available and are environmentally safe. This paper deals with the preparation of protonated cross linked chitosan beads for the removal of chromium ions from aqueous solution. The effect of process parameters such as initial metal ion concentration, contact time, pH and temperature were studied on the performance of percentage removal of chromium. Adsorption isotherms and kinetic studies were established to test the solute interaction with solvent and rate of the reaction respectively. Thermodynamic parameters were also determined to find the nature and spontaneity of the reaction.

**Keywords:** chitosan, protonated beads, chromium, isotherms, kinetics.

## Introduction

Water contamination is a major environmental problem since it affects the environment and human health. Among the various contaminants the heavy metal contamination becomes a very serious problem because it is not deteriorated by natural phenomena called biochemical decomposition. Among various toxic heavy metals, chromium is the most important because of its carcinogenetic nature and also wide application in industries<sup>1</sup>. Chromium exists in two forms viz Cr (III) ions and Cr (VI) ions, which are generated from various industrial processes such as electroplating, leather tanning, mining, dyes and pigments, steel fabrication, canning industries etc. Cr (III) ions are non toxic and play an essential role in the metabolism of plant and animals. Cr (VI) ions are highly toxic. Inhalation of Cr (VI) ions leads to the carcinogenetic problem. Other health effects of Cr (VI) ions are the skin allergy, liver and stomach problems<sup>2,3</sup>.

Due to its severe toxicity, Environmental Protection Agency Cincinaati OH USA, set the tolerance limit for the discharge of Cr (VI) ions into surface water is 0.1mg/l and in potable water is 0.05 mg/l<sup>4</sup>. Therefore it is desired to remove the traces of chromium from the effluent.

A number of methodologies with varying degrees of success have been developed to manage water pollution. Some of them involve coagulation, foam floatation, filtration, ion exchange, sedimentation, solvent extraction, adsorption, electrolysis, chemical oxidation, disinfection, chemical precipitation and

membrane process. One of the efficient methodologies is adsorption because of convenience, easy operation and simplicity of design. Further the process can remove or minimize different type of pollutants at lower concentration level and thus it has a wider applicability in water pollution control<sup>5,6</sup>.

Many natural adsorbents have been investigated for the removal of heavy metals from water. Some of them are chitin, chitosan, natural zeolites, perlite, rice hull, saw dust, bio mass etc. Chitosan, a bio polymer of glucosamine, has received considerable attention for metal ion removal due to its excellent metal binding capacities and its ready availability. It has been widely used as an adsorbent for transition metal ions and organic species. Cross linking agents like glutaraldehyde, epichlorohydrin etc., are used to enhance the stability of chitosan in acidic medium by forming Schiff base reactions<sup>7,8</sup>.

Hence in this present study, Chitosan beads cross linked with glutaraldehyde and protonated in acidic medium was prepared and used for the removal of chromium ions in aqueous solution.

## Material and Methods

Chitosan flakes were provided by "The Medica" Chemicals Limited Chennai (India). The chemicals used in this study such as nitric acid, sulphuric acid, acetic acid, sodium hydroxide, acetone etc were supplied by Merck, India. Potassium dichromate was used for the preparation of Cr (VI). The AR grade of 1, 5-diphenyl carbazide was used for analyzing

chromium. Glutaraldehyde was used as a cross linking agent. Double distilled water was used to prepare all the solutions.

**Preparation of Protonated Cross linked Chitosan beads (PCCB):** Protonated Chitosan beads (PCCB) were prepared by dissolving 3.5 wt % of chitosan in acetic acid. The chitosan gel was then dropped into 2M NaOH which was remained for 12 hrs and washed with distilled water to remove excess NaOH. Then it was cross linked with glutaraldehyde solution (5g/gdry chitosan) for 24hrs. The beads were then cautiously washed with distilled water. The material was then protonated by 30min gentle stirring in a 0.3N hydrochloric acid solution<sup>9</sup>. Then it was dried and stored for further use.

**Batch experiments:** Batch adsorption studies were conducted to determine the percentage removal and adsorption capacity of Cr (VI) ions using PCCB. 2g of PCCB was added to the known concentration of Cr (VI) ions at pH 2 in a reaction mixture and agitated at a speed of 300 rpm. The sample was collected at known interval of time and was analysed using systronics UV-VIS spectrophotometer-119. The amount of adsorption at equilibrium,  $q_e$  (mg/g) and percentage removal (%) were calculated using the equation 1 and equation 2.

$$q_e = (C_0 - C_e)V/m \quad (1)$$

$$\text{Percentage removal} = [(C_0 - C)/C_0] \times 100 \quad (2)$$

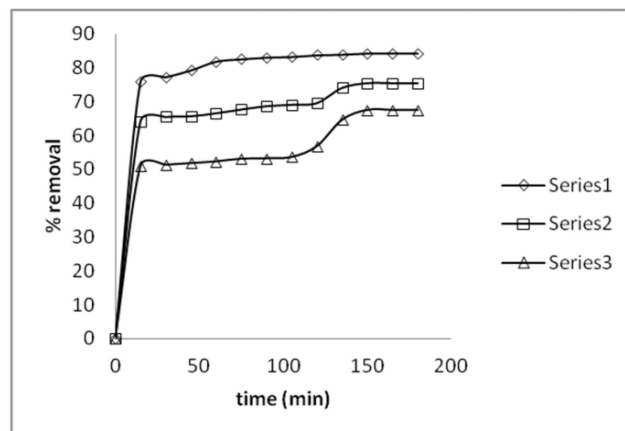
where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations (mg/l),  $V$  is the volume of solution (l),  $q_e$  is the adsorption capacity (mg/g),  $m$  is the weight of adsorbent (g) and  $C$  is the solution concentration at the end of the adsorption process (mg/l).

## Results and Discussion

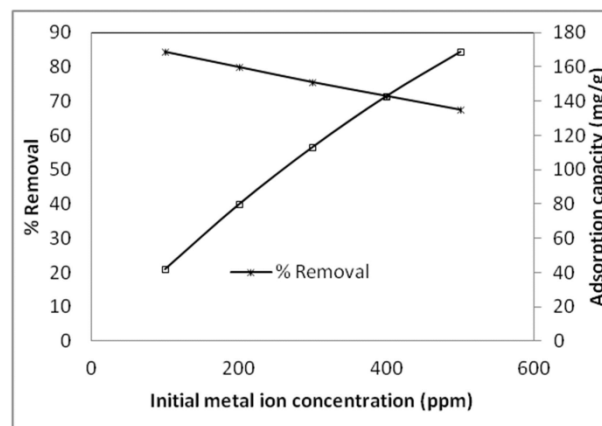
**Effect of contact time:** The effect of contact time on percentage removal of Cr (VI) ion using PCCB was studied for 100 ppm, 300 ppm and 500 ppm of initial metal ion concentration at 2g/l of adsorbent dosage at 2.0 pH and agitation speed of 300 rpm in order to determine the equilibrium time. The results are shown in figure1. It is observed that the rate of adsorption initially increased and then gradually remained constant with increase in contact time and reached the equilibrium nearly at 150 min. This may be due to the availability of a large number of vacant sites initially for adsorption, later the adsorption capacity tailed off due to the saturation of vacant sites.

**Effect of initial metal ion Concentration:** Figure 2 represent the effect of initial metal ion concentration on adsorption capacity and percentage removal of Cr (VI) ion using PCCB. The adsorption capacity of Cr (VI) ions was increased and the percentage removal of Cr (VI) ions was decreased with increased metal ion concentrations. The increase in adsorption capacity may be due to the higher adsorption rate and utilization of all active sites available for the adsorption at higher

concentration and also the higher initial adsorbate concentration provided higher driving force to overcome all mass transfer resistances of the metal ions from the aqueous to the solid phase resulting in higher probability of collision between Cr (VI) ions and the active sites. The decrease in percentage removal may be due to the limited number of active sites in the adsorbent attained saturation above certain concentration.



**Figure - 1**  
Effect of contact time on % removal for Cr (VI) ions using PCCB



**Figure - 2**  
Effect of initial metal ion concentration on percentage removal for Cr (VI) ions using PCCB

**Effect of pH:** The effect of pH on adsorption capacity of Cr (VI) ion using PCCB is shown in figure3. The maximum percentage removal of Cr (VI) ion was obtained at lower pH.

This may be due to the surface positive functional group carries the negatively charged anion by electrostatic force of attraction and the pH decreased, the protonation of the amino groups increased, which increased the percentage removal. The adsorption mechanism probably an acid-base reaction involving amine groups. At higher pH, the protonation of adsorbent decreased which leads to decrease in percentage removal<sup>10</sup>.

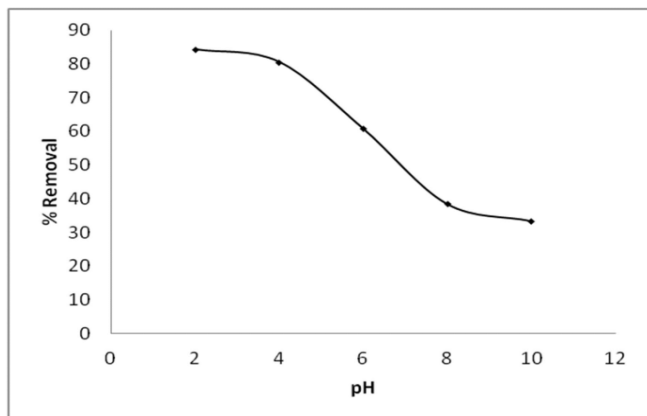


Figure-3

Effect of pH on percentage removal of Cr (VI) ions using PCCB

**Effect of temperature:** Figure 4 represents the effect of temperature on removal of Cr (VI) ions for various initial metal ion concentrations. It was observed that the percentage removal increased with increase in temperature for all initial metal ion concentration. This may be due to the generation of new active sites on the surface of the adsorbent and also increased rate of pore diffusion of the adsorbent which leads to the endothermic adsorption.

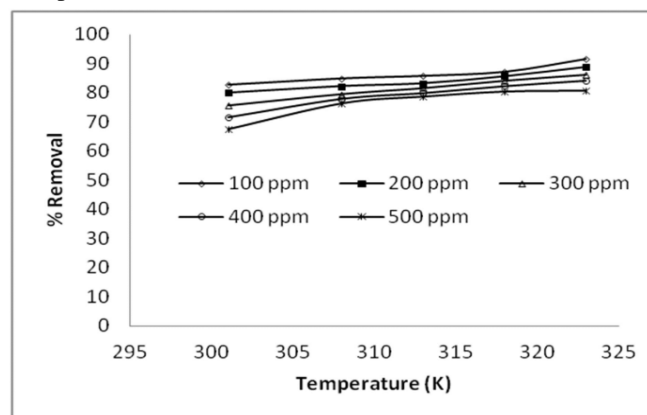


Figure-4

Effect of temperature on % removal of Cr (VI) ions using PCCB for various initial concentration

**Adsorption isotherms:** Adsorption isotherm describes the interaction of solute in the liquid phase and the adsorbent in solid phase. Various adsorption isotherm models are available to fit the experimental data. In this present study, the following isotherms were used to fit the experimental data<sup>11</sup>.

The generalised equation of Langmuir isotherm is given by equation (3).

$$q_e = \frac{\theta b C_e}{1 + b C_e} \quad (3)$$

The linearised form of Langmuir isotherm is given by equation (4).

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

where  $\theta$  (mg/g) is the measure of adsorbed quantity under the experimental conditions and  $b$  is a constant related to the energy of adsorption.

The generalised equation of Freundlich isotherm is given by equation (5).

$$q_e = K C_e^{1/n} \quad (5)$$

The linearised form of Freundlich isotherm is given by equation (6)

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \quad (6)$$

where  $n$  is indicative of bond energies between metal ion and the adsorbent and  $K$  is related to bond strength.

The generalised equation of Redlich Peterson isotherm is given by equation (7)

$$q_e = \frac{A C_e}{1 + B C_e^g} \quad (7)$$

The linearised form of Freundlich isotherm is given by equation (8)

$$\ln \left( A \frac{C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln B \quad (8)$$

where  $B$  ( $\text{cm}^3/\text{mg}$ )<sup>g</sup> and  $g$  are Redlich Peterson constants.

The various isotherm constants were calculated and presented in table 1.

Table-1

Parameter values for various isotherms

Isotherm models	Constants for PCCB	r <sup>2</sup>
Langmuir isotherm	$\theta$ ( $\text{mg g}^{-1}$ )= 250, $b$ ( $\text{L mg}^{-1}$ )= 0.012	0.9929
Freundlich isotherm	$1/n=0.5955$ , $K$ ( $\text{mg g}^{-1}$ )= 8.486,	0.9950
Redlich Peterson isotherm	$g = 0.4073$ , $B = 28.916$ ,	0.9965

Figure 5 shows the theoretical isotherms and equilibrium data for adsorption of Cr (VI) ions using PCCB. From figure, it is observed that the Freundlich and Redlich Peterson isotherms were almost overlapped and seemed to be best fitting models for the experimental data. This reveals the multilayer adsorption of Cr (VI) ions on PCCB adsorbent.

**Adsorption Kinetics:** The linearized forms of pseudo first order, pseudo second order and elovich adsorption kinetic models are given in equations (9), (10) and (11) respectively<sup>12</sup>.

$$\ln(q_e - q_t) = \ln q_e - K_{1ad} t \quad (9)$$

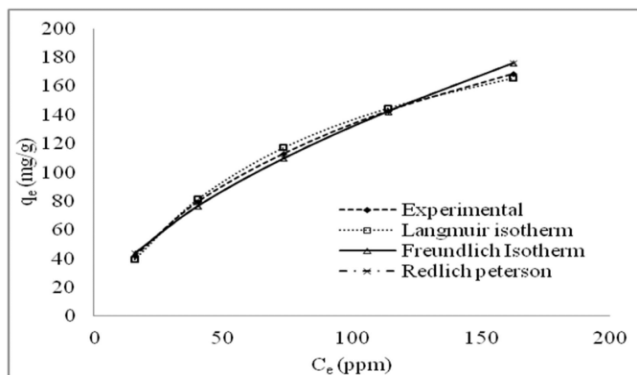


Figure- 5

**Theoretical Isotherms and experimental data for adsorption of Cr (VI) ions using PCCB**

where  $q_t$  is adsorbed quantity at time  $t$  (mg/g) and  $K_{lad}$  is the pseudo-first-order rate constant in  $\text{min}^{-1}$

$$\frac{t}{q_t} = \frac{1}{K_{2ad} \cdot q_e^2} + \frac{t}{q_e} \quad (10)$$

$K_{2ad}$  is the pseudo-second-order rate constant in  $(\text{g mg}^{-1} \text{min})$

$$q_t = \alpha + \beta \ln t \quad (11)$$

where  $\alpha$  and  $\beta$  are the simple elovich kinetic constants.

Table 2 represents the results obtained from various adsorption kinetic models.

**Table-2**  
**Constants for various adsorption kinetic models**

Kinetic models	Constants	Value
Pseudo first order	$K_{lad} (\text{min}^{-1})$	-0.0067
	$R^2$	0.2712
Pseudo second order	$K_{2ad} (\text{g mg}^{-1} \text{min})$	0.011
	$q_e (\text{mg/g})$	42.5
	$R^2$	0.9998
Simple elovich	$\beta$	1.8765
	$\alpha$	32.796
	$R^2$	0.9533

From the table, it is confirmed that the adsorption of Cr (VI) ions using PCCB followed the pseudo second order reaction. The pseudo second order model indicates the adsorption of Cr (VI) ions on the surface of PCCB is chemical adsorption and is shown in figure 6.

**Intraparticle diffusion:** The possibility of intra-particle diffusion was explored by using the intra-particle diffusion model<sup>12</sup> as given in equation (12).

$$q_t = K_{id} t^{1/2} + C \quad (12)$$

where  $K_{id}$  is the intra-particle diffusion rate constant in  $\text{mg g}^{-1} \text{min}^{-1/2}$  and  $C$  is the intercept. From Figure 7, it is observed that there are two separate regions i.e. the initial portion is attributed to the bulk diffusion ( $k_{id,1}$ ) and the final portion to intra-particle diffusion ( $k_{id,2}$ ) which is also evident from the experimental data followed by Freundlich isotherm (multilayer adsorption).

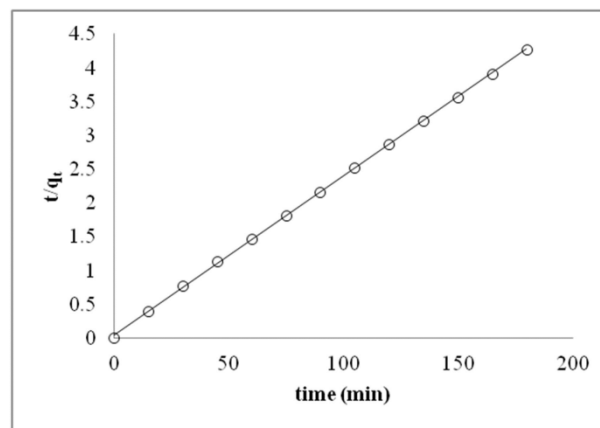


Figure- 6

**Pseudo second order kinetics of adsorption of Cr (VI) ions using PCCB**

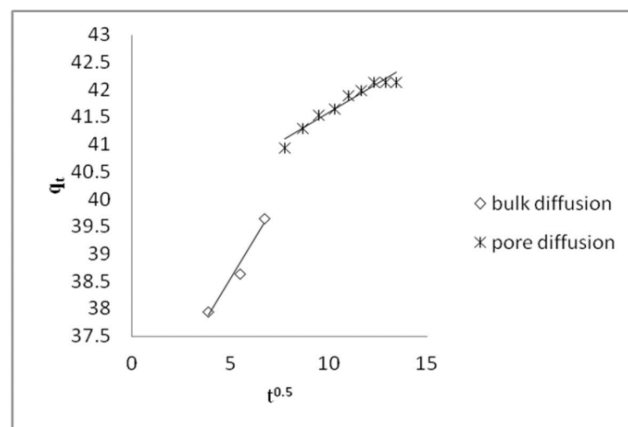


Figure-7

**Intraparticle diffusion for adsorption of Cr (VI) ions using PCCB**

The values of  $k_{id,1}$ ,  $k_{id,2}$ ,  $C_1$  and  $C_2$  using Eq.(4) were found to be  $0.5915 \text{ mg g}^{-1} \text{min}^{-1/2}$ ,  $0.2145 \text{ mg g}^{-1} \text{min}^{-1/2}$ ,  $35.584$  and  $39.436$  respectively from figure 6.

**Thermodynamic Parameters:** The thermodynamic parameters for the adsorption of Cr (VI) ions were determined using the following equations<sup>13</sup> (13), (14) and (15).

$$K_D = \frac{q_e}{C_e} \quad (13)$$

$$\Delta G^\circ = -RT \ln K_D \quad (14)$$

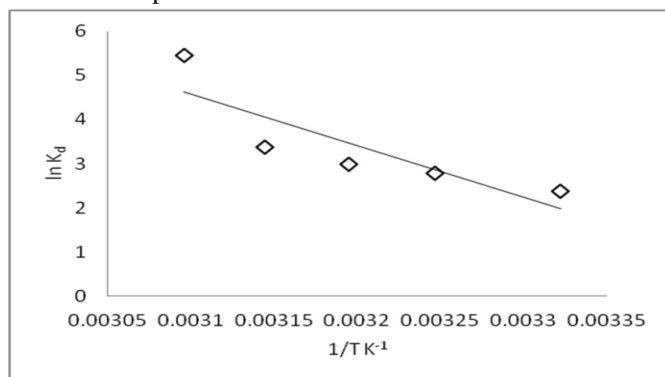
$$\ln K_D = \Delta S^\circ / R - \Delta H^\circ / R.T \quad (15)$$

where  $K_D$  is the distribution coefficient for the adsorption in  $\text{g/l}$ ,  $\Delta G^\circ$  is the Gibbs free energy in  $\text{J/mol}$ ,  $R$  is the gas constant in  $\text{J/mol.K}$ ,  $T$  is the absolute temperature in  $\text{K}$ ,  $\Delta S^\circ$  is the entropy change in  $\text{J mol}^{-1}\text{K}^{-1}$  and  $\Delta H^\circ$  is the enthalpy change in  $\text{KJ/mol}$ .

**Table-3**  
**Thermodynamic parameters for the adsorption of Cr (VI) ions at various temperatures**

S.No	T (K)	$\Delta G^\circ$ J/mol	$\Delta H^\circ$ KJ/mol	$\Delta S^\circ$ J mol <sup>-1</sup> K <sup>-1</sup>
1	301	-5939.88	1410.9	4.925
2	308	-7143.04		
3	313	-7797.75		
4	318	-8925.56		
5	323	14641.9		

The thermodynamic constants were determined from figure 8 and the results for various temperatures are listed in table 3. The positive values of  $\Delta H^\circ$  for all the temperatures indicate the feasibility of the process and the reaction is endothermic. The positive value of  $\Delta S^\circ$  indicate the structural change occurs on the surface of the adsorbent and increased randomness during the adsorption process. The negative values of Gibbs free energy  $\Delta G^\circ$  change indicate the feasibility and spontaneous nature of adsorption.



**Figure- 8**

**Thermodynamic parameters for adsorption of Cr (VI) ions using PCCB**

## Conclusion

This study showed that protonated cross linked chitosan beads can remove the chromium ion. Percentage removal and adsorption capacity were more at low pH values. Percentage removal decreased with increased in initial metal ion concentration and adsorption capacity increased with increased in initial metal ion concentration. Equilibrium adsorption data for chromium removal was best represented by Freundlich isotherm and Redlich Peterson isotherm which reveals multilayer adsorption and is confirmed in intraparticle diffusion. Adsorption kinetics was found to fit suitably in a pseudo second order kinetic model. Thermodynamic studies reveal the endothermic, increased in randomness, spontaneous nature of the adsorption processes.

## Acknowledgements

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