# Preparation, characterisation and chromium (VI) sorption activity of Heptylidene chitosan

P. Alikutty and N. Nasiya

Department of Chemistry, MES Mampad college, Kerala – 673 635

**Abstract:** Heptylidene chitosan was prepared by the condensation of the bio-polymer chitosan with heptaldehyde. It was characterized by FTIR, SEM and DSC and was evaluated for chromium (VI) sorption capacity from aqueous solutions. pH of the solution and metal concentration play an important role in chromium(VI) sorption. Heptylidene chitosan sorbe Cr (VI) at an optimum pH value of 4. Isotherm data fit to Langmuir model which indicate monolayer sorption. The rate studies show that the derivative follows pseudo second order kinetics. Since Heptylidene chitosan is insoluble in acid pH range, it can be effectively used for the removal of chromium (VI) from acid effluents.

**Key words:** Bio-polymer, Heptylidene chitosan, Sorption capacity, Langmuir isotherm, Pseudo second order kinetics

## Introduction

Chitosan is a nontoxic and biodegradable biopolymer produced by alkaline N-deacetylation of chitin, the most abundant natural polymer after cellulose. Chitin is present in the exoskeleton of crustaceans such as the crabs, prawns and shrimps, the cuticles of insects and the cell walls of most fungi [1] and is a cheap resource available in seafood industries. Chitosan consist of 2-amino-2-deoxy (1-4) $\beta$-D glucopyranose residues and has no or small amounts of N-acetyl glucosamine units. Degree of deacetylation varies in different forms of chitosan and derivatives. Chitosan is soluble in acid pH range but insoluble in the neutral or basic range.

As a cheap natural and renewable resource, chitosan and its derivatives posses unique properties such as biocomapatibility, biodegradability and film forming ability and has many applications in biomedicine, agriculture, waste water purification, environmental protection and biotechnology [2]. Chitosan based sorbents have exhibited relatively high sorption capacities for heavy metals due to their high nitrogen content and porosity [3-5]. Metal ion sorption may proceed through different mechanisms: metal cations are adsorbed through a

*Corresponding Author: P. Alikutty E-mail: alikutty.p@gmail.com*

chelation mechanism, while metal anions can be removed by ion exchange reactions. In acidic solutions metal anions can be exchanged with counter anions on the protonated nitrogen.

Heavy metals are not biodegradable and tend accumulate in living organisms, causing various diseases and disorders. Greater awareness of the ecological effects of toxic metals and their biomagnification through food chain has led to a demand for the decontamination of heavy metals in surface waters and industrial effluents. Chromium, the metal known to man from the very early civilization, may enter the environment at any point during mining, refining, geological erosion, manufacturing processes and industrial wastes. Trivalent chromium is required in trace amounts for sugar metabolism in humans. But hexavalent chromium is very toxic and mutagenic. [6-9]

Chitosan has been widely used for the removal of heavy metals from neutral and basic solutions. Since chitosan is soluble in acidic media, attempts have been made by various researchers to chemically modify chitosan so that the derivatives can be used in acidic effluents as sorbents. The use of derivative as sorbent also has environmental significance [10-13].

Tito et al., prepared chitosan with different deacetylation degree (DD) from shrimp wastes and used to remove Cr(VI) from aqueous solution by adsorption.The adsorption data showed that the maximum sorption capacity was 97.4 mg/g on chitosan of 95% DD at pH3 at 298K. The kinetic data was fitted to pseudo second order model.[14] C. Namasivayam and M. V. Sureshkumar used surfactant modified coconut coir pith as biosorbent for the removal of chromium(VI) from water and waste water[15]. C. Gerente and co-workers discussed the application of chitosan as adsorbent for the removal of heavy metals from waste waters[16]. Shafqat et al., investigated kinetic and equilibrium aspects of adsorption of Cr(III) and Cr(VI) on red rose waste biomass.[17]. G. N. Kousalya and co-researchers worked on modified chitosan beads to remove chromium from aqueous solutions. They prepared protonated chitosan beads, carboxylated chitosan beads and grafted chitosan beads, evaluated for Cr(VI) sorption and sorption capacities were found to be 3239, 3647 and 4057 mg/kg respectively.[18]

This work consist of preparation of a Schiff base from chitosan and heptaldehyde, Heptylidene chitosan and its characterization by Fourier Transform Infrared Specroscopy (FTIR), Scanning Electron Microscopy (SEM) and Differential Scanning Calorimetry (DSC).

*Corresponding Author: P. Alikutty E-mail: alikutty.p@gmail.com*

The derivative was evaluated for its chromium (VI) sorption capacity from aqueous acid solutions Sorption experiments for the optimization of parameters viz: pH and contact time were done initially and then carried out the kinetic and equilibrium studies. Sorption isotherms and rate studies were performed. The experimental data were applied to Langmuir model and Kinetic parameters were also evaluated [19,20].

**Materials and Methods**

Materials

Chitosan with 85 percent degree of deacetylation and heptaldehyde were purchased from Sigma Aldrich Co; USA and used as such. Potassium dichromate, ethanol, sodium hydroxide, sulphuric acid and acetic acid were AnalaR quality of Merck, India. All other chemicals used were of analytical grade. All reagents were prepared in de-ionized water.

Instrumental Methods

FTIR spectra of the samples were recorded by diluting in KBr pellets using a Fourier Transform IR Spectrometer (Model-Jasco FT/IR 4108). SEM images of chitosan and the schiff base were taken using a field emission scanning electron microscope (Hitachi SU - 6600 FESEM). Differential scanning calorimetric experiments were carried out in a Perkin Elmer made (Model: DSC 4000) instrument in the temperature range $30 - 375\ ^0C$ under an atmosphere of flowing nitrogen. Microcal Origin software (version 6) was used for computation.

Preparation of Heptylidene chitosan

2g of chitosan was dissolved in 50 mL 5% acetic acid (v/v). 2.92 mL heptaldehyde (twice the equivalent of Glc.N) in 50 mL methanol was added and stirred 2 hours. Kept overnight at low temperature ($5\text{-}8^0C$). The turbid solution was adjusted to pH 10 by addition of NaOH solution when heptylidene chitosan was precipitated. Filtered the precipitate, washed with methanol and then with deionised water to neutrality and dried in an air oven at $60^0C$ for 24 hours. Yield: 2.5432 g. (67.71 %).

Sorption experiments

A stock solution of 500 mg/L potassium dichromate was prepared in de-ionized water. All other concentrations were prepared from this solution by dilution. Optimization of

*Corresponding Author: P. Alikutty E-mail: alikutty.p@gmail.com*

parameters viz, pH and contact time were carried out initially. The effect of contact time on sorption capacity of the schiff base was studied in range of 0-4 h at an initial Cr(VI) concentration of 100 mg/L (50 mL) at pH = 4 with a sorbent dose of 50 mg. For pH studies, 50 ml of 100 mg/L Cr (VI) solution with a sorbent dose of 50 mg was shaken for 2.5 h in an orbital shaker. The pH was varied by concentrated $H_2SO_4$ and NaOH from 1 to 9 and was determined using a pH meter. Equilibrium sorption experiments at pH = 4 were carried out in a 50 ml of Cr(VI) solution in 20-200 mg/L concentration range with 50 mg of heptylidene chitosan by shaking for 2.5 h using an orbital shaker at moderate speed in 125 mL borosilicate glass stoppered bottles at room temperature. Each experiment was duplicated under identical conditions. The aqueous phase Cr (VI) ion concentration was analyzed spectrophotometrically using 0.25% diphenyl carbazide and 6N sulphuric acid at 540 nm.

For kinetic studies 50 mL of 100 mg/L Cr (VI) solution with 50 mg derivative was shaken for 4 h at room temperature at pH = 4. 1 ml of the sample was withdrawn in every half an hour and concentrations and amount of sorption were determined ($q_t$).

The amount of sorption at equilibrium $q_e$ (mg/g) was obtained from the mass balance equation, $q_e = [(C_i-C_e)V]/W$ where $C_i$ is the initial concentration of Cr(VI) in the aqueous phase in mg/L, V is the volume of the solution (L) and W is the weight of the derivative used.

**Results and discussion**

Characterization of heptylidene chitosan

The amino group of chitosan condense with the aldehyde group of heptanal to form the Schiff base.The biopolymer derivative formed was pale yellow in colour, stable in air and insoluble in common organic solvents and in mineral and organic acids which shows the absence of free amino group. FTIR, SEM and DSC were used to confirm the structure of the derivative. The band around 3415 cm$^{-1}$ corresponding to OH and NH stretching vibration in chitosan was shifted to higher frequency 3429.78 cm$^{-1}$ in the FTIR spectra of derivative (Figure 1). Both the spectra exhibit the absorption peaks around 1153, 1100, 1020 and 896 cm$^{-1}$ which can be assigned to saccharide moiety. The new band in the spectra of heptylidene chitosan at 1635.34 cm$^{-1}$ can be assigned to the characteristic C=N group of the Schiff base.

The SEM image of heptylidene chitosan was given in the Figure. 2 which shows that the surface morphology of the derivative is different from that of chitosan. The derivative was more porous and smooth and are capable of accommodating metal ions. The thermal behavior

*Corresponding Author: P. Alikutty E-mail: alikutty.p@gmail.com*

of the Schiff base can be investigated by DSC of the sample which is shown in figure 3. The endotherm observed in the curve around 100 $^0$C was due to the evaporation of water contained in the sample. Carbohydrate polymers usually contain water in them. The endotherm is followed by an exotherm around 300 $^0$C which represent the degradation of the polymer. DSC experiments shows that Schiff base is thermally less stable than chitosan.
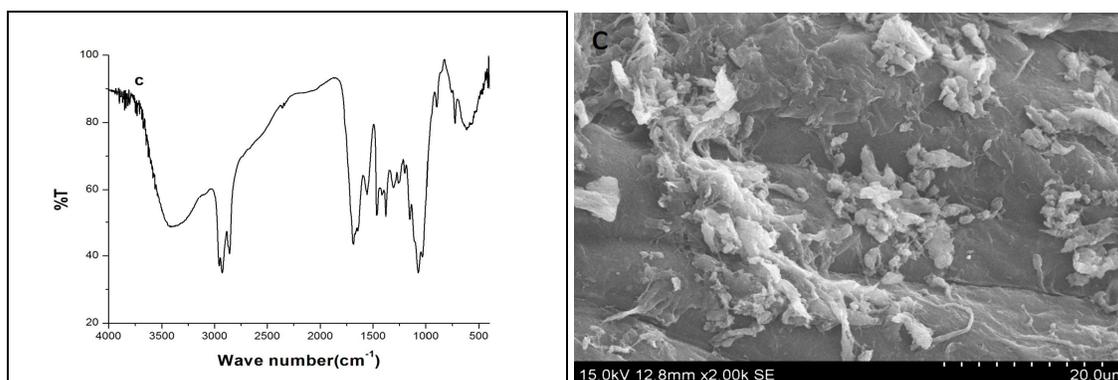


Fig. 1 FTIR spectra of heptylidene chitosan



Fig. 2 SEM image of heptylidene chitosan
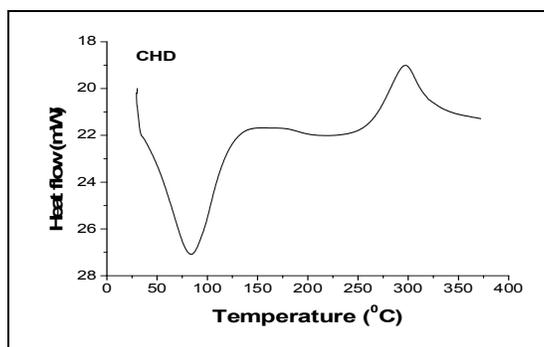


Fig. 3 DSC curve of heptylidene chitosan

Effect of Contact time

Sorption capacity of heptylidene chitosan was determined by varying the contact time from 0 to 4 h and observed that the sorption capacity increased sharply during the first hour, after that a slow increase was observed until it reach a saturation in 2.5 h. Hence 2.5h was fixed as the contact time for the entire work. The sorption capacity in 2.5 h was 68.52 mg/g at pH = 4.

*Corresponding Author: P. Alikutty E-mail: alikutty.p@gmail.com*

Effect of pH

The chromate removal from aqueous solutions is very much dependent on solution pH. So pH study on removal of metal ions is significant. In aqueous solutions Cr(CVI) exist mainly as $HCrO_4^-$ at pH < 6 while the predominant species of Cr(VI) is $CrO_4^{2-}$ at pH > 6 when concentration of Cr(VI) is around 100 mg $L^{-1}$. The optimum pH for chromium(VI) sorption on heptylidene chitosan was pH = 4 and sorption capacity at this pH is 63 mg $g^{-1}$.

Sorption kinetics

The kinetics of sorption of Cr(VI) on heptylidene chitosan indicated a rapid initial binding followed by a slow increase until a state of equilibrium was reached in 2.5 h. After 2.5 h no appreciable change in concentration was observed. Sorption data were fitted to a pseudo second order kinetic model.

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

where $k_2$ is the pseudo second order rate constant.( mg $g^{-1}h^{-1}$), $q_e$ and $q_t$ are the amount of metal ion sorbed (mg $g^{-1}$) at equilibrium and at time $t$ respectively. From the second order model $t$ vs $t/q_t$ curve can be drawn, $k_2$, the pseudo second order rate constant can be calculated from the intercept and $q_e$, the equilibrium sorption capacity from the slope. Fig. 4 shows the plot. The pseudo second order rate constant for Cr(VI) sorption was found to be 0.02203 mg $g^{-1}h^{-1}$ at pH = 4 and $q_e$ = 63 mg $g^{-1}$.

Sorption isotherm

Langmuir isotherm has been adopted to quantify the sorption capacity of heptylidene chitosan for Cr(VI) sorption. The data fitted to the isotherm equation. The linearized Langmuir isotherm equation is shown below

$$\frac{C_e}{q_e} = \frac{1}{Q.b} + \frac{1}{Q} C_e \qquad (2)$$

where $q_e$ is the amount of solute sorbed (mg $g^{-1}$) at equilibrium and $C_e$ is the equilibrium conc. (mg $L^{-1}$), the values of the empirical constants Q and b denote monolayer sorption capacity and energy of sorption respectively and were calculated from the slope and intercept of the plot between $C_e$ and $C_e/q_e$ (Fig. 5). From the plot, Q, the maximum monolayer sorption capacity was found to be 130.37 mg $g^{-1}$ and Langmuir constant b = 0.0297 L $mg^{-1}$ at pH = 4. Langmuir fitting indicated homogeneity of the sorbent surface and monolayer sorption.

*Corresponding Author: P. Alikutty E-mail: alikutty.p@gmail.com*

Heptylidene chitosan is efficient at removing chromate from acidic effluents. The results obtained were comparable to the sorption capacities reported on some other derivatives of chitosan.
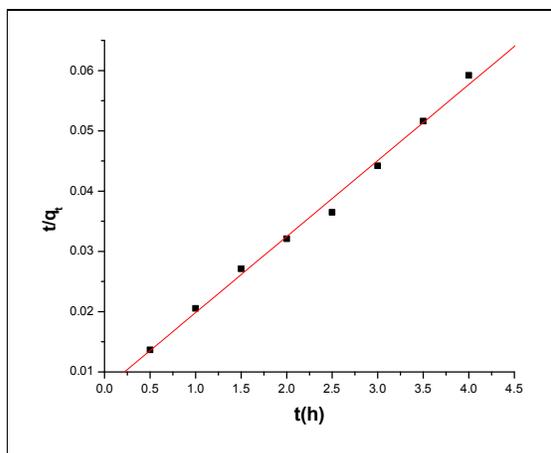


**Fig. 4** Sorption kinetics(pseudo second order)          Fig. 5 Langmuir isotherm plot
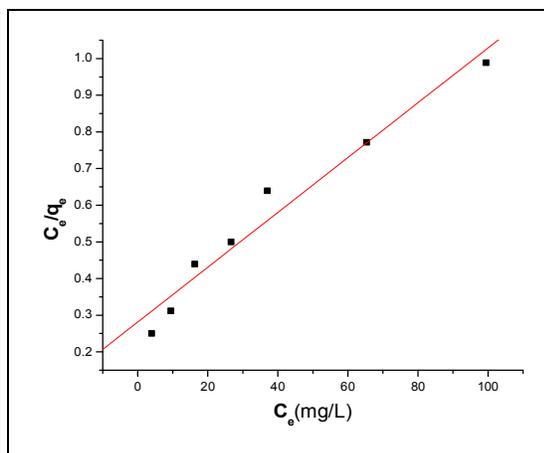
**Conclusion**

A Schiff base of chitosan with heptaldehyde, heptylidene chitosan was prepared and characterized by Fourier Transform IR spectroscopy, scanning electron microscopy and differential scanning calorimetry. The derivative was evaluated for chromium (VI) sorption. The sorption occurred and the sorbent is efficient at removing chromate anions from dilute solutions through electrostatic attraction and anion exchange processes at acidic pH range. The sorption followed pseudo second order kinetics. Sorption kinetics is strongly controlled by the pH. Sorption data fitted to Langmuir isotherm and the maximum sorption capacity was found to be 130.37 mg/g at pH = 4. Isotherm data indicates the interaction of anionic species with the protonated derivative. The values were comparable with some other forms of chitosan and chitosan modifications.  Heptylidene chitosan is an efficient, cheap and biodegradable sorbent for chromium (VI) ions in acid medium.

*Corresponding Author: P. Alikutty E-mail: alikutty.p@gmail.com*

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*Corresponding Author: P. Alikutty E-mail: alikutty.p@gmail.com*