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# Preparation, Characterization and Cr(VI) Sorption Activity of Chitosan-Citral Schiff Base

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**ABSTRACT**

A Schiff base of chitosan with citral was prepared and characterized by Fourier Transform IR spectroscopy and Scanning Electron Microscopy (SEM). The Schiff base was evaluated for Cr(VI) sorption. The sorption occurred. Sorption data fitted to both Freundlich and Langmuir isotherm models. The best fitting is to Langmuir model. Maximum sorption occurred at acidic pH (58.82 mg/g). Isotherm studies indicated that the Schiff base has different binding sites having different binding affinities. Thus, the Schiff base from chitosan and citral was found to be an efficient and cheap sorbent for Cr(VI).

*Keywords*: Biodegradable polymer, Fourier Transform IR Spectroscopy, Scanning Electron Microscopy, Freundlich isotherm, Langmuir isotherm

## INTRODUCTION

Chitosan is a nontoxic and biodegradable biopolymer produced by alkaline N-deacetylation of chitin, the most abundant natural polymer after cellulose (Hengameh & Barikani, 2009; Ngo *et al*., 2015). 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 and is a cheap resource available in seafood industries. Chitosan consists of 2-amino-2-deoxy (1-4) β-D glucopyranose residues. Chitosan is soluble in acid pH range, but insoluble in the neutral or basic ranges.

As a cheap natural and renewable resource, chitosan and its derivatives possess unique properties such as biocompatibility, biodegradability and film forming ability and has many applications in biomedicine, agriculture, waste water purification, environmental protection and biotechnology (Mujeeb *et al*., 2014). Chitosan-based sorbents have exhibited relatively high sorption capacities for heavy metals due to their high nitrogen content and porosity.

Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. 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 (Kosla *et al*., 2018). But hexavalent chromium is very toxic and mutagenic (Rumpa *et al*., 2011). 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. Here, we prepared a Schiff base from chitosan and citral (CCSB). Both chitosan and citral are naturally occurring and biodegradable. The use of Schiff base as sorbent also has environmental significance.

## METHODOLOGY

The Schiff base was characterized by SEM and FTIR and evaluated for its chromium (VI) sorption capacity. Sorption experiments for the optimization of the parameters viz., contact time, sorbent dose and pH were done initially and then carried out the equilibrium studies. The experimental data were applied to Langmuir (Langmuir, 1916) and Freundlich models (Freundlich, 1906) and evaluated.

CCSB was prepared by stirring chitosan dissolved in acetic acid and citral in methanol (in equimolar ratio) and purified by vacuum distillation. It was characterized by FTIR and SEM. CCSB was evaluated for the removal of CR(VI). 0.05g of Schiff base was shaken for 4 hrs with 0.05L of potassium dichromate solution in 0.125L stoppered bottle using an orbital shaker (KEMI make). Equilibrium studies were conducted by carrying out the experiment with five different concentrations ranging from 20-100 mg/L dichromate solutions. The sorption experiments were carried at three different pH values viz., 3, 7 and 10. The equilibrium concentrations were determined calorimetrically by a spectrophotometer (Systronics make) using 6N sulphuric acid and 0.25% diphenyl carbazide as colouring agents. The amount of sorption was calculated using the equation $q_e=(C_0-C_e)V/W$ where $C_0$ and $C_e$ are initial and equilibrium concentrations in mg/L, V volume of solution in L and W mass of the sorbent in g.

## RESULT AND DISCUSSION

### Characterization of Schiff base

In the Schiff base formation, the amino group of chitosan condenses with the aldehyde group of citral. The biopolymer Schiff base formed was brownish 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. The FTIR spectroscopy was used to confirm the structure of the Schiff base. In the FTIR spectra of the Schiff base, new absorption peaks appear at 1648.84 and at 1612.2 $cm^{-1}$. The former represents C=N stretching vibration of imine group and the latter C=C stretching vibration. The SEM images of chitosan and the Schiff base that the surface morphology of the Schiff base is different from that of chitosan. The Schiff base was more porous and smoother and is capable of accommodating metal ions.

### Effect of contact time and sorbent dose

Sorption capacity of Schiff base was determined by varying the contact time from 0 to 8h. The results shows that sorption capacity increased sharply during the first hour, after that a slow increase were observed until it reaches saturation in 4h. Sorption experiments by varying adsorbent dose from 25 mg to 100 mg shows that sorption capacity decreased with increase in weight of the sorbent.

**Effect of pH**

The metal ion removal from aqueous solutions is very much dependent on solution pH. Effluents from industries and urban discharges are having very high or low pH. So pH study on removal of metal ions is significant. We evaluated the sorption capacity of Schiff base for the sorption of Cr(VI) at different pH values. Maximum sorption was observed at pH 3.

**Sorption isotherm**

Equilibrium studies were carried out at pH 3, 7 and 10. In each case five different concentrations of dichromate ranging from 20-100 mg/L were shaken 4 hrs after adjusting the desired pH using conc. $HNO_3$ and NaOH. Sorption data were applied to Langmuir and Freundlich isotherm models. Langmuir model was more fitted to the experimental data. The linearised Langmuir equation $C_0/q_e=(1/K_LQ)+C_e/Q$ was used to evaluate Langmuir parameters $K_L$ and Q where Q represent sorption capacity of the sorbent.

From the Langmuir isotherms ploted, we observed the sorption capacity Q of the Schiff base for Cr(VI) as 58.82 mg/g at pH 3, 33.3 mg/g at pH 7 and 38.6 mg/g at pH 10. Results show that maximum sorption occurred at acidic pH. This was due to the swelling behaviour of the polymer at low pH.

**CONCLUSION**

The study shows that the maximum sorption of chitosan derivative by Cr(VI) occurs at pH 3 which is considered to be due to the swelling behaviour of the polymer at low pH.

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