Hexavalent Chromium Interaction with Chitosan

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Synopsis

Chitosan prepared from fresh water crab shells was used for hexavalent chromium removal. Kinetic studies indicated a rapid removal of chromium from aqueous solutions. The first-order rate constant for chromium removal was calculated to be 1.92 h^{-1}. Sorption isothermal data could be interpreted by the Langmuir relationship. Drastic decrease in chromium removal was observed with the increase in pH. Sorption was almost 90% at pH 3 at an initial chromium concentration of 5 mg/L and reduced to 10% at pH 7 and above. Presence of electrolytes and chloride significantly affected the chromium removal, indicating the electrostatic attraction as the main removal mechanism. Regeneration of the sorbent with alkali was not very effective as only 60–65% of sorbed chromium could be recovered.

INTRODUCTION

The use of chromates and dichromates in plating and as corrosion control agents in cooling waters is quite extensive. It is known that hexavalent chromium is toxic to living systems and must be removed from industrial wastewaters before these are discharged to surface waters. Treatment for hexavalent chromium generally involves chemical reduction to Cr^{3+} at acidic pH. The Cr^{3+} is then precipitated as hydroxide at alkaline pH with either caustic or lime.[1,2] Nonreductive treatments include anion exchange[3,4] and adsorption.[5-7] It is reported that tertiary and quaternary ammonium groups can be introduced to polysaccharides and these derivatives can be used for the removal of metal anions.[8] Many researchers have explored the possibility of using naturally occurring polysaccharide chitin and its deacetylated product, chitosan, for metal cation removal.[9-11] Chitin occurs abundantly in crustaceans, insects, fresh water and marine crabs, prawns, and similar organisms. It is prepared from shells, which is a waste product of the crab meat canning industry. Its deacetylated product, chitosan, has amino groups, which in protonated form may act as a good metal anion scavenger. This aspect has not been studied in detail. In this communication, removal of hexavalent chromium by chitosan is reported.

EXPERIMENTAL

Materials. Chitosan was prepared in the laboratory from fresh water crab shells. Stock chromium solution was prepared in distilled water using potassium dichromate and working solutions were prepared by diluting this stock solution.

Analysis of solutions for hexavalent chromium was carried out colorimetrically using diphenyl carbazide reagent by adapting the procedure described in Standard Methods for the examination of water and wastewaters.[12]

Sorbent Preparation. Chitosan was prepared from fresh water crab shells, which were crushed to required particle size. The powder was washed with distilled water and then treated with $1N$ HCl to remove calcium carbonate. This was followed by repeated washings with distilled water. This acid treated material was digested with 50% NaOH (5 vol per unit weight) at 80°C in the presence of nitrogen for 5 h. The product, chitosan, was washed with distilled water to remove excess alkali, followed by alcohol and acetone. Chitosan was dried at 40°C for 12 h and stored at room temperature.

Batch Sorption Tests. Batch sorption experiments were conducted at room temperature (25 ± 2°C) in a rotary shaker using 300 mL glass bottles. Reaction volume consisted of 150 mL containing 500 mg/L sorbent. For the sorption kinetic studies, initial concentrations of chromium was kept in the range of 1–5 mg/L. After required contact time, supernatant was analyzed for chromium. Sorption equilibrium studies were conducted using a contact time of 12 h. Isotherm studies were conducted with a constant sorbent concentration and varying initial concentrations of chromium.

Effect of pH of the suspending medium on chromate removal was studied in the pH range of 3–9. Initial solution pH was adjusted to required pH levels using either $0.01N$ HCl or $0.01N$ NaOH. Chitosan was equilibrated at the particular pH for 24 h before the addition of sorbate. Solution pH was also maintained at the required level by including appropriate buffers such as 5 mL of $0.1M$ acetate (pH 4, 5), $0.1M$ phosphate (pH 6, 7), and $0.1M$ borate (pH 8, 9) with chromium solution.

Effect of ionic strength (as sodium perchlorate) and chloride on chromium sorption were studied by adding different concentrations of these to 5 mg/L chromium solution. Equilibrium contact time of 12 h was given in all these experiments.

For desorption studies, initially 1.5 g of chitosan was loaded with chromium using 600 mL of 100 mg/L chromium solution and a contact time of 12 h was given. Chromium-laden chitosan was collected, washed with distilled water, and air-dried. The amount of chromium adsorbed per gram of chitosan was determined by measuring the supernatant chromium concentration. Chromium was desorbed from 500 mg/L chitosan with distilled water (pH adjusted to 4.0), $0.01M$ NaCl, $0.01M$ Na_2SO_4, and $0.01N$ NaOH using a procedure as described in batch sorption experiments. Supernatant was analyzed for chromium after required contact time.

RESULTS AND DISCUSSION

Sorption Kinetics. Important physicochemical parameters, which help in the evaluation of basic qualities of a good sorbent, are sorption kinetics and equilibria. Removal of chromium (VI) by chitosan as a function of time at pH 4.0 at various initial concentrations is presented in Figure 1. Results indicate that the removal of chromium is very rapid initially, with more than 80% of total removal being within 1 h at all concentrations. The color of the adsorbent was changed from pale white to yellowish brown on sorption of chromium.

At an initial concentration of 5 mg/L ($0.96 \times 10^{-4}M$), chromium removal was as high as 8 mg/g chitosan at pH 4.0. Huang and Wu[6] observed that 0.5 mg Cr^{6+} was removed per gram of calcinated coke at concentration of $1 \times 10^{-4}M$ at pH 2.0. Pandey et al.[7] have reported a removal of 0.271 mg/g flyash wallostonite at an initial Cr^{6+} concentration of $1.6 \times 10^{-4}M$ at pH 2.0. These researchers had maintained a background ionic strength of $10^{-2}M$ in the adsorption experiments. In the present investigation, experiments were designed to study the interaction of hexavalent chromium with chitosan in the absence of any interfering ions or background electrolytes.

The rate of removal of hexavalent chromium by chitosan was determined using Lagergren's equation[6]

$$\log(q_e - q) + \log q_e - Kt/2.3 \tag{1}$$

where q_e is the amount of sorbate adsorbed per unit weight of sorbent at equilibrium (mg/mg), q is the amount of sorbate uptake per unit weight of sorbent at any time t (mg/mg), t is the time taken for sorption (h), and K is the rate constant.

Using the kinetic data presented in Figure 1, K was calculated to be 1.92 h^{-1} for initial Cr^{6+} concentration of 5 mg/L.

Sorption Equilibriam. Sorption isotherms of chromium chitosan system using two different particle size are presented in Figure 2. A slight increase in capacity for the smaller particles can be due to the increase in surface area, which is expected with nonporous materials like chitosan.

Experimental data were used in the linear forms of Langmuir as well as Freundlich equations [eqs. (2) and (3)]
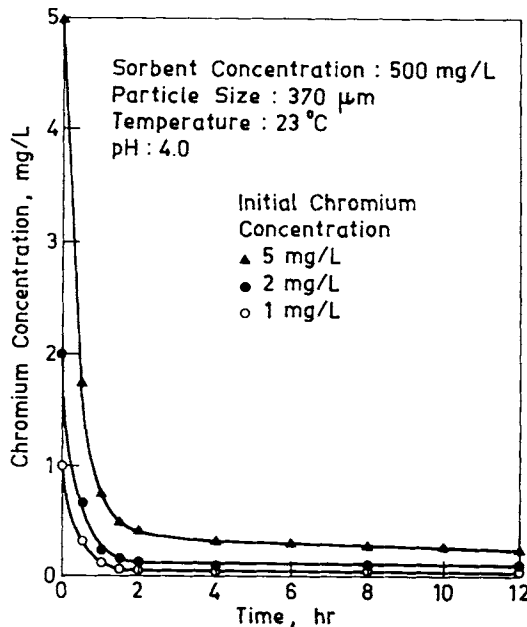
$$\frac{C}{q_e} = \frac{C}{q_0} + \frac{1}{bq_0}$$

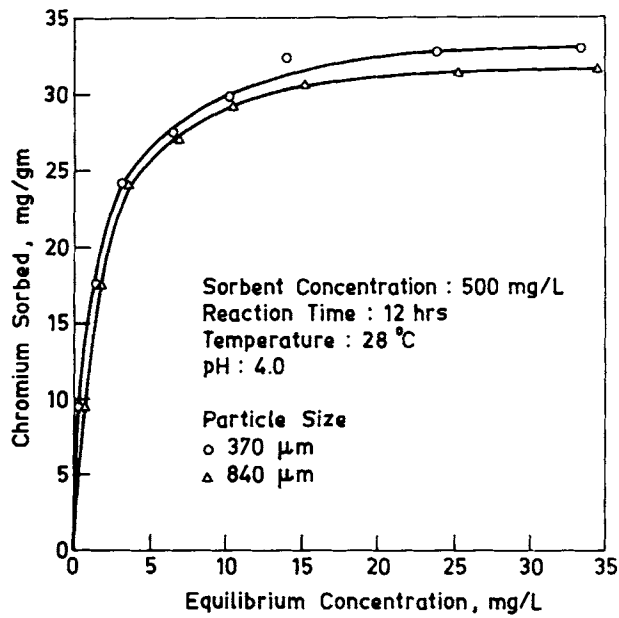Fig. 1. Sorption kinetics of chromium on chitosan at different initial concentrations.
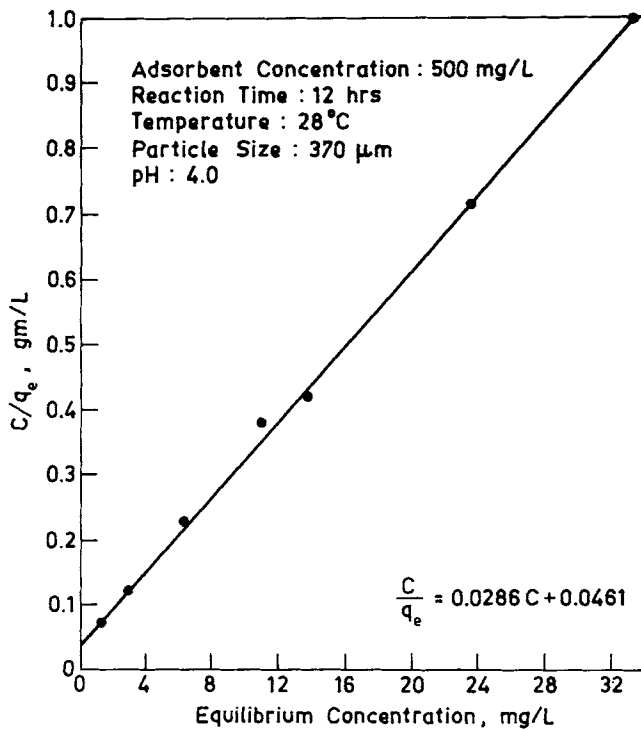
Fig. 2.   Saturation cures for chromium sorption.

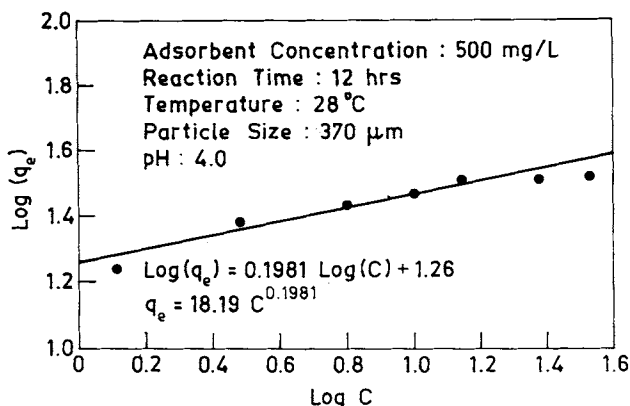Fig. 3.   Linearized form of Langmuir isotherm for chromium sorption on chitosan.

Fig. 4.   Linearized Freundlich isotherm.

where q_e is the mg of chromium adsorbed per unit weight at equilibrium concentration C, q_0 is mg of chromium adsorbed per unit weight of adsorbent forming a complete monolayer on the surface, b is a constant related to the energy or net enthalpy, and C is the measured concentration of chromium in solution at equilibrium:

$$\log q_e = \log K + (1/n)\log C \qquad (3)$$

q_e and C are as described earlier, K is a constant which gives a measure of sorption capacity, and $1/n$, also a constant, gives a measure of sorption intensity.

Figures 3 and 4 show the experimental data fitted into the linearized form of Freundlich and Langmuir relationships. Correlation coefficients were calculated to be 0.9995 for Langmuir's and 0.9648 for Freundlich's, indicating that the Langmuir relationship gives a better fit to the experimental data than the Freundlich. From the slope and intercept of Langmuir isotherm, the values of q_0 and b were calculated to be 34.9 and 0.62, respectively.

The essential features of Langmuir isotherm can be expressed in terms of an equilibrium parameter R (dimensionless),[7] which is expressed as $R = 1/(1 + bc_0)$, where b is the Langmuir's constant and c_0 is the initial concentration of sorbate (mg/L). The value of R was calculated to be 0.244 for initial chromium concentration of $0.96 \times 10^{-4}M$ (5 mg/L), which is indicative of a favorable adsorption.[13]

These results show that kinetics, capacity as well as equilibria, are favorable for using chitosan as a sorbent for the removal of hexavalent chromium.

Effect of Solution pH. Effect of pH on chromium removal was studied in the pH range of 3–9 and results are presented in Figure 5. In unbuffered system, hexavalent chromium uptake by chitosan decreased as the pH increased from 3 to 5. Between pH 5 and 6, a sharp decrease in the removal was observed and at pH 7, removal was only 5–6% to that observed at pH 3. Experiments conducted in the presence of buffers also yielded similar results. However, at pH 4.0, there was about 30% decrease in chromium removal in the presence of buffer as compared to the control, and this can be due to the
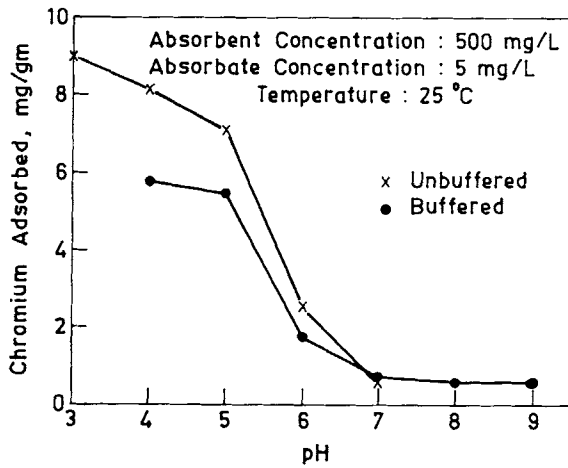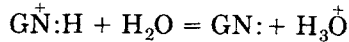
Fig. 5.   Effect of pH on chromium sorption.

presence of acetate anions which can compete with dichromate ions for interaction with chitosan.

Representing the chitosan monomer as GN, dissociation equation of the amine could be represented by

$$GN\overset{+}{:}H + H_2O = GN\!: + H_3\overset{+}{O}$$

pH_{zpc} of chitosan prepared from crab shells has been reported to be 6.3.[14] From pK_a value, it can be calculated that the extent of protonation is 9, 50, 91, and 99% at pH of 7.3, 6.3, 5.3, and 4.3, respectively. Sorbate, chromium, forms stable complexes such as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-} and $HCr_2O_7^-$; the fraction of any particular species is dependent upon chromium concentration and pH (Fig. 6). Below pH_{zpc} of chitosan, sorbent is positively charged, whereas the sorbate is negatively charged. This leads to the electrostatic interaction between the sorbent and the sorbate. Beyond pH_{zpc}, sorbent will also be negatively charged. Hence chromium removal will be drastically reduced. The experimentally observed steep decrease in chromate removal can be explained by rapid changes in protonated and unprotonated forms of chitosan. The effect of pH on hexavalent chromium removal by starch based
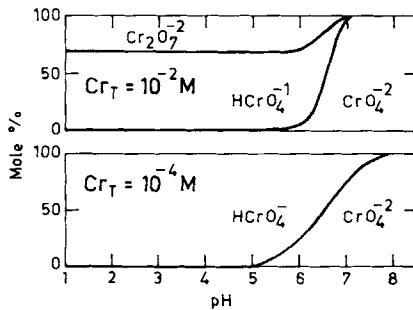

Fig. 6.   Distribution of hexavalent chromium species as a function of pH.
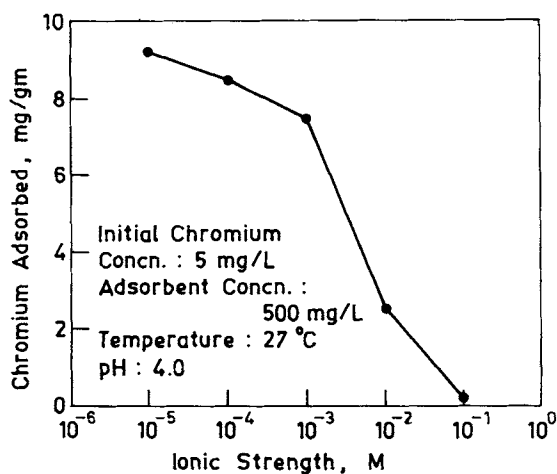
Fig. 7.   Effect of ionic strength on chromium sorption.

anion exchanges is reported to be concentration dependent.[8] At high chromium levels, optimum pH is around 4 and shifts to 7 as initial chromium concentration is lowered. Although it is possible that removal may be more effective with chitosan below pH 3.0, it has been reported that, under certain conditions, dissolution of sorbent can take place in dilute acids.[15] Our observations also indicated that repeated regeneration of cadmium sorbed chitosan with $0.01N$ HCl lead to some weight loss of the sorbent.[16]

Effect of Ionic Strength. Figure 7 shows the effect of ionic strength on the removal of chromium by chitosan. Results indicate that when the ionic strength was increased from 10^{-5} to $10^{-3}M$, there was only an 18% decrease in adsorption capacity and a steep decrease was observed beyond this and reduced to negligible levels at $10^{-1}M$. Changes in background electrolyte concentrations significantly affect the sorbate–sorbent interactions involving the electrostatic attraction. Increase in ionic strength not only decreases the ion activity of dichromate ions but also increases the concentration of competitive perchlorate anions. Our earlier studies with cadmium/chitosan system showed that ionic strength variation did not have any appreciable effect on cadmium binding to chitosan,[16] which indicates that metal cation removal by sorbent is mainly through covalent binding, whereas metal anion uptake is through electrostatic attraction.

Effect of Chloride Ions. Figure 8 illustrates the effect of chloride ion on chromium removal by chitosan. Results were similar to the one that was observed in the presence of ionic strength. However, at equimolar concentrations, chromium removal was decreased only by 5%, showing the high affinity of chitosan for chromium.

Wing and Rayford[8] have reported that sodium chloride is an effective regenerant for hexavalent-chromium-sorbed starch-based cationic quaternary ammonium derivatives and hence these products cannot be useful for industrial effluents with high salt concentrations. Present results also show that chitosan becomes ineffective in removing chromate ions in the presence of very high sodium chloride concentrations.
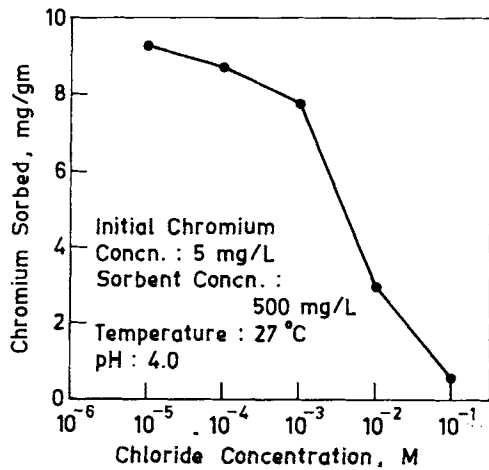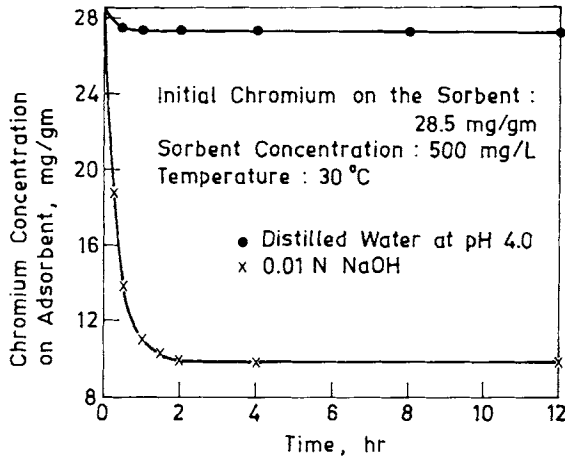
Fig. 8. Effect of chloride concentration.

Fig. 9. Desorption kinetics.

Desorption Studies. Chitosan was saturated with hexavalent chromium as described in Experimental. Chromium adsorbed per gram chitosan was 27.3 mg/g, whereas the q_0 value calculated from the Langmuir isotherm is 34.9 mg/g. Desorption of chromium was negligibly small in distilled water at pH 4, whereas 57.8, 56.2, and 63.5% desorption was observed with $0.01M$ NaCl, $0.01M$ Na$_2$SO$_4$ and $0.01N$ NaOH respectively. Kinetics of chromium recovery with $0.01N$ NaOH is given in Figure 9. Regeneration of sorbent was not very effective after metal anion uptake as compared to metal cations as 88% desorption of cadmium could be achieved from the sorbent with $0.01M$ HCl.[16]

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