

Interaction of Heavy Metals With Chitin and Chitosan.

III. Chromium*

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Synopsis

The interaction of the natural marine polymer chitin and its deacetylated derivative chitosan with chromium has been investigated. The uptake of chromium from aqueous solution was determined from changes in concentration as measured by atomic absorption spectroscopy. The uptake of Cr(III) on chitosan was significantly greater than that on chitin. The smaller the size fraction of the chitin/chitosan, the greater the uptake of Cr(III). The Cr(III) uptake increased with increasing solution pH. Minimal desorption of chromium was observed on washing previously chromium-equilibrated chitosan with distilled water. The uptake of Cr(III) by chitosan was enhanced in the presence of phosphate, whereas the converse was not observed. Minimal uptake of Cr(VI) as dichromate by chitin and chitosan was measured. Cr-containing nodules were noted in the SEM/EDAX analysis for Cr(III)-equilibrated chitosan. Cr-containing clusters were detected for Cr(III)- plus phosphate-equilibrated chitosan. XPS results supported the conclusions drawn from the isotherm studies.

INTRODUCTION

The natural chelating marine polymer chitin, poly(*N*-acetyl-D-glucosamine), and its deacetylated derivative chitosan may be useful for removing heavy metal ion wastes from discharge water. Many researchers have explored the feasibility of this approach. Muzzarelli has reviewed much of this work and, in addition, has compiled an excellent and comprehensive summary of the characteristics and properties of chitin and related materials.¹ Hauer conducted experiments involving Kytex H chitosan with a number of heavy metals including Cd, Cr, Cu, Pb, and Zn.² Masri and Randall have explored the possibility of heavy metal ion removal from actual waste materials from manufacturing plants.³ A recent report by Kurita and co-workers⁴ has demonstrated that Cu(II) and Hg(II) are adsorbed by chitin and its congeners varying in amino group content. Eiden, Jewell, and Wightman have recently reported on the uptake of Cr(III) and Pb(II) by chitin and chitosan.⁵ This study indicated that uptake of the metal ion on chitosan was much greater than that on chitin and suggested that the metal uptake mechanism involves nucleation and growth of nodules on the polymer surface.

In order to further study nodular formation and attempt to establish the uptake mechanism, we report here a study of the uptake of Cr(III) by chitin and

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chitosan. During this investigation, the effects of concentration, agitation, particle size, pH, and anion present on the uptake isotherms were also studied. SEM/EDAX and XPS were used to characterize chitin and chitosan before and after equilibration with the metal ions.

EXPERIMENTAL

Materials

Chitin was obtained from the Velsicol Chemical Corporation in the form of large flakes. It was ground in a blender and sieved to consistent particle sizes before use. Chitosan (Velsicol Chemical Corporation) was received in a finely divided state and was sieved to constant particle size before using. All other reagent grades used were from Fisher.

Procedure

Stock solutions of the equilibrating ions were prepared and standardized against commercial standards. These stock solutions were then diluted to give standards of the appropriate concentrations. Fifty-milliliter aliquots of each of these standard solutions were placed in stoppered 125-mL Erlenmeyer flasks and equilibrated with 0.100 g chitin or chitosan for approximately 24 h. Unless otherwise noted, the samples were shaken on an automatic shaker at room temperature during the equilibration period. The equilibrated supernate was decanted or filtered from the polymer samples before analysis. It was necessary to filter the liquid from the polymer when very small particle sizes were used, otherwise consistent analyses could not be obtained. Metal ions were analyzed using either a Varian 175 or a Varian Techtron 1100 atomic absorption spectrophotometer. Phosphate analyses were done using a modified Fiske-Subbarow method.⁶ After determining the change in the metal ion molar concentration (ΔC) due to equilibration with W grams (0.1 g) of polymer, the quantity $V\Delta C/W$ was calculated, where V is the solution volume (0.05 L). This quantity corresponds to the moles of metal ion taken up per gram of polymer.

Sodium hydroxide (10^{-2} M) or nitric acid (10^{-2} M) was used to correct the pH in all runs that were made at constant pH. The effect of the addition of various concentrations of phosphate and phthalate ion on Cr(III) uptake was determined. Likewise, the effects of Cr(III) on phosphate uptake was studied.

Samples of chitin, chitosan, and these two polymers after equilibration with all the solutions studied in this work were examined using an AMR 900 scanning electron microscope (SEM) with an International 7070A energy dispersive analysis of X-rays (EDAX) accessory. After filtering, washing with deionized water, and air drying, the equilibrated polymer samples were mounted on probes with copper conductive tape. The Cr(III) equilibrated samples were coated with carbon to minimize sample charging.

X-ray photoelectron spectroscopy (XPS) was also used to characterize the polymer samples. A du Pont 650 electron spectrometer with a magnesium X-ray

source was used for this determination. The carbon 1s photoelectron peak at 284.6 eV was used to reference the binding energies for the other elements examined. The polymer samples were mounted on double-sided tape for analysis.

RESULTS

Effect of Particle Size

In Figures 1 and 2, the effects of particle size on the uptake of Cr(III) nitrate by chitin and chitosan are given. The term "uptake" is meant to imply removal of ions from aqueous solution in the presence of chitin or chitosan. For chitin (curves \diamond , Δ , and \circ in Fig. 1), three particle size groups were used (<0.42 , 0.42 – 1.00 , and 2.00 – 4.00 mm); and, as expected, the smaller the particle size, the greater the uptake of Cr(III). However, the effect of particle size is not nearly as great as expected from calculations of relative surface areas assuming cubic particles. An examination of dozens of flakes of chitin under a microscope showed that the chitin is made of several very thin sheets of material loosely bound together. Using a microscope and colored solutions, we were able to observe that even with flakes as large as 1 cm^2 , liquids flowed freely between the layers and, in fact, were drawn between the layers and by capillary action. Thus, reducing the particle size did not increase the effective surface area as much as expected. Similar results were observed for chitosan (Fig. 2). Even though the particle size effect is small, all the other uptake runs reported here were made with polymers having a 0.42 – 1.00 mm particle size.

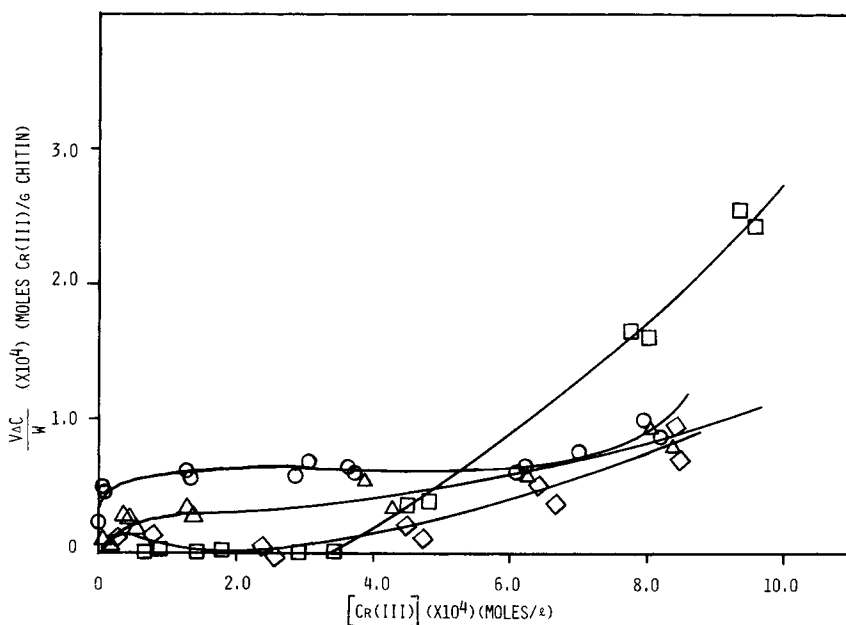


Fig. 1. Isotherms of Cr(III) uptake on chitin. Particle size: (O) <0.42 mm; (Δ) 0.12 – 1.00 mm; (\diamond) 2.00 – 4.00 mm; (\square) 0.42 – 1.00 mm with 0.05 M PO_4^{3-} and pH 5.0.

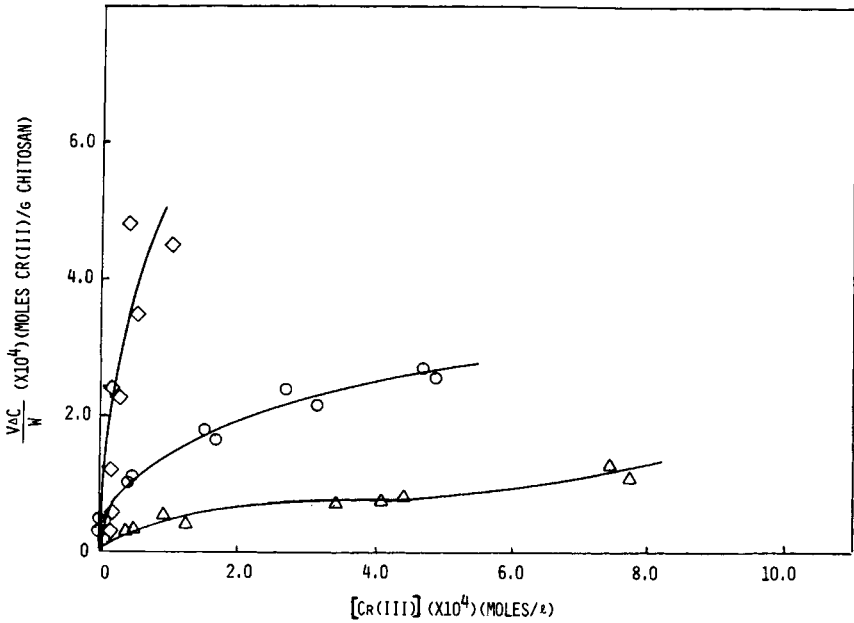


Fig. 2. Isotherms of Cr(III) uptake on chitosan. Particle size: (O) <0.42 mm; (Δ) 0.42–1.00 mm; (◇) 0.42–1.00 mm with 0.05 M PO_4^{3-} and pH 5.0.

Effect of pH

There is a dramatic increase in the amount of Cr(III) taken up by both chitin and chitosan as the pH increases, as shown in Figure 3. However, one needs to

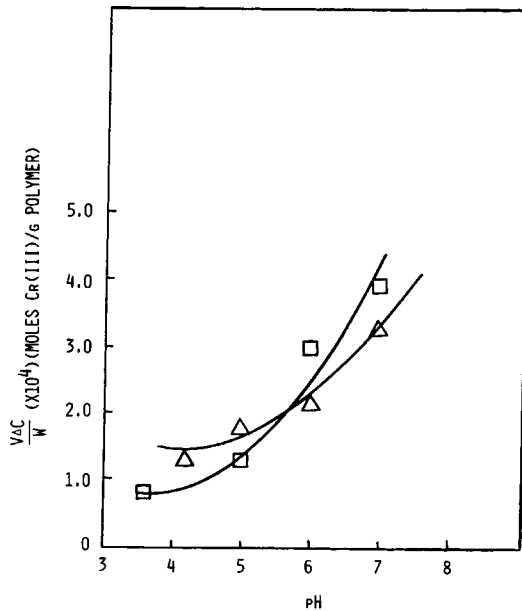


Fig. 3. Uptake of Cr(III) on chitin and chitosan as function of pH. (□) chitin; (Δ) chitosan.

be very careful in interpreting such data, since precipitation of metal hydroxides occurs simultaneously with uptake at high metal ion concentrations and at higher pH values. This was very apparent with equilibrium runs which had both a high concentration of Cr(III) ($10^{-3} M$) and a high phosphate concentration ($10^{-1} M$). In these cases, cloudiness and precipitate formation were sometimes, but not always, observed even at pH values as low as 5.0. The fact that a simultaneous precipitation and uptake of the metal ions occurred was shown by carefully isolating samples of equilibrated polymer from several cloudy equilibrium runs with the Cr(III)- PO_3^{3-} system and then determining the Cr(III) taken up directly. This was done by destroying the polymer in concentrated HCl and then determining the amount of metal ion present by atomic absorption. In one series of runs, twice as much Cr(III) was precipitated out as was taken up. Because of this precipitation problem, any equilibration run which resulted in a cloudy solution was disregarded and all pH-controlled runs were done at lower pH values usually ≤ 5.0 . Experimental runs without pH control are reported since it may not be desirable to control the pH of an industrial effluent before removing the waste metal ions.

As reported previously,^{1,5} it was observed that the final pH values for the equilibrated solutions without pH control were higher as the initial (or final) concentration of the metal ion became smaller. This is what would be expected since the metal ions studied are Lewis acids, and the lower the concentration, the higher the pH.

Release of Ions from Equilibrated Polymers by Water

For the chromium, phosphate, dichromate, and chromium-with-phosphate systems studied, at least one set of equilibrated polymer samples was isolated without washing and then shaken with 50 mL water at 25°C for 24 h to see if the ions were released from the polymer once they were taken up. In no case was a significant concentration of the ions desorbed by water. In fact, the ions which were detected were probably due to those remaining in the original equilibrating liquid which had adhered to the surface of the polymers during isolation.

Uptake of Cr(III) Nitrate on Chitin and Chitosan

The uptake isotherms for Cr(III) on chitin and chitosan at equivalent particle sizes are given by curves (O) and (Δ) in Figure 1 and by curves (O) and (Δ) in Figure 2, respectively. It is evident from these isotherms that the uptake of Cr(III) on chitosan is significantly greater than that on chitin. In an effort to eliminate the need to adjust the pH in these uptake measurements every 3 or 4 h, commercial pH buffers having nominal values of 4.0, 5.0, 6.0, and 7.0 were employed in one set of runs with Cr(III) on both chitin and chitosan. In the pH 4.0 equilibration, no Cr(III) was taken up by either chitin or chitosan. In the pH 5.0, 6.0, and 7.0 runs, uptake was changed drastically. The magnitude and direction of the change depended on the polymer and the pH (results not shown). Upon further investigation, it was learned that the pH 4.0 buffer was a phthalate-based one, while the buffers for pH 5.0, 6.0, and 7.0 were phosphate based. The bidentate phthalate ion may have complexed the Cr(III) ion and thereby completely stopped the sorption of Cr(III) by both polymers. This preclusion

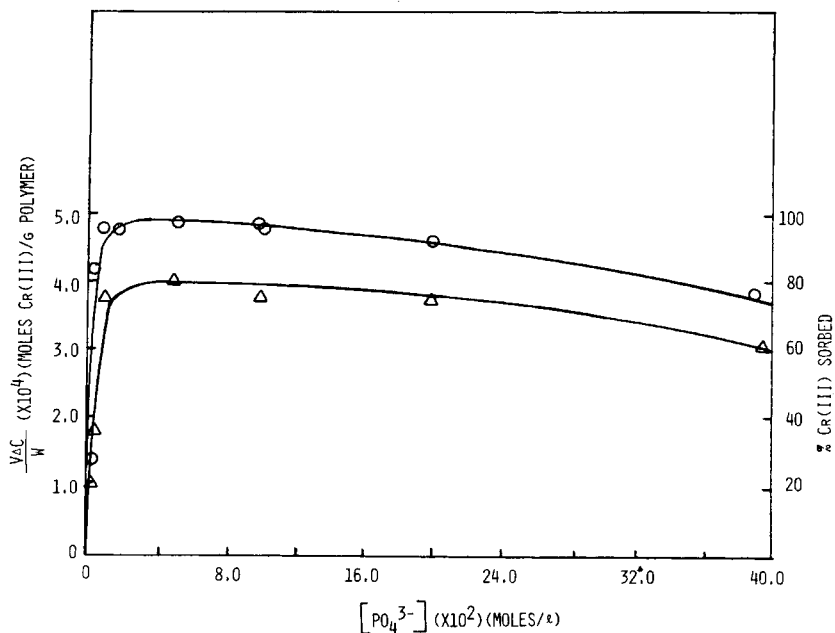


Fig. 4. Uptake of Cr(III) as function of phosphate concentration. Initial Cr(III) concentration $1 \times 10^{-3} M$; pH 5.0: (Δ) chitin; (O) chitosan.

of Cr(III) removal is not a simple pH effect; for, as discussed above (see Fig. 3) in the absence of phthalate ion at pH 4.0, an appreciable amount of Cr(III) was removed by both chitin and chitosan. The phosphate ion, on the other hand, indicated a complex behavior which led to a detailed study of its interaction with chitin and chitosan in the presence and absence of Cr(III).

Uptake of Cr(III) in the Presence of Phosphate Ion

As noted above, Cr(III) in the presence of phosphate ion gave cloudy solutions, with precipitate formation at higher pH values. Thus, all the work with this system was done at a pH close to 5.0. In Figure 4, the uptake of Cr(III) by chitin and chitosan is given as a function of initial phosphate concentration. The initial Cr(III) concentration for each run was $1 \times 10^{-3} M$, and the phosphate concentration was varied from 1×10^{-4} to $0.4 M$. A slight decrease in the maximum uptake was noted as the phosphate concentration increased to $0.4 M$ for both chitin and chitosan.

Two sets of uptake isotherms were generated for Cr(III) on chitin and chitosan at constant phosphate concentrations of 0.2 and 0.050 M . The results for the 0.05 M phosphate concentration are given by curve (\square) of Figure 1 for chitin and by curve (\diamond) of Figure 2 for chitosan. The uptake of Cr(III) by chitosan is greatly enhanced by phosphate at all Cr(III) concentrations studied, both with the concentration of phosphate equal to 0.050 M (Fig. 2) and 0.20 M (not shown). In fact, at both concentration of phosphate, essentially all of the Cr(III) was taken up at initial Cr(III) concentrations below $2.5 \times 10^{-4} M$. This type of behavior has not been reported previously, and the explanation may involve more than just the simple enhancement of the uptake of one ion by a second ion.

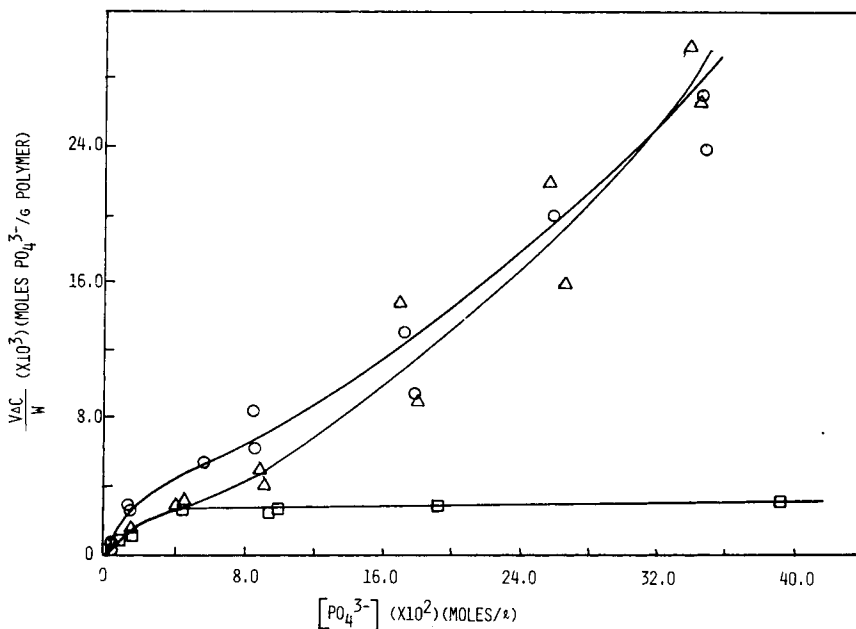


Fig. 5. Phosphate uptake isotherms at pH 5.0: (O) chitosan; (Δ) chitin; (\square) chitosan with $1 \times 10^{-3} M$ Cr(III).

Furthermore, it was found that prior equilibration of either chitin or chitosan with phosphate results in minimal uptake of Cr(III) by either polymer. This series of experiments was conducted in a similar way as those which are reported above, except that the chitin and chitosan samples were first equilibrated with $0.40 M$ phosphate for 24 h at pH 5.0. The polymers were then isolated, washed, and dried, and equilibrium runs as described above were made over the range of Cr(III) concentrations of 1.0×10^{-3} to $1.0 \times 10^{-5} M$. The final concentration of Cr(III) after equilibration was the same as the initial value within experimental error. In order to try to understand this behavior, a set of experiments was done where the uptake of phosphate by chitin and chitosan was measured.

Uptake of Sodium Dihydrogen Phosphate and Potassium Dichromate by Chitin and Chitosan

The uptake isotherms for phosphate ion at pH 5.0 on chitin and chitosan are given in Figure 5. Unlike the cations studied, the uptake of phosphate by chitin is essentially the same as that by chitosan.

Because of the influence of phosphate on Cr(III) sorption discussed above, the effect of Cr(III) on phosphate uptake by chitin and chitosan was studied. The results for chitosan are given in Figure 5. Negligible uptake of phosphate was observed on chitin. Thus, it is seen that Cr(III) drastically depresses the uptake of phosphate on chitosan. This is essentially the reverse of how phosphate affects the uptake of Cr(III).

The uptake isotherms for a second anion, dichromate, on chitin and chitosan are given in Figure 6. Again, as in the phosphate case, the chitin isotherm is essentially identical to that of chitosan.

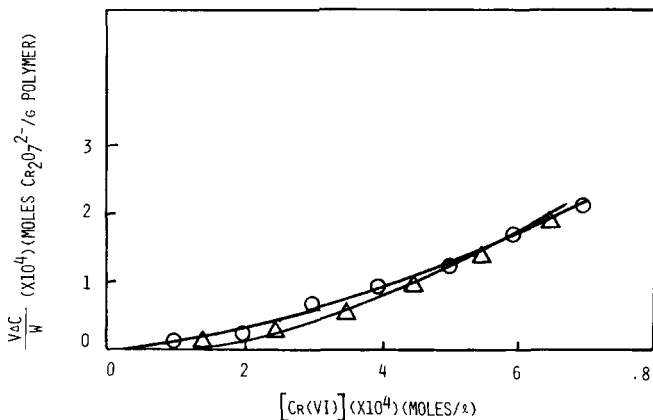


Fig. 6. Dichromate uptake isotherms on chitin and chitosan: (Δ) chitosan; (O) chitin.

Scanning Electron Microscopy/Energy Dispersive Analysis of X-Rays (SEM/EDAX)

SEM photomicrographs were taken of both chitin and chitosan prior to equilibration with Cr(III) solutions. Representative SEM photomicrographs have been published.⁵ Calcium was detected by EDAX only in the chitosan sample. Small flakelike particles were noted on the surface of the chitosan flakes, which EDAX indicated were high in calcium. No significant concentrations of heavy metals were noted by EDAX for either polymer.

SEM/EDAX analyses were also obtained for Cr(III)-equilibrated polymer samples both with and without phosphate ion present. A large number of small nodules are noted in the SEM photomicrograph in Figure 7 for chitin equilibrated with Cr(III). The EDAX spectrum of the small surface nodules indicates a high Cr content. When phosphate is present, the nodules are much larger and more flocculent in appearance than in the absence of phosphate. EDAX analysis indicates a high concentration of P and a lesser concentration of Cr in the nodules, with lower concentration of these two elements on the general surface of the polymer.

X-Ray Photoelectron Spectroscopy (XPS)

The XPS results for chitosan equilibrated with various solutions are listed in Table I. The Cr(III) concentrations were equivalent, whereas the phosphate concentrations were not. The Cr/N atomic fraction ratio increases from 0.054 for the zero phosphate case to 0.36 when phosphate is present. Thus, the XPS results are consistent with the isotherm results in that the uptake of Cr(III) by chitosan is enhanced by the presence of phosphate.

DISCUSSION

Numerous models have been proposed for the adsorption of gases on solid surfaces.⁷ In contrast, there are few models to describe adsorption of ions from aqueous solutions. Healy and co-workers^{8,9} have addressed this problem as

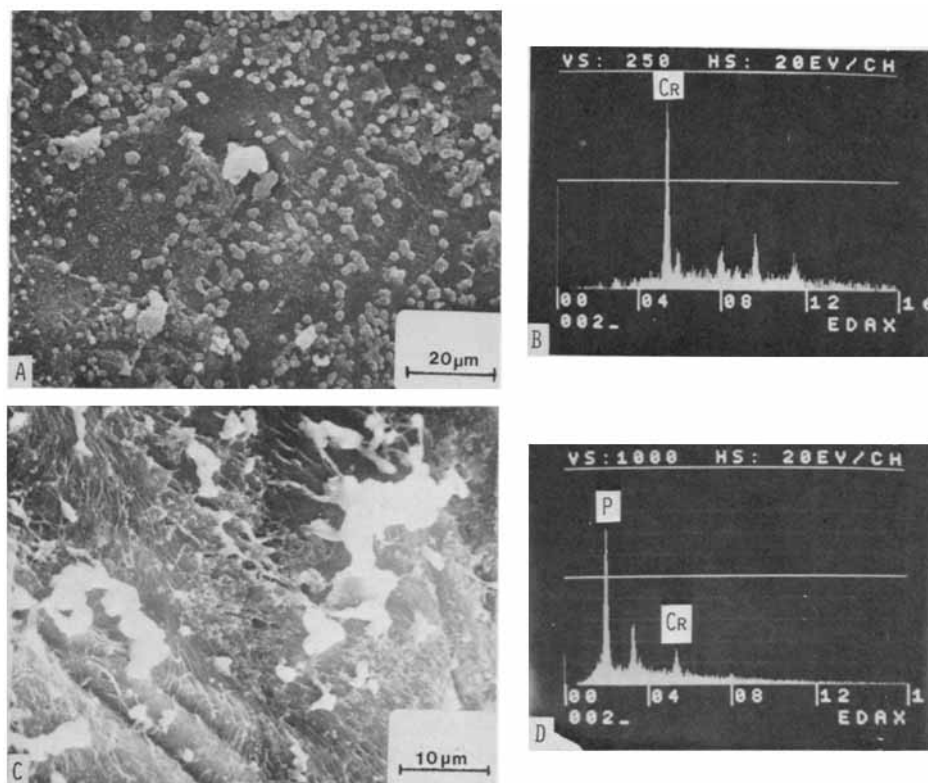


Fig. 7. SEM photomicrograph of chitosan with Cr(III) (A) and EDAX spectrum (B); SEM photomicrograph of chitosan with Cr and phosphate (C) and EDAX spectrum (D).

applied to a variety of oxide surfaces. The use of polymers as adsorbents and in particular of chitin and chitosan is an enormous complicating factor.

The quantitative differences in the measured uptake isotherms suggest that the uptake process is a complex one. Nonetheless, uptake mechanisms can be proposed based on the isotherm results coupled with the SEM/EDAX and XPS results. Simple ion adsorption on the chitin or chitosan surface does not appear to be the dominant mechanism as is inferred from much of the literature. This conclusion is based primarily on the SEM/EDAX analysis, where under moderate magnification metal-containing aggregates are observed on the polymer. Thus,

TABLE I
XPS Parameters for Chitosan, Cr(III)/Chitosan, PO_4^{3-} /Chitosan, and Cr(III) + PO_4^{3-} /Chitosan^a

Photopeak	Chitosan ^b		Cr(III)/Chitosan		PO_4^{3-} /Chitosan		Cr(III) + PO_4^{3-} /Chitosan	
	B.E.	A.F.	B.E.	A.F.	B.E.	A.F.	B.E.	A.F.
N 1s	399.0	0.042	399.5	0.037	400.0	0.040	400.4	0.033
O 1s	532.2	0.177	532.1	0.217	532.1	0.277	532.0	0.312
Cr 2p 3			577.2	0.002			577.7	0.012
P 2p 3					133.0	0.036	133.3	0.055

^a B.E. = binding energies in eV; A.F. = atomic fraction, balance due to carbon.

^b From Ref. 4.

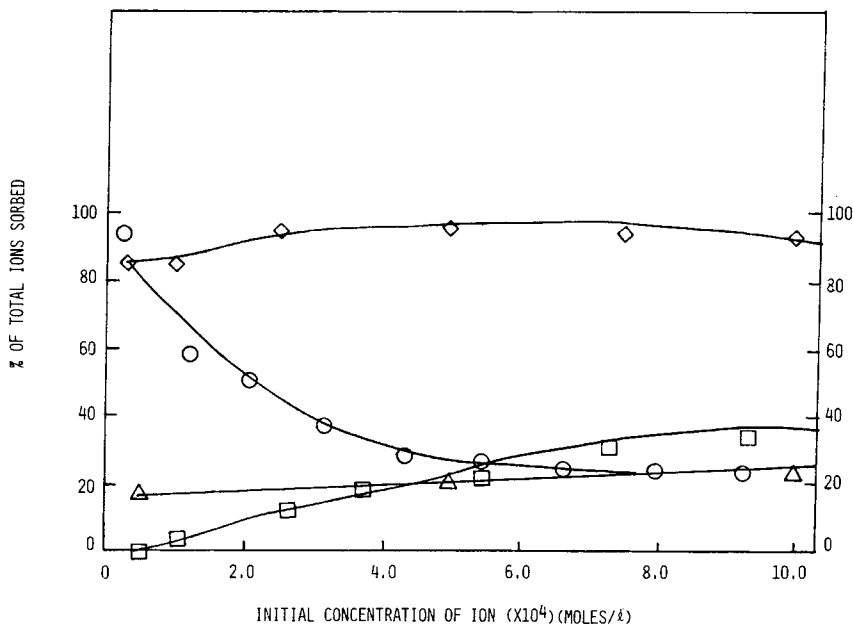


Fig. 8. Percentage of ion uptake by chitosan: (○) Cr(III); (□) $\text{Cr}_2\text{O}_7^{2-}$; (△) PO_4^{3-} ; (◇) Cr(III) with 0.50 M PO_4^{3-} .

the formation of metal-containing nodules on the polymer surface has to be considered a possible uptake mechanism. Secondly, careful visual microscopic examination of freshly cut, highly colored equilibrated polymer samples of chitosan indicated that the metal ions penetrated the polymer to a considerable depth. In one case, a dried piece of chitosan from a Cr(III)-phosphate run appeared to have the characteristic dark-green color penetrating the piece to a depth of at least 0.1 mm, and the fresh-cut face was not more than 0.3 mm square. Thus, absorption presumably by diffusion of metal ions into the polymer can be considered a second plausible uptake mechanism. Thus, a combination of nodular formation, ion adsorption, and ion absorption account for the total uptake.

The greater uptake by chitosan compared to chitin may well be due to differences in the nitrogen moiety of the two polymers. The *N*-acetyl-D-glucosamine groups of the chitin could act as specific chemical binding sites for metal ions capable of forming complex ions but would not be expected to be as efficient as the free amine sites in chitosan. That is, the free amine groups in chitosan are much better ligands for binding to metal ions than the *N*-acetylated amine groups would be. This is particularly true for a hard acid like Cr(III).

The effectiveness of chitin and chitosan at removing the ions studied is shown in Figures 8 and 9. The lower concentration end of these graphs from zero to $1 \times 10^{-4}\text{ M}$ corresponds to Cr(III) concentrations of zero to 5.2 ppm, respectively. In this range, chitosan appears to be quite effective at removing the ions, while chitin is less effective except at the extremely low concentrations. Since this concentration range for metal ions corresponds to that of many waste waters, chitosan would appear to merit further investigation as a sorbent to remove metal ions. At higher concentrations of the metal ions and for all concentrations of

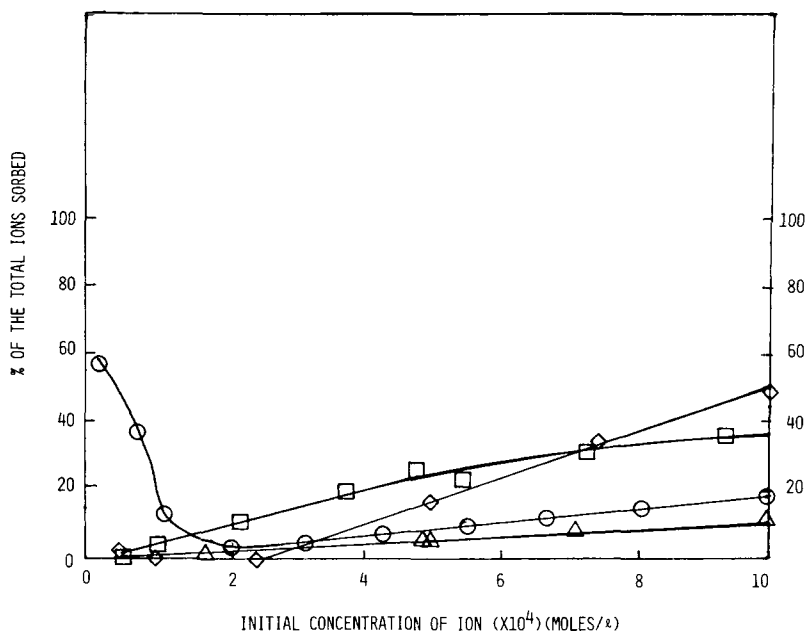


Fig. 9. Percentage of ion uptake by chitin: (O) Cr(III); (\square) $\text{Cr}_2\text{O}_7^{2-}$; (Δ) PO_4^{3-} ; (\diamond) Cr(III) with 0.50 M PO_4^{3-} .

the anions studied, the effectiveness of these polymers is considerably lower, except for the special case of Cr(III) in the presence of phosphate. As the work with the Cr(III)-phosphate system shows, other ions present in the solution could drastically affect the uptake of heavy metals by chitin and chitosan. Thus, the determination of the usefulness of these polymers in the treatment of specific waste waters will require both cation and anion analysis.

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