

# Interaction of Lead and Chromium with Chitin and Chitosan\*

CATHERINE A. EIDEN, CAROLYN A. JEWELL, and J. P. WIGHTMAN,  
*Chemistry Department, Virginia Polytechnic Institute and State  
University, Blacksburg, Virginia 24061*

## Synopsis

The interaction of the natural marine polymer chitin and its deacetylated derivative chitosan with lead and chromium has been investigated. The uptake of lead and chromium was determined from changes in concentration as measured by atomic absorption spectroscopy. A significant uptake of Pb(II) on both chitosan and chitin was observed. However, the uptake of Pb(II) on chitin was approximately 21% of that on chitosan. The number of N atoms in chitin and chitosan per number of Pb(II) ions sorbed was 115 and 29, respectively. The number density of flakes observed in the scanning electron microscope and characterized by an intense Pb signal in energy dispersive analysis of x rays (EDAX) was greater on the surface of chitosan [containing  $1.7 \times 10^{-4}$  mole Pb(II)/g chitosan] than chitin [containing  $3.5 \times 10^{-5}$  mole Pb(II)/g chitin] after equilibration with Pb(II) solution. The bonding state of lead on chitosan as determined by electron spectroscopy for chemical analysis (ESCA) is similar to the bonding of lead in PbO based on the Pb  $4f_{7/2}$  binding energy. A significant shift in the O 1s binding energy from 532.2 to 531.4 eV was observed for chitosan after equilibration with Pb(II) solution. The calculated values of the N/Pb ratio from ESCA spectra were 0.5 and 11, for chitosan and chitin, respectively. A significant uptake of Cr(III) on chitosan was observed and a significant increase in the pH of solutions of Cr(III) on equilibration with chitosan occurred. A high number density of nodules characterized by an intense Cr signal in EDAX was observed in chitosan [containing 2.5 mole Cr(III)/g chitosan] after equilibration with Cr(III) solution. The calculated values of the N/Cr ratio from ESCA spectra was 18 for chitosan.

## INTRODUCTION

In the past, work has been done concerning the interaction of metal ions including lead and chromium with the natural chelating polymer chitin (poly-N-acetyl-D-glucosamine) and chitosan, its deacetylated derivative. Muzzarelli<sup>1,2</sup> has given an excellent summary of work in this field. The article by Muzzarelli and Tubertini<sup>3</sup> is of particular interest as regards the rate of adsorption of Hg, Co, Ag, Mo, Ir, Cs, Zn, Fe, Au, Sb, and Cr on chitin and chitosan. A recent report by Kurita and co-workers<sup>4</sup> demonstrated that Hg(II) and Cu(II) are adsorbed by chitin and its congeners varying in amino group content. Hg(II) was found to be adsorbed on the polysaccharides in preference to Cu(II), particularly at lower amino group contents. There is a paucity of data, however, as to how these polymers interact with heavy metals.

The objective of the present work was to study the uptake of Pb(II) and Cr(III) by chitin and chitosan as a function of concentration. Ancillary spectroscopic

\* This research was done in part under the 1979 NSF-Undergraduate Research Participation Program at Virginia Tech, Dr. J. W. Viers, Director.

techniques [scanning electron microscopy/electron dispersive analysis of x rays (SEM/EDAX) and electron spectroscopy for chemical analysis (ESCA)] were used to further characterize the uptake of the metal ions. Particular emphasis was placed on the uptake mechanism.

## EXPERIMENTAL

### Materials

Chitin was obtained as large flakes from the Velsicol Chemical Corp. (Chicago) and cut into smaller chips. The chitosan came as powdered small flakes from the Velsicol Chemical Corp. and was used in this form.

### Procedure

Stock solutions of  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Cr}(\text{NO}_3)_3$  were made up to a concentration of  $1 \times 10^{-2}M$ . Dilution of these stock solutions with distilled water were made in the concentration range  $10^{-3}$  to  $10^{-5}M$ . The polymer (0.1 g), either chitin or chitosan, separately was added to 50-ml aliquots. The remaining solution was used for calibration. The samples were shaken manually once each hour for 3 hr and were then equilibrated for approximately 24 hr.

The absorbance data of the calibration and equilibrated solutions were taken using a Varian AA-175 atomic absorption (AA) spectrophotometer. A Varian lead hollow cathode tube was used. A Varian multielement hollow cathode tube was used for chromium. The order of taking absorbance readings was as follows: the initial (before polymer addition) solution of the metal salts, the equilibrated solutions, and then the initial solutions again to check instrument stability. Standard curves were drawn and the final concentration ( $C_f$ ) of the samples were interpolated from these. The change in concentration of Pb(II) or Cr(III) was then calculated. The results were plotted as  $V\Delta C/W$  vs.  $C_f$ . Here, the volume ( $V$ ) is 50 ml,  $\Delta C$  is the change in metal ion concentration on equilibration with  $W$  grams of polymers, and  $C_f$  is the final concentration of metal ion after equilibration.

The pH values of selected solutions were measured with a Beckman Zero-Matic pH meter. The pH of the initial Cr(III) solutions was adjusted by addition of  $\text{HNO}_{3(\text{aq})}$ . The pH values of the initial Pb(II) solutions ranged from 4.8 to 5.0, and the initial Cr(III) solutions from 3.5 to 5.1.

Samples of chitin and chitosan, both before and after equilibration with Pb(II) and Cr(III) solutions, were run in an AMR model 900 scanning electron microscope with an International model 7070A energy dispersive analysis of x-ray accessory. The polymer samples were filtered and washed several times with distilled water and air dried. The samples were mounted on copper conductive tape and coated with Au/Pd alloy to minimize sample charging.

The ESCA spectra of samples of chitin and chitosan, both before and after equilibration with Pb(II) and Cr(III) solutions, were analyzed in a du Pont model 650 electron spectrometer using a magnesium x-ray source. The C 1s photopeak taken as 284.6 eV was taken as the references for binding energy calibration. The samples were mounted on double-sided tape after preparation, as described above for the SEM work.

## RESULTS AND DISCUSSION

## Sorption Isotherms of Pb(II)

The results for the uptake of Pb(II) on chitosan are shown in Figure 1. The plotted results suggest a Langmuir-type isotherm.<sup>5</sup> However, it is not certain that the uptake of Pb(II) is in fact limited to the surface of chitosan. The results in Figure 1 are shown linearized in Figure 2. A plot of  $C_f/(V\Delta C/W)$  vs.  $C_f$  produces a straight line whose slope is the reciprocal of  $(V\Delta C/W)_{\max}$ , which is the limiting value for the amount of Pb(II) sorbed onto chitosan. The average limiting value of  $(1.9 \pm 0.1) \times 10^{-4}$  mole Pb(II)/g chitosan listed in Table I is the average of seven separate isotherms.

The results for the uptake of Pb(II) on chitin are shown in Figure 3. Again, the shape of the isotherm is suggestive of Langmuir-type behavior. The linearized isotherm is shown in Figure 2. The average limiting value of  $3.9 \times 10^{-5}$  mole Pb(II)/g chitin listed in Table I is the average of four separate isotherms.

The significant conclusion here is that the uptake of Pb(II) on chitin is only approximately 21% of that on chitosan. The greater uptake of Pb(II) on chitosan is consistent with the results of Muzzarelli<sup>1</sup> and is attributed to the reduced availability of the nitrogen electrons in chitin owing to the acetyl group.

A further analysis of the isotherm results can be made in terms of the number of Pb(II) ions sorbed per number of N atoms in the bulk polymer. There are  $3.2 \times 10^{21}$  N atoms/g chitosan based on a nitrogen content<sup>1</sup> of chitosan of 7.4%. A value of  $1.1 \times 10^{20}$  Pb(II) ions/g chitosan is calculated from the limiting ratio in Table I. Thus, the ratio of N atoms in the polymer to the number of sorbed Pb(II) ions is 29 as listed in Table I. Clearly, there is not saturation of total N atom sites in chitosan by lead. A similar analysis for chitin based on a N content<sup>1</sup> of chitin of 6.26% leads to a ratio of 115. Again, the amount of Pb(II) sorbed by chitin does not represent saturation of the total N atom sites in chitin.

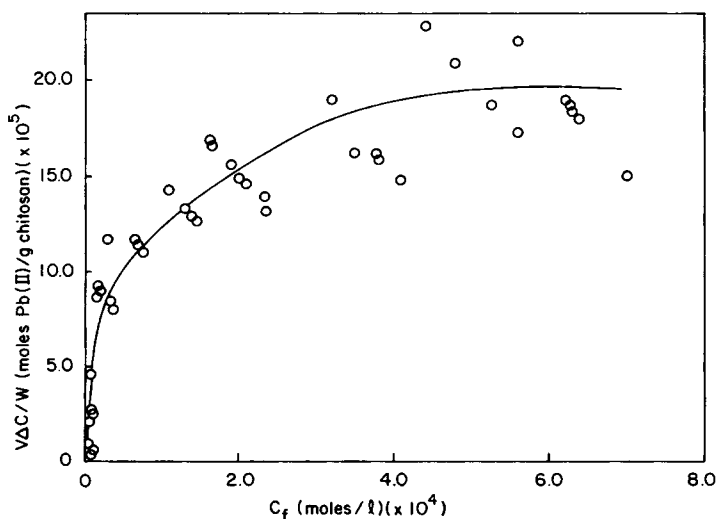


Fig. 1. Uptake of Pb(II) on chitosan.

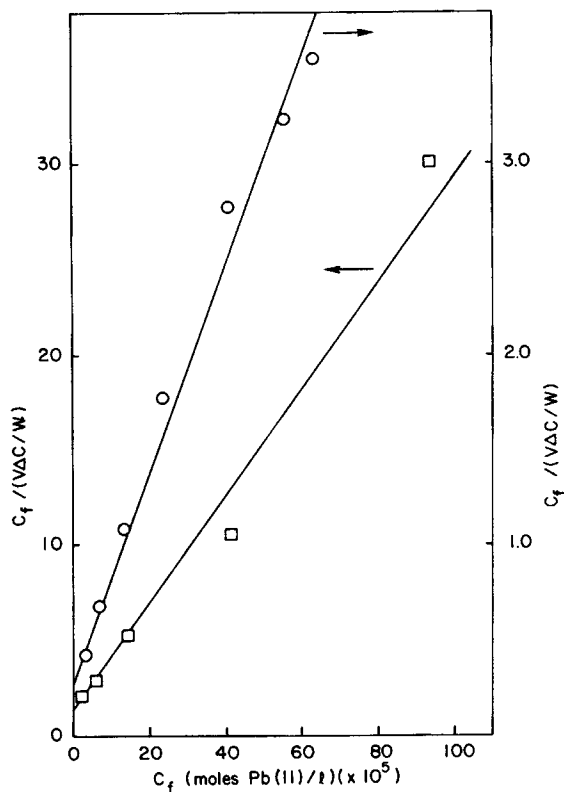


Fig. 2. Linearized plot for uptake of Pb(II) by chitosan (O) and chitin (□).

### Sorption Isotherms of Cr(III)

The results for the uptake of Cr(III) by chitosan are shown in Figure 4. The shape of the isotherm here is quite different from that observed for Pb(II) (cf. Figs. 1 and 3). At low concentrations of Cr(III), there appears to be the onset of a plateau, but then the uptake increases sharply and the isotherm rises steeply. Linearization of the isotherm in Figure 4 is precluded since no limiting plateau was reached. The uptake of Cr(III) on chitin was not reproducible.

TABLE I  
Limiting Uptake of Pb(II) by Chitosan and Chitin and Values of N/Pb and N/Cr Ratios  
Calculated from Uptake and ESCA Results

	$(V\Delta C/W)_{\max}$ (mole Pb(II)/g)	$(N/Pb)_{\text{uptake}}$	$(N/Pb)_{\text{ESCA}}$	$(N/Cr)_{\text{uptake}}$	$(N/Cr)_{\text{ESCA}}$
Pb(II)/chitosan	$(1.9 \pm 0.1) \times 10^{-4}$	29	0.51	—	—
Pb(II)/chitin	$(3.9 \pm 0.1) \times 10^{-5}$	115	11	—	—
Cr(III)/chitosan	—	—	—	21	18

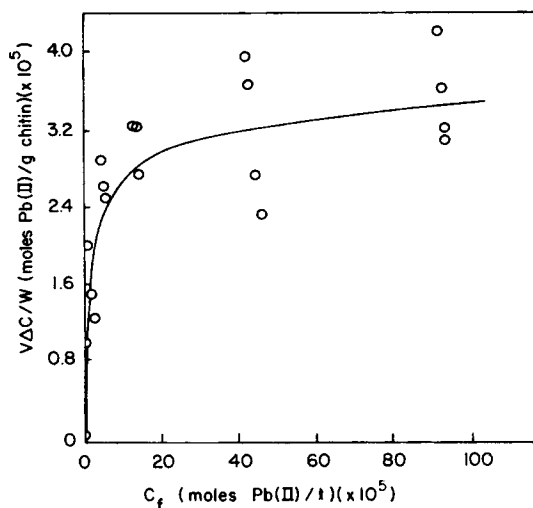


Fig. 3. Uptake of Pb(II) on chitin.

### pH Study

A knowledge of pH was important in this study because of the dependence of the number and kind of hydrolysis species on pH and concentration. It was noted that the pH values of the equilibrated solutions of Cr(III) were considerably different from the pH values before chitosan addition. The results of pH measurements are summarized in Table II. The Cr concentration before chitosan addition is  $C_0$  with a corresponding acidity of  $pH_0$ . The adjusted pH is  $pH_a$ . The measured pH after equilibration is  $pH_f$  at a concentration of  $C_f$ . There is

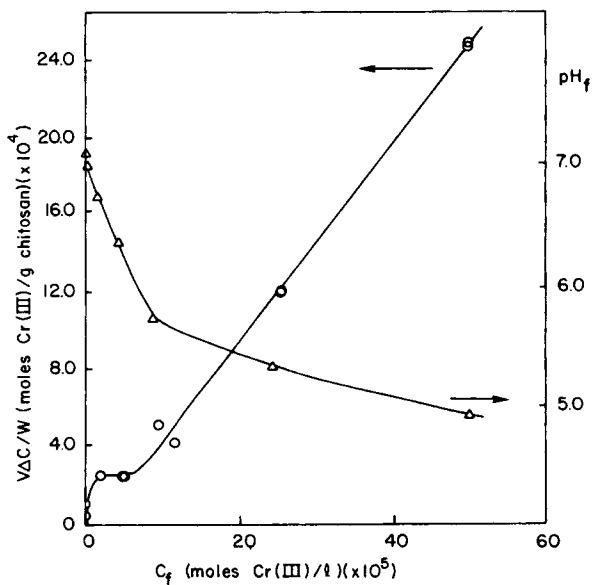


Fig. 4. Uptake of Cr(III) on chitosan.

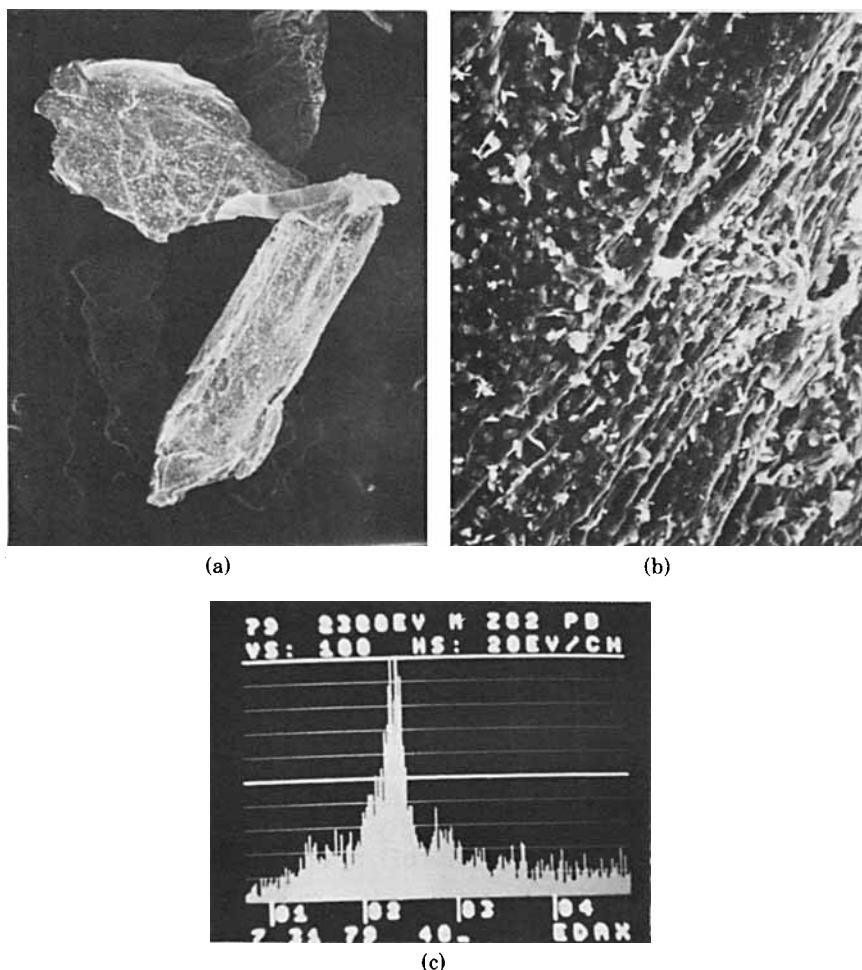


Fig. 5. SEM photomicrographs at 50 $\times$  (a) and 500 $\times$  (b) of chitosan showing Pb in the EDAX spectrum (c).

a significant increase in the pH of Cr(III) solutions on equilibration with chitosan. It is instructive to plot the pH results on the uptake isotherm for Cr(III) as is done in Figure 4. Note that the initial apparent plateau region in the uptake isotherm is characterized by a sharp change in the value of  $pH_f$ . Further work is necessary to interpret these results.

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

SEM photomicrographs of chitin and chitosan were obtained and no significant difference in surface morphology of the two polymers was noted. Calcium was detected by EDAX in both polymers, but no lead or chromium was detected. The SEM photomicrographs of chitosan after equilibration with Pb(II) solution are shown in Figure 5. Based on the uptake isotherm (Fig. 1), the Pb content

TABLE II  
pH Values of Cr(III) Solutions before and after Chitosan Addition

$C_0 (\times 10^{-5}) (M)$	pH <sub>0</sub>	pH <sub>a</sub>	pH <sub>f</sub>	$C_f (\times 10^{-5}) (M)$
100	3.5	3.6	4.85	50
50	3.8	3.6	5.0	25.5
20	4.0	3.5	5.8	9.5
10	4.2	3.6	6.8	5.0
5	4.5	3.6	7.0	1.9
2	4.8	3.6	7.1	<1
1	5.1	3.5	7.1	<1

of the chitosan sample was  $17 \times 10^{-5}$  mole Pb(II)/g polymer. A particularly striking feature of these photomicrographs is the appearance of flakes on the chitosan particles. A smaller number of similar flakes was noted on chitin after equilibration with Pb(II) solution. A lead signal was noted in the EDAX spectrum of the flakes on both chitosan and chitin. The intensity of the Pb signal observed in the EDAX spectrum of chitosan was stronger than that of chitin. This result is consistent with the isotherm studies above.

The origin of the flakes is unclear. Are the flakes formed during the sorption process? Do the flakes form during sample preparation? If the flake formation results from sample preparation, it would seem as if the same result would be observed with chitin as with chitosan. This was not the case as has been noted above.

The SEM photomicrographs and the Cr EDAX spectrum of chitosan after equilibration with a Cr(III) solution are shown in Figure 6. Based on the uptake isotherm (Fig. 4), the Cr content of this sample was  $2.5 \times 10^{-4}$  mole Cr/g chitosan. The chitosan surface appears littered with whitish nodules. The EDAX spectrum of these nodules showed an intense Cr signal as illustrated in Figure 6. The presence of a high Cr(III) content on chitosan is consistent with the uptake isotherm (see Fig. 4).

We have shown that the uptake of both Pb(II) and Cr(III) on chitosan leads to the formation of discrete aggregates on the chitosan surface. This phenomenon which may be referred to as the Eiden–Jewell effect could represent a new model for the uptake of heavy metals by chitosan and chitin.

### Electron Spectroscopy for Chemical Analysis (ESCA)

A summary of the corrected (C 1s = 284.6 eV) binding energies and surface atomic fractions calculated from the narrow scan ESCA spectra of chitin and chitosan is given in Table III. The atomic fraction of the  $i$ th species was calculated using

$$AF_i = A_i / \sum A_i \quad (1)$$

where

$$A_i = bhS/2\sigma \quad (2)$$

In eq. (2), the parameters  $b$  and  $h$  are the base and height of the triangulated photopeak,  $S$  is the sensitivity (counts/sec/cm), and  $\sigma$  is the value of the photoelectron cross section.<sup>6</sup>

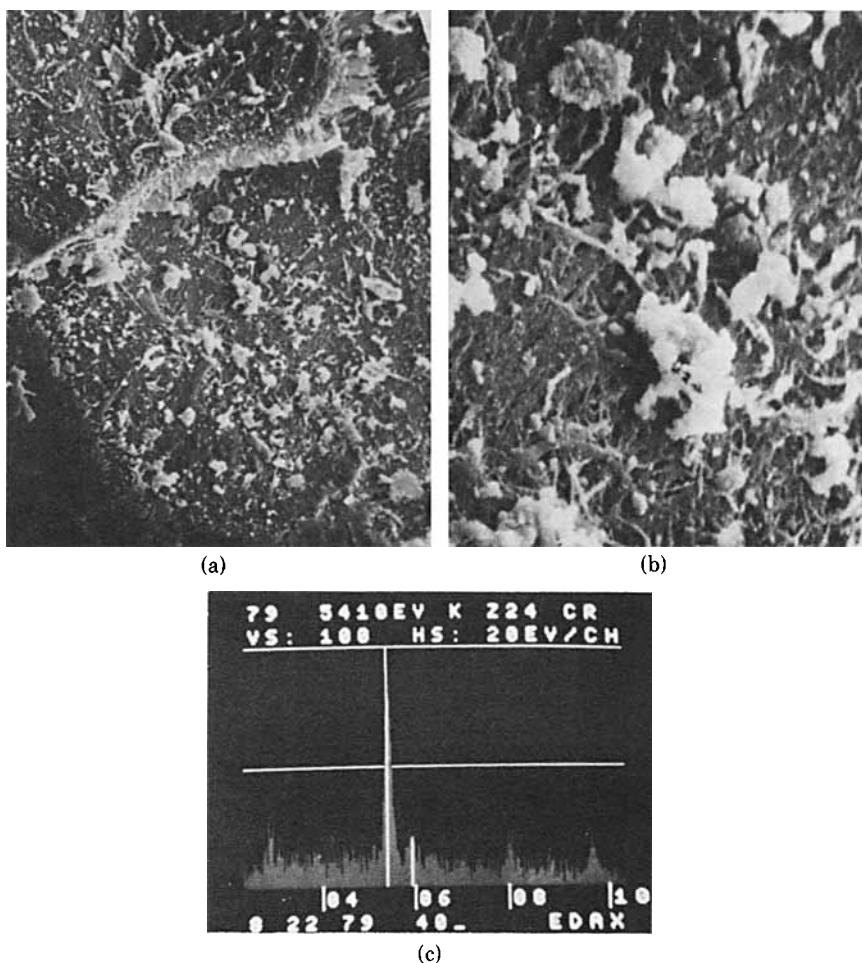


Fig. 6. SEM photomicrographs at 500 $\times$  (a) and 2000 $\times$  (b) of chitosan showing Cr in the EDAX spectrum (c).

There is no significant difference in the N 1s binding energy in chitin and in chitosan. The 0.5-eV difference in the O 1s binding energy in the two polymers may be significant.

Trace amounts of Ca were observed in both polymers consistent with the EDAX results noted above. No detectable quantities of Cl were measured in either polymer. For chitosan, no detectable quantities of K or Na were measured. The absence of these elements rule out their role in explaining the pH changes noted above.

The major photopeaks observed for chitin after equilibration with Pb(II) solution and for chitosan after equilibration with Pb(II) and Cr(III) solutions are shown in Figures 7, 8, and 9, respectively. A summary of the corrected binding energies and surface atomic fractions calculated from the narrow scan ESCA spectra of all samples is given in Table III.

A strong Pb  $4f_{5/2,7/2}$  photopeak was observed for both chitin and chitosan after



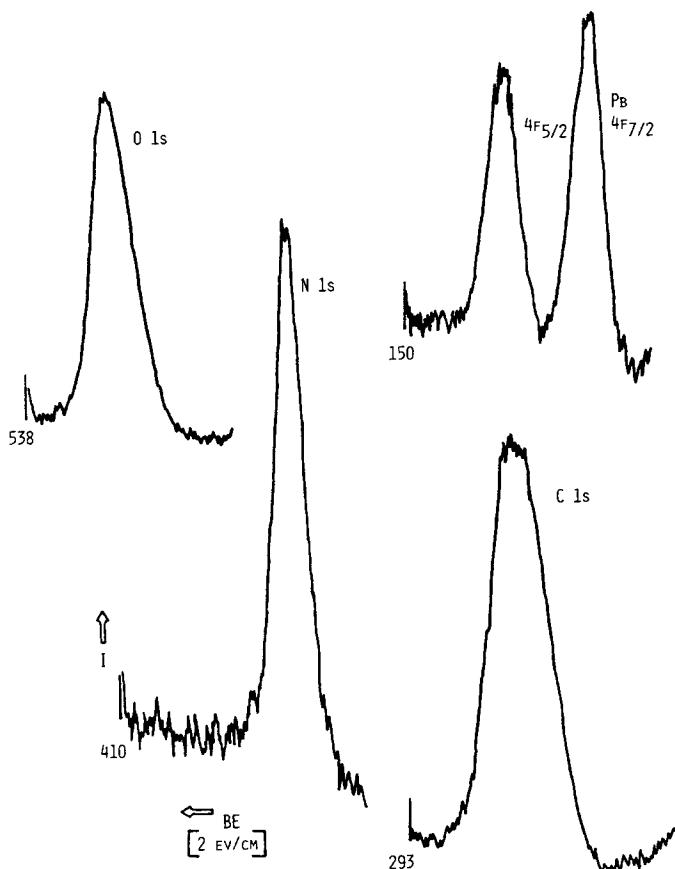


Fig. 7. Major ESCA photopeaks of chitin after equilibration with Pb(II) solution.

equilibration with Pb(II) solution. The average binding energy of 138.3 eV for the Pb  $4f_{7/2}$  photopeak on chitin and chitosan is in good agreement with the value of 138.0 eV reported<sup>7</sup> for PbO. The argument suggests that the bonding state of the lead associated with both chitin and chitosan is Pb(II) as in PbO. It is now speculated that the whitish flakes observed on chitosan are aggregates of Pb(OH)<sub>2</sub>.

There was no significant shift in the binding energies of the N 1s or O 1s photopeaks on equilibration of chitin with Pb(II) solution. On the other hand, there was a significant decrease in the O 1s binding energy from 532.2 to 531.4 eV on equilibration of chitosan with Pb(II) solution. This shift might be expected if Pb(OH)<sub>2</sub> flakes cover the chitosan surface. There was no shift in the binding energy of the N 1s photopeak.

Based on the uptake isotherms (Figs. 1 and 3), the Pb contents of the chitin and chitosan samples were  $3.5 \times 10^{-5}$  and  $17 \times 10^{-5}$  mole Pb(II)/g polymer, respectively. The calculated N/Pb ratios for chitosan and chitin based on uptake are 29 and 115, respectively. The N/Pb ratio can also be calculated from the ESCA surface atomic fractions. The calculated N/Pb ratios for chitosan and chitin based on ESCA are 0.51 and 11, respectively. The results are summarized in Table I.

TABLE III  
ESCA Parameters for Chitosan, Pb(II)/Chitosan, Cr(III)/Chitosan, Chitin, and Pb(II)/Chitin

Element	Chitosan		Pb(II)		Cr(III)		Chitin		Pb(II)	
	$\overline{B.E.}(eV)$	A.F.	$\overline{B.E.}(eV)$	A.F.	$\overline{B.E.}(eV)$	A.F.	$\overline{B.E.}(eV)$	A.F.	$\overline{B.E.}(eV)$	A.F.
N 1s	399.0	0.042	398.8	0.021	399.5	0.037	398.9	0.043	398.9	0.055
O 1s	532.2	0.177	531.4	0.228	532.1	0.217	531.7	0.255	531.8	0.258
C 1s	(284.6)	0.774	(284.6)	0.709	(284.6)	0.744	(284.6)	0.700	(284.6)	0.677
Ca 2p <sub>3/2</sub>	346.8	<0.01					346.5	<0.01	346.8	<0.01
Pb 4f <sub>7/2</sub>			138.4	0.041					138.2	0.005
Cr 2p <sub>3/2</sub>					577.2	0.002				

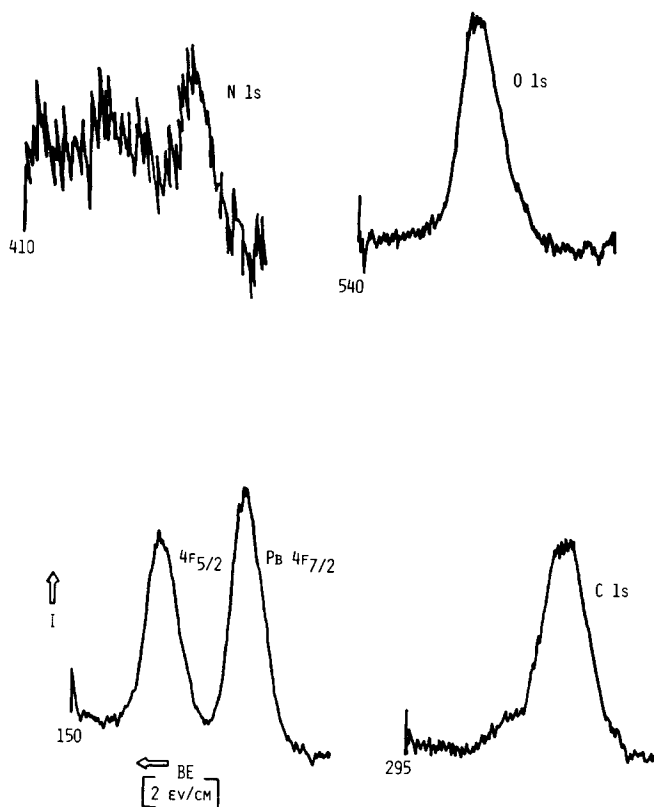


Fig. 8. Major ESCA photopeaks of chitosan after equilibration with Pb(II) solution.

The discrepancy between the uptake and ESCA ratios are rationalized by the fact that the uptake value was calculated assuming a uniform distribution of Pb throughout the polymer. Secondly, ESCA is a surface sensitive technique, and if, as the SEM photomicrographs suggest, Pb is segregated on the surface of the polymer particle, the much smaller values of the N/Pb ratios are reasonable. On the other hand, there is a consistency in that the ESCA ratios support the greater uptake of Pb by chitosan over chitin.

A Cr  $2p_{3/2}$  photopeak at 577.2 eV was observed for chitosan after equilibration with Cr(III) solution. Carlson<sup>8</sup> lists a value of 577.0 eV for Cr<sub>2</sub>O<sub>3</sub>. The apparent agreement may be fortuitous. Further work on model compounds is necessary to establish the bonding state of Cr on Chitosan. It can be speculated, however, that the nodules observed on chitosan are aggregates of Cr(OH)<sub>3</sub>. There was no significant shift in the binding energy of either the N 1s or the O 1s photopeaks on equilibration of chitosan with Cr(III) solution. The fact that a shift was noted for Pb(II) and not for Cr(III) could be attributed to the smaller atomic fraction of Cr compared to Pb (see Table III). But similar densities of flakes were noted (cf. Figs. 5 and 6) in the SEM photomicrographs for Pb(II) and Cr(III), suggesting that a shift ought to have been observed.

Based on the uptake isotherm (Fig. 4), the Cr content of the chitosan sample was  $2.5 \times 10^{-7}$  mole Cr(III)/g chitosan. The calculated N/Cr ratio based on up-

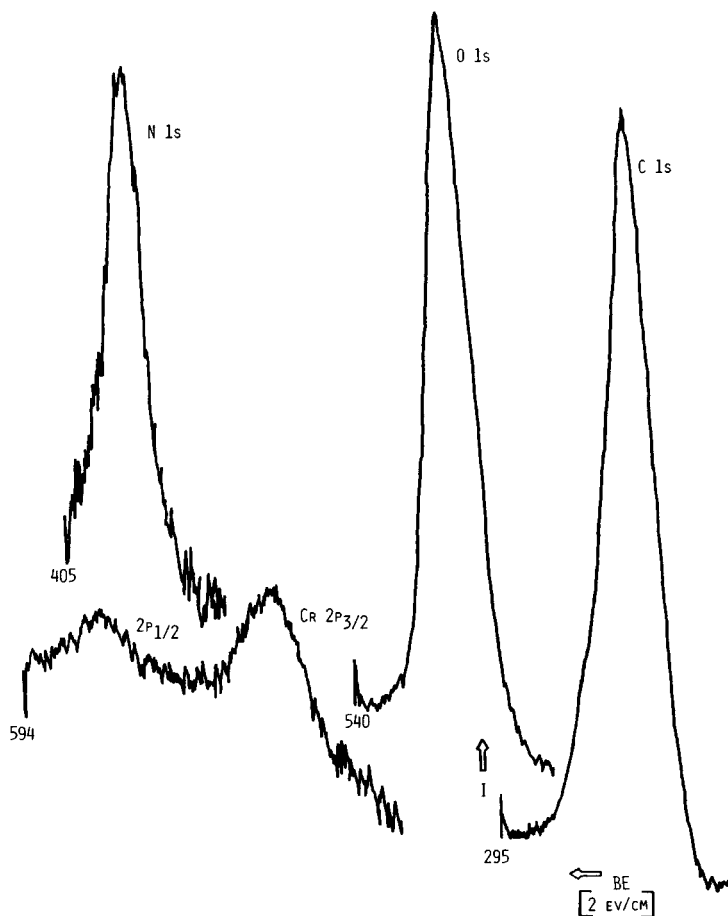


Fig. 9. Major ESCA photopeaks of chitosan after equilibration with Cr(III) solution.

take is 21 and is listed in Table I. The calculated N/Cr ratio for chitosan based on ESCA is 18. The agreement is interesting, but based on the SEM photomicrographs and the analogous Pb(II)/chitosan system, one might have expected a greater divergence of the two ratios.

The authors wish to thank the National Science Foundation for partial financial support of this research and in particular for a summer stipend for one of us (C.A.E.). Our efforts in this ten-week summer research program were aided greatly by a number of persons at Virginia Tech, including Betty Bartschmid, John Mason, and Frank Mitsiansis (SEM). The continuing interest of Peter Perceval in this research is appreciated.

### References

1. R. A. A. Muzzarelli, *Natural Chelating Polymers*, Pergamon, Oxford, 1973.
2. R. A. A. Muzzarelli, *Chitin*, Pergamon, Oxford, 1976.
3. R. A. A. Muzzarelli and O. Tubertini, *Talanta*, **16**, 1571 (1969).
4. K. Kurita, T. Sannan, and Y. Iwakura, *J. Appl. Polym. Sci.*, **23**, 511 (1979).

5. S. Brunauer, *The Adsorption of Gases and Vapors*, Princeton U. P., Princeton, NJ, 1945, p. 60ff.
6. J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 129 (1976).
7. M. E. Counts, J. S.-C. Jen, and J. P. Wightman, *J. Phys. Chem.*, **77**, 1924 (1973).
8. T. A. Carlson, *Photoelectron and Auger Spectroscopy*, Plenum, New York, 1975.

Received November 14, 1979

Revised January 2, 1980