

# Preparation of Polyacrylamidoxime Chelating Cloth for the Extraction of Heavy Metals from Water

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**ABSTRACT:** Woven polyacrylamidoxime cloth was prepared from the polyacrylonitrile precursor via reaction in methanolic hydroxylamine. Preparation was controllable and reproducible and the reaction conditions were optimized with respect to the time of conversion, the concentration of  $\text{NH}_2\text{OH} \cdot \text{HCl}$ , and the temperature of conversion. The cloth produced had a large capacity for Cu(II) and Pb(II) of 71.2 and 450  $\text{mg g}^{-1}$  (1.12 and 2.17  $\text{mmol g}^{-1}$ ) respectively, and adequate physical properties suitable for rigorous use. Sorption profiles of Pb(II) and Cu(II) were similar to those of chelate ion exchange resins and fibers containing the amidoxime group. The rate of uptake of metals by the cloth was found to be dependent on the percent surface area converted to amidoxime groups, the concentration and type of metal being tested for, and the time of exposure. Anomalous kinetics of sorption for Pb(II) and Cu(II) by cloth of increasing amidoxime group content were explained by a two-part sorption mechanism. Distribution coefficients of  $3.5 \times 10^6$  and  $1.5 \times 10^6$  for Cu(II) and Pb(II) were observed, and the average rates of uptake for Cu(II) and Pb(II) were 600 and 200  $\mu\text{g g}^{-1} \text{day}^{-1}$  (9.4 and 0.96  $\mu\text{mol g}^{-1} \text{day}^{-1}$ ), respectively, from dilute solution ( $[\text{Cu}] = 5.9 \mu\text{g L}^{-1}$ ,  $[\text{Pb}] = 2.8 \mu\text{g L}^{-1}$ ). Treatment of the cloth with aqueous NaOH did not improve the capacities for Pb(II) and Cu(II). © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1175–1192, 1997

**Key words:** amidoxime; chelating adsorbent; water analysis; trace metal; polyacrylonitrile

## INTRODUCTION

Recent work by Lin on the use of polyacrylonitrile fibers containing the amidoxime group for the extraction of Au from water,<sup>1–3</sup> and by others for the preconcentration of U from seawater,<sup>4–11</sup> has suggested to us that it may be possible to use a woven chelating cloth containing the amidoxime group as a device for the passive *in situ* concentration of trace metals in water.

Although there has been substantial work in the past with regards to fibers and resins containing the amidoxime group for metal extraction from water,<sup>12–18</sup> our work was focused on the development of a practical and possible commercial

concept, thus a common textile was chosen. Polyacrylonitrile was chosen for the backbone of the material based on the past work with fibers and the fact that a textile is self-supporting, whereas fibers as well as chelating resins necessitate some form of containment for deployment. The physical properties of the textiles also allows the design of a device which can be directly introduced into the sample cavity of an XRF spectrometer for analysis of the metals taken up. As well, work in our lab with activated carbon cloth for the extraction of VOC from air has demonstrated some advantages of using textiles for monitoring purposes.<sup>19,20</sup>

The goal of this article was to develop a means for the preparation of polyacrylamidoxime cloth to be used in a device for the *in situ* concentration of trace metals in water. Several criteria were deemed important in the preparation process. These were the ease and cost associated with

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manufacture on a relatively large scale as well as reproducibility between successive batches of cloth. Other properties were a large capacity for trace metals and adequate physical strength.

## EXPERIMENTAL

### Reagents

Reagents used in the conversion of the nitrile groups on the polyacrylonitrile cloth to amidoxime chelating groups,  $\text{NH}_2\text{OH} \cdot \text{HCl}$ ,  $\text{NH}_4\text{OH}$ ,  $\text{NaOH}$ , and ethanol (95%) were reagent grade (Fisher) while methanol (100%) used was electronic grade (Fisher). Metals used in the kinetic experiments and in standard solutions were prepared from the nitrate salts and were reagent grade (Fisher). Solutions used in AA were prepared in analytical-reagent grade  $\text{HNO}_3$  (Mallinckrodt), while those used in Graphite Furnace Atomic Absorption (GFAA) spectroscopy were prepared in environmental grade  $\text{HNO}_3$  (Anachemia).

Water used for the *in vitro* tests in the flow chambers was derived from reverse osmosis feed-stock (ro). Water used in the standards for GFAA, and in the conversion process, was further purified by passage through a four-stage Barnsted Nano-Pure II purification system (nanopure).

The film used in the preparation of samples for wavelength dispersive X-ray fluorescence (WDXRF) spectroscopy was 6.3  $\mu\text{m}$  X-ray polypropylene film supplied by Chemplex Industries Inc., NY.

### pH Measurement

An ORION expandable ionanalyzer EA 940 was used for the measurement of solution pH.

### Radioisotope EDXRF Spectroscopy/WDXRF Spectroscopy

An energy dispersive X-ray fluorescence (EDXRF) spectrometer, consisting of an annular 0.5 Ci  $^{241}\text{Am}$  source, a New England Nuclear Si(Li) semiconductor detector, a Nuclear Semiconductor 512 amplifier, and a Tracor Northern TN 1705 pulse-height analyzer, were used to measure the amount of metal taken up by the cloth from solution. An arbitrary time of 3000 s for data acquisition was chosen for sensitivity and convenience. Representative blanks were recorded for all samples.

Wavelength dispersive XRF spectroscopy was also used as a means of analysis of the cloth. An American Research Laboratories spectrometer

with a 50-sample capacity autosampler was used. Spectral acquisition was done by recording spectra for three 30-s intervals for each element examined. Representative blanks were recorded for all analysis.

Quantitation of XRF results for Cu and Pb was carried out by prior calibration in order to relate XRF results with absolute amounts of the metal present on the cloth. This involved quantitative (>95%) acid extraction of metals from selected samples whose XRF spectra were recorded previously, followed by AA or GFAA analysis of the extract.

### AA Spectroscopy/GFAA Spectroscopy

Analysis of the solutions used in batch experiments, acid extracted metals from cloth samples, and the test solutions used in the flow chamber were carried out using a Varian SpectrAA-20 Atomic Absorption Spectrometer equipped with a Varian GTA-96 Graphite Tube Atomizer and an autosampler. Standards were prepared by serial dilution of stock 1000  $\text{mg L}^{-1}$  solutions. Solutions for GFAA were adjusted to 0.5%  $\text{HNO}_3$  (v/v). Solutions for AA were adjusted to 5% and 20%  $\text{HNO}_3$  (v/v).

### Fourier Transform Infrared Spectroscopy

Infrared spectra were recorded on a Bomen, Hartmann, Brawn, Michelson MB Series, Fourier Transform Infrared Spectrometer (FTIR). Pieces of cloth were cut into strips, placed in liquid nitrogen, and once frozen, ground into a powder. The powder was combined with a small amount of KBr and pressed into a thin glass pellet. FTIR spectra were recorded from 600 to 4000  $\text{cm}^{-1}$  at a resolution of 2  $\text{cm}^{-1}$ .

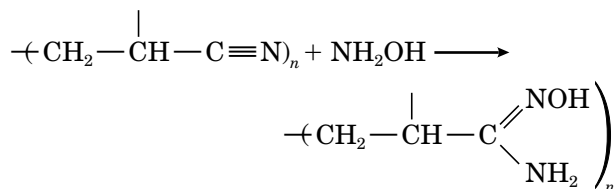
### Scanning Electron Microscopy

Cloth samples were prepared with a Au/Pd coating via Ar plasma. Photographs were obtained on a Stereoscan 120 Scanning Electron Microscope coupled to a IBAS Kontron Elektronik Image Analyser.

## RESULTS AND DISCUSSION

### Preparation of Polyacrylamidoxime Chelating Cloth

The preparation of the cloth began with the conversion of the nitrile groups on the surface of the polyacrylonitrile cloth to amidoxime groups via the reaction in methanolic hydroxylamine as described by Lin, Lu, and Zeng.<sup>1</sup> The reaction is depicted below in Scheme 1.

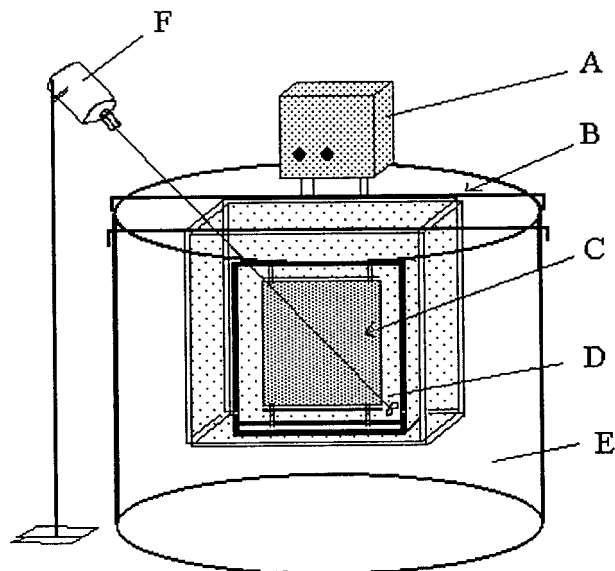


**Scheme 1** Reaction of a polyacrylonitrile monomer unit with hydroxylamine to produce polyacryloamidoxime.

Orlon cloth (polyacrylonitrile) was obtained from Test Fabrics Inc. and used as received; the properties of the cloth are given in Table I.<sup>21</sup> Cloth pieces were cut from the supplied material and the edges fused with a flame heated stainless steel spatula. After this, opposite ends of the cloth were sewn, using cotton thread, around a glass frame in order to expose the entire surface area of the cloth to the hydroxylamine solution. Solutions of hydroxylamine in 50% methanol/water or 50% ethanol (95%)/water (v/v) were prepared by adding a fixed amount of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  with an equal molar amount of  $\text{NaOH}$  or  $\text{NH}_4\text{OH}$  to water,  $\text{pH} = 7$ , followed by the addition of methanol or ethanol. A diagram of the batch reactor is given in Figure 1.

After conversion the cloth was washed with water (ro) and allowed to dry in air, and in the case of later-produced cloth (batches 28–35) dried in a vacuum oven at  $65^\circ\text{C}$ . A total of 35 batches of cloth were manufactured using this batch process. Reaction conditions for each batch of cloth, the type of tank used, the degree of conversion, and general observations are given in Table II. After the conversion process was complete, small pieces of the amidoxime containing cloth were cut into  $2 \times 2 \text{ cm}^2$  squares for use in both the flow and batch laboratory experiments.

In order to quantify the effect of the different reaction conditions on the degree of conversion of nitrile groups to amidoxime groups, the cloth was weighed before and after the conversion process.



**Figure 1** Diagram of the batch reactor. (A) Circulating water heater; (B) Glass tank; (C) Cloth on glass frame; (D) Glass stirring rod; (E) Reservoir; (F) Motor.

The percent conversion, a measure of the degree of conversion, was calculated using the method as described by Lin, Lu, and Zeng.<sup>1</sup>

$$\begin{aligned} \% \text{ Conversion} &= \frac{W_1 - W_0}{W_0} \times \frac{M_0}{M_1} \times 100 \\ &= \frac{W_1 - W_0}{W_0} \times 160.6 \end{aligned}$$

where  $W_0$  is the weight of polyacrylonitrile cloth before conversion,  $W_1$  is the weight of polyacrylonitrile cloth after conversion,  $M_1$  is the molecular weight of hydroxylamine ( $33 \text{ g mol}^{-1}$ ), and  $M_0$  is the molecular weight of acrylonitrile monomer unit ( $53 \text{ g mol}^{-1}$ ).

#### Characterization by FTIR Spectroscopy

FTIR spectra were taken of some of the samples of cloth before and after varying degrees of conver-

**Table I** Properties of the Polyacrylonitrile Cloth Used

Material	Properties
Orlon Cloth Manufactured by Test Fabrics Inc., P.O. Box 420, Middlesex, NJ, 08846	Orlon Type 75, 100% Acrylic, style #864, lot #8400
Orlon Fibers Manufactured by Dupont Canada Inc., P.O. Box 2100, Kingston, Ont. Canada, K7L 4Z6	Spun Orlon, Type 75, Dupont yarn, acrylic yarn, 30/2 warp—44 end/inch, 30/2 warp—40 pick/inch, 30/2 = 19.68 Tex $\times$ 2-ply yarn

**Table II** Reaction Conditions and Properties of the Cloth Produced

Batch No.	Mass Cloth (g)	Mass NH <sub>2</sub> OH · HCl (G)	Base <sup>a</sup>	Solvent <sup>b</sup>	Conditions	Percent <sup>c</sup>	Cloth Properties
1	6.26	63.1	NaOH	MeOH	45°C × 48	10	soft, yellow
2	6.92	3.0	NaOH	MeOH	45°C/5 days	7	soft, white
3	6.84	20.0	NH <sub>4</sub> OH	MeOH	45°C × 29 h	50	soft, beige
4 <sup>d</sup>	6.81	from batch 3	NH <sub>4</sub> OH	MeOH	60°C × 2 h 90°C × 4 hours	70	brittle, yellow
5 <sup>d</sup>	7.07	from batch 3	NH <sub>4</sub> OH	MeOH	20°C × 3 hours 80°C × 2 hours	28	stiff, yellow
6	6.72	6.05	NaOH	EtOH	45°C × 24 hours 40°C × 10 hours	7	soft, yellow
7 <sup>d</sup>	6.48	from batch 6	NaOH	EtOH	60°C × 4 hours 65°C × 24 hours	22	soft, yellow
8	5.87	6.0	NaOH	EtOH	65°C × 7 hours	30	soft, beige
9	5.69	20.04	NH <sub>4</sub> OH	MeOH	43°C × 8 hours 70°C × 39 hours	11	soft, beige
10	6.36	29.61	NH <sub>4</sub> OH	MeOH	65°C × 24 hours	16	soft, beige
11	5.34	40	NH <sub>4</sub> OH	MeOH	65°C/24 hours	14	soft, yellow
12	6.28	30	NH <sub>4</sub> OH	MeOH	85°C/22 hours	90	brittle, yellow
13	6.81	30	NH <sub>4</sub> OH	MeOH	60°C × 48 hours	62	soft, yellow
14	5.77	30	NaOH	MeOH	68°C × 14 hours	14	brittle, yellow
15	5.75	30	NaOH	MeOH	64°C × 2 hours 74°C × 2 hours	57	stiff, yellow
16	5.53	30	NaOH	MeOH	60°C × 4 hours	5	soft, white
17	4.98	30	NaOH	MeOH	65°C × 24 hours	100	brittle, white
18	3.59	30	NaOH	MeOH	65°C × 7 hours	48	soft, beige
19	3.57	30	NaOH	MeOH	43°C × 8 hours 70°C × 39 hours	30	soft, white
20	2.28	60	NaOH	MeOH	65°C × 24 hours	44	soft, white
21	3.06	60	NaOH	MeOH	54°C × 15.7 hours	84	brittle, white
22	3.09	60	NaOH	MeOH	55°C × 7.7 hours	14	soft, white
23	2.90	60	NaOH	MeOH	54°C × 12.3 hours	46	soft, white
24	2.93	60	NaOH	MeOH	55°C × 10.3 hours	21	soft, white
25	5.15	60	NaOH	MeOH	55°C × 12 hours	73	flexible, white
26	4.88	60	NaOH	MeOH	55°C × 12 hours	42	soft, white
27	4.85	60	NaOH	MeOH	56°C × 12 hours	47	soft, white
28	4.80	60	NaOH	MeOH	54°C × 12 hours	47	soft, white
29	4.83	60	NaOH	MeOH	54°C × 12 hours	(5)	damaged
30	4.85	60	NaOH	MeOH	54°C × 12 hours	47	soft, white
31	4.90	60	NaOH	MeOH	54°C × 12 hours	52	soft, white
32 <sup>e</sup>	4.93	60 + batch 31	NaOH	MeOH	55°C × 12 hours	100	stiff, white
33	4.85	60	NaOH	MeOH	55°C × 26 hours	100	brittle, white
34	4.92	60	NaOH	MeOH	55°C × 21.3 hours	100	brittle, white
35	4.94	60	NaOH	MeOH	56°C × 12.3 hours	63	soft, white

<sup>a</sup> Base: solution adjusted to pH = 7.

<sup>b</sup> Solvent used with water, 50% (v/v), EtOH = ethanol (95%), MeOH = methanol.

<sup>c</sup> Degree of conversion in percent, see text for formula.

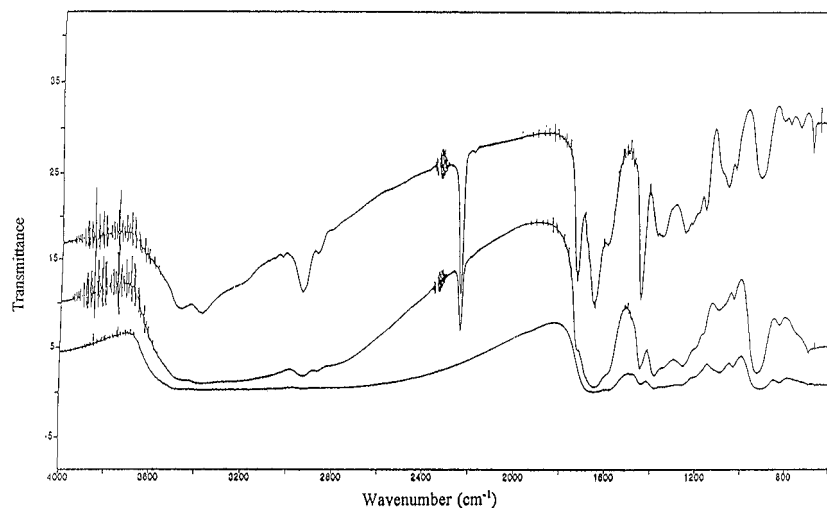
<sup>d</sup> Hydroxylamine solution reused from previous batch.

<sup>e</sup> Cloth damaged while drying at 120°C for 5 min.

sion in order to qualitatively monitor the conversion process. Representative spectra are presented in Figure 2. The use of an attenuated total

reflectance cell to record spectra on the cloth was attempted without success.

Examination of the FTIR spectra recorded on



**Figure 2** FTIR spectra recorded on three different batches of cloth. Degree of conversion = 17% (upper), 57% (middle), and 100% (lower), respectively.

three batches of converted cloth of differing degrees of conversion provides a qualitative and semi-quantitative account of the conversion process. The peak at  $\sim 2240\text{ cm}^{-1}$ , which corresponds to the nitrile group of the Orlon cloth, is seen to decrease as the degree of conversion increases, while at the same time the peak at  $1600\text{ cm}^{-1}$ , which corresponds to  $\text{C}=\text{N}$ , broadens considerably. These results are similar to those reported by Lin, Lu, and Zeng.<sup>1</sup>

### Initial Observations

The method of conversion was based on the literature method used for the treatment of polyacrylonitrile staple fibers and thus was not directly applicable to the conversion of the textile.<sup>22,23</sup> The reason for this is that the textile is made up of thread woven from the staple fiber and thus possesses its own physical properties, an extension of those of both the thread and the fiber.

From the results of the conversion of several batches of cloth presented in Table II, several observations were made. The physical properties of the Orlon cloth, which was quite flexible and white in color originally, changed markedly during the conversion process. Depending upon the degree of conversion to amidoxime groups, the cloth became increasingly less flexible, and it was observed that at higher degrees of conversion ( $>50\%$ ) the cloth also became brittle.

The color of the cloth was observed to change from white to tan, to a light yellow in color, depending on the reaction conditions. The color change was originally attributed to the increase

in the degree of conversion; however, later experiments indicated that the color change may also have been due to the prolonged heating of the cloth at temperatures  $> 60^\circ\text{C}$ , conditions which favor saponification.<sup>24,25</sup>

The choice of methanol as the solvent used with water seemed to produce a slightly better cloth than when ethanol was used. The cloth produced with methanol seemed to be more flexible and softer in texture. The use of  $\text{NH}_4\text{OH}$  as opposed to  $\text{NaOH}$  as the choice of neutralizing base produced no noticeable differences in the cloth.

The cloth was also observed to contract in size during the course of treatment, even enough to crack the glass frame supporting it. This effect is based on the physical nature of the thread and fibers which make up the thread. During manufacture, the fibers are produced by a hot extrusion process, which results in the manufacture of a fiber in an elongated form. The reason for this is that a high degree of order is introduced into the polyacrylonitrile chains during the extrusion process due to the high crystallinity that the polymer possesses.<sup>24,25</sup> The polymer is thus said to be placed in a high energy metastable state. When subjected to a wet heating process the polymers relax to a lower energy state, and thus the fibers will contract. This is the effect observed during the conversion process and the result is a contraction of the cloth.

Because of the two processes which occurred during conversion, the contraction of the cloth, as well as actual conversion of nitrile groups, the optimization experiments were performed. This was carried out in order to gain a better under-

standing of all of the processes which occurred during the conversion and to identify some of the variables involved regarding these processes. The eventual goal was the production of a cloth with good physical characteristics, such as flexibility, while having a high percentage of amidoxime groups. Another factor was that the production would be able to reproducibly manufacture cloth of similar characteristics in different batches in order to simplify calibration during the deployment of a large number of monitors.

### Optimization of Reaction Conditions

A number of variables were investigated in an attempt to reproducibly manufacture cloth with good physical characteristics and a high degree of conversion of nitrile groups to amidoxime groups. Parameters investigated were the effects of initial pH, concentration of hydroxylamine, time of conversion, and temperature of conversion. For these experiments small pieces of plain Orlon cloth were cut from the supplied material into squares  $\sim 6.13 \text{ cm}^2$  with the edges fused by a hot spatula. Conversion was carried out in 140-mL beakers containing 100 mL of the appropriate hydroxylamine solution.

### Effect of Initial pH

The effect of varying the initial pH of the hydroxylamine solution on the degree of conversion was investigated. Hydroxylamine solutions of pH = 2–10 were prepared via addition of dilute HCl or  $\text{NH}_4\text{OH}$  to a stock solution of 2% (w/v) of hydroxylamine in 50% (v/v) ethanol (95%)/water. Conversion was carried out in 100 mL each of the solutions for 63.25 h at  $50^\circ\text{C}$  followed by 9.75 h at  $60^\circ\text{C}$ .

From the results regarding the effect of the initial pH on the degree of conversion as shown in Figure 3, it was observed that at a pH of 7 the highest degree of conversion was obtained. This was presumed to be due to the mechanism of the reaction being an  $\text{S}_{\text{N}}2$  type of reaction, with the hydroxylamine attacking the nitrile carbon, which is preferentially favored at a neutral pH. Thus a pH of 7 was chosen for the conversion of the cloth. This is similar to results obtained for the conversion of polyacrylonitrile staple fibers.<sup>1</sup>

### Hydroxylamine Concentration

The effect of the initial concentration of hydroxylamine on the degree of conversion and the physi-

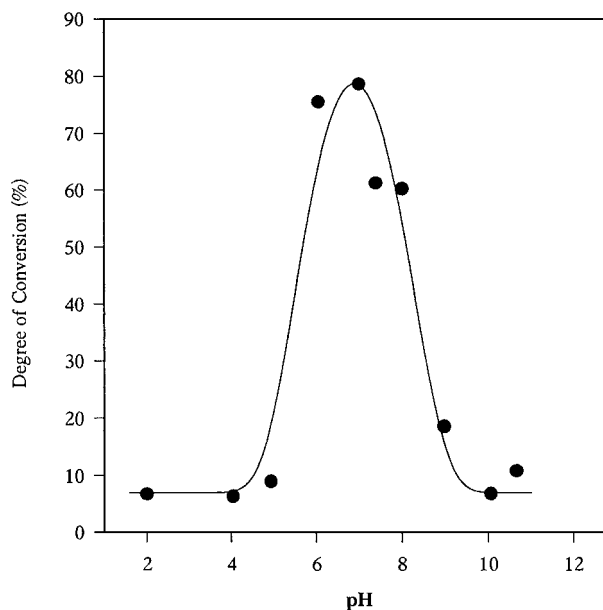
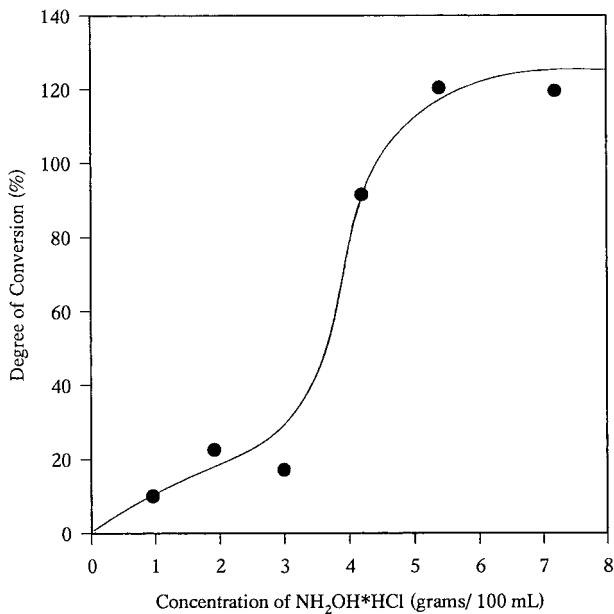


Figure 3 Effect of pH on the degree of conversion.

cal properties of the cloth were investigated. The initial concentration of hydroxylamine was varied between  $\sim 1$  and 7 wt % in 100 mL of solution via serial dilution of a freshly prepared 1-L stock solution of hydroxylamine 3% (w/v) in 50% (v/v) ethanol/water. Conversion was carried out in 100 mL solutions, each of differing concentrations, for 1.5 h at  $80^\circ\text{C}$ .

Several observations were made with respect to the effect of the initial concentration of  $\text{NH}_2\text{OH} \cdot \text{HCl}$  on the degree of conversion, as can be seen in Figure 4. It was observed that the degree of conversion initially was relatively slow up to a concentration of  $\sim 3.5\%$  (w/v) after which the conversion increased substantially, reaching a plateau at  $>6\%$  (w/v). The slow initial rate was presumed to be due to the diffusion of  $\text{NH}_2\text{OH}$  through solution being rate limiting. After the steep rise, the surface reaction was presumed to be the rate-limiting step. These results are similar to the results observed on the conversion of polyacrylonitrile staple fibers.<sup>1</sup>

Another interesting fact was that the degree of conversion was observed to be  $>100\%$  for cloth produced at concentrations of  $\text{NH}_2\text{OH} \cdot \text{HCl} > \sim 4.5\%$  (w/v). The cloth produced at these higher concentrations was also observed to be smooth and brittle compared to the cloth produced at lower concentrations of  $\text{NH}_2\text{OH} \cdot \text{HCl}$ . This higher than theoretically possible degree of conversion may be attributed to the formation of ring and ladder structures, the result is the linking the amidoxime groups on the surface of the cloth,



**Figure 4** Effect of the concentration of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  on the degree of conversion.

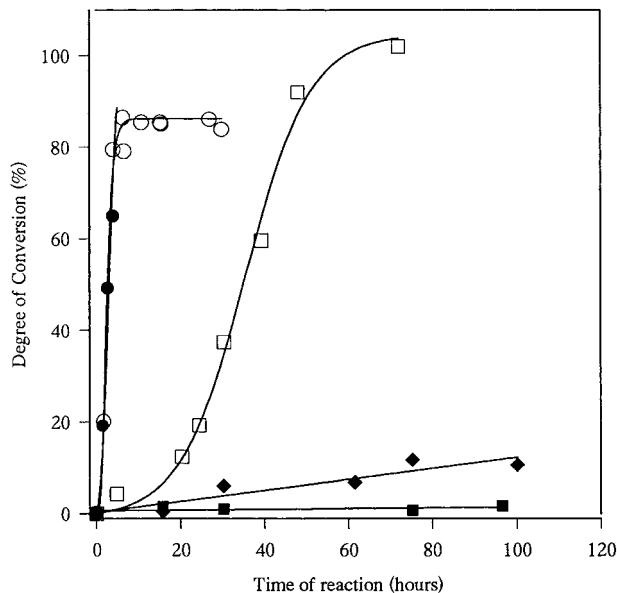
something that has been observed with the conversion of fibers.<sup>26,27</sup> A side effect of this process is the production of a cloth that is unsuitable for use in the monitors.

Because the production of the secondary structures was undesirable, a concentration of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  of 2% (w/v) was deemed optimal for the reproducible production of cloth with the desired properties. At this concentration the conversion process was slower, and thus deemed more controllable.

**Time and Temperature of Conversion**

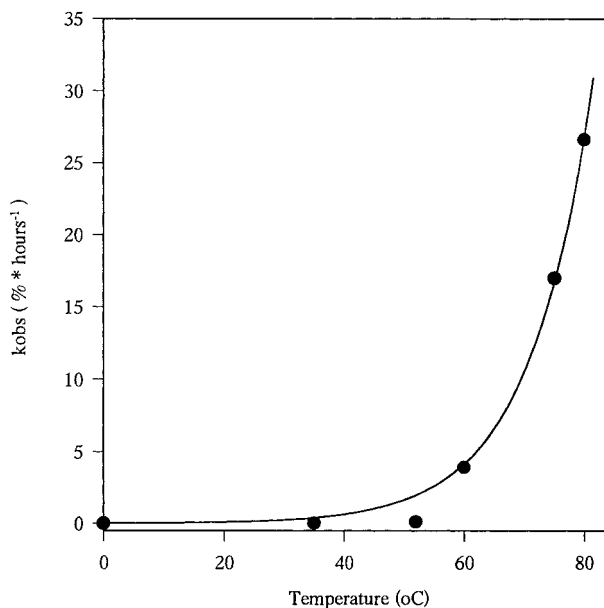
Both the time of conversion and the temperature of conversion were investigated as to their effect on the degree of conversion and the physical properties of the cloth. The conversion of the cloth was carried out at different temperatures (35, 52, 60, 75, and 80°C) over different time intervals of up to 5 days, in order to observe the effect of each variation, and to try and optimize the manufacturing procedure. Initially, 100-mL hydroxylamine solutions were used to treat small pieces of cloth. The conversion was carried out by heating the solutions on hot plates without stirring. Results are shown in Figure 5. The rate of conversion was calculated from the linear slope of each of the curves derived for the different temperatures. The results are shown in Figure 6.

It can be seen in Figure 5 that, as the tempera-



**Figure 5** Effect of temperature on the degree of conversion. Temperature: (■) 35°C; (◆) 52°C; (□) 60°C; (●) 75°C; (○) 80°C.

ture of the reaction was increased, the degree of conversion increased linearly with the exception of the results at 60°C. The change in the slope at 60°C was presumed to be due to a slow initial hydration process of the cloth, which is relatively hydrophobic, followed by the more rapid reaction with hydroxylamine. The degree of conversion at the low temperatures was observed to be exceedingly slow, while at the higher temperatures the



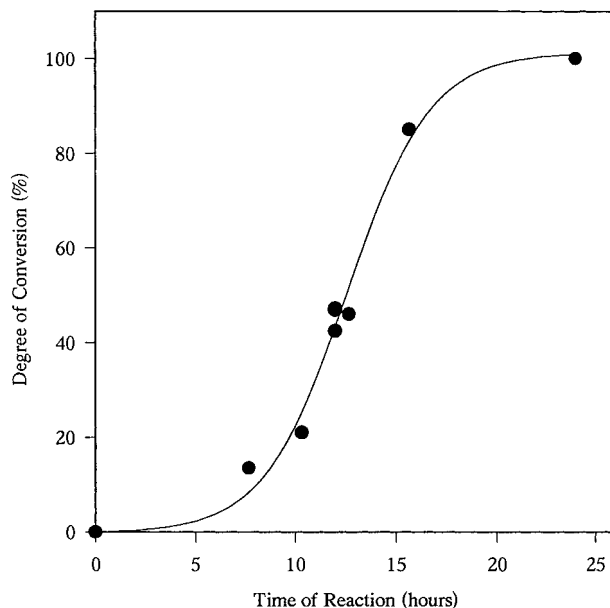
**Figure 6** Rate conversion at different temperatures.

rate was too fast and the cloth produced was brittle. The cloth produced at 60°C seemed to be the best compromise between speed of conversion and quality of the cloth produced.

From previous research, it was observed that at higher degrees of conversion (>50%) the cloth actually became less receptive to the uptake of metal ions from solution as well as becoming more brittle, something that was confirmed here.<sup>22,23</sup> It was thought that, as the degree of conversion is increased, a side reaction involving the fusing of the cloth fibers took place, thus decreasing both the nominal surface area of the cloth and resulting in the cloth's brittleness. This then resulted in a decrease in the effective chelating surface area of the cloth and a subsequent reduction in the uptake of metals. Evidence to support this is found in the differences in the maximum degree of conversion as measured at 65°C and 80°C from the results presented in Figure 5. It can be seen that at 65°C the conversion process is relatively slow, which allows the entire bulk of the textile to react with hydroxylamine, resulting in a degree of conversion approaching 100%. However, at 80°C, the upper limit of conversion approached only ~85%. The reason for this is twofold, the first of which is contraction of the cloth due to the thermal shrinkage. The second cause is due to the fusing of the cloth fibers on the surface of the textile as evident in the smoothness of the surface of the cloth after the conversion process at these higher temperatures. This fusing results in decreasing the net effective surface area that may react with the hydroxylamine, and thus decreases the degree of conversion.

The observed rate of conversion was calculated from the linear slopes of each of the curves for the different temperatures used. From the results in Figure 6 it was observed that the rate of conversion was slow initially up to a temperature of ~60°C, after which the rate increased rapidly. Because it was deemed necessary to prepare the cloth as reproducibly as possible, the lower temperatures of conversion were chosen. The other criterion for the conversion of the cloth was that the conversion process should not be too long. For these reasons a temperature of 55°C was chosen as being optimum, as this allowed more control in the manufacture of different batches of cloth with the same degree of conversion while possessing good physical properties.

It is noted that the results of the optimization experiments were extended to the larger scale batch processes with similar results at 55°C (Fig. 7). From these results it is clear that the pro-



**Figure 7** Large scale results for batch conversion at 55°C.

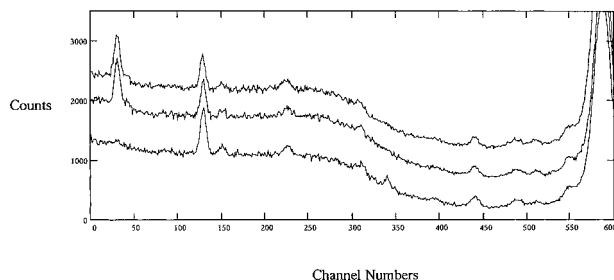
cesses involved with the smaller scale conversion experiments are the same as those of the larger scale experiments. As the time of conversion at 55°C was increased, so did the degree of conversion up to a point past ~50%, where the cloth became less flexible and more brittle. From these results an optimum time of conversion of 12 h was chosen. The 12-h time interval was also chosen for convenience.

### Conditioning With HCl

Treating the cloth with a dilute solution of HCl was done in order to observe the effect of acid treatment on the physical properties of the cloth, and on the resulting uptake of metals from solution. Pieces of cloth (batch 13, ~62% conversion) were placed in 200 mL of ~1.2M solution of HCl for 5 and 30 min. The monitors, along with ones that were not treated with HCl, were then exposed to the flow chamber in order to sorb Pb and Cu.

The EDXRF spectra of the cloth before and after 5 and 30 min of treatment in HCl are shown in Figure 8. It was observed that although the cloth was washed after the treatment process, there was a detectable amount of Cl present, which suggests that the amine part of the amidoxime group is in its protonated form. During the course of treatment with HCl the cloth was observed to swell considerably and then collapse after washing with water. The physical properties of the cloth were observed to degrade with the





**Figure 8** EDXRF Spectra recorded on monitors before (lower) and after treatment in HCl for 5 (middle) and 30 (upper) minutes. Peaks correspond to Cl and Ti at 40 and 120 channel numbers, respectively.

HCl treatment. It is noted that there was no discernible difference in the cloth treated for 5 min compared with the cloth treated for 30 min.

The EDXRF spectra recorded on the HCl-treated cloth and untreated cloth after exposure to the flow chamber are shown in Figure 9. It was observed that after exposure there was a complete loss of the Cl peak, as the remaining HCl was presumably removed from the cloth into solution. It was also observed that the amounts of Cu and Pb sorbed by the treated cloth were greater than the amount taken up by the untreated cloth. This was due to the treatment process in which the amine groups were protonated, which resulted in the cloth becoming more hydrophilic, and thus decreased the resistance to solvation by water. The net result was a reduction in the boundary diffusion layer between the cloth and solution. This ultimately allowed more solution to flow within the confines of the fibers within the cloth. These results are similar to the observations made with respect to an increase in the amount of metals sorbed because of an increase in the hydrophilicity of a fiber.<sup>28,29</sup> It is noted that the HCl treatment would also remove any bound Na present on the cloth as a result of the NaOH neutralization of the  $\text{NH}_2\text{OH} \cdot \text{HCl}$  used in the preparation process. The HCl treatment, although it produced a better cloth with respect to the amount of metals sorbed, resulted in the partial degradation of the physical strength of the cloth, and thus was not further investigated.

#### Conditioning with NaOH and $\text{NH}_4\text{OH}$

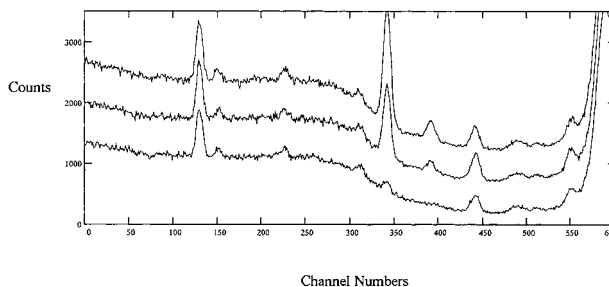
Conditioning of the converted cloth with dilute NaOH and  $\text{NH}_4\text{OH}$  was carried out in order to investigate the resulting effects on the uptake of metals and the physical properties of the cloth. For the NaOH and  $\text{NH}_4\text{OH}$  treatment, small

pieces of converted cloth ( $2 \times 2$  cm, batch 24, 21% conversion) were placed in  $\sim 200$  mL of a 0.1M solution of either NaOH or  $\text{NH}_4\text{OH}$  for periods up to  $\sim 8$  h.

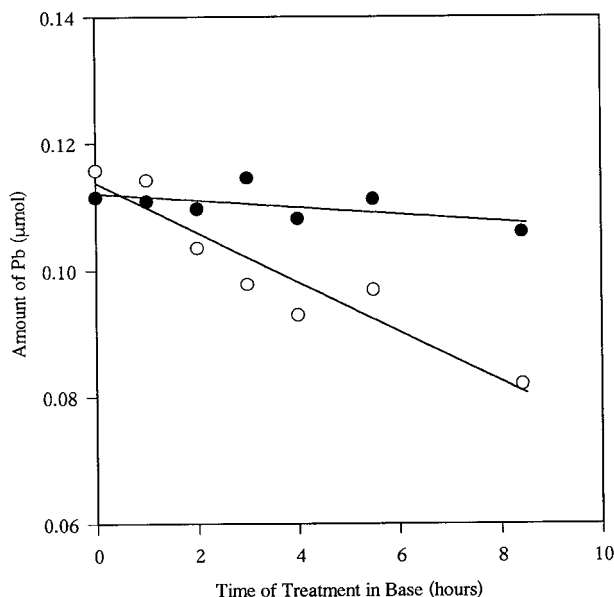
After treatment with base, the cloth pieces were washed with 0.1M HCl and then with water until neutral. The cloth pieces were then grouped together and placed in 250 mL of a dilute solution of Pb(II),  $[\text{Pb(II)}] = 60 \text{ mg L}^{-1}$ , at pH  $\sim 5.0$ , for 5 h on a shaker so that sorption of Pb(II) could occur. Analysis of Pb(II) taken up was done by acid extraction followed by GFAA spectroscopy.

During the treatment process with NaOH, the cloth was observed to become progressively yellow/orange in color as the length of treatment increased. This was presumed to be from the  $\text{Na}^+$  ions present on the cloth, as the  $\text{NH}_4\text{OH}$  treatment produced no noticeable color change. After washing in dilute HCl, the cloth returned to its original white color and was observed to swell slightly.

The results are presented in Figure 10 for NaOH and  $\text{NH}_4\text{OH}$  treatment. It was observed that both the NaOH and the  $\text{NH}_4\text{OH}$  treatments resulted in a decrease in the amount of Pb initially sorbed by the cloth. The slight difference in the effect of NaOH versus  $\text{NH}_4\text{OH}$  was due to the increased base strength of NaOH. It is noted that these results were contradictory to previous findings in which the amount of  $\text{UO}_2(\text{VI})$  sorbed generally increased with an increasing time of alkaline treatment.<sup>10,26,28,29</sup> The difference arises due to the fact that  $\text{UO}_2(\text{VI})$  forms a different chelate complex with the amidoxime groups compared to Pb(II) and Cu(II). As well,  $\text{UO}_2(\text{VI})$  favors the formation of complexes with the imidedioxime group, which is a by-product of the preparation and NaOH treatment.



**Figure 9** EDXRF spectra recorded on an untreated monitor (lower), and HCl treated monitors (5 min, middle; 30 min, upper) after exposure to the flow chamber. Peaks correspond to Cl, Ti, Cu, Zn, and Pb at 40, 120, 340, 380, and 440 channel numbers.



**Figure 10** Effect of NaOH/NH<sub>4</sub>OH on the amount of Pb taken up by the cloth.

### Characterization by SEM

Characterization of the cloth by SEM was done in order to draw a comparison between the cloth and a commercially available chelate ion exchange resin particles, and to see if there were any observable physical changes in the fibers which occurred during the conversion process and during subsequent treatment with NaOH or HCl. Photographs of a piece of cloth produced under the optimized reaction conditions (47% conversion), at increasing magnification, are given in Figure 11. At low magnification the weave of the cloth and the dog-bone shape of the fibers are apparent, while at higher magnification the irregular surface of the fibers can be seen.

SEM photographs of two commercially available chelating resin beads are given in Figure 12. These can be compared with SEM photographs of the cloth at varying degrees of conversion, shown in Figure 13. Past work with fibers have indicated that they possess similar physical properties to macroporous chelating resins. It can be seen that although the surface of the cloth here is not identical to that of Chelite-N, a macroporous resin containing the amidoxime group, it is considerably more pitted than the surface of the normal chelating resin Chelex 100, which contains the iminodiacetate group. This is consistent with the physical properties of the cloth with respect to the uptake of metals from solution.

Photographs of fibers of cloth with varying degrees of conversion from 21%, 47%, 52%, and 84%

are given in Figure 13 along with a photograph of the polyacrylonitrile precursor. It was observed that as the degree of conversion increased there appeared to be an increase in the physical degradation of the fiber, represented here as a pitting of the surface. This is consistent with the increase in brittleness as the degree of conversion increased, results which are consistent with those reported by Lin, Lu, and Zeng.<sup>1</sup>

Figure 14 shows a photograph of a sample of cloth, 47% conversion, which had been heated after conversion in an oven at  $\sim 120^{\circ}\text{C}$  for 5 min. The cloth which was heated was observed to be more similar in physical appearance to the cloth of 84% conversion rather than the cloth of 47% conversion. This indicates that the physical destruction of the fiber during conversion is primarily dependent on the length of time the cloth is exposed to elevated temperatures and not the conversion process itself.

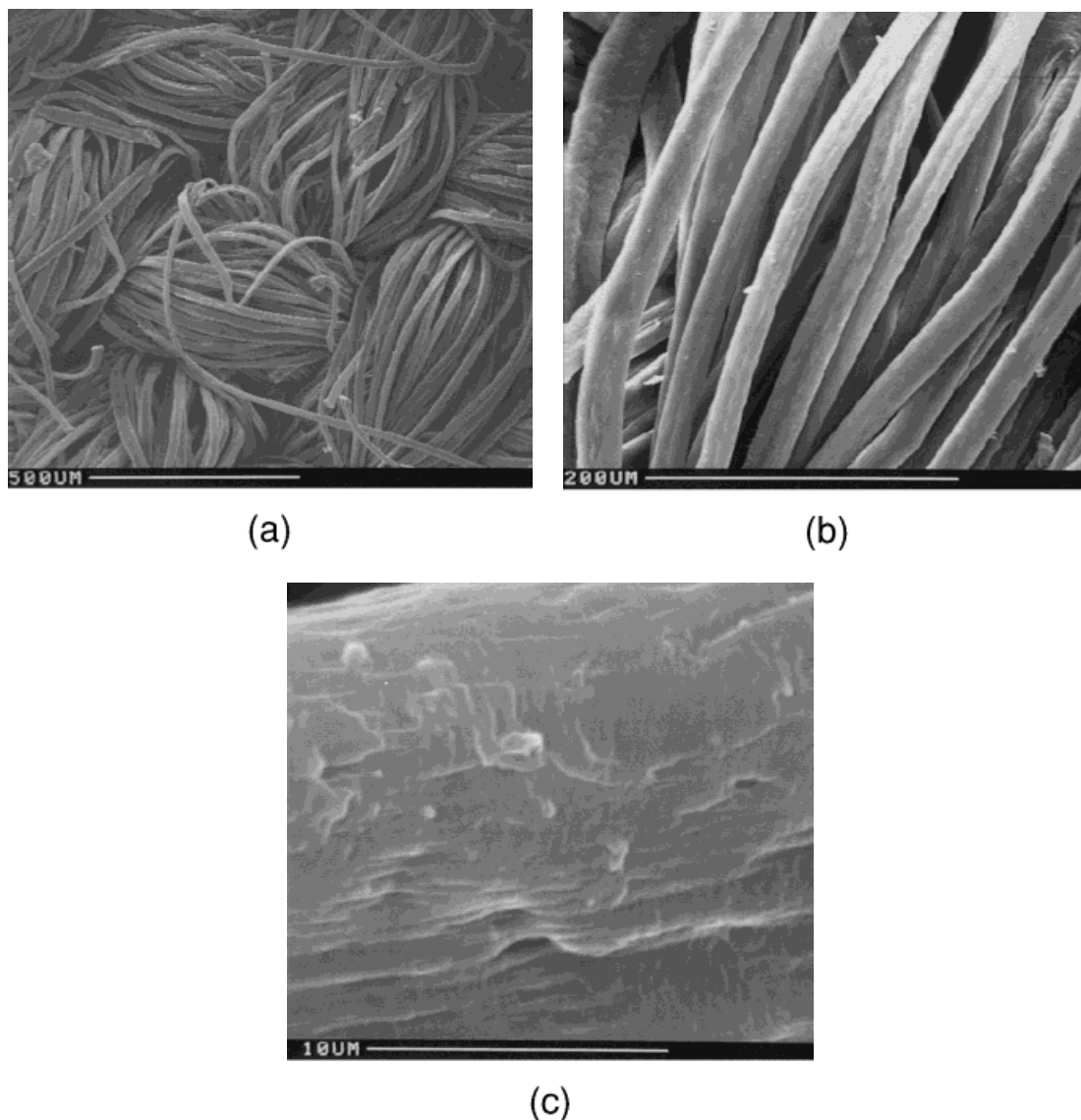
SEM photographs of cloth which had been treated with HCl and NaOH are shown in Figure 15. It is noted that in both cases the treatment was relatively extreme. The result of the treatment is apparent in what appears to be the melting (fusing) of the cloth during the treatment process, as evidenced by the fused fibers. In both cases the cloth was brittle and not suitable for use.

### Chemical Properties

In order to test the physical properties of the cloth with respect to the sorption of different metals from solution, a series of both batch and flow experiments were used. Amidoxime-containing cloth, with varying degrees of conversion as prepared in the preceding section, were used for all experiments. The two metals, Pb(II) and Cu(II), were chosen for two different reasons, Pb(II) because of its environmental significance and Cu(II) because it is the metal of choice for the study of the chelating properties of resins, etc. In addition, Pb(II) and Cu(II) bind with different degrees of stability to amidoxime resins, with Cu(II)  $\gg$  Pb(II) in stability, and thus should provide a representation of all the metals which chelate with the amidoxime group.<sup>30,31</sup>

### Capacity Measurements

The effect of a large excess concentration of metal in solution on the amount of metal sorbed by the cloth was investigated using Pb(II) and Cu(II).



**Figure 11** Photographs of a sample of cloth (47% conversion) at different magnifications. (A) 60 $\times$ ; (B) 225 $\times$ ; (C) 4350 $\times$ .

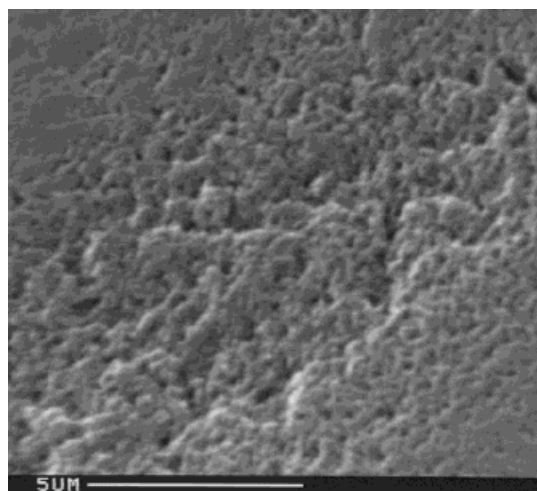
From this experiment an estimate of the capacity of the cloth for Cu(II) and Pb(II) was calculated.

A solution of 100 mL  $\sim 0.2$  mol L $^{-1}$  in Pb(II) was prepared and adjusted to pH = 5.0 in a 250-mL conical flask. Two pieces of cloth, one each from batch 23 and 28 (46 and 47% conversion, respectively), were placed in the solution on a shaker for 7 days. Analysis of the metals sorbed was done by acid extraction of the cloth, followed by AA.

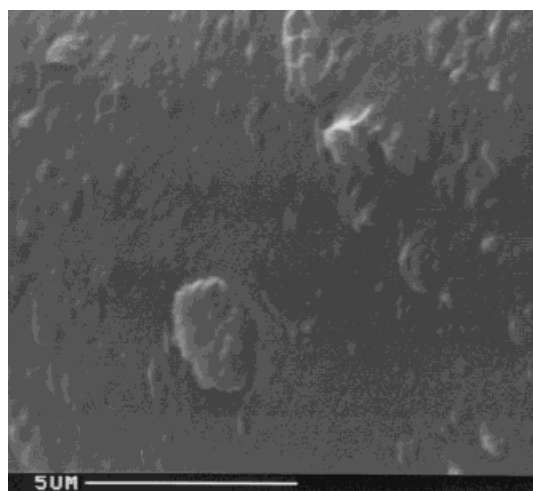
A slightly different procedure was used for Cu(II). A series of solutions of 100 mL each, 0.04 mol L $^{-1}$  Cu(II) were prepared and adjusted to pH = 5.0. Two cloth pieces, one each from batch 23 and 28 (46 and 47% conversion, respectively),

were placed in one of the solutions on a shaker for a period of  $\sim 48$  h. The cloth pieces were then removed and placed in a fresh solution of Cu(II) for 24 h. The process was repeated until a total time of exposure of 7 days had passed, after which the cloth samples were dried and analyzed as described above.

The results for the 7 days of exposure are presented in Table III. The total amount of Pb(II) and Cu(II) sorbed was relatively high at 450 and 71.2 mg g $^{-1}$ , respectively. The difference in the amount of Cu(II) and Pb(II) sorbed may be attributed to a difference in the number of chelating groups bound to the metal. In the case of Pb(II) a 1 : 1 chelate complex with amidoxime is preferred,



(a)



(b)

**Figure 12** Photographs of two commercial chelating resins. (A) Chelate-N, macroporous containing the amidoxime group. (B) Chelex 100, containing the aminodi-acetate group.

while in the case of Cu(II), two amidoxime groups are preferred.<sup>31</sup> This corresponds to the results given here, where the capacity of the cloth for Pb of 2.17 mmol g<sup>-1</sup> is almost double the capacity for Cu of 1.12 mmol g<sup>-1</sup>. The fact that Cu(II) and Pb(II) chelate in a different manner supports the previously stated results suggesting a different rate of uptake by the cloth.

### Kinetics of Metal Uptake

The effect of the length of time of deployment on the amount of metal taken up by the monitors

exposed to a constant flowing stream containing trace amounts of Pb(II) and Cu(II) was investigated. The flow chamber in Figure 16 was used, with the flow rate of solution fixed at ~ 4.75 L min<sup>-1</sup>, with a linear velocity of ~ 51.8 cm min<sup>-1</sup>. The initial concentrations of Pb and Cu in the barrel/flow chamber were determined with GFAA to be 3.5 and 4.8 μg L<sup>-1</sup> (0.017 and 0.075 μmol L<sup>-1</sup>) respectively, in ~ 190 L. Pieces of cloth (batch 6, 7% conversion) were exposed for times ranging from 7 to 44 days. After exposure, they were removed from the chamber and dried in air. Analysis of the amounts of metals sorbed during exposure was done with EDXRF using a spectral acquisition time of 3000 s.

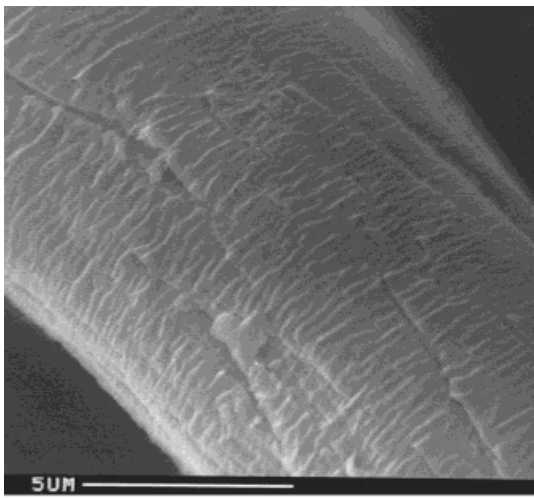
The results showing the dependence of the amount of Pb and Cu sorbed on the cloth with respect to the time of exposure are presented in Figure 17. The amount of Pb and Cu sorbed were represented in the form of the equilibrium distribution coefficient  $K_d$ .<sup>17,32</sup>

$$K_d = \frac{(\mu\text{mol metal/g cloth})}{(\mu\text{mol metal/mL solution})}$$

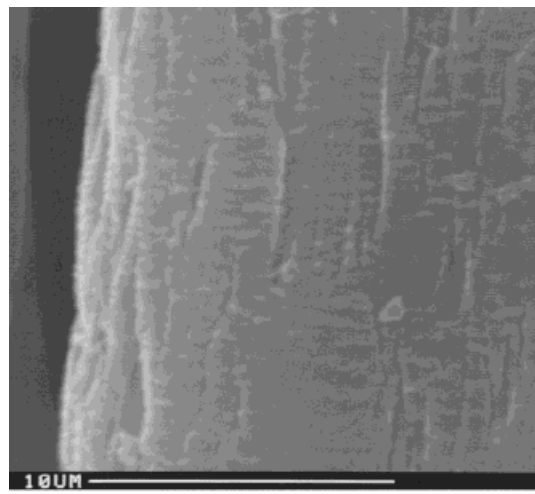
It is noted that this measure provided only an estimate of  $K_d$ , as equilibrium had not yet been reached, as indicated by the upward slope of the graph. These results also provide a measure of the degree of sample preconcentration from solution, and at the same time normalize the results with respect to the initial concentration of metals in solution.

The general shapes of the curves in Figure 17 indicate that the rate of uptake of Cu and Pb were initially quite rapid. After this the rate is observed to decrease somewhat but does not appear to approach a limiting value. The kinetic profile observed was similar to the general shape of results reported by others with respect to the rates of metal uptake by chelating polymers such as resins and fibers.<sup>4-7,10,11</sup>

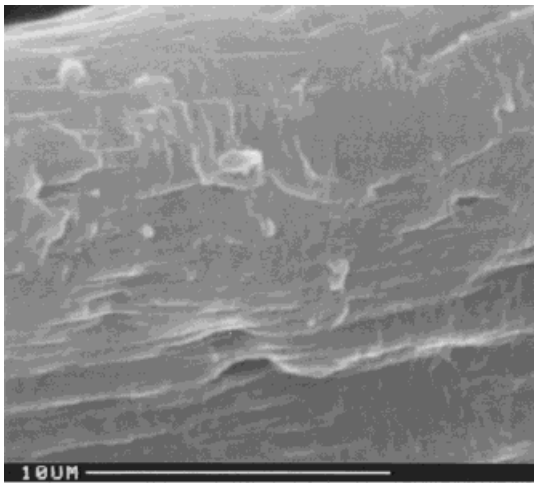
The rate of metal uptake was calculated from an averaged daily value for the duration of exposure. The values were 600 and 200 μg g<sup>-1</sup> day<sup>-1</sup> (9.4 and 0.96 μmol g<sup>-1</sup> day<sup>-1</sup>), respectively, from dilute solution ([Cu] = 5.9 μg L<sup>-1</sup>, [Pb] = 2.8 μg L<sup>-1</sup>), values in the same range as those observed for the sorption of UO<sub>2</sub>(VI) of 200 μg g<sup>-1</sup> day<sup>-1</sup> (0.84 μmol g<sup>-1</sup> day<sup>-1</sup>) from seawater.<sup>33</sup> The rates of uptake normalized to the average concentration of metal in solution were 100 (μmol g<sup>-1</sup> day<sup>-1</sup>)/μM for Cu and 71 (μmol g<sup>-1</sup> day<sup>-1</sup>)/μM for Pb. The total amount of Cu sorbed was observed to



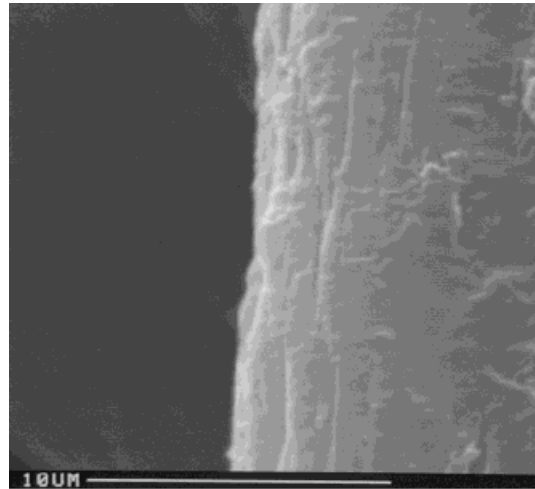
(a)



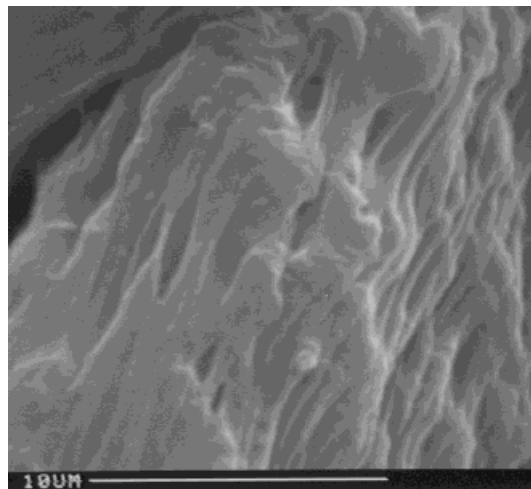
(b)



(c)

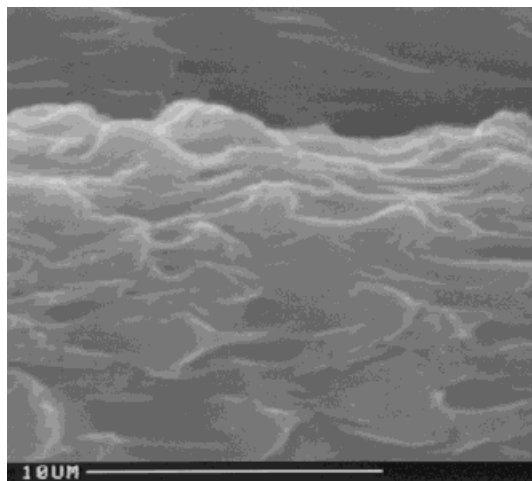


(d)



(e)

**Figure 13** Photographs of cloth at increasing degrees of conversion to amidoxime groups. (A) Polyacrylonitrile precursor; (B) 22% conversion; (C) 47% conversion; (D) 52% conversion; (E) 84% conversion.



**Figure 14** Photograph showing the effect of heat on a sample of cloth. Degree of conversion = 47%, heated at  $\sim 120^{\circ}\text{C}$  for 5 min.

be much greater than Pb, even after only a few days of exposure. The value at 30 days  $K_d = 3.5 \times 10^6$  for Cu was approximately double that of the value  $K_d = 1.5 \times 10^6$  for Pb, values which are in agreement with those observed for the sorption of  $\text{UO}_2(\text{VI})$ .<sup>17,31</sup> The value  $K_d$  Cu was greater than  $K_d$  Pb because Cu(II) is known to form a much stronger chelate complex with amidoxime than Pb(II).<sup>27,30,31</sup>

It was observed that there was a great deal of variability in the results. One source of variation was attributed to the cloth used for each sampler, specifically, differences in the tightness of the weave of the cloth which was introduced during the manufacturing process. This variation would have resulted in slightly different effective surface areas for chelation of the metals by the cloth. There was also a relatively large amount of noise present in the spectra which resulted in a relatively large error during spectral analysis.

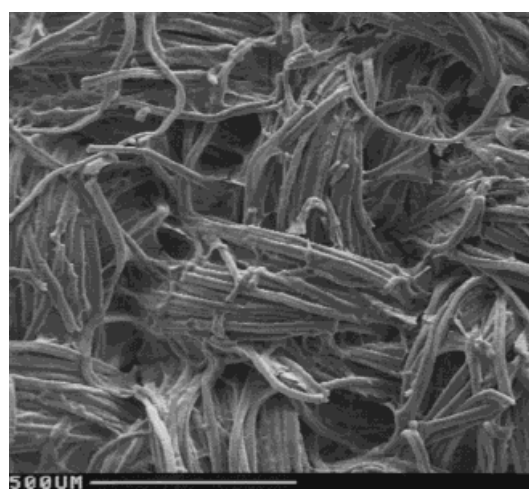
Another source of variation was due to a noticeable amount of turbulent flow present within the flow chamber. As the cloth pieces were exposed at different locations within the flow chamber they would experience different degrees of turbulence. This difference would affect the results substantially as the rate-limiting step of metal uptake was presumed to be diffusion.

#### Kinetics of Metal Uptake/Degree of Conversion to Amidoxime Groups

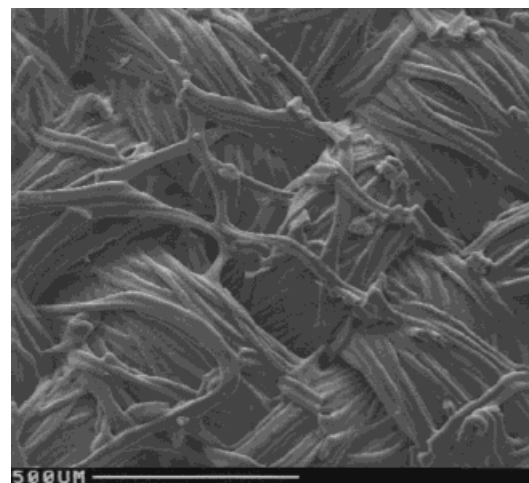
An experiment was performed in order to investigate the effect of the amount of amidoxime groups present on the surface of the cloth versus the

amount of Pb(II) and Cu(II) taken up by the cloth. Monitors were prepared with cloth of different degrees of conversion to amidoxime groups (batches 6, 7, 5, and 3; 7, 22, 28, and 50% conversion, respectively). They were then exposed for varying lengths of time, of 7, 17, and 24 days, to the flow chamber under the same conditions as before. Analysis of the amounts of metals sorbed during exposure was done with EDXRF spectroscopy.

The results showing the dependence of the amount of Pb(II) and Cu(II) sorbed with respect to the time of exposure using cloth of increasing degrees of conversion are shown in Figures 18 and 19. The general shapes of the curves are similar to those observed earlier in this work. The amount



(a)



(b)

**Figure 15** Photographs of cloth samples after being treated. (A) HCl treatment; (B) NaOH treatment.

**Table III Capacities of Cloth for Cu and Pb Exposed for 7 Days**

Cloth Used Batch, %	Amount Sorbed (mg/4 cm <sup>2</sup> piece)		Amount Sorbed (mmol/g)		% Theoretical Capacity <sup>a</sup>		% Theoretical Capacity <sup>b</sup>	
	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb
	23, 46	5.9	33	0.93	1.59	16	28	32
28, 47	7.1	45	1.12	2.17	20	38	40	76

Conditions were pH = 5.0 for both Cu and Pb solutions.

<sup>a</sup>Theoretical capacity of 5.66 mmol g<sup>-1</sup> cloth was calculated from the weight percent of amidoxime groups per gram of cloth, assuming a 1 : 1 complex.

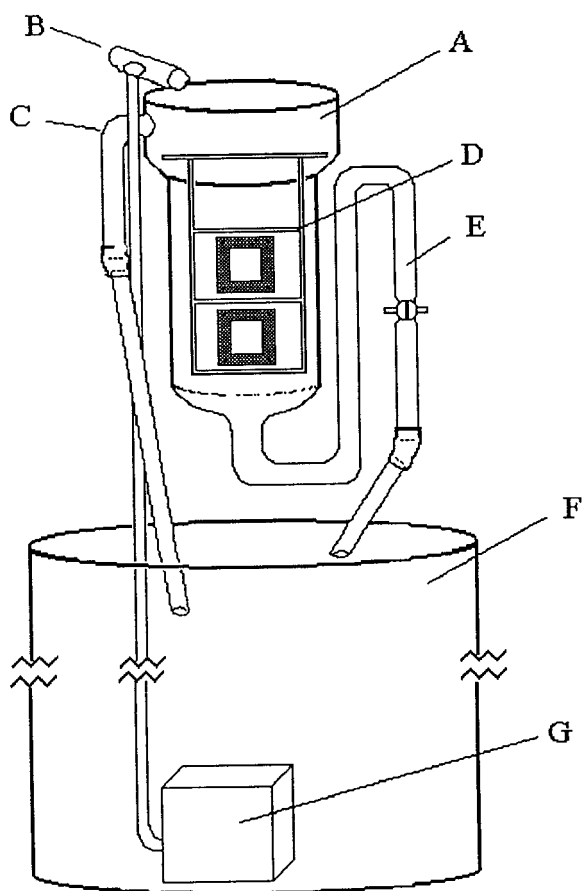
<sup>b</sup>Theoretical capacity of 5.66 mmol g<sup>-1</sup> cloth was calculated from the weight percent of amidoxime groups per gram of cloth, assuming a 1 : 2 complex.

of Pb sorbed was observed to increase with an increasing degree of conversion, whereas the amount of Cu sorbed appeared to be independent of the degree of conversion with the exception of the results at 24 days.

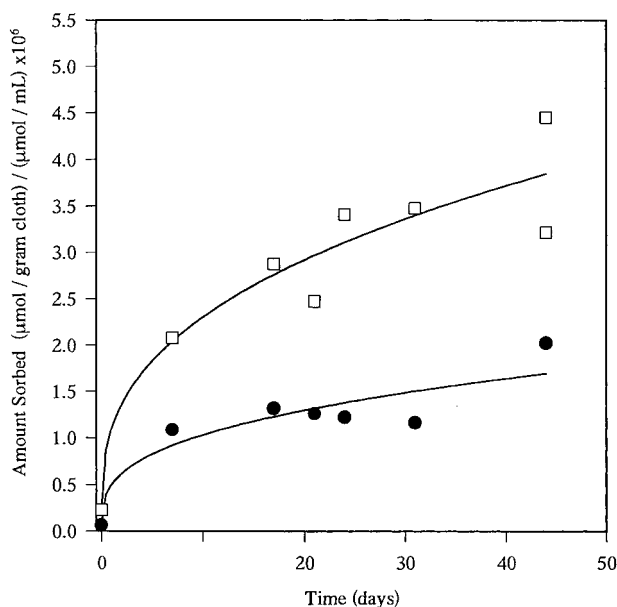
In the case of the Pb results, the shape of the

curve is representative of the process of sorption where a weak complex is formed and the rate of sorption is similar to the rate of desorption, whereas the Cu results are indicative of the formation of a strong complex where the rate of sorption is much larger than the rate of desorption.

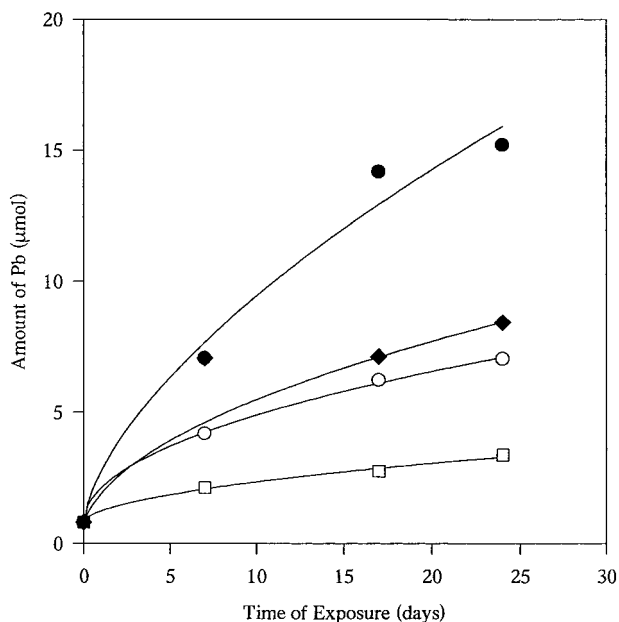
The results showing the dependence of the amount of Pb(II) sorbed with respect to the degree of conversion are given in Figure 20. It was observed that the relationship between the amount of Pb sorbed and the degree of conversion was linear, a phenomenon observed with heterogeneous kinetics where adsorption is the rate-limiting step. The results for the uptake of Cu with respect to the degree of conversion, as shown in Figure 21, were observed to be somewhat different. It appears that, for each increasing degree



**Figure 16** Diagram of the flow system. (A) Flow chamber; (B) Water inlet; (C) Overflow; (D) Glass rack with monitors; (E) Drain with stopcock; (F) Reservoir; (G) Submersible pump.



**Figure 17** Sorption profiles for (●) Pb(II) and (□) Cu(II) by the cloth.



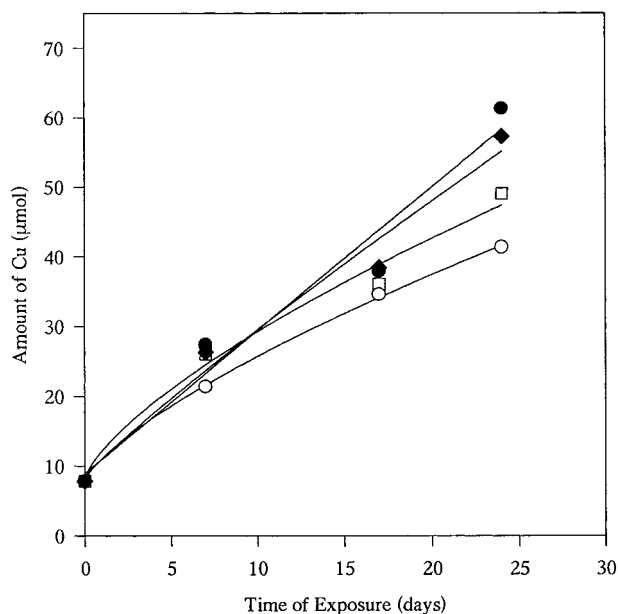
**Figure 18** Amount of Pb(II) sorbed by cloth of increasing degrees of conversion. Degree of conversion: (□) 7%; (○) 22%; (◆) 28%; (●) 50%.

of conversion, Cu reaches a limiting value with respect to the amount sorbed by the cloth, a phenomenon which is observed in heterogeneous kinetics in which a strong complex is formed and the formation of the complex is rate limiting.

The explanation for the differences in the observed Pb and Cu sorption curves is based on two facts. The first is that, during the conversion process, the outer portion of the cloth may be considered to be fully converted to amidoxime chelating groups. Thus, after a given degree of conversion, for example 10%, the surface of the cloth had been fully converted to amidoxime groups and any subsequent conversion took place with the nitrile groups toward the center of the cloth.

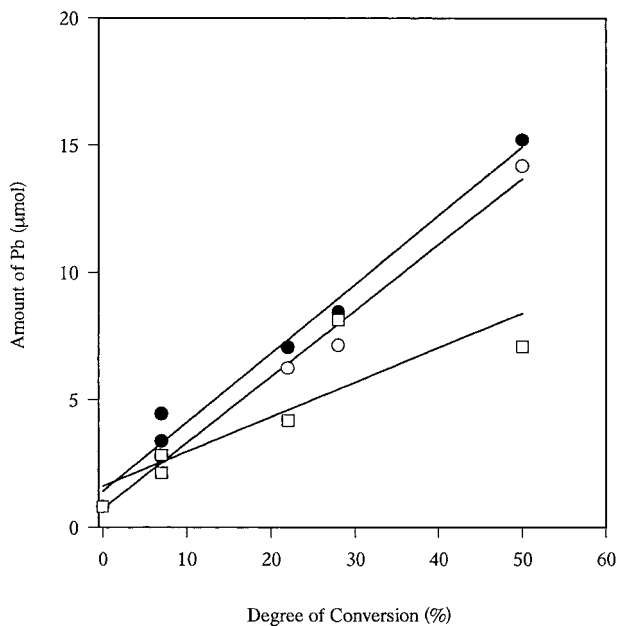
The second reason is due to the relative stabilities of the complexes formed by Pb(II) and Cu(II) with the amidoxime group and hence the resulting kinetics involved. It is known that Pb(II) prefers the formation of a complex with a single amidoxime group, ( $K_d \text{ Pb} > K_d \text{ Cu}$ ); whereas Cu(II) preferentially forms complexes with two or three amidoxime groups ( $K_d \text{ Cu} > K_d \text{ Pb}$ ).<sup>31</sup> The result is that the overall stability of the Pb-(amidoxime) complex is much less than that of the Cu-(amidoxime)<sub>2</sub> complex due to the increased stability of the latter from the chelation with the second amidoxime ligand.

The sorption of Cu and Pb from solution may be expected to involve first, the saturation of the more readily accessible sites on the outer surface



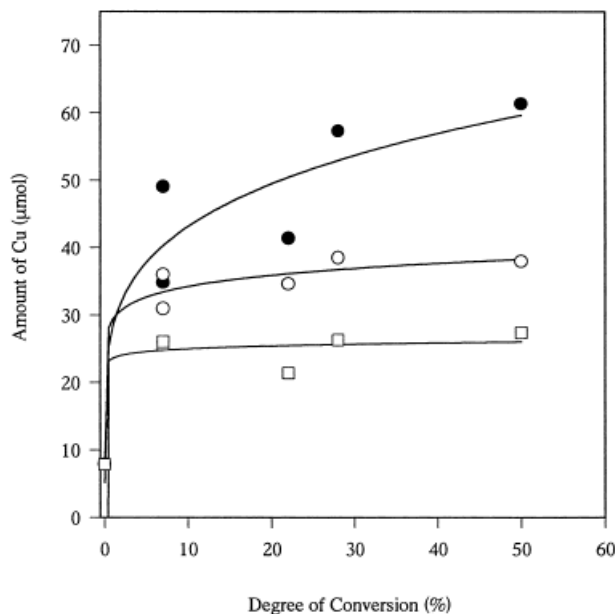
**Figure 19** Amount of Cu(II) sorbed by cloth of increasing degrees of conversion. Degree of conversion: (□) 7%; (○) 22%; (◆) 28%; (●) 50%.

of the cloth, followed by interaction with sites within the interior. The rate of migration of ions to the interior of the cloth will depend on the rates of adsorption and desorption from exterior surface sites as well as the rate of diffusion into the interior from the bulk solution.



**Figure 20** Effect of the degree of conversion on the sorption of Pb(II). Time of exposure: (□) 7; (○) 17; and (●) 24 days.





**Figure 21** Effect of the degree of conversion on the sorption of Cu(II). Time of exposure: (□) 7; (○) 17; and (●) 24 days.

In the case of Pb, where a weak complex is formed relative to the Cu–amidoxime complex, assuming a similar rate of sorption, the rate of desorption will be much larger. Thus, the surface-complexed Pb is able to desorb and migrate at a relatively fast rate toward the interior of the cloth compared to Cu. This is confirmed in Figure 20, where it is shown that the amount of Pb sorbed is linearly dependent on the increasing degree of conversion of the amidoxime groups.

In the case of Cu, assuming a similar rate of sorption, the rate of desorption will be much smaller due to the strength of the Cu–(amidoxime)<sub>2</sub> complex compared to that of the Pb–amidoxime complex. Because of this behavior, Cu will not desorb to the same extent and will migrate at a much slower rate toward the center of the cloth only after surface saturation. This corresponds to the limiting values of the curves observed in Figure 21, where the initial Cu sorbed may be expected to be found only on the surface of the cloth, which is essentially saturated with amidoxime groups. The curves obtained for 17 and 21 days suggest a slow rate of migration into the interior of the cloth after the initial surface saturation.

## CONCLUSIONS

The net result of the research into the parameters involved with the preparation of the chelating

cloth was the production of a material suitable for the extraction of Cu(II) and Pb(II) from water. The preparation of the cloth and the subsequent monitors proved to be relatively easy, controllable, and cost-effective. The following conditions were deemed optimal for the conversion process: concentration of  $\text{NH}_2\text{OH} \cdot \text{HCl} = 2.0\%$  (m/v) in 50% (v/v) methanol/water,  $\text{pH} = 7$ ,  $T = 55^\circ\text{C}$  for 12 h. The final process used had a reproducibility of  $\sim 2\%$  and can be adapted to a commercial scale. The cloth produced at  $\sim 45\%$  conversion has good physical properties with respect to strength and a relatively large capacity for metals of 1.12 and 2.17  $\text{mmol g}^{-1}$  for Cu(II) and Pb(II), respectively (71.2 and 450  $\text{mg g}^{-1}$ ).

Use of EDXRF and WDXRF as the methods of analysis for metals bound to the cloth proved to be relatively easy and sensitive. It was found that the EDXRF instrumentation was easier to use but was not as sensitive as the  $\lambda$ DXRF instrument which was used a tube as the X-ray source. It was also observed that due to the high intensity of the tube source used in the  $\lambda$ DXRF instrument the cloth samples changed in appearance. This was attributed to a radiation-induced reaction within the cloth such as fusing or crosslinking.<sup>9</sup> The result of this was the reduced possibility of reusing the monitors for more than one deployment and analysis.

Processing the cloth with HCl resulted in a slight improvement in the amount of metals taken up but at the same time caused the cloth to swell and then contract, which produced a cloth with poorer physical properties. Treatment with NaOH or  $\text{NH}_4\text{OH}$  was also found to degrade the physical properties of the cloth without providing any real benefit for the sorption of Pb(II) and Cu(II).

The choice of amidoxime as a ligand was acceptable and proved to be selective to metals of interest. The kinetics of metal sorption, capacities, and distribution coefficients for Cu and Pb were similar to those of resins and fibers which contained amidoxime groups, with  $K_d$  values in the  $10^6$  range for Cu and Pb.

Thus it was found that the physical properties of the cloth made it suitable for the construction of a device for the passive monitoring of trace metals in water, work that is explained in detail elsewhere.<sup>34,35</sup>

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