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THE USE OF CHITOSAN COLUMNS FOR THE REMOVAL OF MERCURY FROM WATERS

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SUMMARY

The experimental conditions for the removal of ionic mercury from waters have been studied. Columns containing 1–15 g of chitosan were used to lower the mercury concentration from 1 to 0.02 ppm, with volume reduction factors of 2000 to 10,000. Recycling of columns was carried out with 10 m*M* potassium iodide solution; other inorganic and organic eluting agents were also studied. The analytical instrumental techniques employed were flameless atomic-absorption spectrometry and radiochemistry.

INTRODUCTION

Chitosan is a natural chelating polymer that has been proposed for use in inorganic chromatography for the prevention and survey of pollution by toxic metals[1,2]. The present work deals with the extension of its applications to the removal of ionic mercury from waters.

New approaches to the isolation of mercury are not frequently encountered in the literature: the sedimentation of mercury compounds of poly(amino acids)[3] and the extraction of mercury with sulphide-treated polyurethane foams[4] are rare examples. Methods for the removal of mercury from electrolytic cell brines are mainly based on reductions carried out with iron or formaldehyde, on amalgam formation with sodium and on precipitation of mercury in the form of sulphide[5].

Hence little effort seems to have been made to find efficient ways of selectively removing mercury from waters, in comparison with the extensive studies on improvements to the analytical procedures used in detecting mercury at very low levels in waters and biological materials [6–19].

EXPERIMENTAL

Instrumentation

A Perkin-Elmer 305 atomic absorption spectrometer equipped with an HGA-70 hot graphite atomizer and a Hitachi Perkin-Elmer 56 recorder was used. Volumes

of 20 μl of samples were introduced into the graphite atomizer with an Eppendorf pipette, together with 20 μl of 0.1 *M* ammonia solution in order to form mercury(II) oxide and depress the volatility of mercury. The addition of ammonia was omitted for samples that contained iodide. The HGA-70 programme was No. 1 with a 60-sec drying time at 60° and 12-sec atomization at 4.5 V and 500 A. Scale expansion for 1.0 ppm mercury solutions was about one third of the maximum. The reproducibility of the signals was good, their linearity was verified up to 2.5 ppm of mercury, and the background interference was about 2%, as shown in Fig. 1. A second signal was present in all readings obtained on potable water, but it was independent of the mercury concentration. Ultrapure nitrogen was as good as argon for purging the atomizer.

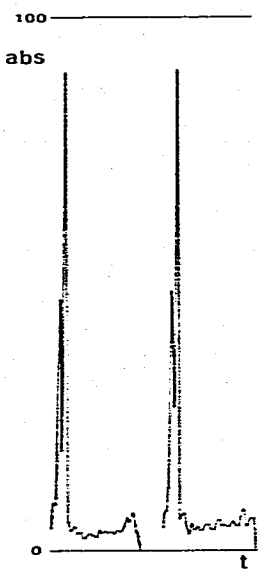

Fig. 1. Hot graphite atomic-absorption spectrometry readings of 0.1 ppm mercury in 10 m*M* potassium iodide solution. Atomic absorption (%) *versus* time (sec).

The eluates containing sulphuric acid were analyzed with an alternative apparatus consisting of a quartz cell connected to an air pump and a reduction flask. Several versions of this apparatus have been described[20–22]; in the present work the one officially recognized in Italy was adopted[23,24].

The eluates containing cyanide were analyzed by γ-ray spectrometry on ^{203}Hg-labelled solutions, as previously described[2].

Solutions

Tap water (39°F hardness), previously passed through a chitosan cartridge so as to eliminate mainly copper, zinc and iron, was used to prepare solutions of mercury(II) chloride, mercury(II) acetate or ethylmercury chloride solutions with mercury concentrations of 4.0, 1.0 or 0.1 ppm. The pH was 7.0 and in a few instances it was adjusted to 4.0 or 8.0 with hydrochloric acid or sodium hydroxide solution.

The solutions were passed through the chitosan columns and collected into erlenmeyer flasks; a representative aliquot of each 1-l fraction was taken for analysis.

Columns

Chitosan was supplied by the Food, Chemical & Research Laboratories, Seattle, Wash., U.S.A. Glass columns of 6 × 1, 12 × 1, 12 × 0.4 and 20 × 2 cm were filled with 100–200 mesh powder and operated under reduced pressure.

RESULTS AND DISCUSSION

Collection of mercury on chitosan columns

The breakthrough curves for mercury in tap water at a concentration of 4.0 ppm for 6 × 1 cm columns of 1 g of chitosan at a flow-rate of 100 ml·min^{-1} are shown in Fig. 2. Curves a and b refer to solutions of pH 4.0 and 8.0, respectively. Curve c refers to solutions of pH 7.0 for which the mercury concentration in the first 7 l of the effluent is less than 0.02 ppm.

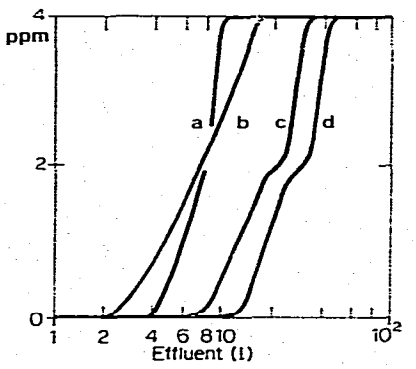

Fig. 2. Breakthrough curves for mercury at a concentration of 4.0 ppm for 6 × 1 cm columns containing 1 g of chitosan. (a) pH 4.0, 100 ml·min^{-1}; (b) pH 8.0, 100 ml·min^{-1}; (c) pH 7.0, 100 ml·min^{-1}; (d) pH 7.0, 50 ml·min^{-1}. Mercury concentration *versus* litres of effluent.

When the flow-rate is 50 ml·min^{-1} (curve d), the breakthrough point is at 13 l. The capacity, C, for water containing 4.0 ppm of mercury passed at a flow-rate of 50 ml·min^{-1} through a 6 × 1 cm chitosan column is therefore given by

$$C = \frac{\frac{1}{2}(V_1 + V_2)\cdot c_{Hg}}{ml_{chitosan}}$$

$$= \frac{\frac{1}{2}(43 + 13)\cdot 4\cdot 10^{-2}}{4.4}$$

$$= 0.26 \text{ mequiv.}\cdot ml^{-1} \text{ of mercury}$$

corresponding to 114 mg of mercury per gram of chitosan. V_1 and V_2 are the initial and final volumes of the breakthrough curve in litres and c_{Hg} is the mercury concentra-

tion in mequiv.·l^{-1}. This means that the chitosan powder collects mercury and has a capacity as high as 11% of its weight under these conditions.

pH values higher or lower than 7 anticipate the breakthrough point, as shown in Fig. 2, curves a and b. No effect due to chloride or acetate anions was observed. Zinc and copper ions that are fixed on the column under the same conditions do not disturb the fixation of mercury: this was verified at concentrations of 4.4 and 0.1 ppm, respectively.

When tap water that contained 1.0 ppm of mercury was used, the curves in Fig. 3 were obtained: curve a represents a 6 × 1 cm column containing 1 g, curve b a 12 × 0.4 cm column containing 1 g, curve c a 12 × 1 cm column containing 2 g and curve d a 20 × 2 cm column containing 15 g of chitosan. These curves, which exhibit a typical shoulder, are not affected by the flow-rate. For the longer, narrower columns, the breakthrough point is higher and, in fact, the reduction in diameter leads to an increased capacity, *C*.

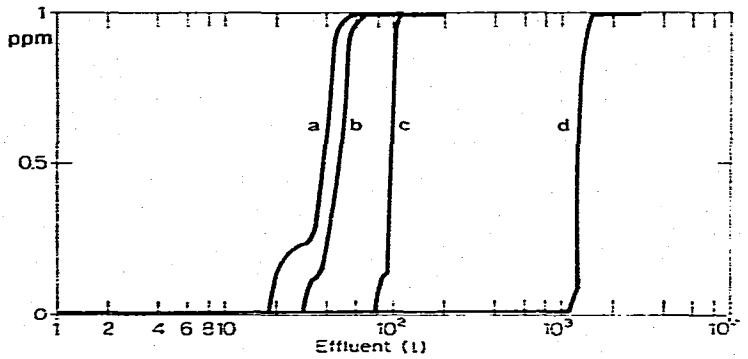

Fig. 3. Breakthrough curves for mercury at a concentration of 1.0 ppm. Chitosan columns: (a) 1 g, 6 × 1 cm; (b) 1 g, 12 × 0.4 cm; (c) 2 g, 12 × 1 cm; (d) 15 g, 20 × 2 cm. Mercury concentration *versus* litres of effluent.

For 12 × 1 cm columns containing 2 g of chitosan, the slope of the curve is steeper, as can be seen in Fig. 3, curve c, because of the more favourable length to diameter ratio, and mercury can be detected in the effluent after 80 l have passed. The reduction in mercury concentration is from 1.0 to 0.02 ppm.

For 20 × 2 cm columns containing 15 g of chitosan, the breakthrough point is reached after 1100 l have passed. This column contains 7.5 times more chitosan than the 12 × 1 cm column containing 2 g, but it purifies thirteen times more water. These results demonstrate that not only the amount of chitosan but also the dimensions of the columns must be taken into account for optimum results.

When treating water containing 0.1 ppm of mercury, the effluent contains a constant concentration of 0.02 ppm of mercury: for 6 × 1 cm columns containing 1 g of chitosan, the breakthrough point is at 120 l and saturation is reached after 140 l have passed.

Waters containing 1.0 ppm of mercury in the form of ethylmercury chloride are not appreciably purified, as mercury is present in the fourth litre of effluent.

TABLE I

ELUTION OF MERCURY FROM 6 × 1 cm COLUMNS CONTAINING 1 g OF CHITOSAN
Absolute amount of mercury 3 μg. Reference solution containing 0.03 ppm of mercury. Elution performed with 50 ml of 2 *N* sulphuric acid or 15 ml of 10 m*M* potassium iodide solution.

Cycle No.	*Hg eluted (%)*		*Hg in washings (%)*		*Hg in column (%)*	
	KI	H_2SO_4	*KI*	H_2SO_4	*KI*	H_2SO_4
1	100	100	0	0	0	0
2	98	40	0	15	0	45
3	100	50	0	11	0	39
4	98	50	0	11	0	39
5	100	46	0	11	0	43
6	101	39	0	11	0	50
7	100	43	0	11	0	46
8	99	39	0	11	0	50
9	102	43	0	11	0	46
10	97	40	0	11	0	49
11	100	49	0	11	0	40
12	100	43	0	11	0	46
13	97	49	0	10	0	40
14	100	39	0	11	0	50
15	100	43	0	11	0	46

Elution of mercury and column recycling

The complete elution of mercury can be performed with 10 m*M* potassium iodide solution; 15 ml of this solution are enough for the complete washing of a 6 × 1 cm column containing 1 g of chitosan. The recoveries for the first fifteen cycles are reported in Table I. Potassium cyanide solution is also suitable for the elution of mercury from chitosan and elution curves for 0.01 and 0.10 *M* solutions are shown in

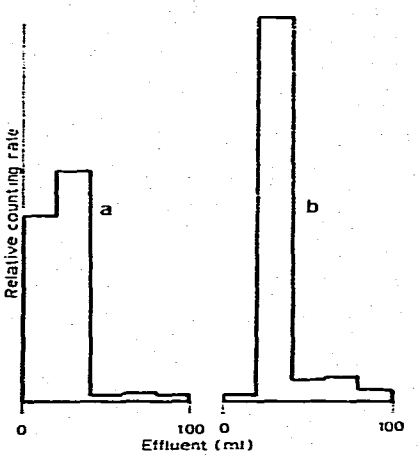

Fig. 4. Mercury elution curves for 1 g, 6 × 1 cm columns containing 1 g of chitosan. ^{203}Hg-labelled solutions. (a) Elution performed with 0.01 *M* potassium cyanide solution, recovery 98%; (b) elution performed with 0.10 *M* potassium cyanide solution, recovery 94%. Relative counting rate *versus* millilitres of effluent.

Fig. 4: 100 ml of the 0.01 *M* solution permit the recovery of 98% of the mercury, the major part of which is in the first 40 ml of effluent.

Sulphuric acid is a good eluent for removing several metals from chitosan; however, mercury can be partially removed from chitosan, as shown in Table I, after the first cycle. The first regeneration of chitosan is complete, but the mean recovery for the subsequent cycles is 43%. This was verified for sulphuric acid concentrations in the range 1–8 *N*, as shown in Table II.

Organic complexing agents were found of no use for the elution of mercury, 1% solutions of succinimide, 2-aminopyridine and diphenylcarbazide giving recoveries as low as 21, 15 and 5%, respectively.

CONCLUSIONS

Ionic mercury can be efficiently removed from hard waters at neutral pH. A 1-g amount of chitosan in a 12 × 0.4 cm column yields 30 l of water the mercury

TABLE II

ELUTION OF MERCURY FROM 6 × 1 cm COLUMNS CONTAINING 1 g OF CHITOSAN

Absolute amount of mercury 3 μg. Reference solution containing 0.03 ppm mercury. Elution performed with 50 ml of sulphuric acid.

Normality of H_2SO_4	*Cycle No.*	*Hg eluted (%)*	*Hg in washings (%)*
1	1	100	0
	2	32	10
	3	43	11
2	1	100	0
	2	40	9
	3	90	10
3	1	100	0
	2	43	12
	3	61	7
4	1	100	0
	2	43	11
	3	61	7
5	1	100	0
	2	42	9
	3	42	15
6	1	100	0
	2	43	11
	3	43	10
7	1	100	1
	2	40	9
	3	45	11
8	1	100	0
	2	43	12
	3	43	11

content of which is reduced from 1.0 to 0.02 ppm; the corresponding amount of mercury can be eluted with 15 ml of 10 m*M* potassium iodide solution, and the column recycled. The volume reduction factor in this instance is 2000, while for 15 g of chitosan eluted with 100 ml of solution it is over 10,000. Elution can be also performed with potassium cyanide solution, but of course it would be less widely applicable.

While recycling with potassium iodide solution is a very simple and trouble-free procedure, elution with sulphuric acid is satisfactory only for the first cycle of unused chitosan columns. The chromatographic behaviour of chitosan in sulphuric acid deserves further study[25].

The high affinity of the chelating polymer toward mercury is shown by the low ability of well known complexing agents to elute mercury from chitosan. Chitosan, therefore, qualifies as a most useful and effective polymer for the removal of ionic mercury from waters.

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