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EVALUATION OF POLYMERIC SUPPORTS FOR IMMOBILIZING BIOMASS TO PREPARE SORBENT MATERIALS FOR METALS

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Five polymeric materials, namely, styrene divinylbenzene, ethyl acrylate-ethylene glycol dimethacrylate, ethyl acrylate-methyl methacrylate-ethylene glycol dimethacrylate, polysulfone, and silica gel, were evaluated as supports for immobilizing biomass of the common brown seaweed alga, *Sargassum fluitans*, for use as metal sorbents. Small ion exchange columns were prepared containing one gram of sorbent. Solutions of metal ions at pH of 5.5, with the exception of gold for which a pH of 2 was used, were passed through the columns to trap the metals. Bound metals were subsequently stripped from the columns with 1 M nitric acid. Styrene divinylbenzene, polysulfone, and silica gel were found to be the most ideal matrices for immobilizing biomass. Breakthrough curves for the polymeric sorbents were similar to an iminodiacetic acid chelating resin, but the total metal adsorbing capacity of each biosorbent was considerably less than chelating resin. However, the resin swelling commonly associated with chelating resins when using strong acid stripping agents was not observed.

KEYWORDS: Polymer support, biomass, biosorbent, metals.

INTRODUCTION

The powerful metal-binding characteristics of certain types of biomass are well known. The uptake of metals from solution by algae have been studied¹⁻³. Seaweed algae have been found to be effective binders of metal ions⁴. Kuyucak and Volesky surveyed a large number of marine algae for cobalt and gold binding ability^{5,6}. In their studies the brown alga *Ascophyllum nodosum* had a very high capacity for cobalt and another brown alga *Sargassum natans* was able to accumulate gold from solution to the highest degree of all organisms studied. For ions with a positive charge, a strong pH effect on metal binding by seaweed algae was observed⁴ with maximum binding occurring at pH5-6. Metal ions such as gold, which exist in solution as negatively charged ions, show an inverse or no pH effect and can be stripped from biomass with complexing agents^{7,8}. The dependence of binding on pH has

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led to the preparation of biosorbents based on the immobilization of nonliving biomass of algae, and fungi in porous, stable and inert matrices such as silica gel^{7,9,10}. Such sorbent materials can efficiently concentrate metals from solution by binding the metals at a pH between 5 and 6. The metals can subsequently be stripped at a pH less than 2 or with a complexing agent to facilitate analysis⁹. Recent work has demonstrated the usefulness of a porous polysulfone polymer for immobilizing biomass for use as a "biosorbent"¹¹.

In the study described herein the characteristics of five polymeric materials, namely, styrene divinylbenzene, ethyl acrylate-ethylene glycol dimethacrylate, ethyl acrylate-methyl methacrylate-ethylene glycol dimethacrylate, polysulfone, and silica gel were evaluated for immobilizing biomass of the common marine alga, *S. fluitans*. The degree of retention of a large number of metal ions by each biosorbent was studied. Comparisons of metal-binding properties and capacities of biosorbents containing differing weight percentages of biomass were made.

MATERIALS AND METHODS

Preparation of S. fluitans biomass

A large quantity of *S. fluitans* was collected along the Louisiana gulf coast. The seaweed was washed thoroughly in the laboratory, first with tap water and then doubly-deionized water. The seaweed was allowed to air dry and then was ground to a fine powder with a laboratory grinder. The powder was screened through a set of standard testing sieves into the following mesh sizes: 9–32, 32–35, 35–60, 60–115, 115–150, 150–170, 170–250, and smaller than 250 mesh. For the preparation of biosorbents the finest-sized powder was used.

Purification of monomers and preparation of materials

Styrene Styrene monomer as obtained contained 10–15 ppm p-tert-butyl catechol as an inhibitor. The inhibitor was removed by washing the monomer with 10% aqueous NaOH. A drying agent such as Na₂SO₄ was added (100 g/L). The drying was complete in 0.5 hour. After adding about 1 g/L CuCl stabilizer the monomer was distilled under dry nitrogen at 26.3°C in a vacuum (20 torr).

Divinyl benzene The monomer was inhibited with less than 1500 µg/g p-tert-butyl catechol. It was removed as described above.

Ethyl acrylate The monomer contained 15–20 µg/g hydroquinone monoethylether (4-ethoxyphenol) as an inhibitor. The inhibitor was removed by washing with dilute NaOH and drying under anhydrous Na₂SO₄. It was distilled at 85°C without using a vacuum pump.

Ethylene glycol dimethacrylate The monomer contained 100 µg/g hydroquinone monoethylether inhibitor. It was distilled at 50–60°C under vacuum at 20 torr.

Methylmethacrylate The monomer contained 10 $\mu\text{g/g}$ hydroquinone monoethylether inhibitor. It was washed with 10% NaOH, dried with anhydrous Na_2SO_4 , and distilled between 60 and 80°C with a vacuum pump.

Potassium persulfate It was purified by crystallization as a saturated solution in water at 0°C.

Preparation of biomass-immobilized polymers

Styrene divinylbenzene copolymers The procedure of Collins *et al.*¹² was used as a guideline for the preparation of biomass immobilized in a styrene divinylbenzene copolymer. Approximately 5 g of deionized water, 2.925 g of sodium lauryl sulfate, 25 g of styrene (previously distilled under vacuum to remove inhibitor), and 0.125 g of divinylbenzene were mixed in a blender until a stable emulsion was formed. The emulsion was then placed in an addition funnel connected to a three-neck flask. The flask was purged with nitrogen, followed by the addition of 18.75 mL of deionized water, 0.0025 g Na-EDTA, and enough biomass (smaller than 250 mesh) to give weight percentages of 1, 5 and 10%. Initially, 10% of the emulsion (3.315 g) was added to the flask and the contents heated to 60°C under nitrogen purge. A mixture of potassium persulfate, 0.125 g, and sodium metabisulfite, 0.05 g dissolved in 6.25 mL distilled water, was quickly added to the mixture in the flask. When the temperature had stabilized, as evidenced by a bluish color, the remainder of the emulsion was added at a rate of 5 mL/min. The temperature was then increased to 80°C for 20–30 min. After cooling to room temperature, the reaction mixture was poured slowly with agitation into a hot (95°C) aluminum sulfate solution (0.625 g aluminium sulfate dissolved in 187.5 mL distilled water). The precipitated polymer was filtered through a Buchner funnel and washed several times with hot water to remove the emulsifier. The polymer support with the biomass sorbent was dried in a vacuum oven, pulverized to a fine powder, and sieved into the following mesh sizes: larger than 32, 32–60, 60–115, and smaller than 115.

Ethyl acrylate-ethylene glycol dimethacrylate copolymers After purging the reaction flask with nitrogen, 58.75 mL of distilled water, 4.25 g sodium lauryl sulfate, 0.25 g of purified potassium persulfate, 0.1 g sodium metabisulfite, and 0.5 g *S. fluitans* were added. The mixture was heated to 65°C. A monomer mixture was prepared by adding the following to an addition funnel: 25 g ethyl acrylate and 0.75 g ethylene glycol dimethacrylate. The monomer mixture was then added to the reaction flask slowly and steadily at about 2 mL/min. The rate of addition was decreased if the temperature rose appreciably above 65°C. The entire mixture was added to the flask over a 15–20-min period of time. Then the reaction mixture was cooled to room temperature.

After all materials had been added, the temperature was increased to 80°C for 20–30 min. Then the reaction mixture was cooled to room temperature. Following this, 1.25 g aluminum sulfate was dissolved in 375 mL distilled water and heated to 95°C. The reaction mixture was poured into the aluminum sulfate solution with agitation. The solution was filtered through a Buchner funnel and washed several times with hot water until no more emulsifier detergent was removed. The polymer obtained was dried in a vacuum oven for 24 hrs at 80°C. If the procedure is followed as described and the monomers are purified free of inhibitor before use,

the molecular weight of the polymer obtained will be very high ("rubber-like"). To avoid this, 0.5% retarder (nitrobenzene) was added to the monomer mixture. The polymers obtained by this procedure were not separated into mesh sizes for the reasons to be explained below. Polymers containing 2 and 10% biomass by weight were prepared.

Ethyl acrylate-methyl methacrylate-ethylene glycol dimethacrylate copolymer The preparation procedure was essentially the same as in (b) above except that the monomer mixture contained 17.5 g ethyl acrylate, 7.5 g methyl methacrylate, 0.75 g ethylene glycoldimethacrylate, and 0.5% nitrobenzene (0.128 g) as retarder. The polymer obtained was sieved into two mesh sizes—32–60 and 60–115. The biomass-immobilized polymeric product contained 2% biomass by weight.

Polysulfone resin The easiest biosorbent to prepare was based on polysulfone resin. Polysulfone resin (Scientific Polymer Products, Inc.) was dissolved in warm (60°C) chloroform. Dried biomass, in amounts calculated to yield 10, 25 and 50% biomass by weight in the final polymer, was added to the solution. The solution was slowly precipitated in methanol. The precipitated polymer containing the immobilized biomass was filtered and dried at 70°C for 24 hours in a vacuum oven. A very light, porous polymer was obtained. No mesh size differentiation was attempted because of the physical nature of the material.

Silica gel Biosorbents based on silica gel were prepared by the procedure of Walton¹³. Varying amounts of dried and powdered *S. fluitans* (0.5 to 5 g) to yield final biomass percentages of 10, 30, and 52% were mixed with 25 mL of 6N H₂SO₄. While stirring the suspension rapidly, 25 mL of 1:1 sodium silicate solution was added. The resulting mixture was continually stirred until gelled (usually about one hour). The gel was allowed to age overnight, then it was cut into small pieces and thoroughly washed with water until all the sulfuric acid was removed, as evidenced by a change in color of thymol blue indicator from orange to yellow. The washed pieces were then dried in an oven at 80°C for 48 hours. After drying the pieces were ground gently to a fine powder and sieved into the following mesh sizes: larger than 32, 32–60, 60–115, and smaller than 115.

Preparation of chelating resin

The chelating resin, obtained in the sodium form (Sigma Chemical, no. C-7901), was prepared for use by soaking overnight in water, followed by several rinses with 1 M nitric acid, and then 2 M ammonium acetate. Before use the columns were rinsed with 0.05 M ammonium acetate at pH 5.5.

Column studies

All columns were prepared by placing one gram of sorbent in a small amount of water to form a slurry. The slurry was poured into a small plastic tube (6×120 mm) fitted with a stopcock. The sorbents were preconditioned overnight in water and cleaned of any sorbed

metals by several rinses with 1 M nitric acid (pH = 1.4). Before use the columns were adjusted to pH 5.5 with 0.05 M ammonium acetate solution. For gold the columns were adjusted to pH 2 with acetate solution. Five mL of metal solutions, 5, 10, or 20 ppm, was added to the top of the column. The first 5-mL fraction collected was called the eluate. Next, 5 mL of pH 5.5 acetate solution (pH 2 acetate for gold) was allowed to flow through the column. This was collected and referred to as the rinse. Finally, successive 5-mL portions of stripping agent were added. The fractions were collected and referred to as strip 1, strip 2, etc. The percentage of metal in each fraction was determined by flame atomic absorption (Pb, Cu, Zn, Cd, K, Au, and Ag) or inductively coupled plasma emission spectrometry (Hg, Na, Ca, Mg, Ba, Sr, Cr, Co, Mn, Al, and Li).

Breakthroughs of biosorbent columns.

The capacities of silica gel and polysulfone columns for Pb, Cu, Zn, and Cd were evaluated by immobilizing *S. fluitans* biomass in each matrix and packing the biosorbents in small plastic columns fitted with stopcocks. Standard solutions of each metal, 5–20 ppm, were added to the top of the columns in 5-mL aliquots and the effluent of each increment collected. The flow rate depended somewhat on the nature of the packing material, but it was usually in the range of 1.2–1.4 mL/min. Each fraction was analyzed for residual metal content by atomic absorption or ICP emission spectrometry.

RESULTS

Five different polymeric materials were evaluated in this study as supports for immobilizing biomass to prepare biosorbents for metal removal from aqueous solutions. Silica gel was the first support material evaluated following the pioneering studies of Darnall *et al.*⁷ Silica gel is very easy to prepare. It can be separated into the mesh sizes previously described and functions extremely well as an adsorbent in the column mode. It does not swell when using nitric acid eluants as do iminodiacetic acid chelating resins. Silica gel-based biosorbent can be stored dry for several months and then reused. The precision of ten repetitive uses as an adsorbent was excellent⁹.

The two biosorbents prepared with ethyl acrylate-ethylene glycol dimethacrylate copolymer were found to be unsatisfactory. The first one prepared had too little crosslinking and would not allow liquid to pass when wetted in a column. The particles appeared to stick together when wetted. The second polymer of this type contained too much crosslinking because it had a "rubber-like" character. It could not be ground into the necessary mesh-size ranges. A "triple copolymer" sorbent was prepared with ethyl acrylate-methyl methacrylate-ethylene glycol dimethacrylate using nitrobenzene as inhibitor to reduce crosslinking. Its performance will be described below.

Styrene divinylbenzene was found to be a useful support material for preparing biosorbents. It could be prepared rather easily and biomass could be incorporated into the polymer during polymerization.

Table 1 Summary of preliminary results of polymer columns containing 1 to 10% *S. fluitans* by weight.

Polymer	Weight percentage of loaded metal eluted in each fraction ^a				
	Pb	Cu	Zn	Cd	
Styrene divinylbenzene (1%, 32–60 mesh)	Eluate	34	30	26	28
	Rinse	26	28	34	24
	Strip 1	42	35	26	18
	Strip 2	8	12	12	8
Styrene divinylbenzene (5%, 32–60)		2	2	2	0
		6	2	2	2
		20	32	34	28
		34	39	44	36
Styrene divinylbenzene (5%, 60–115)		0	0	0	2
		0	0	0	2
		8	76	93	82
		46	38	8	26
Styrene divinylbenzene ^b (10%, 60–115)		2	2	0	2
		0	0	0	0
		6	20	30	40
		40	56	34	42
		20	12	2	2
Ethyl; acrylate-methyl methacrylate- ethylene glycol dimethacrylate (2%, 32–60 mesh)		5	8	20	18
		15	26	35	34
		42	61	34	26
		9	8	8	5

^a Five-ppm mixed metal standard was used.

^b Three stripping steps were used for this polymer.

A preliminary evaluation of the performance of five polymer columns, four styrene-divinylbenzene and one ethyl acrylate-methyl methacrylate-ethylene glycol dimethacrylate polymer, containing various weight percentages of immobilized *S. fluitans* biomass for Pb, Cu, Zn, and Cd is summarized in Table 1. It is apparent from these results that the greater the amount of biomass, the more efficient the column. At least a 5% amount of biomass was necessary to trap efficiently the four metals studied. Also, the positive effect of smaller mesh size is seen in the case of the styrene divinylbenzene columns. A 60–115 mesh range was more efficient than 32–60 mesh size. The performance of the ethyl acrylate-methyl methacrylate-ethylene glycol dimethacrylate “triple” polymer was not as good as the styrene divinylbenzene columns and was thus not used for any further experiments.

A comparison of several different immobilizing materials containing 10% by weight *S. fluitans* is made in Table 2 for Pb, Cu, Zn, and Cd. The results with the iminodiacetic acid chelating resin are also included for comparison purposes. The silica gel, styrene divinylbenzene, and polysulfone columns all worked well at the level of metal concentrations used (5 ppm) and compared quite favorably with the chelating resin. The performance of the ethyl acrylate-ethylene glycol dimethacrylate column was distinctly inferior to the others.

Table 2 Performance of silica, ethyl acrylate-ethylene glycol dimethacrylate, styrene divinylbenzene, and polysulfone columns containing 10% *S. fluitans* for Pb, Cu, Zn, and Cd, and comparison with chelating resin column.

Element	Weight percentage of loaded metal eluted in each fraction ^a					
	Silica	Eegdm ^b	Sdvb ^c	Polysulfone	Chelating	
Pb	Eluate	0	20	26	6	6
	Rinse	0	8	1	1	0
	Strip 1	72	64	96	74	88
	Strip 2	26	6	6	30	12
	Strip 3	2	2	0	4	0
	Strip 4	0	0	0	1	0
	Strip 5	0	0	0	1	0
Cu	0	14	0	0	0	
	0	6	0	0	0	
	60	78	100	68	92	
	27	6	2	24	6	
	2	2	0	4	0	
	0	0	2	0	0	
	0	0	0	0	0	
Zn	0	26	0	0	0	
	0	16	0	0	0	
	70	40	99	66	80	
	12	6	1	20	4	
	0	2	0	4	0	
	0	2	0	2	0	
	0	2	0	2	0	
Cd	0	26	0	0	1	
	0	12	0	0	0	
	72	46	99	68	90	
	26	6	1	18	6	
	2	2	0	2	1	
	0	2	0	0	0	
	0	2	0	0	0	

^a Five-ppm mixed metal standard was used.

^b Ethyl acrylate-ethylene glycol dimethacrylate copolymer.

^c Styrene divinylbenzene copolymer.

A comparison of the performance of silica, styrene divinylbenzene, polysulfone, and chelating columns for the elements Cr, Co, Mn, Ni, and Al is shown in Table 3. It is clear from these tables that the polysulfone column did not perform as well as the other three. It is also seen that Cr was not retained well by any of the columns. The other elements were retained efficiently by all columns. The results for Li, Na, K, Ca, Mg, Ba, and Sr using the same columns are presented in Table 4. It is apparent that monovalent ions in general were not retained well by any of the columns. The divalent cations were retained to a much higher degree by all columns. Again, the performance of the polysulfone columns was inferior to the other columns.

Table 3 Performance of silica, styrene divinylbenzene, and polysulfone columns containing 10% *S. fluitans* for Cr, Co, Mn, Ni, and Al, and comparison with chelating resin column.

Element	Weight percentage of loaded metal eluted in each fraction ^a			
	Silica	Sdvb	Polysulfone	Chelating
Cr				
Eluate	31	23	24	18
Rinse	34	36	5	12
Strip 1	18	22	16	18
Strip 2	7	7	6	8
Strip 3	3	8	2	4
Strip 4	2	2	1	3
Strip 5	1	1	1	2
Co				
	0	0	13	0
	0	0	6	0
	88	97	69	92
	14	7	17	5
	1	0	2	0
	0	0	0	0
	0	0	0	0
Mn				
	0	0	22	0
	1	0	1	0
	86	89	70	92
	9	6	15	5
	0	0	2	0
	0	0	0	0
	0	0	0	0
Ni				
	0	0	1	0
	0	0	4	0
	85	94	68	96
	19	7	19	5
	1	0	2	0
	0	0	0	0
	0	0	0	0
Al				
	1	1	0	1
	0	0	0	1
	72	99	58	97
	41	23	37	20
	8	8	6	6
	3	5	1	4
	3	3	0	3

^a Ten-ppm mixed metal standards were used.

Breakthrough curves for Pb, Cu, Zn, and Cd using a column containing approximately 15% by weight *S. fluitans* immobilized in silica gel are shown in Figure 1. Breakthrough curves for the same metals using a 10% by weight *S. fluitans*/styrene divinylbenzene column are shown in Figure 2. These curves are similar qualitatively to those previously obtained using columns of lichen biomass (about 15% by weight) immobilized in silica⁹. It is seen

Table 4 Performance of silica, styrene divinylbenzene, and polysulfone columns containing 10% *S. fluitans* for Li, Na, K, Ca, Mg, Ba, and Sr, and comparison with chelating resin column.

Element	Weight percentage of loaded metal eluted in each fraction ^a			
	Silica	Sdvb	Polysulfone	Chelating
Li				
Eluate	49	39	28	11
Rinse	49	60	61	42
Strip 1	1	3	11	41
Strip 2	0	1	1	2
Strip 3	0	0	0	0
Strip 4	0	0	0	0
Strip 5	0	0	0	0
Na				
	32	26	39	13
	42	72	82	44
	4	5	20	51
	1	1	4	3
	0	0	2	1
	0	0	1	1
	0	0	1	1
K				
	34	26	20	10
	59	72	66	43
	4	5	1	40
	1	1	1	3
	1	0	1	2
	0	0	0	1
	0	0	0	0
Ca				
	0	1	4	1
	1	0	15	0
	54	76	83	73
	5	4	17	7
	1	1	4	1
	0	0	3	0
	0	0	2	0
Mg				
	0	0	6	1
	21	1	39	0
	72	89	64	86
	6	6	12	10
	1	1	2	0
	0	0	1	0
	0	0	1	0
Ba				
	0	0	7	0
	0	0	15	0
	58	75	73	71
	9	4	14	7
	0	1	2	0
	0	0	0	0
	0	0	0	0
Sr				
	0	0	2	0
	0	0	11	0
	54	72	74	67
	5	3	11	5
	0	0	1	0
	0	0	0	0
	0	0	0	0

^a Ten-ppm mixed metal standards were used.

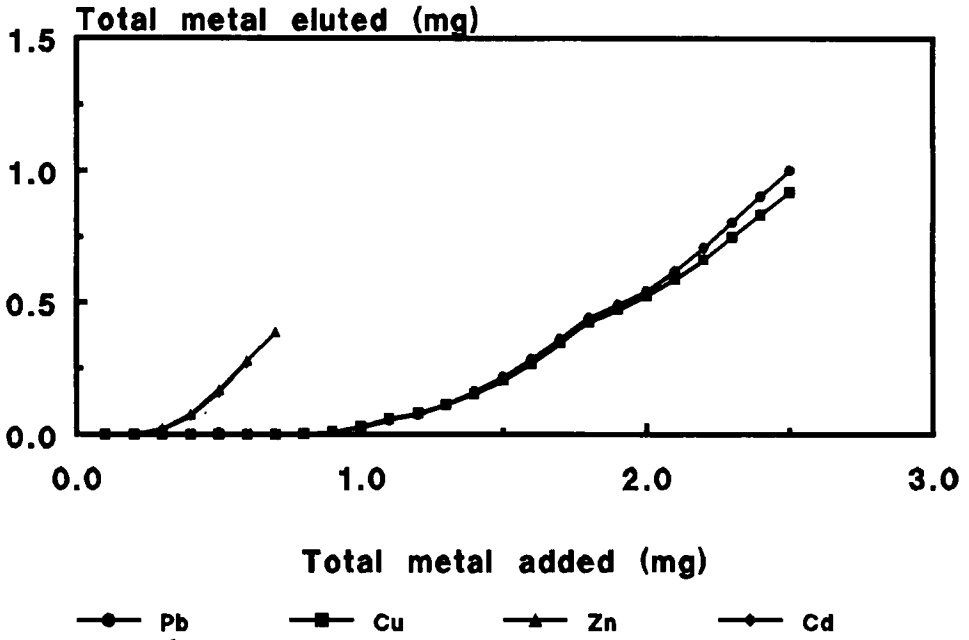


Figure 1 Breakthrough curves for Pb, Cu, Zn, and Cd on a column containing 15% *S. fluitans* immobilized in

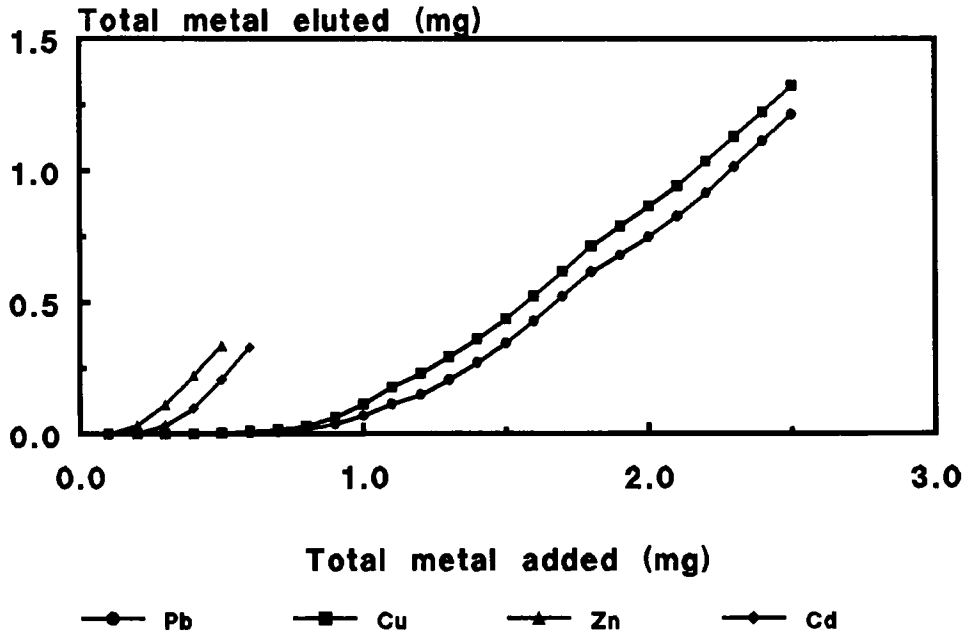


Figure 2 Breakthrough curves for Pb, Cu, Zn, and Cd on a column containing 10% *S. fluitans* immobilized in styrene divinylbenzene.

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from these figures that the capacity of both biocolumns was greatest for Pb. Lead and Cu behave in a very similar fashion on both columns, as do Zn and Cd. When a chelating resin was used, essentially no breakthrough was observed for any of the four metals, even at 3 mg of added metal.

In the next series of experiments the amount of *S. fluitans* biomass by weight was varied. Three different amounts of biomass by weight, 10, 25–30, and 50–52%, were incorporated in polysulfone and silica gel. The results for the polysulfone columns are shown in Figure 3 a–d for Pb, Cu, Zn, and Cd. The breakthrough curves shown indicate that for all four metals the capacity of the 25% column was greater than the 10% column. This was an expected result since the more biomass available, the greater the amount of metal bound. Surprisingly, a 50% column showed less metal binding than the 25% column for all four metals. The 25% column displayed a greater capacity for all four metals than the 10 and 50% columns. A second 50% resin was prepared to see if perhaps the first sorbent had been somehow incorrectly prepared. The second biosorbent performed in a very similar fashion to the first; in other words, the 50% column was again intermediate in performance between the 10 and 25% columns. Apparently, between 25 and 50% biomass by weight the physical structure of the adsorbent changes, leading to less metal binding. It is thought that as the percentage of biomass reaches 50%, the formation of aggregates of biomass within the polymeric matrix reduces the available surface area, and thus leads to reduced metal binding.

Breakthrough curves were also obtained for different percentages of *S. fluitans* immobilized in silica gel. In Figure 4 a–d a comparison of the capacities of silica columns for Pb, Cu, Zn, and Cd containing three different amounts of *S. fluitans* biomass is made. Again, the column with intermediate weight percentage, the 30% column, performed better than both the 10% and 52% columns. However, the differences between all columns was much less for silica gel support than for polysulfone. Also, in comparing Figures 3 and 4, it is seen that the capacities of the polysulfone columns were much greater than the silica gel columns and the breakthrough points were three to four times later for polysulfone compared to silica gel.

In Figure 5 a–c the breakthrough curves for Ag, Au, and Hg using a silica gel column are shown. For these three elements the 52% column performed better than either the 10 or 30% columns, a behaviour in contrast to that observed for Pb, Cu, Zn, and Cd using both polysulfone and silica gel columns. The nature of these differences is not understood but it is known that these three metals are classified as “soft” ions because they can form covalent complexes with nitrogen and sulfur⁷. Thus, their binding is less pH dependent and they may bind at more than one site on biocell walls. Electron microscope investigations of metal binding to these biosorbents should prove useful in elucidating the nature of intermetal differences.

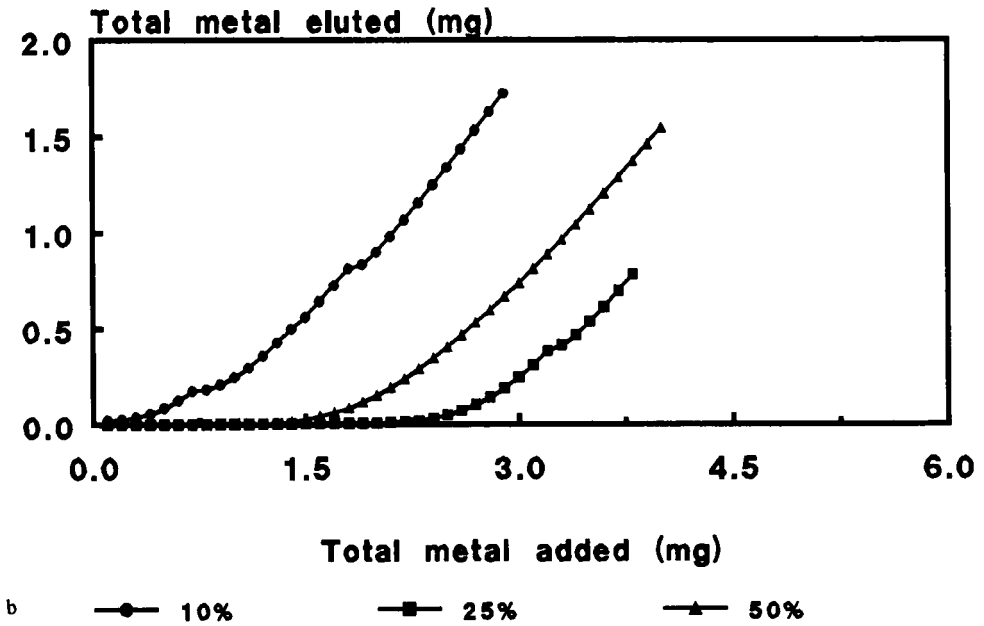
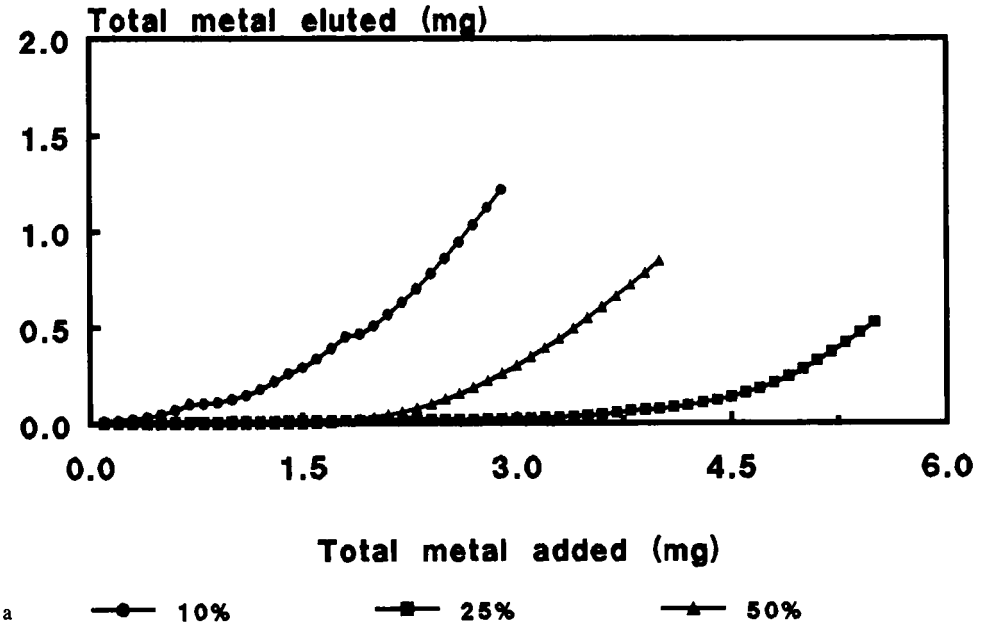
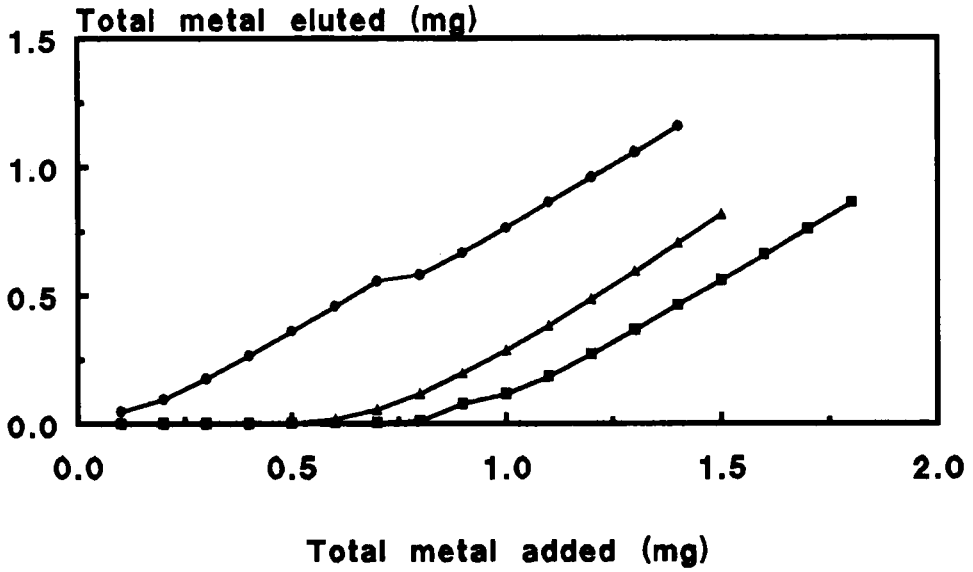
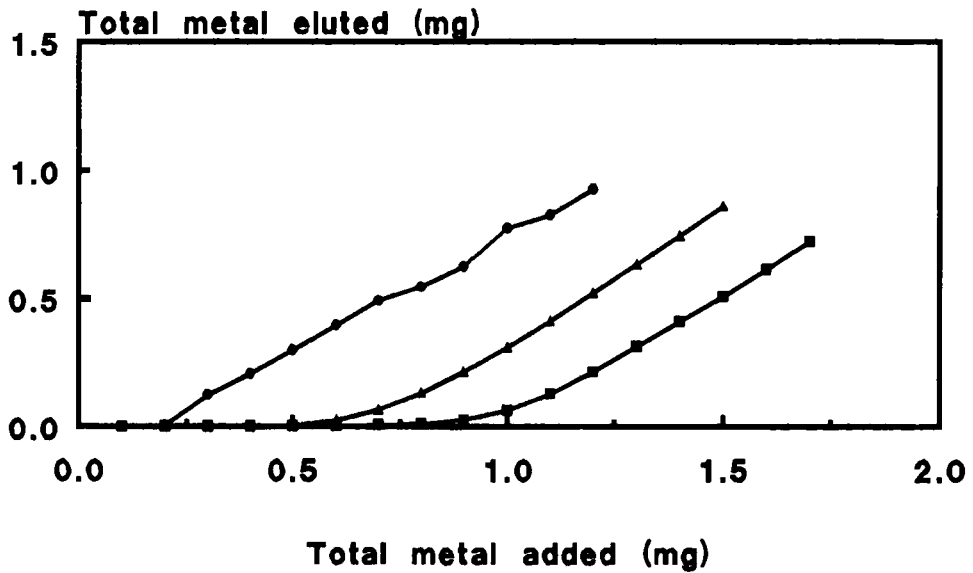


Figure 3 Breakthrough curves for a) Pb, b) Cu, c) Zn, and d) Cd on columns containing 10%, 25%, and 50% *S. fluitans* immobilized in polysulfone.

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c ● 10% ■ 25% ▲ 50% (II)



d ● 10% ■ 25% ▲ 50%

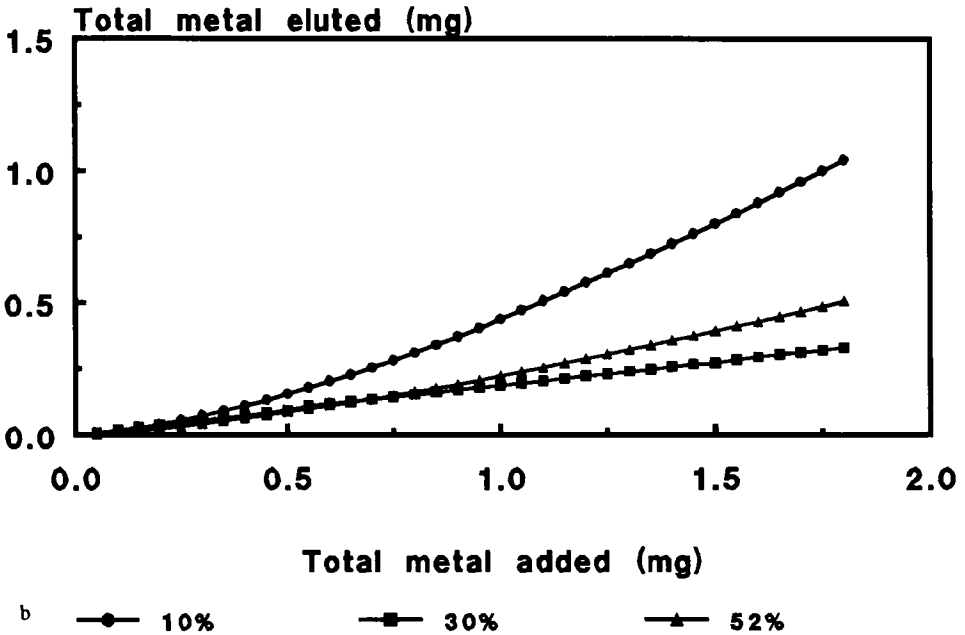
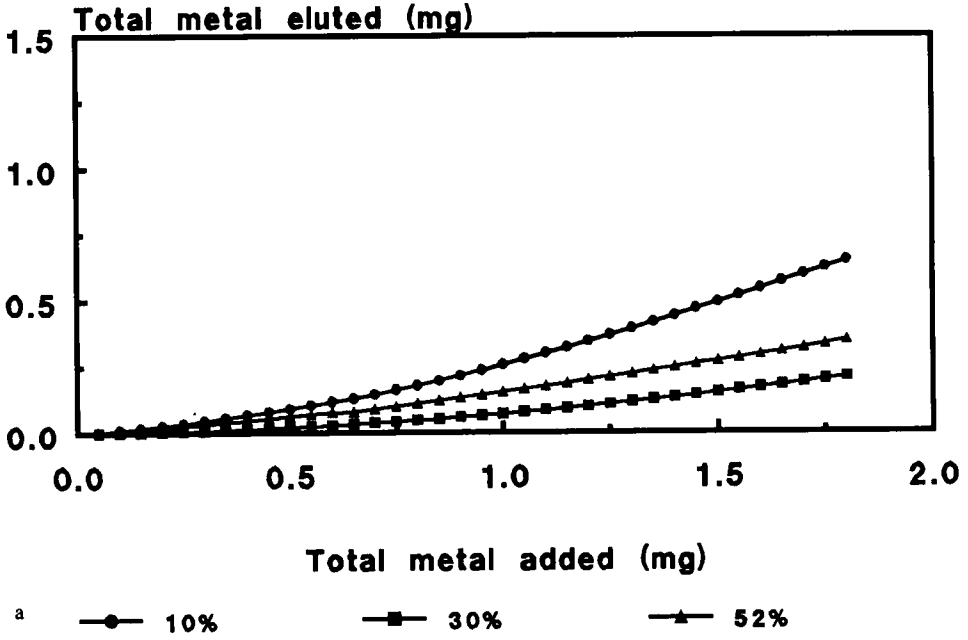
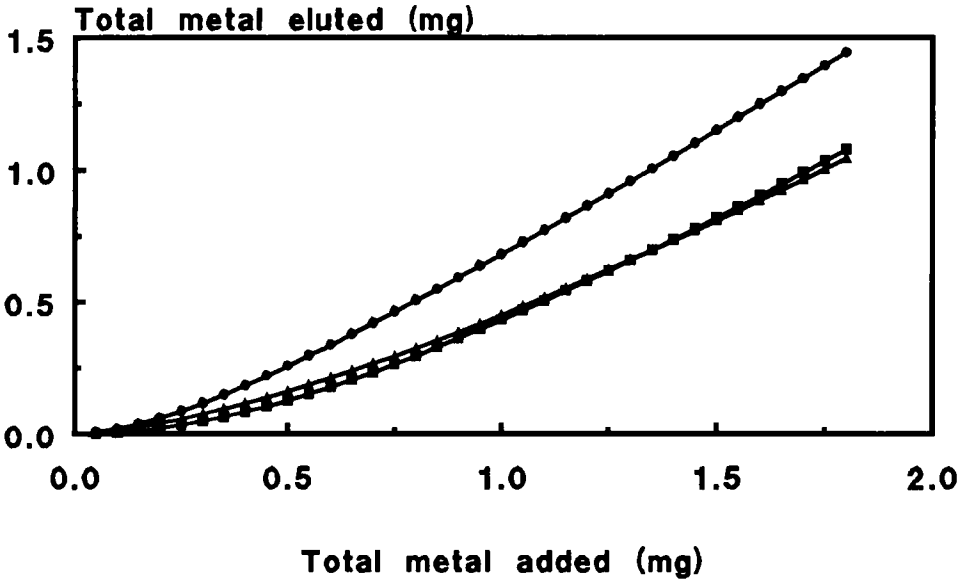
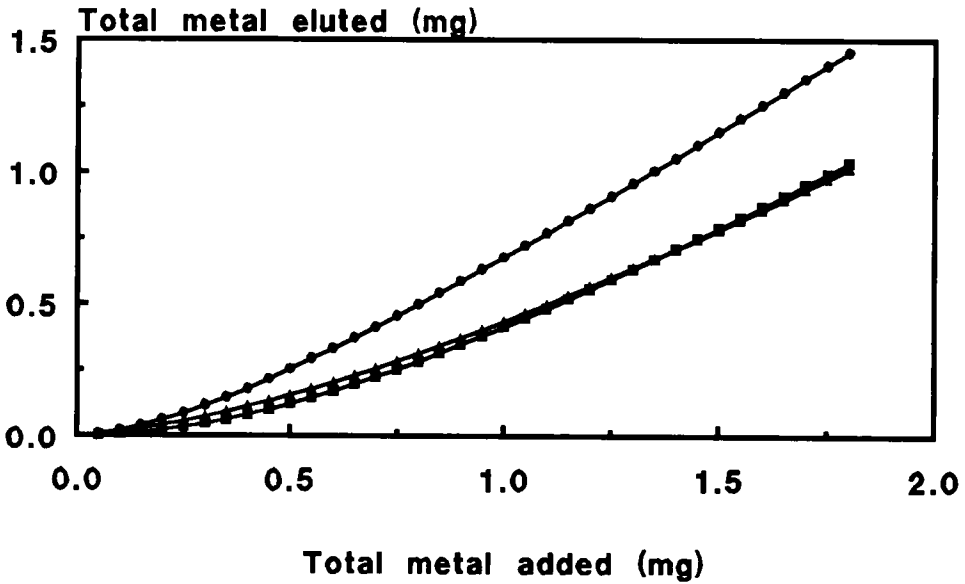


Figure 4 Breakthrough curves for a) Pb, b) Cu, c) Zn, and d) Cd on columns containing 10%, 30%, and 52% *S. fluitans* immobilized in silica gel.

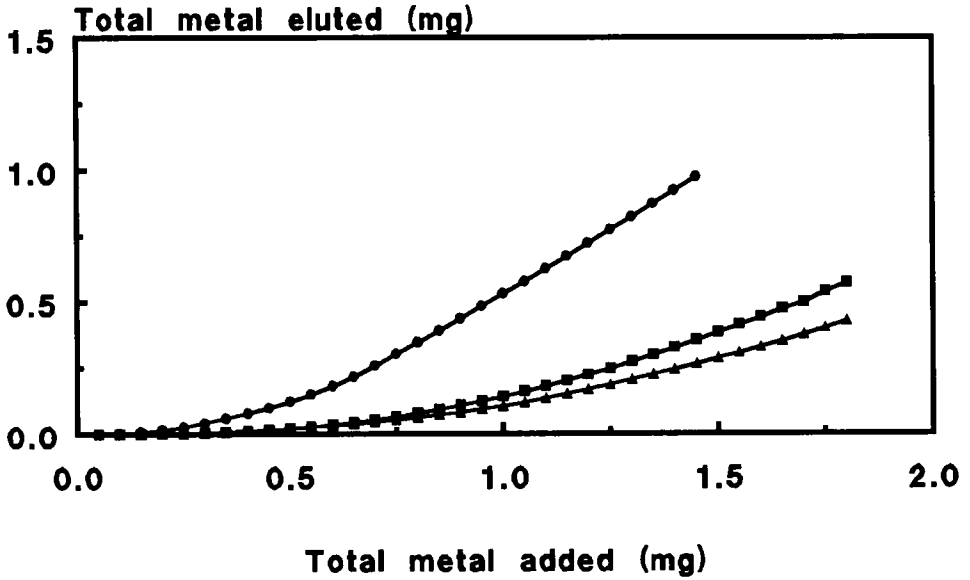
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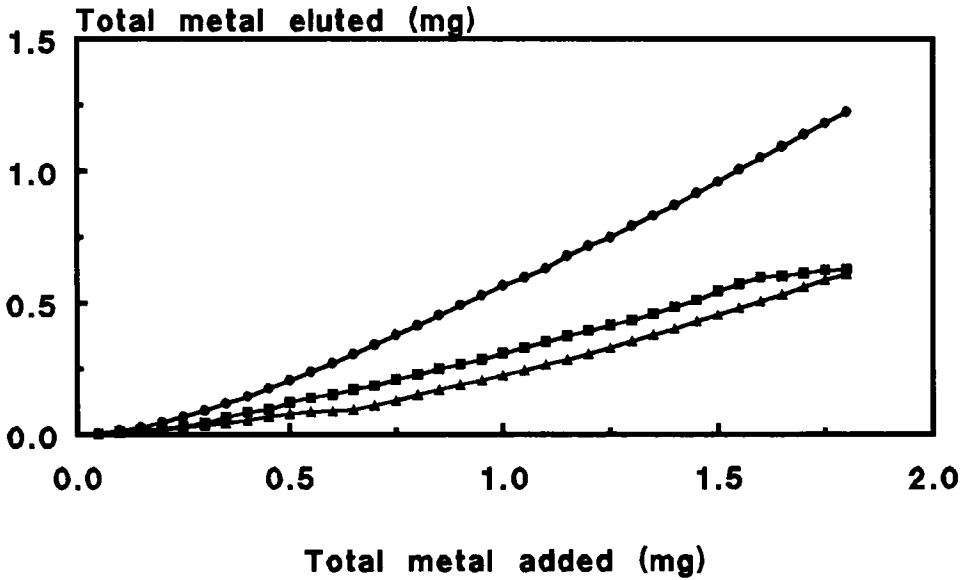
c ● 10% ■ 30% ▲ 52%



d ● 10% ■ 30% ▲ 52%

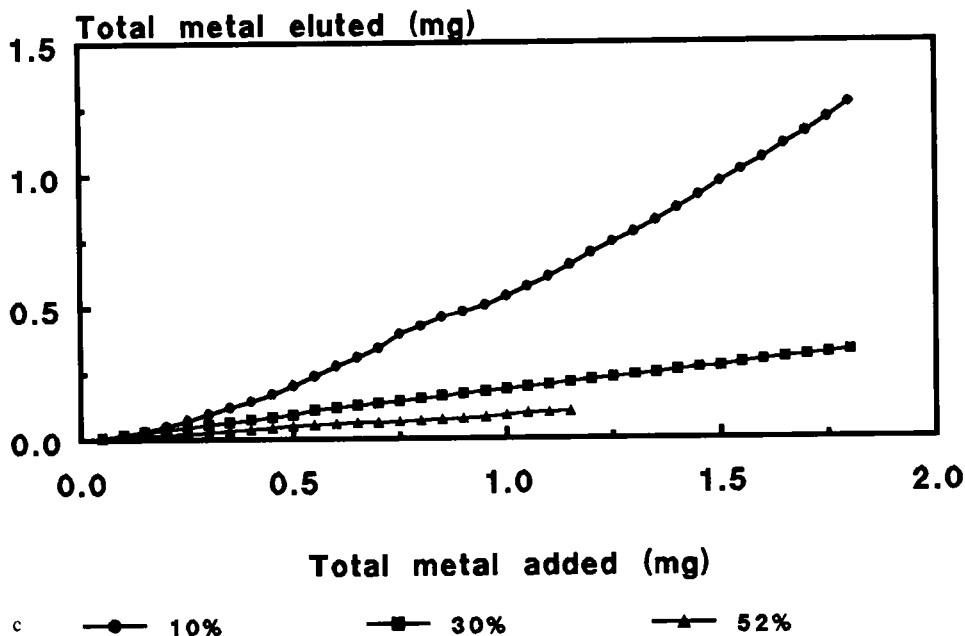


a ● 10% ■ 30% ▲ 52%



b ● 10% ■ 30% ▲ 52%

Figure 5 Breakthrough curves for a) Ag, b) Au, and c) Hg on columns containing 10%, 30%, and 52% *S. fluitans* immobilized in silica gel.



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