

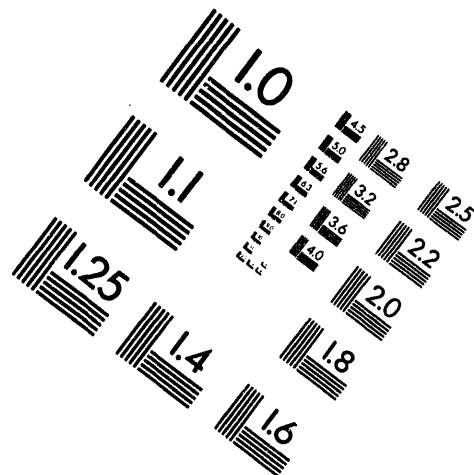
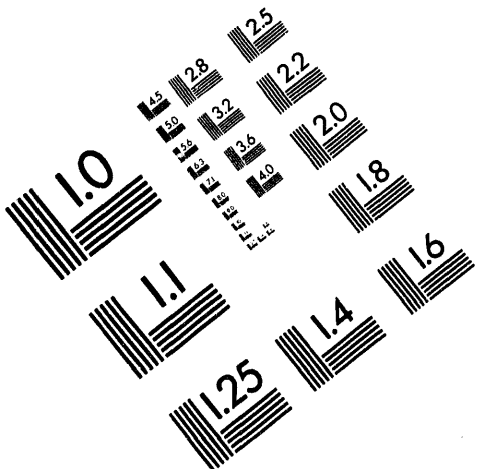


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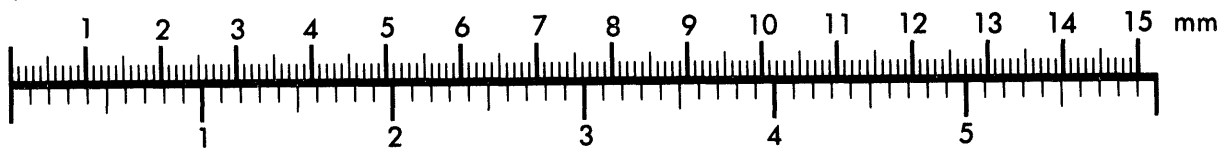
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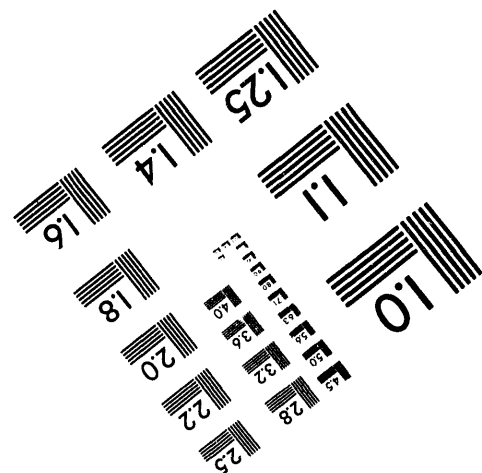
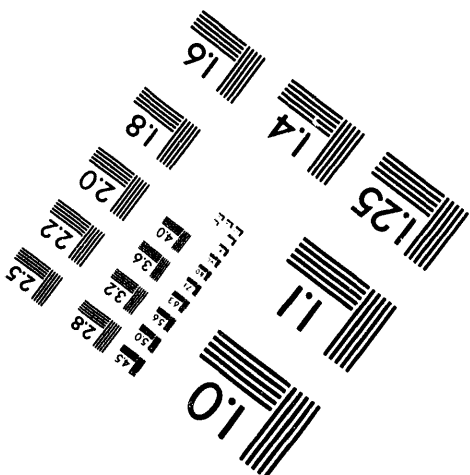
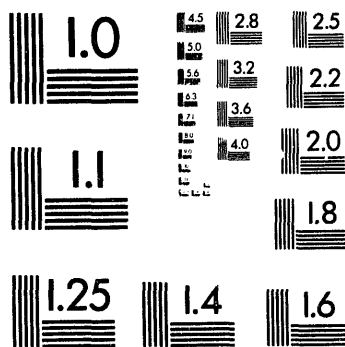
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READINESS THROUGH RESEARCH

**METAL ION SORPTION BY UNTREATED
AND CHEMICALLY TREATED BIOMASS**

by

J. J. Kilbane

J. Xie

Paper Presented at the

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METAL ION SORPTION BY UNTREATED
AND CHEMICALLY TREATED BIOMASS

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ABSTRACT

The metal-binding ability of biosorbents is well known; however, in comparison with commercial ion-exchange resins the capacity of biosorbents is low. The purpose of this research was to examine chemically modified biosorbents and biosorbents prepared from microorganisms isolated from extreme environments to determine if significant improvements in metal-binding capacity or biosorbents with unique capabilities could be produced. Chemical treatments examined included acid, alkali, carbon disulfide, phosphorus oxychloride, anhydrous formamide, sodium thiosulfate, sodium chloroacetic acid, and phenylsulfonate. Biosorbents were prepared from microorganisms isolated from pristine and acid mine drainage impacted sites and included heterotrophs, methanotrophs, algae, and sulfate reducers. Chemical modification with carbon disulfide, phosphorous oxychloride, and sodium thiosulfate yielded biosorbents with such as much as 74%, 133%, and 155% improvements, respectively, in metal-binding capacity, but the performance of these chemically modified biosorbents deteriorated upon repeated use. A culture isolated from an acid mine drainage impacted site, IGTM17, exhibits about 3-fold higher metal-binding capacity in comparison with other biosorbents examined in this study. IGTM17 also exhibits superior metal-binding ability at decreased pH or in the presence of interfering common cations in comparison with other biosorbents or some commercially available cation-exchange resins. Some biosorbents, such as IGTM5, can bind anions! To our knowledge this is the first demonstration of the ability of biosorbents to bind anions. Moreover, preliminary data indicate that the chemical modification of biosorbents may be capable of imparting the ability to selectively bind certain anions. Further research is needed to optimize conditions for the chemical modification and stabilization of biosorbents.

METAL ION SORPTION BY UNTREATED AND CHEMICALLY TREATED BIOMASS

INTRODUCTION

In today's industrial society, metals are among the most commonly used raw materials. They are introduced into the environment during mining and refining of ores and from other sources, such as the combustion of fossil fuels, industrial processes, spraying of pesticides, and the disposal of industrial and domestic wastes. In the last few decades, metals have been mined and used extensively by mankind. The combination of rapidly expanding industry and increases in domestic activities has caused significant environmental problems due to metal ion pollution and critical losses of non-renewable metal resources [4].

The binding of metals to microorganisms in wastewater treatment plants was noted as early as 1965 [6]. Since then, the idea of using microorganisms to accumulate metals from solution has been a very attractive topic, not only for water purification, but for the recovery of valuable or economically important metals [1-3].

The use of bioadsorbents in continuous or semi-continuous treatment systems has been attempted using immobilized cell cultures; however, most of these systems employ living/functional microorganisms [11-13]. The chief limitations of these immobilized cell systems are those inherent in the use of living cells: susceptibility to cell death, contamination, low mechanical strength of immobilized particles, and the requirement of certain conditions and nutrients to maintain cellular activity. Indeed, metal ions are known to be toxic to microorganisms, including those species that are recommended for use in metal waste treatment systems [15-18].

The use of dried biomass immobilized in various fashions has been reported in systems employing algae [5], bacteria [1,7,8,9,19], and fungal cells [1,21]. The results obtained using some of these systems confirm that this may well be the most practical application of bioadsorbents for the economical treatment of metal-contaminated wastewater, as this bioadsorbent technology is just beginning to be used commercially [1-3].

Bioadsorbents clearly show great promise for use in removing and recovering metal ions from contaminated water, although much remains to be done. While the ability of biosorbents to bind heavy metal cations is well documented, the binding capacity of biosorbents in comparison with commercially available cation-exchange resins is generally low. Moreover, commercial ion-exchange resins for the treatment of wastewater containing anions is well known. The binding of anions by biosorbents has not been reported. In this paper, biosorbents modified by various chemical treatments and biosorbents produced from diverse microbial

cultures are examined for increased metal ion-binding capacity, ability to bind anions, and unique metal-binding ability.

MATERIALS AND METHODS

Bacterial Strains and Culture Media

The organisms used in this study were Zoogloea ramigera 115 (ATCC 25935), an algae culture, sulfate reducers, and methanotrophic and heterotrophic cultures isolated from pH neutral and from acid mine drainage site environmental samples. All cultures/biosorbents were designated IGTM1 through IGTM17. The cultivation medium for these cultures has been previously described [10].

Immobilization of Dried Biomass

Biomass (cells plus exopolysaccharides) was harvested by centrifugation at 10,000 X g for 10 minutes and dried under vacuum in a rotary evaporator at 65°C. The dried biomass was ground to a uniform fine powder using a mortar and pestle. Dried, powdered biomass was used as is for some metal-binding experiments or the biomass was first immobilized in polysulfone according to previously described procedures [10].

Chemical Treatment Procedures

The chemical modification of biomass was done according to published procedures in treatments involving CS₂ [22], POCl₃ [19], HOCNH₂ [7], or Na₂CO₃CH₂Cl [19].

For treatments using Na₂S₂O₃, 5 g of biomass were treated with 30 g Na₂S₂O₃ in 300 ml H₂O at 80°C for 72 hours. The treated biomass was centrifuged out and washed with distilled H₂O at least three times, and then dried in an 80°C oven.

For treatments involving sulfonated phenolic resin, a two-step procedure was used.

Step 1. An 80-ml 88% phenol solution was reacted with 40 ml of 98% H₂SO₄ for 40 minutes and then cooled to room temperature; then 80 ml of epichlorohydrin was gradually added to the solution cooled in an ice bath.

Step 2. A 5-g sample of biomass was dissolved in an NaOH solution of 9 g NaOH in 25 ml H₂O. Twenty-five ml of the sulfonated phenolic resin prepared from Step 1 was gradually added to the biomass/NaOH slurry, heated in a boiling bath, and stirred for 1 hour. The mixture was transferred into 2 L of H₂O and then centrifuged. The precipitates were rinsed thoroughly with distilled H₂O and dried in an 80°C oven.

Commercial Ion-Exchange Resins

AG50W-X4, a strongly acidic cation-exchange resin (ion-exchange capacity = IEC = 1.2 meq/ml or 5.2 meq/g), was

purchased from Biorad Chemical Co. IR-122, a strongly acidic cation-exchange resin (IEC = 2.1 meq/ml or 4.4 meq/g) and IRC-76, a weakly acidic cation-exchange resin (IEC = 3.5 meq/ml or 10 meq/g), were purchased from Sigma Chemical Co.

Metal Ion Solutions

The following metal salts were used to prepare aqueous solutions ranging in concentration from 0.001 to 100 ppm: AuCl₃, CdCl₂, CoCl₂·6H₂O, CrCl₃, CuSO₄·5H₂O, HgCl₂, Ni(NO₃)₂·6H₂O, Pb(NO₃)₂, SrCO₃, V₂O₅, ZnSO₄, Na₂AsO₂, Na₂CrO₄·4H₂O, Na₂MoO₄·2H₂O, H₂SeO₃, Na₂WO₄·2H₂O. Stock solutions of 100 and 1000 ppm were prepared of individual metal ion species as well as mixtures of several metal ions.

Analytical Procedures

Atomic Absorption Spectrophotometry (AAS) (Model: 403, Perkin-Elmer Co.) and Inductively Coupled Plasma Emission Spectroscopy (ICPAES) (Model: Atom Scan 25, Thermo Jarrell Ash Co.) were used for metal concentration analyses. Samples had to be diluted to 0.1-1.0 ppm for accurate analysis. To remove the interference from suspended particles, samples were centrifuged (600 rpm, 5 min) and filtered by a 0.45- μ m filter before injection into the AAS or ICPAES apparatus.

Ion-exchange capacity (IEC) was determined by the titration method [20] and by preparing absorption isotherms and breakthrough curves.

Metal Adsorption Studies

Batch studies were performed using either 14 ml (containing 1 g biomass, dry weight) of fresh beads or 100 mg of biomass in a 250-ml Erlenmeyer shaker flask containing 100 ml of 10 to 100 ppm metal solution (pH 6.0 or 4.0) and shaken overnight at a speed of 160 rpm at room temperature. Beads of biomass were allowed to settle and/or were centrifuged, the supernatant was decanted, filtered, and metal ions were then analyzed by AAS or ICPAES.

Continuous-flow metal-binding studies were performed using 100 ml of beads (containing 7 g biomass dry weight) in a 25-cm X 2.5-cm column. Flow rates were adjusted to hydraulic retention times of 15 minutes.

RESULTS AND DISCUSSION

The ability of biosorbents to bind metal cations is well known, but in comparison with commercially available cation-exchange resins, it is generally believed that the metal-binding capacity of biosorbents is low. To examine this further, the ion-exchange capacity of several biosorbents and several cation-exchange resins was determined using two techniques: titration and adsorption isotherms/breakthrough curves. The results are shown in Table 1, which illustrates that the titration method overestimates the IECs of both

Table 1. ION-EXCHANGE CAPACITIES DETERMINED BY TITRATION AND BY ADSORPTION ISOTHERMS (meq/g) SHOW SIGNIFICANT DIFFERENCES

	<u>AG50W-X4</u>	<u>IR-122</u>	<u>IRC-76</u>	<u>IGTM1</u>	<u>IGTM2</u>	<u>Zr115</u>
Titration Method	5.20	3.00	9.7	1.34	1.47	1.20
Absorption Isotherm	4.66	1.79	0.397	0.214	0.178	0.229

biosorbents and cation-exchange resins in comparison with the results obtained from adsorption isotherm/breakthrough curve experiments. This is thought to be due to the fact that the titration method measures all sites capable of exchanging protons without regard to the reactivity of these sites toward metal cations. The titration method is the standard means of determining IECs of commercially produced cation-exchange resins, and the data in Table 1 indicate that, at least for AG50W-X4, the IEC values determined by the titration method and the adsorption isotherm/breakthrough curve method (which involved actual divalent metal cations) agree rather closely. However, the agreement between these two methods is rather poor for the other cation-exchange resins and biosorbents examined. Accordingly, all additional work in this project utilized the adsorption isotherm/ breakthrough curve method to determine IECs because these values are more conservative and more closely predict the performance of cation-exchange resins or biosorbents during normal usage.

The data in Table 1 indicate that the IECs of biosorbents are low in comparison with cation-exchange resins. To see if this situation could be improved, the IECs of a variety of biosorbents and chemically modified biosorbents were determined. Biosorbents were prepared from microorganisms isolated from pristine and acid mine drainage impacted environments and included heterotrophs, methanotrophs, algae, and sulfate reducers. Representative data are shown in Figure 1. The vast majority of biosorbents examined in this study had metal-binding capacities from 10 to 20 mg Cd/g biomass (or IECs of 0.178 to 0.357 meq/g). Data for the metal-binding capacity of moss [5] and apple residue [14] are also included in Figure 1 for comparative purposes to illustrate that most biosorbents fall within a reasonably narrow range of IEC comparable to weakly acidic cation-exchange resins such as IRC-76. However, one biosorbent sample isolated from an acid mine drainage impacted environment, IGTM17, showed superior metal-binding capacity roughly 3-fold higher than other biosorbents. To examine the metal-binding abilities of biosorbents, particularly IGTM17, in greater detail, metal-binding experiments were performed at pH 4 as well as pH 6, and at pH 6 in the presence of various concentrations of commonly occurring cations such as sodium, calcium, or magnesium. The results of metal-binding experiments performed at different pH values are summarized in Figure 2, which shows that while the performance of most

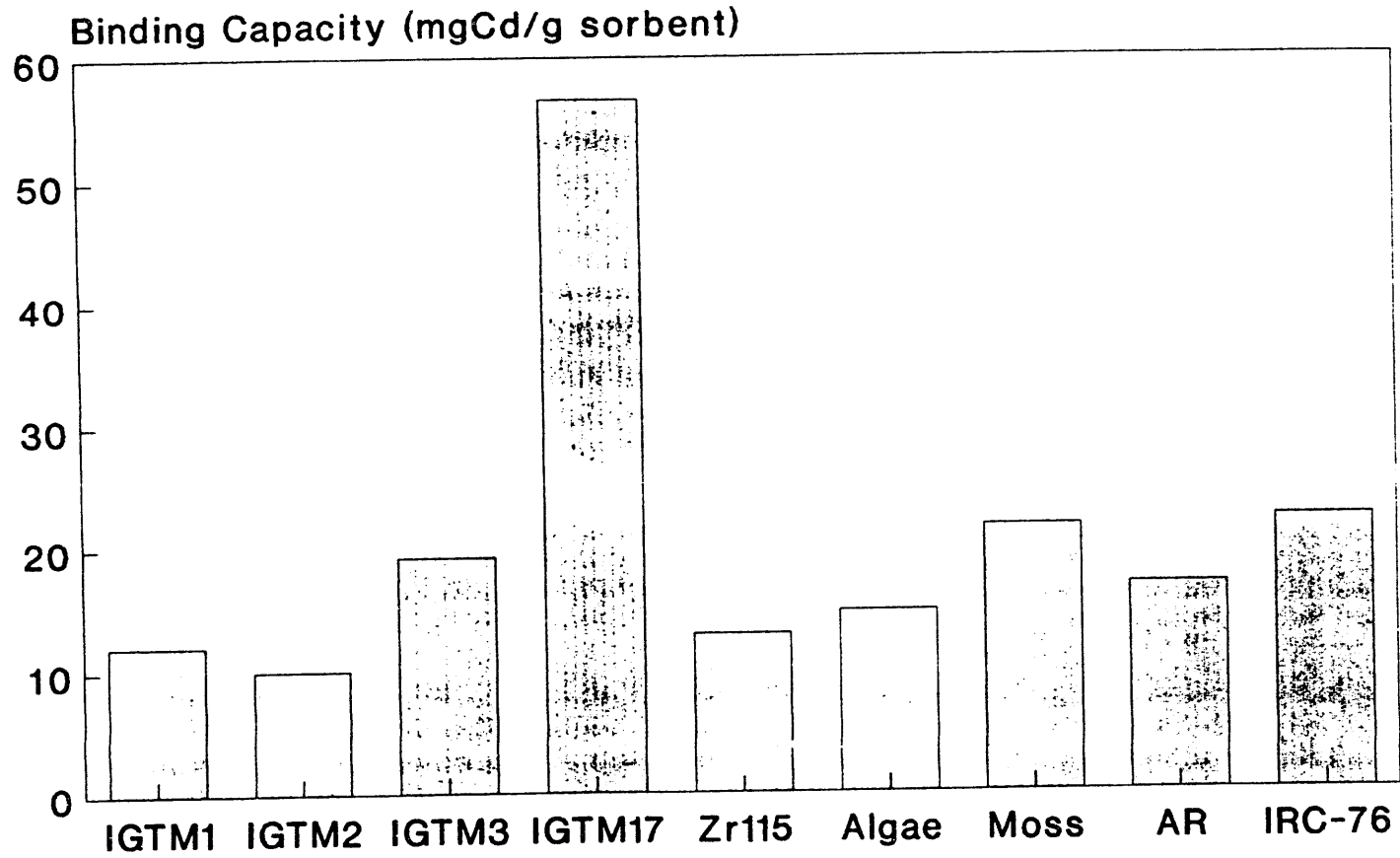


Figure 1. SOME BIOSORBENTS POSSESS SUPERIOR METAL-BINDING CAPACITY

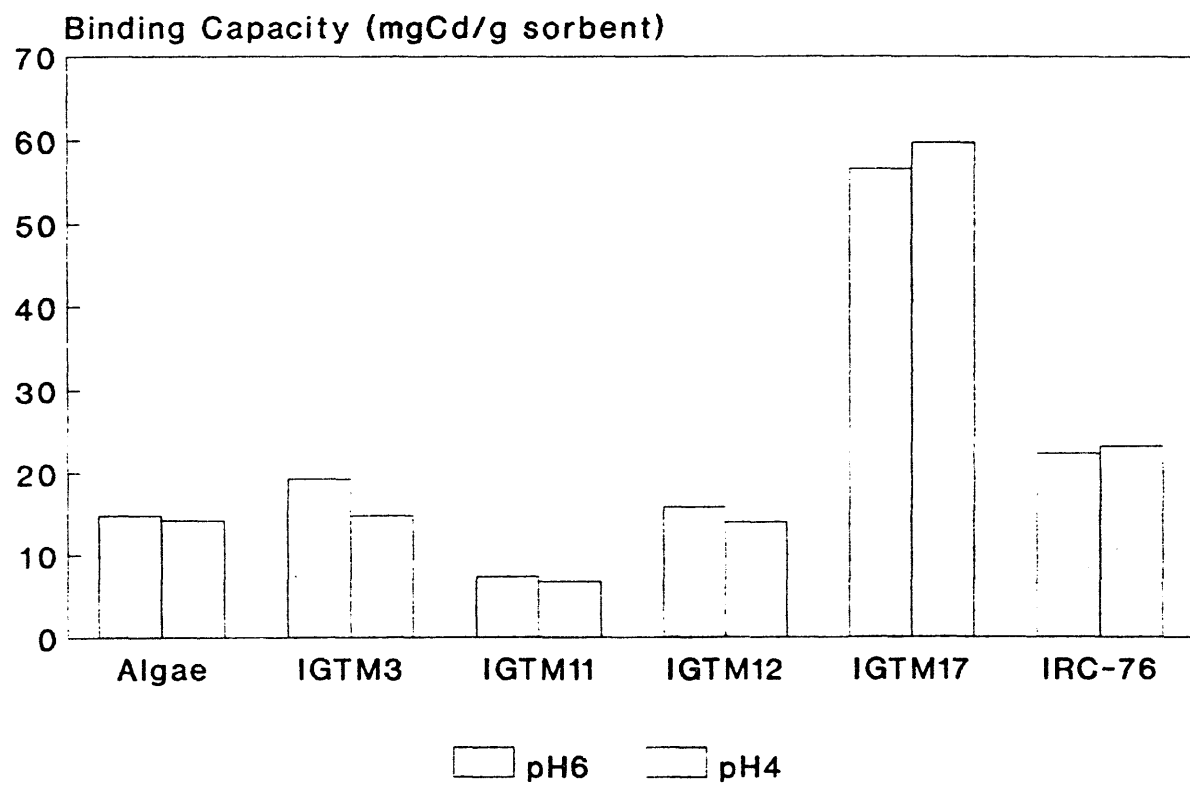


Figure 2. SOME BIOSORBENTS RETAIN METAL-BINDING CAPACITY AT LOW pH VALUES

biosorbents is significantly diminished at pH 4 versus pH 6, IGTM17 retains its metal-binding ability at pH 4. It would be interesting in future experiments to determine if the metal-binding ability of IGTM17, or other biosorbents, is retained at even lower pH values.

Wastewater streams containing heavy metal ions often contain commonly occurring cations such as sodium, calcium, and magnesium that can interfere with the ability of ion-exchange resins to bind heavy metal cations of environmental concern. Numerous experiments were performed to determine the effect of common ion interference on various biosorbents, chemically modified biosorbents, and cation-exchange resins. Representative data are summarized in Figure 3. Common cations interfere to some extent with the binding of heavy metal cations to all sorbent materials; however, as shown in Figure 3, the degree of interference is minor for some biosorbents in comparison with the ion-exchange resin IRC-76.

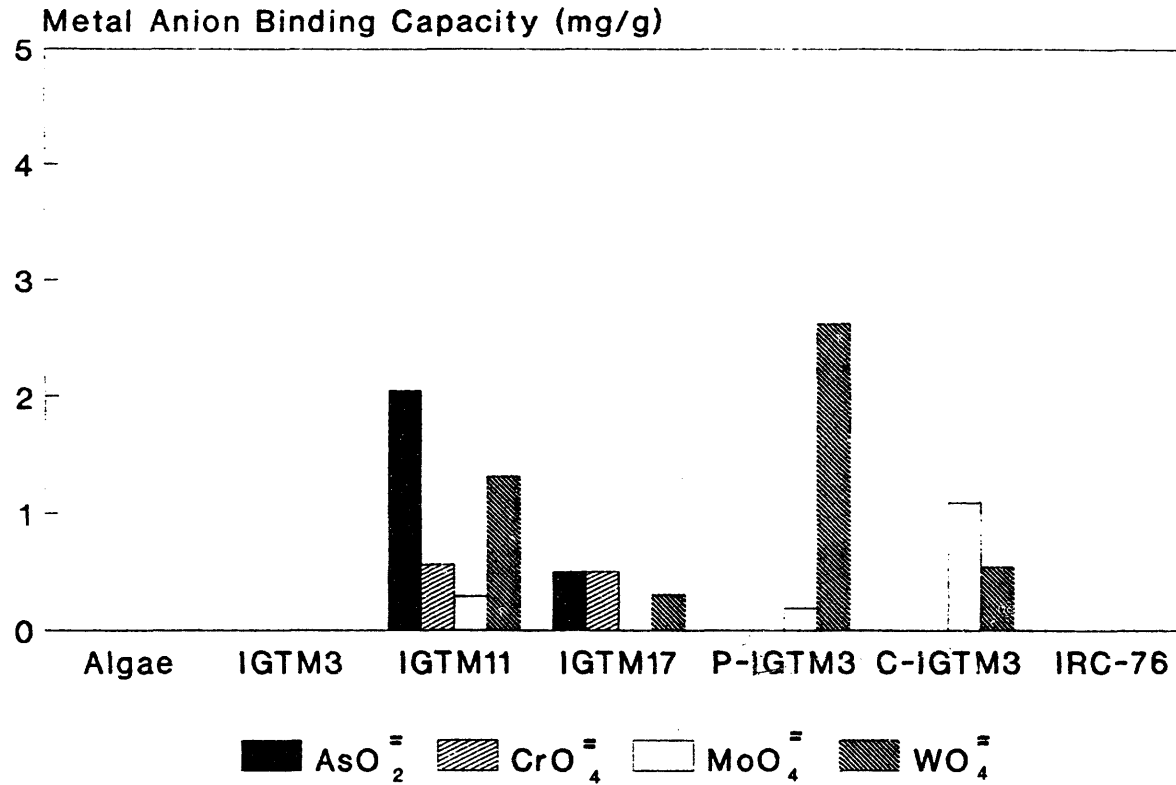
Although the literature contains many examples of the ability of biosorbents to bind heavy metal cations, the binding of metal anions by biosorbents has not been reported. Several biosorbents, chemically modified biosorbents, and a cation-exchange resin were examined for their ability to bind any of a mixture of four anions (AsO_4^- , CrO_4^- , MoO_4^- , and WO_4^-) at pH 6.0, and the results are shown in Figure 4. The vast majority of biosorbents examined in this study failed to bind metal anions; however, some biosorbents were capable of binding all of the metal anions tested. Additionally, preliminary data indicate that the chemical modification of biomass with phosphorus oxychloride can yield biosorbents that can selectively bind WO_4^- . We believe that this is the first demonstration of the ability of biosorbents to bind metal anions, and this important observation should be confirmed by further testing.

The chemical modification of biomass was attempted to determine if biosorbents with enhanced metal-binding capacity and/or unique capabilities could be produced. The various chemical treatments that were examined and the results obtained are listed in Table 2, while Figure 5 illustrates the performance of unmodified versus chemically modified biosorbents. Several chemical modification techniques resulted in significant enhancements in metal cation-binding capacity: sodium chloroacetate, carbon disulfide, phosphorous oxychloride, and sodium thiosulfate. These chemically modified biosorbents perform better than the weakly acidic cation-exchange resin IRC-76; however, chemically modified biosorbents do not appear to be very stable, and their metal-binding capacity deteriorates with time and with repeated use. The degree of improvement afforded, as well as the deterioration of that performance, by the chemical modification of biomass using carbon disulfide, phosphorous oxychloride, and sodium thiosulfate is illustrated in Figures 6, 7, and 8, respectively.



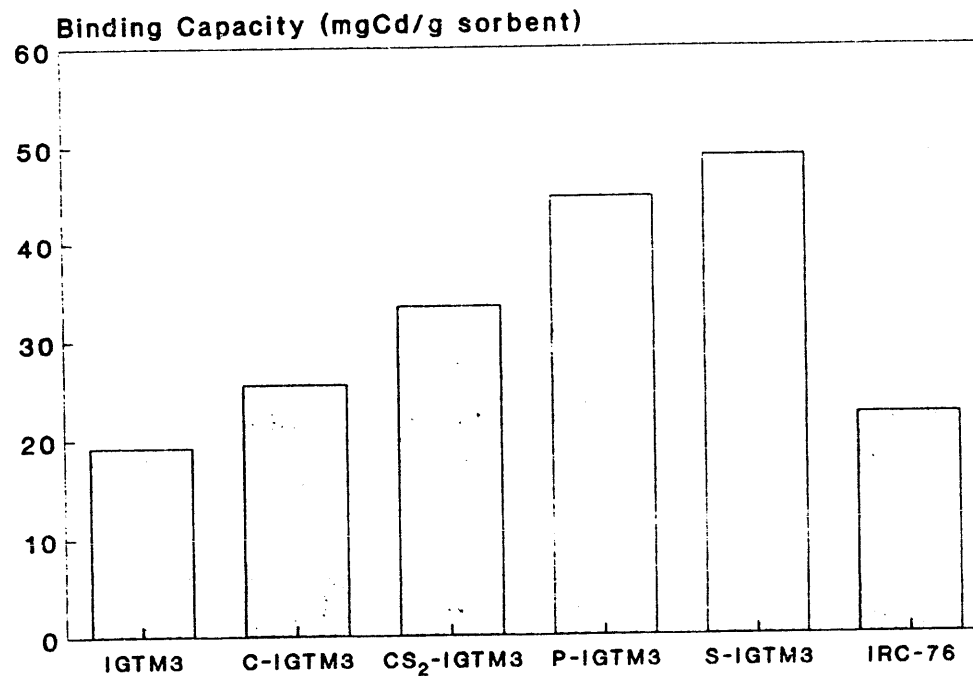
- * IRC-76 = Commercial Ion Exchange Resin
- Chemical modification of biosorbents does not appear to enhance metal binding in the presence of interfering common ions, data using sodium thiosulfate treated biomass is shown to illustrate typical results.

**Figure 3. BIOSORBENTS RETAIN HIGH METAL-BINDING EFFICIENCY
IN THE PRESENCE OF INTERFERING COMMON METAL IONS**



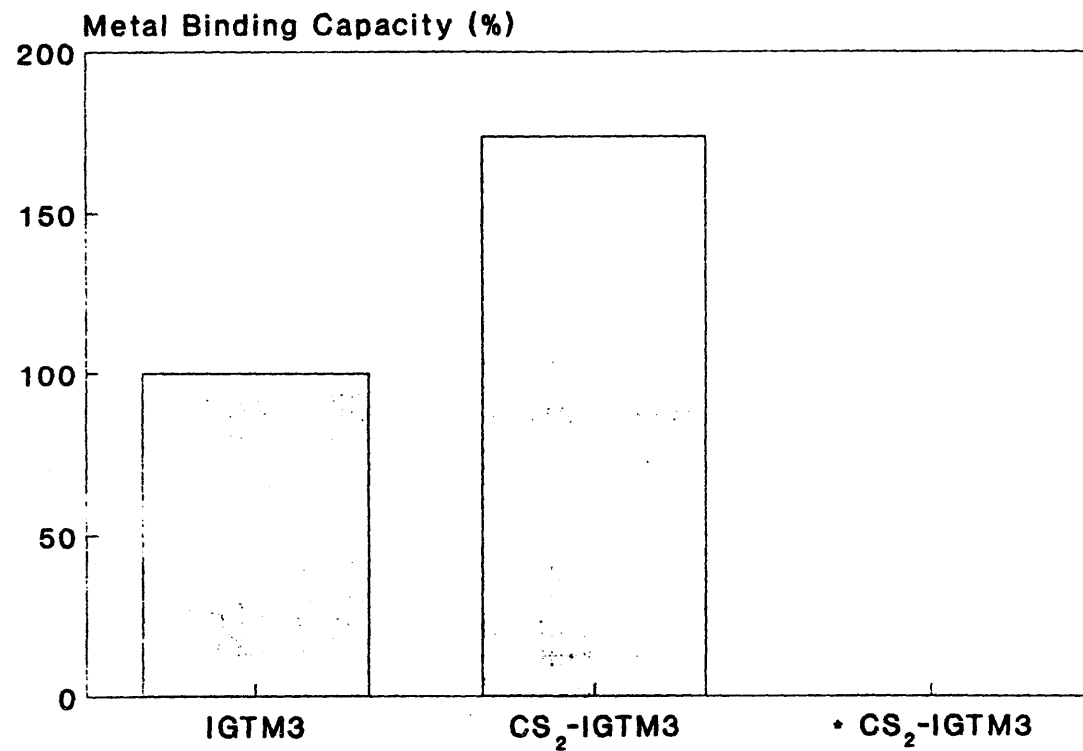
P-IGTM3 = phosphotated IGTM3
 C-IGTM3 = carboxylated IGTM3
 IRC-76 = commercial ion exchange resin

Figure 4. THE ABILITY OF BIOSORBENTS TO BIND METAL ANIONS WAS DEMONSTRATED HERE FOR THE FIRST TIME



C-IGTM3 = Carboxylated
CS₂-IGTM3 = treated with carbon disulfide
P-IGTM3 = phosphotated
S-IGTM3 = treated with sodium thiosulfate
IRC-76 = commercial ion exchange resin

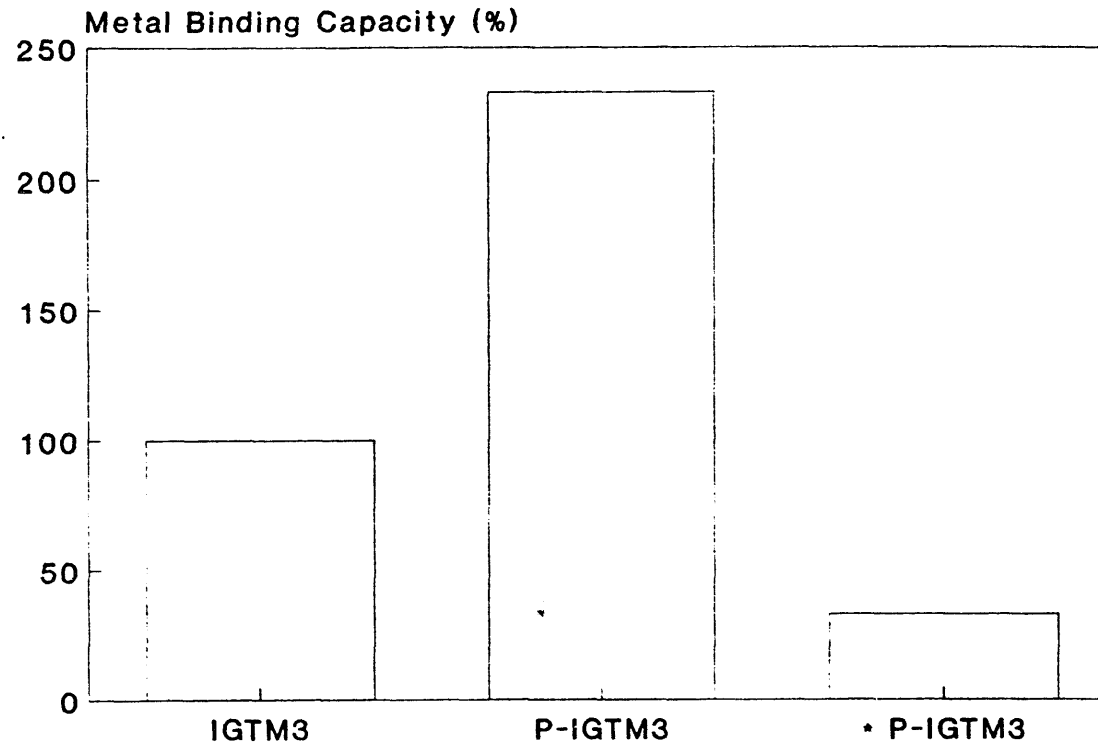
Figure 5. CHEMICAL TREATMENTS CAN DRAMATICALLY INCREASE THE METAL-BINDING CAPACITY OF BIOSORBENTS



CS₂-IGTM3 = IGTM3 freshly treated with carbon disulfide

•CS₂-IGTM3 = CS₂-IGTM3 after repeated use

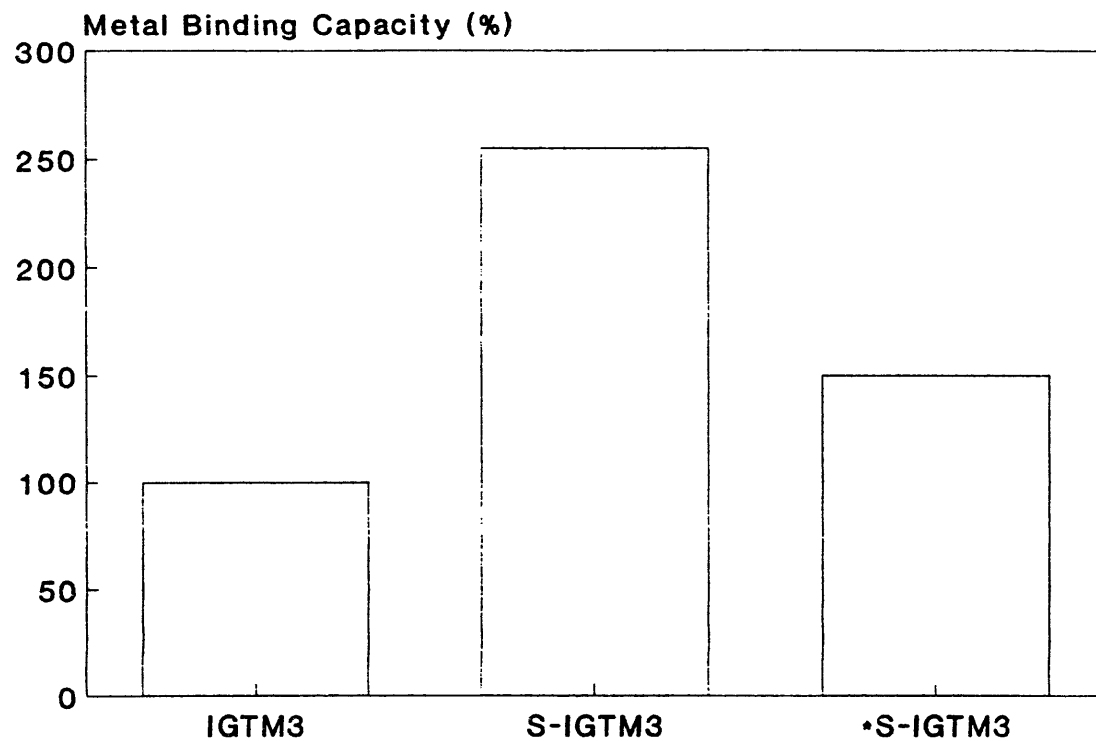
Figure 6. CARBON DISULFIDE INITIALLY ENHANCES BUT EVENTUALLY DESTROYS METAL-BINDING CAPACITY OF BIOSORBENTS



P-IGTM3 = IGTM3 freshly treated with POCl_3

*P-IGTM3 = P-IGTM3 after repeated use

Figure 7. PHOSPHOROUS OXYCHLORIDE TREATMENT CAN INCREASE METAL-BINDING CAPACITY 133%, BUT PERFORMANCE DETERIORATES



S-IGTM3 = IGTM3 freshly treated with sodium thiosulfate

*S-IGTM3 = S-IGTM3 after repeated use

Figure 8. SODIUM THIOSULFATE TREATMENT CAN INCREASE METAL-BINDING CAPACITY 255% AND STILL RETAIN HIGH BINDING EFFICIENCY AFTER REPEATED USE

Table 2. CHEMICAL TREATMENTS USED TO MODIFY BIOSORBENTS

<u>Treatment</u>	<u>Observations</u>
Acid	Strong acids ($\geq 1M$) can destroy the metal-binding capacity of biomass; however, encapsulation in polysulfone renders biosorbents resistant to acids. Dilute acid (0.1M) efficiently elutes bound metals without harming biosorbents.
Alkali	Strong bases ($> 0.1M$ NaOH) can dissolve biomass and destroy metal binding. Mild bases ($< 0.1M$ NaOH) neither improve nor harm biosorbents.
Anhydrous Formamide	Treatments using a 2% formamide solution destroys the metal-binding ability of biomass.
CS ₂	Treatment of biomass with carbon disulfide can yield biosorbents with 74% improvement in metal-binding capacity, but performance deteriorates upon repeated use.
POCl ₃	Phosphorus oxychloride yields phosphotated biosorbents with as much as 133% improvement in metal-binding capacity (this has also been observed by others [14]), however, performance deteriorates upon repeated use to values less than untreated biomass.
Na ₂ S ₂ O ₃	Sodium thiosulfate yields biosorbents with additional sulfhydryl groups resulting in as much as 155% improvement in metal-binding capacity. Improved performance is especially noted at low ion concentrations. Performance deteriorates upon repeated use but is more stable than other chemically modified biomass.
NaCO ₂ CH ₂ Cl	Sodium chloroacetic acid adds carboxyl groups (the functional groups in weakly acidic cation-exchange resins) to biomass to yield about 33% improvement in metal-binding capacity. Performance deteriorates upon repeated use to values less than untreated biomass.
HOC ₆ H ₄ SO ₃	Phenylsulfonate (the functional groups in strongly acidic cation-exchange resins) neither helps nor harms the binding capacity of biosorbents in preliminary tests. Further research to optimize this chemical modification procedure is indicated.

As shown in Figure 6, carbon disulfide-treated biomass has as much as a 74% improvement in metal-binding capacity; however, the modified biomass is highly unstable, particularly

at low pH, and can result in the total loss of metal-binding capacity. The results obtained with phosphorous oxychloride-treated biomass are similar, but as Figure 7 shows, improvements as high as 133% were observed, and while the subsequent deterioration of metal-binding capacity was not quite as severe as with carbon disulfide, it still resulted in biosorbents unable to perform as well as untreated biomass. The most promising chemical treatment revealed by the results obtained thus far is sodium thiosulfate. As Figure 8 shows, metal-binding capacity can be increased by as much as 255%, and treated biosorbents still retain high binding efficiency after repeated use. The kinetics of the deterioration in performance of chemically modified biosorbents remains to be determined, yet with the data currently available it appears that treatment with sodium thiosulfate yields the most stable biosorbents.

The chemical modification of biosorbents has been shown to be advantageous inasmuch as increased metal-binding capacity and the apparent ability to selectively bind WO_4^- was observed; however, further research is needed to more thoroughly examine the chemical modification of biosorbents. The biosorbent with the greatest metal-binding capacity observed in this project thus far was IGTM17; but, unfortunately, this microbial culture was recently isolated, and the chemical modification of IGTM17 biosorbents has not yet been examined. Those chemical modification procedures that yield biosorbents with increased metal-binding capacity all suffer from some degree of instability. Further research to optimize chemical modification procedures, determine the cause and the kinetics of the deterioration of performance, and to enhance stability would be highly beneficial.

ACKNOWLEDGMENT

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CONCLUSIONS

- Biosorbents can outperform weakly acidic cation-exchange resins, and chemically modified biosorbents may be capable of performing as well as or better than strongly acidic cation-exchange resins.
- The ability of some biosorbents to bind anions was demonstrated here for the first time.
- Preliminary data indicate that chemically modified biosorbents may be capable of selectively binding certain anions.
- Chemical modification of biomass using $POCl_3$, $Na_2S_2O_3$, and CS_2 results in significant enhancement of metal-binding

capacity; however, the performance of modified biosorbents deteriorates upon repeated use.

- Further research is needed to optimize conditions for the chemical modification and stabilization of biosorbents.

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