REMOVAL OF HEAVY METALS FROM WATER WITH MICROALGAL RESINS
II. BENCH SCALE TESTING

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14. ABSTRACT
This bioresin technology utilizes immobilized non-living biomass derived from algae to bind heavy metals from dilute solutions. There is significant need for such technology as contamination of water supplies is a broad area of concern in former mining operations, industrial sites, groundwaters and surface waters. Bench scale-tests used immobilized biomass to assess heavy metal binding. Column efficiency was high with 2-10 ppb of copper being passed through these columns in the first 25-50 bed volumes of influent water with 10 ppm Cu^{2+}. Reproducibility within batches and over time was adequate, although measurable variations among batches of bioresins were evident. HCl concentrations of 0.0024N and above were required to elute copper (pH $\leq$ 2.6) from the columns, and the less expensive sulfuric acid was also demonstrated to be effective. Binding of Cu^{2+} at 10 ppm was largely unaffected by roughly equimolar Fe^{2+}, as copper had a particularly high affinity for the tested bioresin. The process appeared to be cation exchange as the oxyanion selenate was not bound. Cost of processing/1000 gal. was calculated to be \$0.42, of which \$0.31 was system capital and the remainder operating cost for a base case of 10 ppm Cu^{2+} and 600 gpm.

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Acknowledgments

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1. Summary

This bioresin technology utilizes immobilized non-living biomass derived from algae to bind heavy metals from dilute solutions. There is significant need for such technology as contamination of water supplies is a broad area of concern in former mining operations, industrial sites, groundwaters and surface waters. Bench scale-tests used immobilized biomass to assess heavy metal binding. Column efficiency was high with 2-10 ppb of copper being passed through these columns in the first 25-50 bed volumes of influent water with 10 ppm Cu^{2+}. Reproducibility within batches and over time was adequate, although measurable variations among batches of bioresins were evident. HCl concentrations of 0.0024 N and above were required to elute copper (pH $\leq$ 2.6) from the columns, and the less expensive sulfuric acid was also demonstrated to be effective. Binding of Cu^{2+} at 10 ppm was largely unaffected by roughly equimolar Fe^{2+}, as copper had a particularly high affinity for the tested bioresin. The process appeared to be cation exchange as the oxyanion selenate was not bound. Cost of processing/1000 gal. was calculated to be $0.42, of which $0.31 was system capital and the remainder operating cost for a base case of 10 ppm Cu^{2+} and 600 gpm. These results compared favorably with the sulfide precipitation method and with previous estimates for bioresin technology.

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2. Background and Objectives

Rationale

The technology studied in this work utilizes immobilized non-living microbial biomass to strip heavy metals from dilute solutions as part of potential remediation efforts. A schematic diagram of such a system is given in Fig. 1. CLF Technologies has a proprietary collection of microbial cultures derived from contaminated sites which can be used to produce and bioadsorbents. Previously, it was pointed out that the key advantage of this type of biomass is the wide range of functional groups present representing a variety of macromolecules present and the substantial evolutionary diversity of the microalgae reinforce the versatility of potential ion-exchange mechanisms that may be utilized in the processing of metals (Brown 1997). Conventional precipitation technology is still used in many applications for metals remediation, but is expensive, labor intensive, and ineffective below ppm levels. Also, biologically-based exchangers are superior to conventional ion-exchangers because they are resistant to competition from total dissolved solids in the waste waters (such as Ca^{2+}- or Mg^{2+}-hardness).

Previous Work

In a previous report, results by other workers using non-living immobilized microalgal biomass to bind heavy metals was extensively reviewed (Brown 1997). Several laboratories demonstrated chromium, cadmium and lead binding. Binding of lead was tested through 20 adsorption elution cycles, but bioresin capacity declined 15% (Mahan and Holcombe 1992). In laboratory tests, Hg, Cr and U were removed from contaminated groundwaters to low ppb levels (Feiler and Darnall, 1991). Field trials with similar materials demonstrated in-situ removal of Hg to below 10 ppb (U. S. EPA, 1990, Barkley, 1991).

In our own work at bench-scale (Brown 1997), cultures of biomass were isolated and bioresins were produced. Four bioresin materials were tested, including materials derived from two different species of microalgae. Bioresins derived from one biomass type (SDW001a) were found to be highly effective in binding Cu, Ni and Pb, but binding of Ni and Cu by biomass SDW017 on silica gel was less efficient. Silica gel without immobilized biomass was a poor adsorbent for Cu. Polymeric resins with immobilized microalgae at a content of 10% of biomass were considerably less effective in sequestering copper. On average, more Cu passed through these bioresin columns than was bound even at this moderate loading. Efficient recovery of Cu from bioresin columns was achieved by elution with 0.012 N HCl. More than 50 bed volumes of 10 ppm Cu could be passed through a column before breakthrough was achieved. Based on data derived native dried biomass, it was calculated that at least 42 bed-volumes of Cu should be bound by this type of biomass. Thus, these results are in good agreement with the data obtained with the non-immobilized, non-living biomass. Good reproducibility in limited testing was shown for at least 15 cycles with these bioresins.

Other experiments with silica bioresin column SDW001a evaluated the effects of other cations such as Na^+ and Ca^{2+} which had little effect (2.6% reduction in complete binding) on the first 114 μg of Cu^{2+} when applied in 44-fold molar excess (Brown 1997). The Na and Ca were added at twelve-fold the column capacity for Cu. Continuing infusion of this mixture (10 ppm Cu, 100 ppm and Na 100 ppm Ca as Cl salts) resulted in some breakthrough of Cu. Overall these results appear promising, and encouraged us to pursue the presently reported work.

Study Goals

The goals of this study were to test the reliability and longer-term performance characteristics of bioresins and protocols developed in previous work by CLF Technologies, to evaluate methodologies for elution of metals, and to address process economics issues. The study of elution included testing of different types and concentrations of acids as eluants, and evaluation of the potential use of a direct current (electroelution) for the recovery of heavy metals

bound to bioresins. Our previous work supported the concept of the use of dilute acid to elute metals (Brown 1997). However, more detailed information would be required to evaluate such a process.

Project Tasks

The project consisted of two tasks. The first task dealt with regeneration and stability of bioresins. The second task dealt with the possibility of electroelution of metals and process economics.

3. Conclusions

- Bioresin columns were effective in reducing Cu^{2+} from 10 ppm to 2-10 ppb

- Reproducibility within batches and over time was adequate, although measurable variations among batches of bioresins were evident.

- Acid concentrations of 0.0024 N and above were required to elute Cu (pH $\leq$ 2.6); this represented one-fifth acid concentration demonstrated previously - a benefit to process economics and environment.

- Hydrochloric acid was successfully replaced with a less expensive acid (sulfuric).

- DC currents not feasible for elution of copper from the bioresin tested.

- Bioresins tested do not show promise for binding Selenium.

- Binding of Cu^{2+} was largely unaffected by roughly equimolar Fe^{2+} ; copper had particularly high affinity for bioresins.

- Cost of processing/1000 gal was $0.42, of which $0.31 was system capital and the remainder operating cost for base case of 10 ppm Cu and 600 gpm.

- Systems are expected to have costs within the range of $0.06/1000 to $2.00/1000 gal. for metals concentrations 0f 1-30 ppm and flows of 50-1000 gpm.

- Results compare favorably with the sulfide precipitation method and with previous estimates for the bioresin technology made by other workers.

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4. Equipment and Methods

General Technical Description of Production and Testing of Bioresins:
The approach includes the following steps:
1) Grow algae biomass.
2) Harvest and dry the biomass.
3) Immobilize algae on support material (bioresin production).
4) Pack bioresins into columns.
5) Test columns for efficiency of uptake.
6) Test regeneration efficiency.

Biomass Production
Cultures were derived from former mining sites in Gilpin County, CO, and numerous isolates obtained as described previously (Brown 1997). Cultures were maintained in Bold's Bristol Medium (BBM), a standard freshwater formulation (Sigma Chemical Co. Product B5282) with 2 mM $NaHCO_3$ added (Nichols, 1973). The pH was adjusted to 7.0 and buffered with 5 mM HEPES buffer (N-[2-Hydroxyethyl]piperazine-N'[2-ethanesulfonic acid]). Cultures SDW001a and SDW0017 were used as a source of biomass for the production of bioresins in this study. Cultures were grown at 25-27° C, at a light intensity of 200 $\mu E \cdot m^{-2} \cdot s^{-1}$ provided continuously.   A solenoid, needle valve and multi-event timer were used for the automated introduction of 5% CO_2 / 95% air into the cultures Brown 1997). This system was programmed for introduction of short gas pulse every 90 minutes. Batches of 4 liters were grown 25-27 °C under approximately 100 μE m^{-2} s^{-1} illuminance from cool-white fluorescent lamps, and continuously stirred with a magnetic stirrer. After 15-17 days, cultures were harvested by centrifugation at 1560 x G for 5 min, washed twice with distilled water and lyophilized. Some cultures are harvested by filtration onto a mesh screen and lyophilized.

Bioresin Production
The algae were immobilized on silica gel using standard methods (Mahan and Holcombe, 1992) which involved wetting a mixture of silica gel and lyophilized biomass (7.4% wt/wt) with ultrapure water, then drying at 105 °C for 20 min followed by repeat of this wetting and drying twice.

Bioresin Testing
Columns were tested according to the protocols given in Tables 4-12. Loading of each eluant or sample was controlled by the use of a peristaltic pump operated at 2.5 mL/min, and calibrated by measuring the eluted volume. All results are presented $\pm$ SD. Copper was supplied to the columns as a solution $CuCl_2$ in ultrapure water except as otherwise indicated.

For competition experiments with Fe (Table 12), trials were done in which two 10 mL aliquots containing 10 ppm Cu as $CuCl_2$ and 10 ppm Fe as $FeSO_4$ were added to a column. A control with two aliquots of 10 ppm $CuCl_2$ alone was also performed. Efficiency of copper binding and elution was evaluated. The Fe^{2+} solution was freshly prepared for this experiment.

Se (as Na_2SeO_4) (Sigma Chemical Co. Product # S-0882) was applied to the columns at 10 ppm (Table 4).

For all experiments, eluants were introduced from reservoirs through a multiport valve operated manually. Semi-automatic operation was effected by the use of an interval timer with relay which provided power to the peristaltic pump. Wetted surfaces were glass, polypropylene, teflon and silicone rubber. A Typical test solution containing 10 ppm metal was provided to the column. The column was regenerated and bound metal is eluted with 0.012 N HCl, and the

eluant tested for quantitative recovery. The column was then flushed with ultrapure water as indicated in the various protocols.

Atomic Absorption Spectrophotometric Analyses.

Hollow cathode lamps were used to analyze for Cu in the model 5000 Perkin-Elmer Atomic Absorption (AA) Spectrophotometer using graphite furnace techniques (Table 1 and Fig. 1) and the flame atomization technique (Table 2 and Fig. 2). The flame technique was used for the analysis of Se (Table 3 and Fig. 6). Standard curves were linear (Figs. 4-6). The volume required for the flame method was 2-3 mL with 0.5-1 mL actually consumed during the analyses. For the graphite furnace technique, the sample volume loaded into the autosampler (polystyrene autoanalyzer cuvettes) was 1 mL with 25 μL being introduced into the graphite furnace for each analysis. All column fractions analyzed by AA were analyzed directly or diluted 1:10 or 1:20 for analysis by flame atomization. Calibration solutions were diluted from AA Certified Standards #C-6024 for Cu (990 ppm) and #S-9760 for Se (980 ppm) from Sigma Chemical Company, St. Louis, MO. Dilutions for standards were made in 0.8% HNO_3 with 0.32% of the non-ionic detergent Triton X-100.

Electroelution

The column system for electroelution experiments included a DC power supply (400 V), luer-lok (Trademark: Becton Dickinson Corp.) fittings, gold-plated or stainless-steel electrodes, silicone rubber sealants. Other materials of construction were polypropylene and Teflon. In in-column experiments, gold-plated electrodes were set in a male luer fitting and glued in place with silicone rubber sealant. Stainless-steel electrodes (size 20 scalpel blades), silicone tubing reservoirs, and 100 mL beakers with teflon-coated stir bars were used in some of these elution experiments. Electrolytes included 40 mM tris(hydroxymethyl)aminomethane acetate (Sigma Chemical Co., Product T-1258, Lot # 56H5706). Other details of these experiments are given in Table 11.

Technoeconomic Analysis

Assumptions used for the technoeconomic analysis are given in Table 13 along with output for the base case of 10 ppm copper and 600 gpm. A simplified model was constructed using Microsoft Excel and a spreadsheet model using assumptions as in Table 13 which typically underlie chemical engineering estimates such as these. More detail of the actual calculations done and formulas embedded in the worksheet are given in Table 14.

5. Results

Initial Column Testing

An initial columns test was performed according to a protocol used previously (Table 4). The protocol was designed to allow a rapid evaluation of column efficiency in comparison to previous results. These trials indicated that efficient binding and elution of Cu was achieved (Fig. 7) in a manner comparable to that reported previously for this column material (Brown 1997). All applied Cu (68 µg) was bound by the column. Within experimental error, recovery of Cu was quantitative. This test, however, was not a complete test of the column as full column capacity was not tested. The next sections describe more complete testing of these columns and assessments of reliability.

Copper Breakthrough Test and Purity of Effluent

In this test (Tables 9 and 10) about 37 bed volumes of copper were passed through the column before leakage started to occur (Fig. 8). Measurements by graphite furnace AA indicated that less than 10 ppb of Cu was present in the effluent stream in the first 25 mL that passed through this column. The concentration of Cu was less that 2 ppb in the first 10 mL.

Column Reproducibility

The protocol given in Table 5 details one strategy used for more extensive column testing with a column denoted as C1. Ten trials were performed in this test. Each trial consisted of infusing enough Cu into the column until breakthrough occurs (Fig. 9). The shape of these curves appears substantially the same through the series of tests. Careful examination of the intercepts revealed a very reproducible breakthrough 54.9 ± 0.3 bed volumes (Fig. 10, lower panel). In addition, Cu was quantitatively eluted from these saturated columns with 0.012N HCl (Fig. 10, upper panel). The variability in the recovery data was larger that in the column breakthrough tests, as each measurement is composed of several individual determination of Cu concentration.

Several columns and column and column treatments were tested. Overall recovery was good for all columns and treatments (Figs. 11-16). A column (C1) that had been used in previously (Fig. 17, leftmost bar), had a lesser capacity after six months of storage (Fig. 11, 16 and 17). Another column (C2) prepared in the same way, had a lesser capacity (Figs. 12 and 17), but the capacity did not diminish as a result of cycling with or without copper added (Fig. 12). This same column exhibited a small decrease in capacity after exposure to 0.48 N HCl for 18 h (Figs. 13 and 17). This suggests a possible low pH method of storage of these columns for regeneration or to prevent biofouling. Another column (C3) had a capacity greater than C2, but less than C1 even though it had been baked at 105 ^{o}C and stored desiccated for 1 year (Figs. 14 and 17). Column C4 had a capacity of about 25 bed volumes of 10 ppm Cu (Figs. 15 and 17). Overall, there was batch-to-batch variation in column capacity, but good cycle-to-cycle reproducibility. There were some changes upon long term storage (at 4 ^{o}C).

Elution of Copper with Acids

According the experimental plan, we proposed to test various eluants for their ability to release Cu bound by bioresins columns. The eluants tested were water, 0.0012 N HCl, 0.0024 N HCl, 0.0036 N HCl, 0.006 N HCl, 0.012 N HCl, 0.006 N H_2SO_4 , and 0.012 N 0.012 N H_2SO_4 (Fig. 18) (protocols in Tables 6 and 7). This corresponded to a pH range of 1.9-5.5 (Fig. 19). A solution of 20 mL of 10 ppm Cu was loaded onto to the column in each case. This is just about the breakthrough for this column of volume 0.75 mL total bed volume. It can be seen that in all cases, total recovery of Cu from the experiment was good to excellent, indicating that an accurate

description of the mass balance of Cu in this system was achieved. Water and 0.0012 N HCl were insufficient to elute Cu from the column (Fig. 4). Acid concentrations of 0.0024 N and above were required for elution. This corresponded to pH's at or below 2.6 (Fig. 19). The critical pH range for elution was pH 2.6-2.9. The lowest acid concentration tested, 0.0012 N HCl, was a marginally effective eluant and had a high standard deviations for efficiency of binding indicating carry-over of Cu between runs. This was confirmed by the fact that the apparent binding efficiency of the first trial with this eluant was high, but that of subsequent runs was lower (the apparent lower binding was carry-over of Cu) (data not shown). Responses to sulfuric and hydrochloric acids appeared to be identical (Figs. 18 and 19).

Elution with Electrical Fields

Nine experiments were done (Table 11). Experiments in which electrodes were positioned in-line at either end of the column were unsuccessful, regardless of the electrolyte because bubbles formed and interrupted the electrical connection (Table 11, expts. 1-3). Electrode and electrolyte testing without bioresins indicated that the combination of stainless steel plate electrodes yielded good current flow and electrode stability (Table 11, expts. 4-7). The most promising result was with the application of 150 V with tris acetate electrolyte resulting in 2.9% of the added copper eluted after 30 min (Table 11, expt. 8). Current was 3-3.5 mA. Some copper leached out in the control with no current (0.32%). An experiment in which the bioresin was extruded from the column into a tris acetate suspension resulted in better current flow, but release of copper was no better than the control (Table 11, expt. 9). Also, shearing forces in the stirred bath resulted in mechanical breakdown of the bioresin. Overall the results do not make a convincing case for the feasibility of this method for elution of copper.

Tests for Binding of Selenate

Se binding was tested on a limited basis with two bioresins. It was found that the selenate anion was very poorly bound, or not at all bound to these two bioresins (Fig. 20). The bioresins appeared to be acting as cation exchangers, since the binding of Cu^{2+} was excellent (Fig. 20), and Ni^{2+} and Pb^{2+} were also bound by bioresins (Brown 1997). It appears from these results that these bioresins do not show much promise for binding Se, especially since the amount of Se used was low (Table 4).

Competition of Iron with Copper Binding

Elution and recovery of Cu^{2+} was similar regardless of whether 10 ppm Cu^{2+} (0.157 mM) or 10 ppm Cu^{2+} with 10 ppm Fe^{2+} (0.179 mM) (Fig. 21). However there was a small decrease in Cu-binding in the presence of Fe^{2+} (Figs. 21 and 22). This was see particularly evident in the second 10 mL fraction where Cu leakage increased from 0.2% to 2.2% (Fig. 22). However, it is remarkable that leakage of copper increased by this small amount, as this column was already near saturation as indicated by the 0.2% leakage. It appears that iron does not occupy the copper sites to any great extent or the affinity for copper was higher than for iron. Protocol for this experiment is in Table 12.

Technoeconomic Analysis

Previous technoeconomic analyses by other workers were re-evaluated based on our own assumptions about the process and these results. Assumptions and base case results are given in Table 13 for the 10 ppm Cu and 600 gpm (base case). Formulas used to construct this spreadsheet are given in Table 14. The analyses indicated that the cost of processing/(1000 gal) was $0.42, of which $0.31 was system capital and the remainder operating cost. A sensitivity analysis of this spreadsheet model was performed in which values for metal concentration and flowrate were varied. Total processing cost was a linear function of metal concentration (Figs. 23

and 24), and cost increased non-linearly at low flowrates (Figs. 24 and 25). Across all combinations of concentrations and flowrate, capital was a larger component of total cost than the operating cost especially at high metal concentration (Figs. 25- 27). Of the components of the operating cost, chemicals and biomass were significant at high metal concentration and labor at low flowrate. These results appear to compare favorably with the sulfide precipitation method and with previous estimates for the bioresin technology made by other workers.

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6. Analysis of Results and Technoeconomic Analysis

Binding Capacity and Reproducibility.

The efficiency of columns in reducing copper from 10 ppm to less than 10 ppb was encouraging (Fig. 8). Reproducibility within batches and over time was considered to be adequate (Figs 7-18), although measurable batchwise variations were evident. Some early work with similar bioresins found measurable diminution of column capacity after only 5-20 cycles with lead (Mahan and Holcombe 1992). Our work with other bioresins and copper detected no such diminution. Whether this is due to greater reactivity of lead under these conditions, or whether differences in bioresins are responsible for these observations is unknown.

Overall capacity of different bioresin batches was 25-50 bed volumes of 10 ppm copper. By comparison, field test of other resins (with considerably different composition) revealed binding of mercury was efficient for up to 500 bed volumes when supplied at between 0.3 and 1 ppm influent concentration (US EPA 1990). The concentration of mercury in their effluent was less than 10 ppb for the first 500 bed volumes. Our results with copper therefore compare very well with the results for lead as the concentration that we used was more than 30-100 fold higher when considered on a molar basis. They used a flow of 6 bed volumes/h. Our flowrate was about 220 bed volumes/h (2.5 mL/min).

Elution Methods

Other workers have used acid as high as 0.5 N to elute lead from bioresins (US EPA 1990), although no data were given indicating whether lower acid concentrations were tested. In a study of similar bioresins a range of acid concentrations between 0.012 and 0.12 N HCl and HNO_3 were found to be effective (Mahan and Holcombe 1992). We extended this range to demonstrate quantitative elution at 0.0024 N HCl (Fig. 18), one-fifth the concentration demonstrated to be effective previously (Mahan and Holcombe 1992, Brown 1997). Also our demonstration of the utility of the less expensive sulfuric acid (Fig. 18) is also significant to the technoeconomic analysis. The demonstrated five-fold reduction in acid requirement is beneficial to both process economics and for environmental considerations.

In a similar attempt to improve process economics and reagent requirements, the possible use of DC current to elute metals was also investigated. The application of DC electric currents applied through electrodes inserted into the ground is becoming a popular method for *in situ* remediation of toxic metals in contaminated soils (Lageman 1993, Cox et al. 1996) and is termed as electrokinetic remediation or electroremediation. Electrodes are inserted into the soil at intervals of several meters and a current is applied for weeks to months and the ions migrate to the cathode. A similar approach has been applied to the enhanced elution (electroelution) of metals complexes from conventional anion-exchange resins (Fleming and Cromberge 1984, Martins 1993). However, this technique has not been applied to the stripping of metals from bioresins of the type described here. The advantage of such an approach would be the minimization or elimination of the use of acidic or basic chemical eluants for the release of metals from the bioresin. Minimization of consumption of reagents could be a significant benefit in materials handling, environmental impact and costs. However, our results did not clearly demonstrate that this is possible (Table 11). At best, it required 150 v for 30 min with 40 mM electrolyte and was less than 3% efficient in elution (Table 12, expt. 8). The chemistry of this process is very complex, and involves the interaction of resin, possible complexing agents, electrolyte, electrode types and system geometry.

Affinity of Selenate and Iron to Bioresin Columns

Non-living biomass has been reported to be effective in binding Se in preliminary work done with some freshwater algae (Mahan et al. 1989). However, for most algae Se-binding was not as effective as the binding of the cationic species such as copper and lead, but greater than the binding of cobalt. There are reasons to believe that Se-binding may be possible. For example, Se exists mostly as selenate in seawater at the extraordinarily low concentration of 30 ppt (Haygarth 1994), and phytoplankton algae can concentrate and utilize Se in the presence of the 900 ppm S (2700 ppm sulfate) in seawater (Riley and Skirrow 1975). This translates to a molar ratio of 13 million:1 for S:Se. In our previous work on freshwater algae, a 2500-fold molar excess of sulfate over selenite failed to have any measurable effect on Se-assimilation in freshwater phytoplankton, nor did a 2500-fold excess of sulfate substitute for the Se requirement (Wehr and Brown 1985). This argues for extremely specific Se-binding polymers in these organisms. This is in sharp contrast to ion-exchange resins which have no specificity for selenate or selenite over sulfate (Maneval et al. 1985). However, even at low total volume of 10 ppm selenate, the vast majority of the selenate was not bound by two bioresins tested. (Fig. 20). At least for these two bioresins, the anion exchange capacity was very low, and would be unusable in any process. There is still some potential based on the literature, but the present work fails to demonstrate effectiveness. These results support the concept that the heavy metal binding is a cation exchange process.

The fact that column efficiency for Cu^{2+} was decreased by only a small amount (2%) in a nearly saturated column in the presence of Fe^{2+} (Figs. 21 and 22) is a positive result for situations when the remediation of the more closely regulated copper is desired in the presence of iron. These data are reminiscent of previous results in which Na^+ and Ca^{2+} had little effect (2.6% reduction in binding) even when applied in 44-fold molar excess (Brown 1997). While the lack of effect of sodium and calcium have been noted previously (US EPA 1990), this is the first report of the relative lack of competition for sites between Cu and Fe. Work on dried marine algal biomass has shown that Cu is bound with higher affinity than Fe, depending on biomass type and pH (Ramelow et al. 1992). Previous work has also shown that both Zn and Cd apparently compete for the same sites as Cu in some processed biomass preparations (de Carvalho et al. 1995). However, copper tends to have a particularly high affinity for bioresins, and has been shown to have a greater affinity than zinc or cadmium ions (de Carvalho et al. 1995), but some preparations have a higher affinity for cadmium than copper (Leusch et al. 1995). Generalized conclusions require study of competition with the same bioresins under carefully controlled conditions. These differences in affinity can be potentially exploited for treatment of particular waste streams.

Technoeconomic Conclusions

Previously, we analyzed some cost data for treatment of copper-containing waste sites at Summitville in Colorado. That process was based on sodium sulfide and ferrous sulfate combined to produce ferrous sulfide, which is then allowed to react to produce insoluble cupric sulfide. We estimated the cost of operation for one of these units is $6.60 to $46 per 1,000 gal treated (calculations in Brown 1997 based on data of Leitz et al., 1995). In previous estimates of bioresin technology, Darnall estimated operating cost for a bioadsorption plant (using immobilized non-living algae) at $0.25-5.00/1000 gal depending on process details (Feiler and Darnall, 1991). Those calculations were based on a 600 gpm unit. Our new analyses indicate a cost per /1000 gal processed of $0.42/1000 gal for the 10 ppm and 600 gpm base case (Table 13) to $1.98/1000 gal. for a 50 gpm system with 30 ppm heavy metal contamination (Fig. 25). It is anticipated that this would be at the lower end of capacity and higher end of concentrations that will be encountered in field situations. Based upon the experimental results of this study, and this new technoeconomic model, the current upper end of the estimate for heavy metals remediation has been reduced to less than $2/1000 gal. compared to the previously reported $5/1000 gal (Feiler and Darnall, 1991). At the low end we calculate a total processing cost of $0.06/1000 gal

for treatment of 1 ppm heavy metal for a 1000 gpm system (Fig. 25). This represent a new lower limit of estimate for such a system. Also, we confirm the general reasonableness of the previous model and report in detail the formulas used to calculate this model (Table 14). Such level of detail has not been reported previously.

The cost analysis has also been affected by the reduction in acid requirement by one-fifth and the possible use of the less expensive sulfuric acid for elution. The observation of the lack of competition between iron and copper binding for one bioresin used (Fig. 22), also has impacts as this observation has a major impact on assessment of column capacity in situations when both of these metals are present. It would be advantageous when copper is the metal of greater environmental importance. However, the use of bioresins with greater affinity of iron is not ruled out by these results.

This project was responsive to the need for improvement of existing processes for treatment of heavy metal contaminated of water supplies. A particular need was seen for processes for removing heavy metals such as copper from mine wastes, industrial waters or soil washing effluents. The present results demonstrate that the use of bioresins has the potential to fulfill the requirements for economically viable recovery for reuse and safe disposal.

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7. References

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Tables and Figures

Table 1. Instrumental operating parameters used for the Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer graphite furnace analyses for Cu.

Instrumental					
Element: Cu					
Instrument Model 5000		Technique: Graphite Furnace	Energy : 67		
Wavelength 324.8 nm peak	Slit 0.7 Low	Signal Measurement: Peak Area	Lamp mA: 25	Lamp: Hollow cathode Cu	
Calibration					
Solution	*Concentration (μg/L)*	*Autosampler Location*	*Volume (μL)*		
Blank	0	1	25		
Standard 1	4.85	2	25		
Standard 2	14.55	3	25		
Standard 3	19.41	4	25		
Standard 4	24.26	5	25		
Samples		Various	25		
Calibration Type: Linear:	Matrix Modifier: none				
Furnace Time/Temperature Program					
Step	*Temperature °C*	*Ramp (s)*	*Hold Time (s)*	*Read Step*	
1	100	30	15		
2	1000	5	15		
3	100	15	10		
4	2300	0	4	Yes	
5	2700	1	4		
Injection Temp: 20 °C	Gas: N$_2$				

Table 2. Instrumental operating parameters used for the Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer flame analyses for Cu.

Instrumental					
Element: Cu					
Instrument Model 5000		Technique: Flame AA	Lamp current 12 mA	Energy: 70	
Wavelength 324.8 nm peak	Slit 0.7 nm	Signal Measurement: Peak Area	Acetylene Fuel Flow: 15 Air Flow: 25	Integration time: 5 seconds	Lamp:hollow cathode Cu
Calibration					
Solution	*Concentration (mg/L)*				
Blank	0				
Standard 1	0.99				
Standard 2	1.98				
Standard 3	2.97				
Standard 4	3.96				
Standard 5	4.95				
Calibration Type: Linear:	Matrix Modifier: none				

Table 3. Instrumental operating parameters used for the Perkin-Elmer Model 5000 Atomic Absorption Spectrophotometer flame analyses for Se.

Instrumental					
Element: Se					
Instrument Model 5000		Technique: Flame AA	Lamp current 12 mA	Energy: 50	
Wavelength 196 nm peak	Slit 2.0 nm	Signal Measurement: Peak Area	Acetylene Fuel Flow: 15 Air Flow: 25	Integration time: 5 seconds	Lamp:hollow cathode Se
Calibration					
Solution	*Concentration (μg/L)*				
Blank	0				
Standard 1	1.96				
Standard 2	3.92				
Standard 3	5.88				
Standard 4	9.80				
Standard 5	24.5				
Calibration Type: Linear:	Matrix Modifier: none				

Table 4. Protocol for loading and elution of Cu or Se from bioresin columns for experiment reported in Figs. 7 and 20. In the experiments described in this report, flow rate was 2.5 mL/min. One or two steps are pooled in each eluant tube.

Elution Step	Pooled Eluant Tube	Eluant Component	Time (min)	Volume of Eluant (mL)	# Dead Volumes of Column System	Pooled Volume in Eluant Tube
1 (loading)	A	10 ppm Cu or Se (loading solution)	2.72	6.8	3	
2 (flush)	A	H_2O	2.72	6.8	3	13.6
3 (acid stripping)	B	0.012 N HCl	2.72	6.8	3	
4 (flush)	B	H_2O	2.72	6.8	3	13.6
5 (flush)	C	H_2O	5.44	13.6	6	13.6

Table 5. Protocol for loading and elution of metals from bioresin columns. In these experiments volume to breakthrough of Cu was determined in consecutive trials (Fig. 9). Flow rate was 2.5 mL/min. Depending on the experiment, some of the early fractions are sometimes pooled.

Elution Step	Pooled Eluant Tube	Eluant Component	Time (min)	Volume of Eluant (mL)	# Dead Volumes of Column System	Pooled Volume in Eluant Tube
1 (loading)	A-I	10 ppm Cu (loading solution)	1.83	4.6	2-6	4.6-13.6
2 (acid stripping)	J	0.012 N HCl	5.5	13.6	6	
3 (flush)	K	H_2O	5.5	13.6	6	13.6

Table 6. Protocol for loading and elution of Cu from bioresin columns. Flow rate was 2.5 mL/min. This was the protocol for elution with test acids (0.0036 N and below and water at pH 5.5). Protocol for Figs. 18 and 19.

Elution Step	Eluant Tube	Eluant Component	Time (min)	Volume of Eluant (mL)	# Dead Volumes of Column System
1 (loading)	A	10 ppm Cu (loading solution)	8	20	9
2 (flush)	B	H_2O	3	7.5	3
3 (test)	C	Test Acid	3	7.5	3
4 (acid stripping)	D	0.012N HCl	3	7.5	3
5 (flush)	E	H_2O	3	7.5	3

Table 7. Protocol for loading and elution 0.006 N acid and higher concentrations (Fig. 18). Flow rate was 2.5 mL/min.

Elution Step	Eluant Tube	Eluant Component	Time (min)	Volume of Eluant (mL)	# Dead Volumes of Column System
1 (loading)	A	10 ppm Cu (loading solution)	8	20	9
2 (flush)	B	H_2O	3	7.5	3
3 (acid stripping)	C	0.012 N HCl	3	7.5	3
4 (flush)	D	H_2O	3	7.5	3

Table 8. Protocol for loading and elution of Cu from bioresin columns used in testing for column efficiency (Figs. 11-17). Flow rate was 2.5 mL/min.

Elution Step	Eluant Tube	Eluant Component	Time (min)	Volume of Eluant (mL)	# Dead Volumes of Column System
1 (loading)	A	10 ppm Cu (loading solution)	8	20	9
2 (loading)	B	10 ppm Cu (loading solution)	3	7.5	3
3 (test)	C	H_2O	3	7.5	3
4 (acid stripping)	D	0.012N HCl	3	7.5	3
5 (flush)	E	H_2O	3	7.5	3

Table 9. Protocol for breakthrough (column saturation) experiment with Cu with bioresin columns. Flowrate was 2.5 mL/min. This was the protocol used for data collection for Fig. 8. These fractions ere analyzed by flame AA.

Test Step	Loading Solution	Time (min)	Volume (mL)	# Dead Volumes of Column System
A-C	10 ppm Cu	2	5	2
D-Q	10 ppm Cu	1	2.5	1
R-V	10 ppm Cu	4	10	4

Table 10. Protocol for breakthrough (column saturation) experiment with Cu with bioresin columns. Flow rate was 2.5 mL/min. This was the protocol used for data collection for Fig. 8. These fractions were analyzed by graphite furnace AA.

Test Step	Loading Solution	Time (min)	Volume (mL)	# Dead Volumes of Column System
A-D	10 ppm Cu	2	5	2

Table 11. Results of electroelution experiments. Experimental conditions of voltage, electrodes and other conditions are given in the table. Current and percent recovery of Cu after application of the electric current and for no voltage controls are given. Overall this technique was not demonstrated to be an effective method for the elution of copper.

Expt. #	Volts	mA	Time (min)	Configuration	Electrodes	Electrolyte	% Recovery of Cu	Control (no voltage)	Comments
1	200	0	20	In column w/ polyethylene frit	Gold-plated pin	water	0.30 ± 0.06	none	Current does not pass through because of bubbles, low conductivity, and column frit
2	300	0	30	In column w/ polyethylene frit	Gold-plated pin	100 ppm NaCl and 100 ppm $CaCl_2$	<4.4	-	Analytical interferences make quantitation difficult. However, current does not pass through because of bubbles, and column frit
3	300	0	30	In column w/ glass fiber frit	Gold-plated pin	40 mM tris acetate	4.4	4.3	Current does not pass through because of electrolytically produced bubbles
4	300	0	5	Test of electrodes in dish	Gold-plated pin	25 mL of ultrapure water	-	-	No copper added (electrode configuration test). Results: conductivity too low
5	175	150	5	Test of electrodes in dish	Gold-plated pin	25 mL of 40 mM tris acetate	-	-	No copper added (electrode configuration test). Results: Good current flow, but electrode pitting
6	25	30	5	Test of electrodes in dish	Gold-plated pin	25 mL of 1000 ppm NaCl	-	-	No copper added (electrode configuration test). Results: cathode consumed
7	30	25	5	Test of electrodes in dish	Stainless steel blade	25 mL of 40 mM tris acetate	-	-	No copper added (electrode configuration test). Results: electrodes stable and current stable
8	150	3-3.5	30	In column w/	Stainless	20 mL of	2.9	0.32	Stable current of 3-3.5 mA

| | | | | glass fiber frit and electrodes in external reservoirs | steel blade | 40 mM tris acetate | | | passes through column if voltage kept ≤ 150 V. Higher voltages cause bubbles which break electrical connection |
| 9 | 30 | 62-92 | 90 | Bioresin extruded into 100 mL beaker with 20 mL of electrolyte. Solution was stirred. | Stainless steel blade | 40 mM tris acetate | 9.8 | 14 | Good electrical connection allows high current flow at low voltage. Shearing caused some mechanical breakdown of bioresin, releasing Cu in both control and experimental |

Table 12. Protocol for loading and elution competition test of Cu and Fe. In experimental trials 10 ppm Fe^{2+} is added as $FeSO_4$ to the 10 ppm Cu^{2+} as $CuCl_2$. Results are given in Figs. 21 and 22.

Elution Step	Eluant Tube	Eluant Component	Time (min)	Volume of Eluant (mL)	# Dead Volumes of Column System
1 (loading)	A	10 ppm Cu (loading solution)	4	10	5
2 (loading)	B	10 ppm Cu (loading solution)	4	10	3
3 (test)	C	H_2O	3	7.5	3
4 (acid stripping)	D	0.012N HCl	3	7.5	3
5 (flush)	E	H_2O	3	7.5	3

Table 13. Assumptions and results for base case economic analysis. A spreadsheet (Microsoft Excel) was constructed which modeled these results under combinations of metal concentration and flowrate. These results are plotted in Figs. 23-28. System capital accounts for $0.31 of the $0.42/1000 gal cost for processing. These costs do not include costs or credits associated with downstream processing or reuse of the metals, or the costs for buildings. See formulas used in Table 14.

Base Case Assumptions:

Flow Rate:	600 gpm
Metal Content:	10 ppm
Breakthrough:	50 pore volumes
Reactor Volume:	17,230 gal
Regeneration:	1 per 24 hours
System Capital:	$800,000
Chemicals	25.40/day
Replacement Time:	1000 cycles (3 years)
Column Capacity:	33.48 grams/day

Base Case Economic Analysis:

	$/lb	*Cap. x10³$*	*$/1000 gal*
Chemicals	0.04	5	0.029
Microalgae	0.01	50	0.050
Labor			0.016
Pump Energy		10	0.020
System Capital		800	0.310
Total			0.425

Table 14. Formulae used in spreadsheet (Microsoft Excel) which modeled bioresin process under combinations of metal concentration and flowrate. These formulas were used to generate the base case (Table 13) and program output (Figs. 23-28). Blank spreadsheet rows are not printed in order to save space.

|	D	E	F	G	H	I	J	K
4	**Base Case Assumptions:**				**Base Case Analysis**	$/lb	Capital M$	$/1000 gal
5	Flow Rate:	600	gpm		Chemicals	0.04	5	=F21/(50*E8/1000)
6	Metal Content:	10 ppm			Microalgae	0.01	50	=0.05*F20
7	Breakthrough:	50 pore volumes			Labor			=0.016*600/E5
8	Reactor Volume:	=17230*E5/600			Pump energy		10	0.02
9	Regeneration:	1 per 24 hours			Operating Cost			=SUM(K5:K8)
10	Capital Cost:	=F31			Capital Costs		=(E10+J8+J6)/1000	=+J10/F22/50/E8*1000
11	Chemical Costs:	=25.4*E5/600	$/day		Total Cost ($/1000gal)			=SUM(K9:K10)
12	Replacement time:	1000 cycles (3 years)						
13	Column Capacity	=33.48*E5/600	grams/day					
17	**Process Input Parameters**							
18	Concentration Cu^{2+}:		10	ppm				
19	Breakthrough:		=10/F18*50	pore volumes				
20	Regeneration:		=50/F19	per day				
21	Chemical costs:		=E11*F20	per day				
22	Column Replacement:		=3/F20	years				
26	**Capital Cost Factors**							
28	**Base Case**		New case					
29	600 gal/min	Factor						
31	800000	0.8	=D31*(E5/600)^E31					
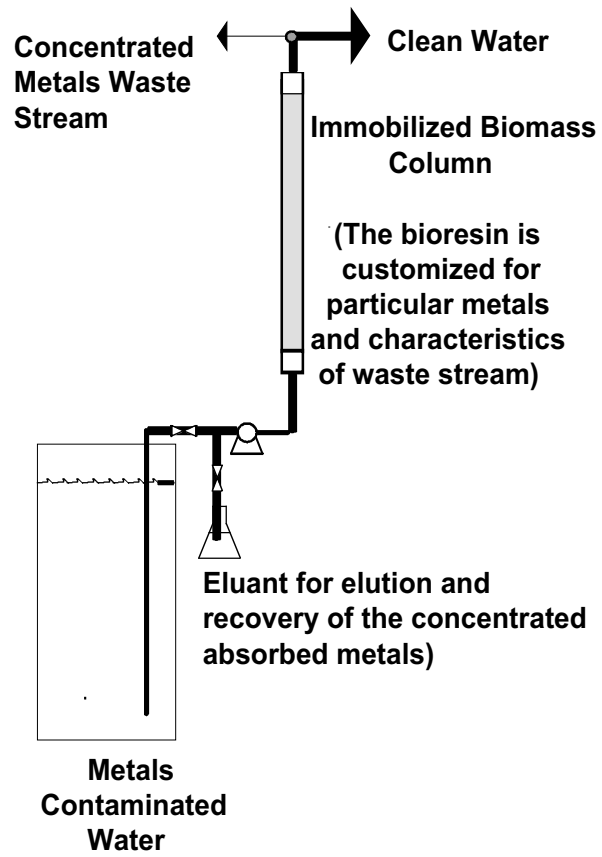
Figure   1.
Schematic of immobilized biomass system for sequestration and recovery of heavy metals.

Column Test System

Eluants

Valve

Column

Pump

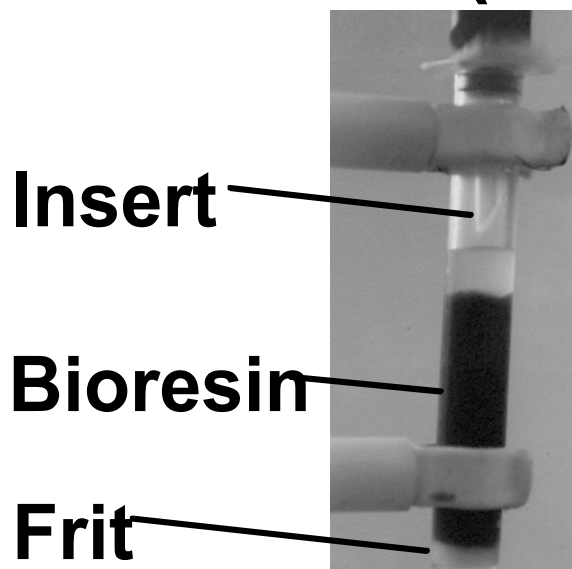Timer

Column (Detail)

Insert

Bioresin

Frit
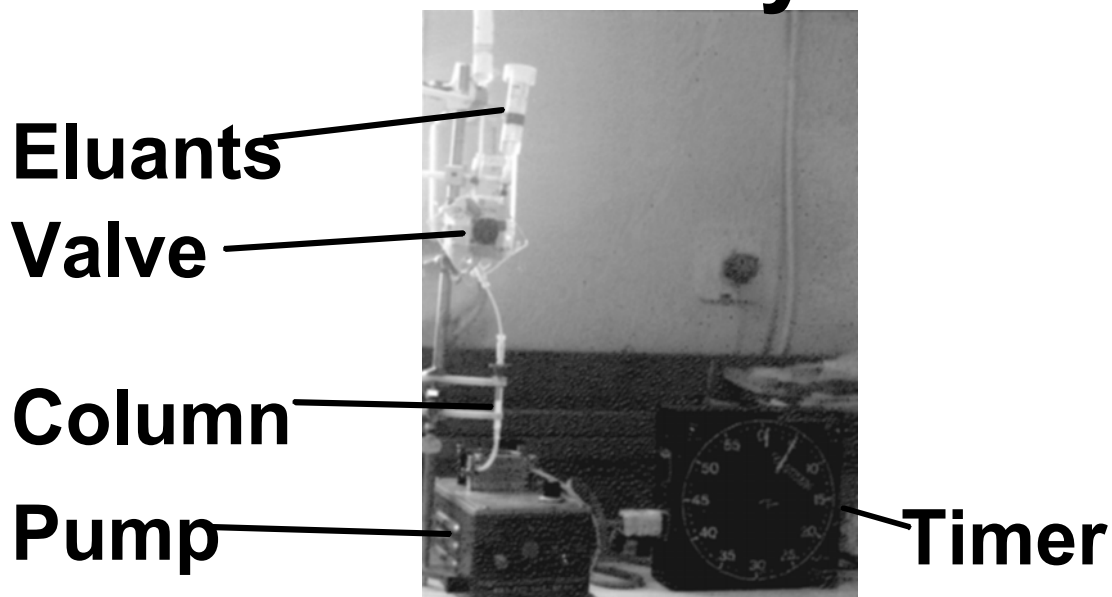
Figure 2. System used to evaluate the efficiency of bioresins. Upper photo shows the complete system including eluant reservoirs, column, peristaltic pump, and timer. The timer controls the operation of the pump. The lower photo shows the detail of the polypropylene column containing silica-based bioresin. System is pictured diagrammatically in Fig. 3.
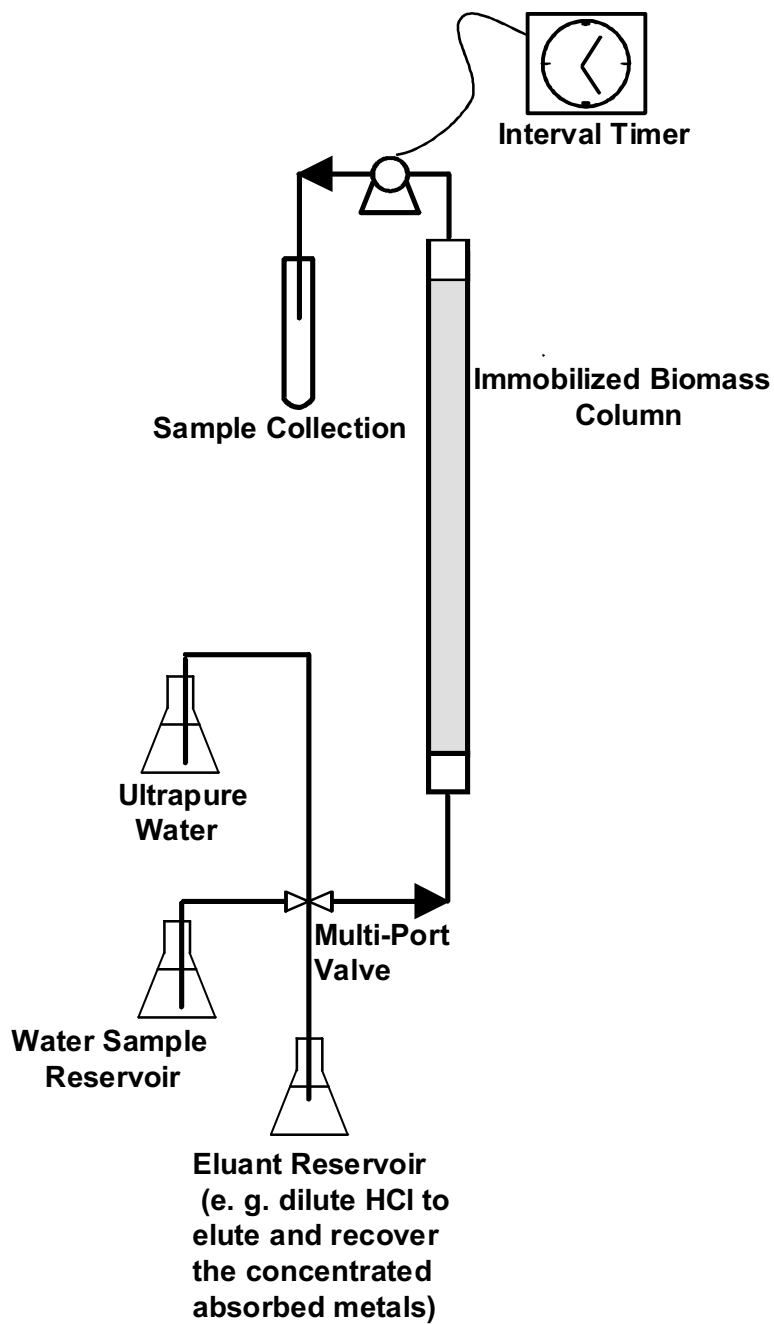
Figure 3. System used to evaluate the efficiency of bioresins. system includes eluant reservoirs, column, peristaltic pump, and timer. The timer controls the operation of the pump. See photos of components in Fig. 2
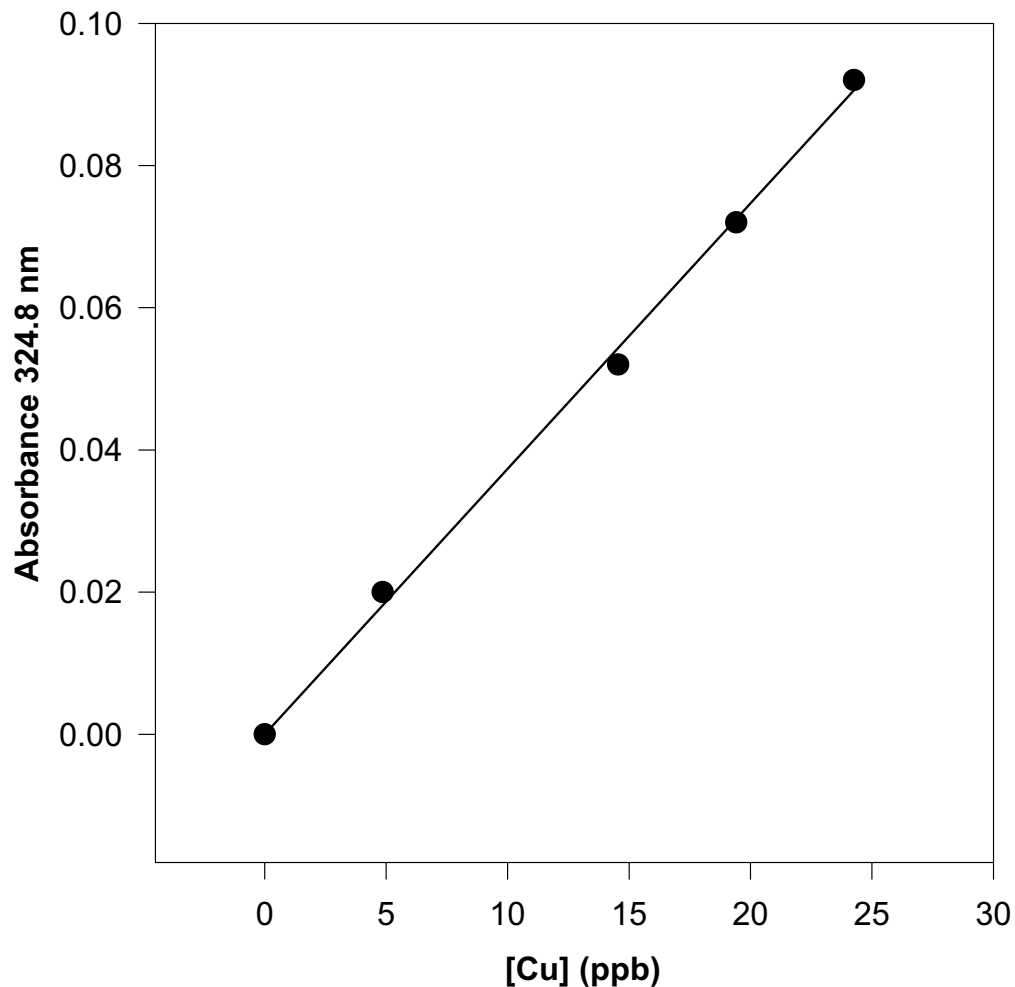
Cu Standard Curve Furnace AA

Figure 4. Calibration curve for copper using the Perkin-Elmer Model 5000 atomic absorption spectrophotometer   A hollow cathode lamp was used to analyze for copper in the model 5000 Perkin-Elmer Atomic Absorption (AA) Spectrophotometer using flame atomization and graphite furnace techniques. Dilution was not often necessary with flame atomization due to the higher capacity of the flame system. Selenium was measured by the flame technique in graphite furnace mode. This instrument provides a reproducible linear response for Cu. A calibration was done for each day's analysis.
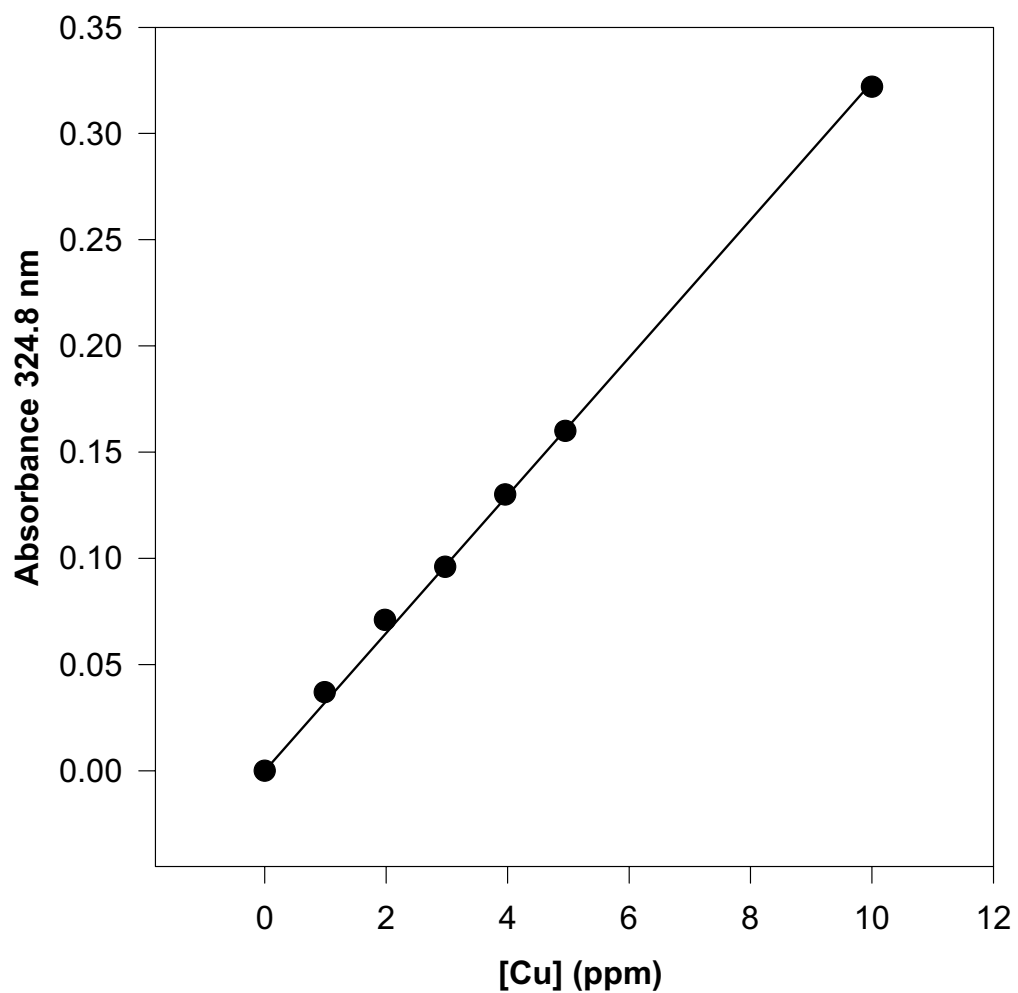
- 34 -

Cu Standard Curve Flame AA

Figure 5. Calibration curve for copper using the Perkin-Elmer Model 5000 atomic absorption spectrophotometer in flame mode. This instrument provides a reproducible linear response for Cu. A calibration was done for each day's analysis.
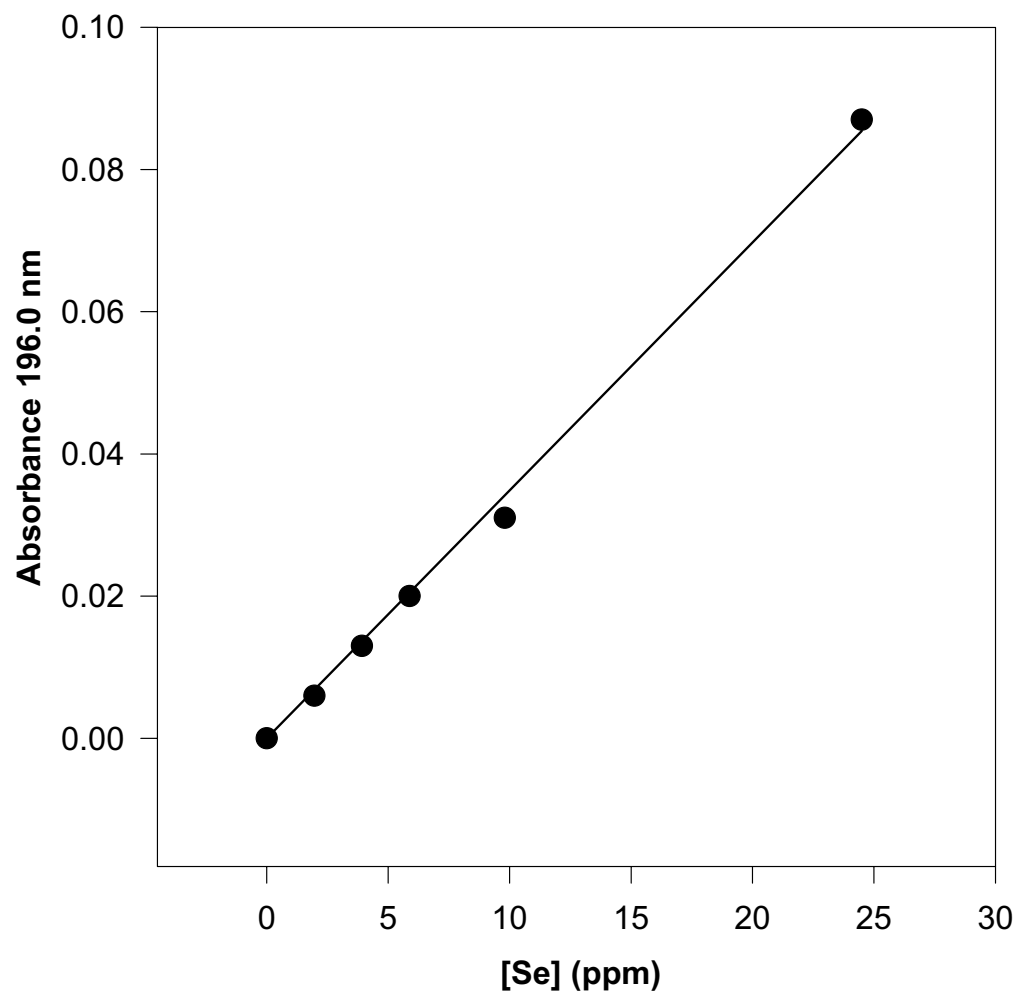
Se Standard Curve Flame AA

Figure 6. Calibration curve for selenium using the Perkin-Elmer Model 5000 atomic absorption spectrophotometer in flame mode. This instrument provides a reproducible linear response for Se. A calibration was done for each day's analysis.
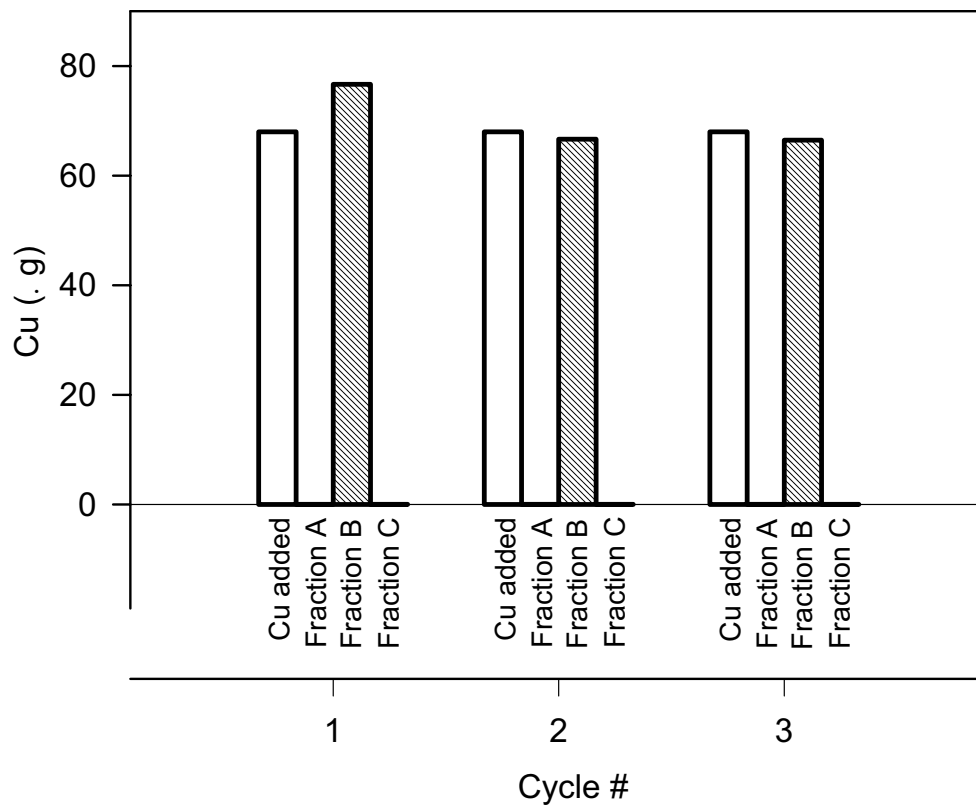
Figure 7. Binding and elution of Cu in experiment done just before breakthrough trials (Fig. 8). Protocol for this experiment is in Table 4. A solution of 10 ppm of Cu is added to a bioresin of SDW001a at a biomass at a loading of 7.4%. An aliquot of 6.88 mL is added to a column at a flow rate of 2.5 mL/min. Fraction A represents the efficient loading of Cu as no leakage of Cu was detected (detection limit was 0.03 ppm). Quantitative elution was achieved in Fraction B.
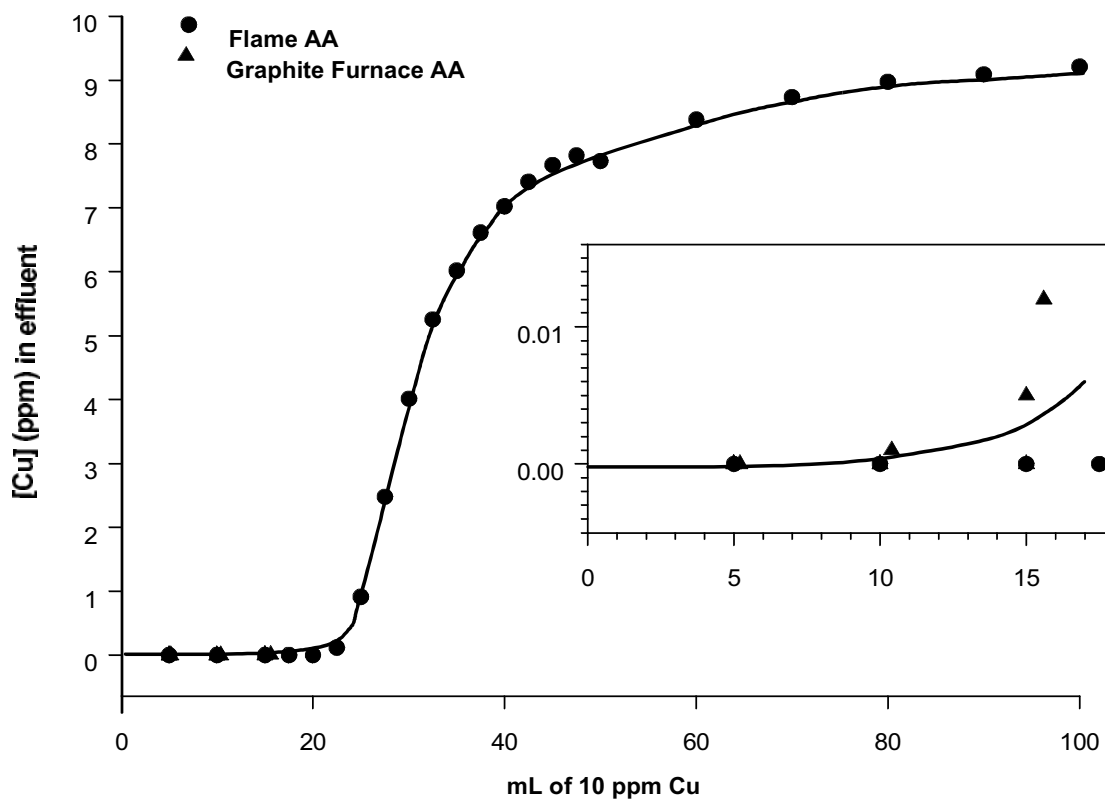
Figure 8. Column capacity test for Cu. A solution of 10 ppm CuCl$_2$ was added to a bioresin of SDW001a biomass at a loading of 7.4%. The column effluent was monitored for Cu, and as shown Cu was below ppm levels until 25 mL had passed through the column. Cu-content of the column effluent was below 10 ppb for the first 15 mL. Bed volume was 0.68 mL. Inset shows and expanded scale for this range. Column C1 of Fig. 17 was used for this test. Protocol for these tests is given in Tables 9 and 10.
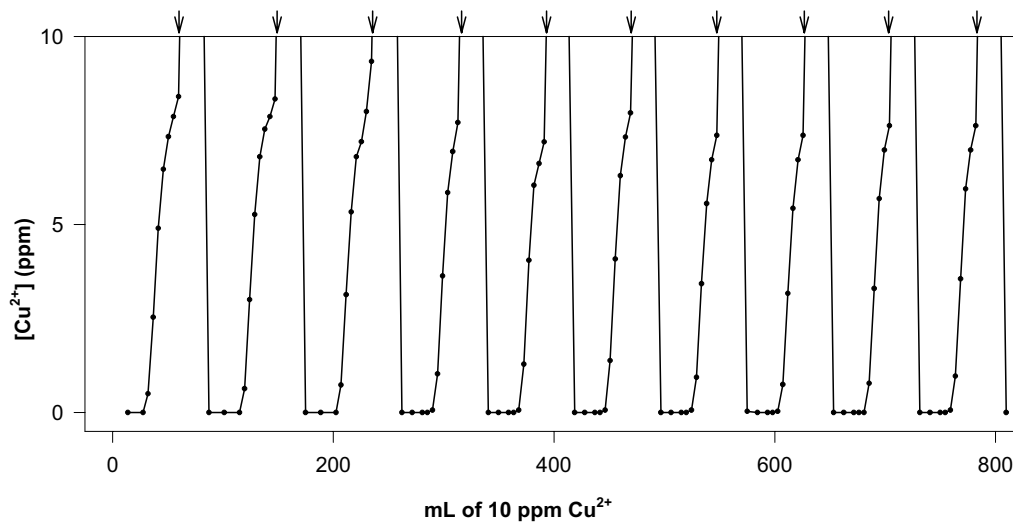
Figure 9. Repeated column capacity, binding and elution tests for Cu. This is the same experimental series as Fig. 10 which shows breakthrough volumes (intercepts) and recovery. First 3 trials were on a different sample collection protocol, so the number of data points is less prior to breakthrough. Elution profiles, breakthrough, etc. are remarkably similar between trials demonstrating the excellent reproducibility of this system. For each trial 0.012 N HCl was added after breakthrough (arrows) to elute Cu followed by a water rinse. See protocol in Table 5. Column C1 (leftmost bar) of Fig. 17 was used for these tests.
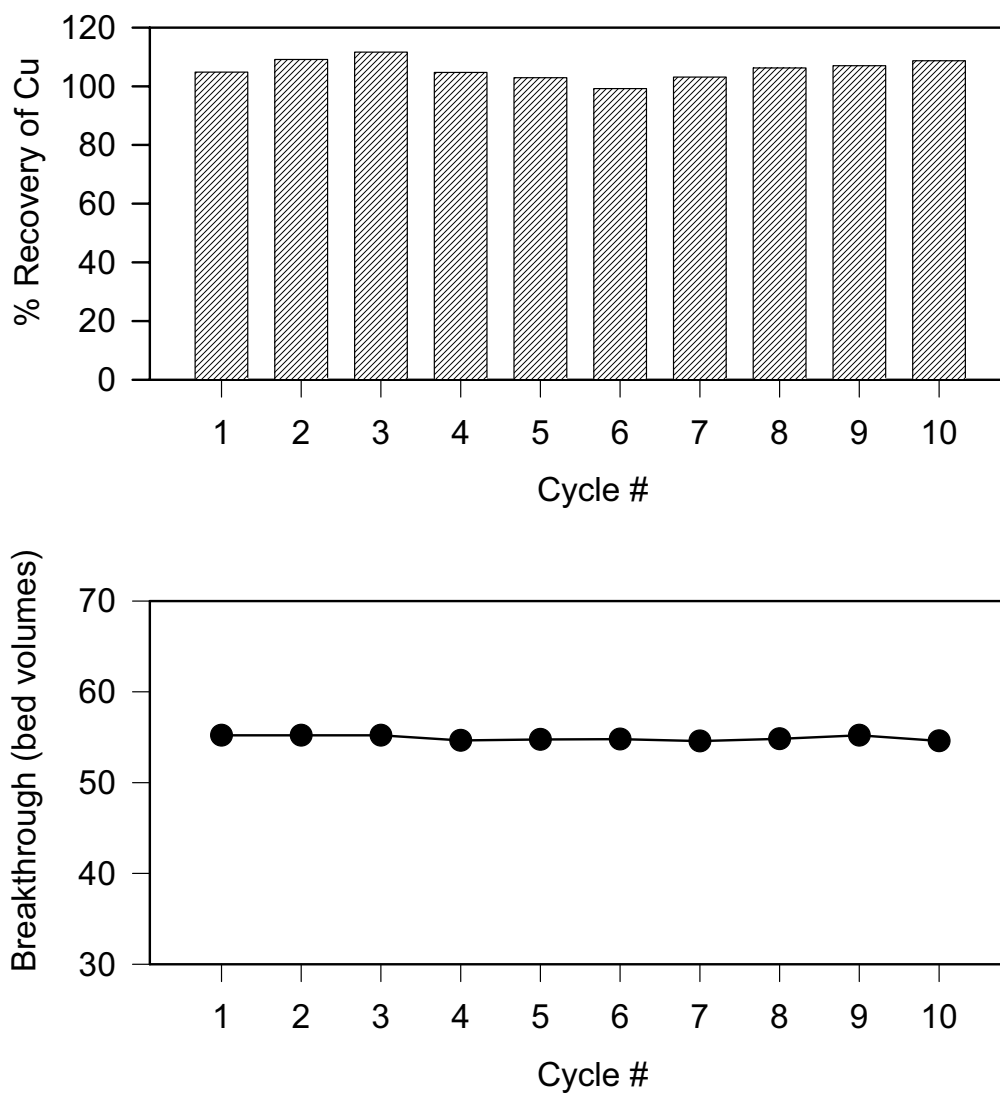
Figure 10. Other measured parameters in column capacity test for Cu. Upper panel represents percentage recovery of Cu from column after breakthrough (for protocol see Table 5). Variability is due to experimental error, as each measurement is comprised of the sum of several measurements for Cu. Bottom panel is calculated breakthrough volumes as determined from the x-intercepts of Figure 9 (first 2 non-zero data points are used in this calculation). Column C1 (leftmost bar) of Fig. 17 was used for these tests.
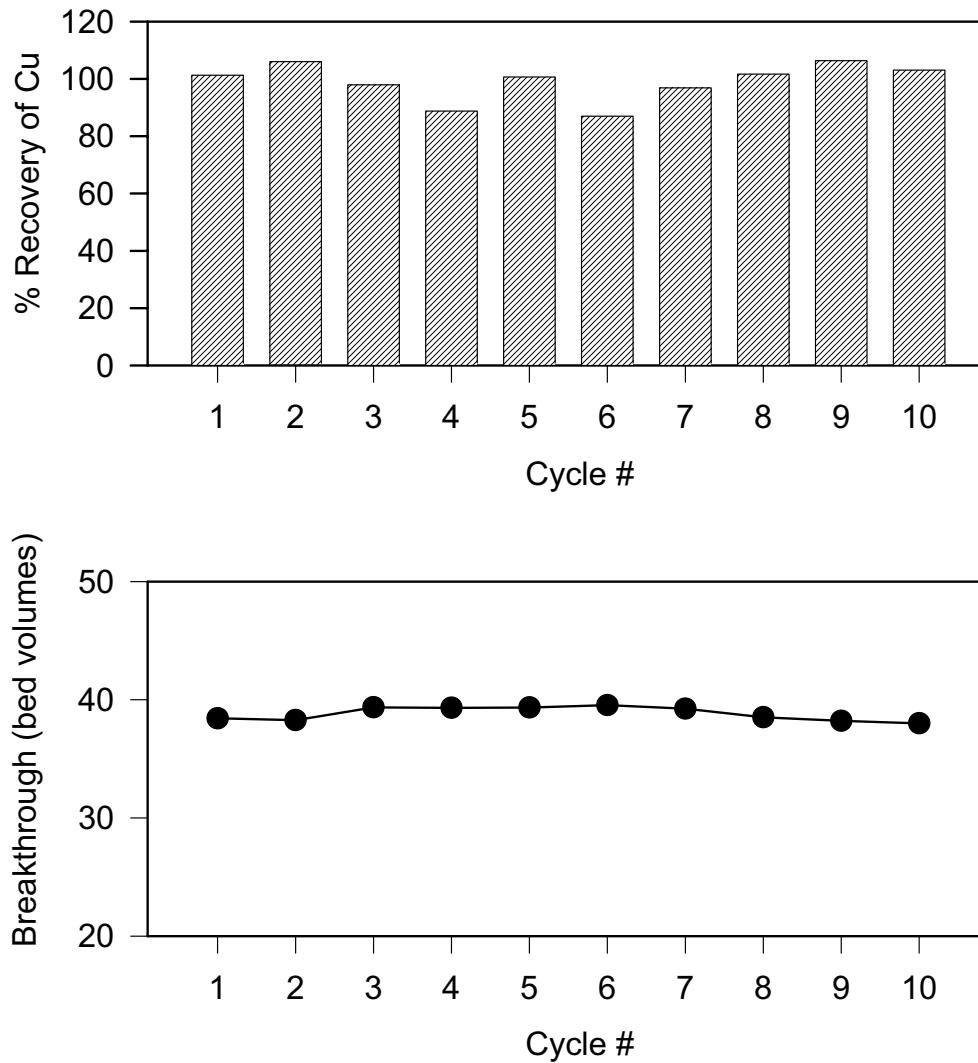
Figure 11. Upper panel represents percentage recovery of Cu from column after breakthrough (for protocol see Table 8). Bottom panel was calculated breakthrough volumes as estimated from amount of Cu leaking through the column in first two fractions (see Table 8). This column (C1 of Fig. 17) had been stored for six months. See comparisons in Fig. 17.
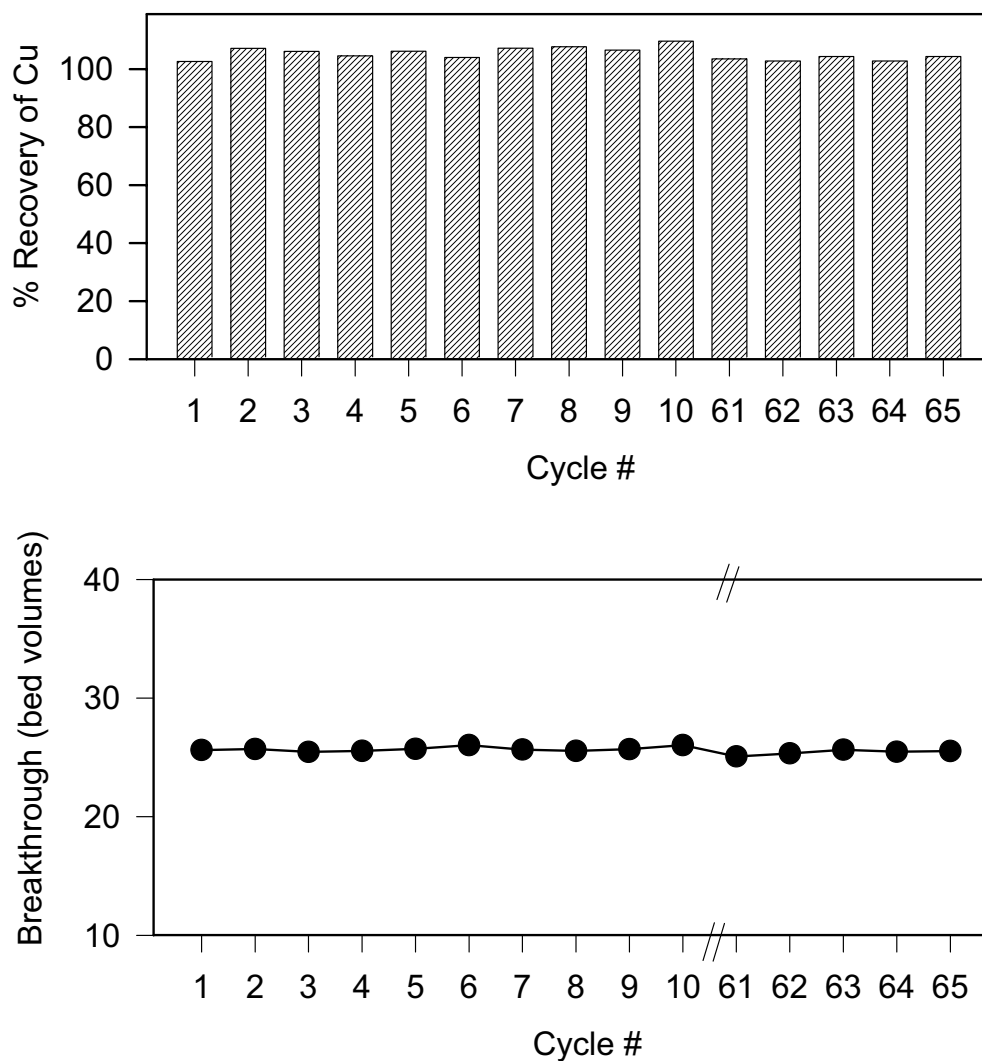
Figure 12. Upper panel represents percentage recovery of Cu from column after breakthrough (for protocol see Table 8). Bottom panel was calculated breakthrough volumes as estimated from amount of Cu leaking through the column in first two fractions (see Table 8). This was a new column prepared in the same manner as all of Fig 17. However, its capacity (breakthrough) was lower than the previous batch (Fig. 10). The first 10 cycle were done on the same day. Broken scale indicates an intervening 50 acid/water cycles without copper. The column was then tested for another 5 cycles. No diminution of capacity or recovery was noted. Column C2 of Fig. 17 was used for this test.
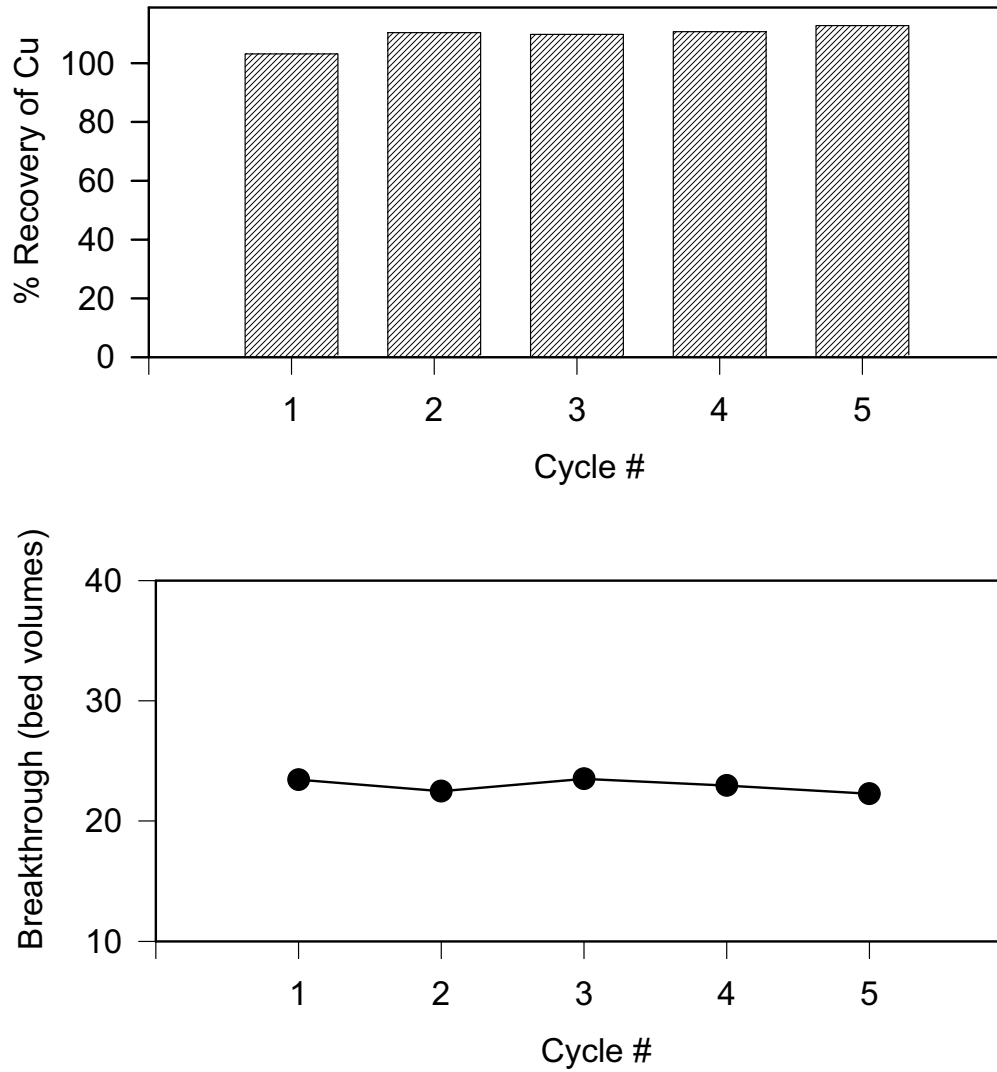
Figure 13. Upper panel represents percentage recovery of Cu from column after breakthrough (for protocol see Table 8). Bottom panel was calculated breakthrough volume as estimated from amount of Cu leaking through the column in first two fractions (see Table 8). This was the same column as Figure 12, but it was treated with 0.48 N HCl for 18 h. Capacity (breakthrough) was reduced compared with previous batch. No diminution of capacity or recovery was noted. Column C2 of Fig. 17 was used for this test.
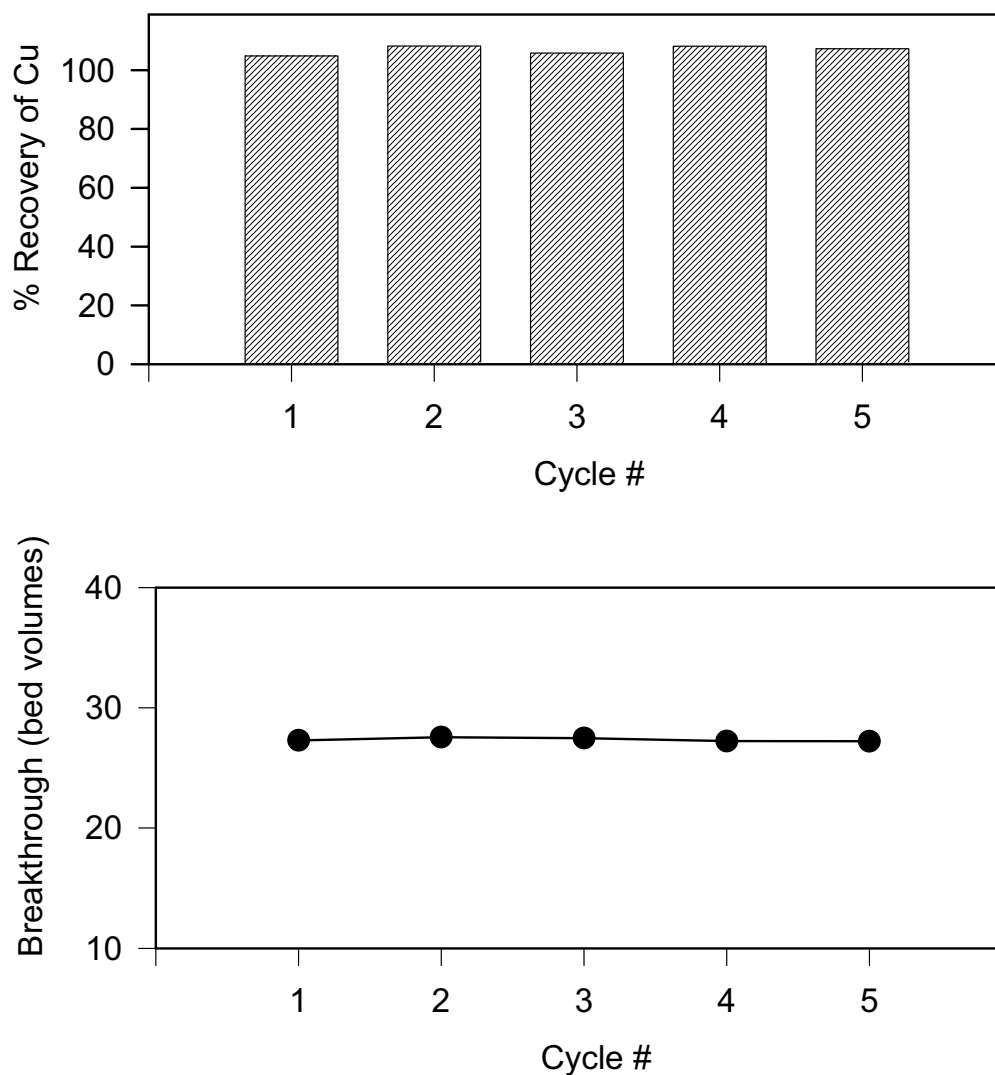
Figure 14. Upper panel represents percentage recovery of Cu from column after breakthrough (for protocol see Table 8). Bottom panel was calculated breakthrough volumes as estimated from amount of Cu leaking through the column in first two fractions (see Table 8). This was a column prepared in the same manner as the others in Fig. 17). However, it was dried at 105 ^{o}C and then stored desiccated. It was rehydrated before this test. The capacity and efficiency of recovery of Cu were not diminished compared to similar columns (Fig. 17). Column C3 of Fig. 17 was used for this test.

Figure 15. Upper panel represents percentage recovery of Cu from column after breakthrough (for protocol see Table 8). Bottom panel was calculated breakthrough volumes as estimated from amount of Cu leaking through the column in first two fractions (see Table 8). This was a freshly-prepared column prepared in the same manner as the others Fig. 17). Column C4 of Fig. 17 was used for this test.
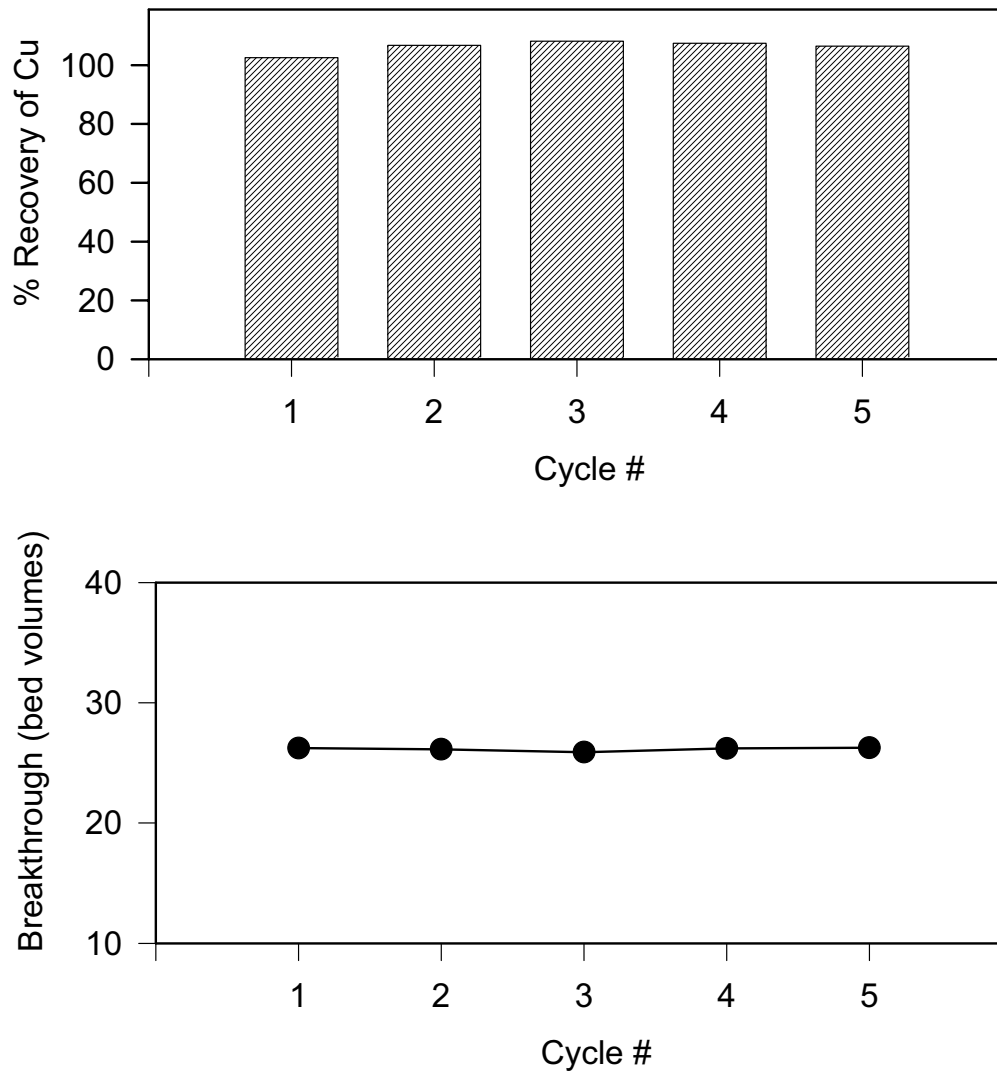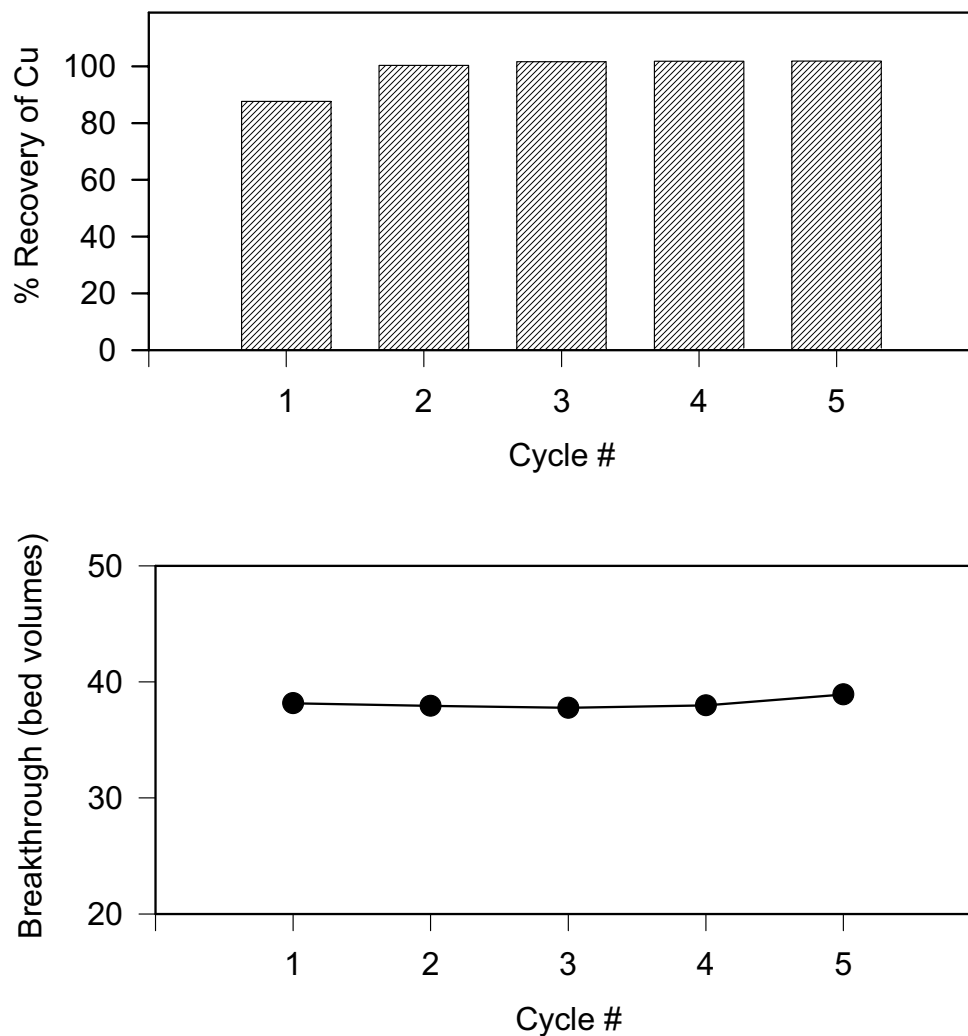
Figure 16. Upper panel represents percentage recovery of Cu from column after breakthrough (for protocol see Table 8). Bottom panel was calculated breakthrough volumes as estimated from amount of Cu leaking through the column in first two fractions (see Table 8). This was the same column as in Figs. 7-11. Column C1 of Fig. 17 was used for this test (last set of bars).
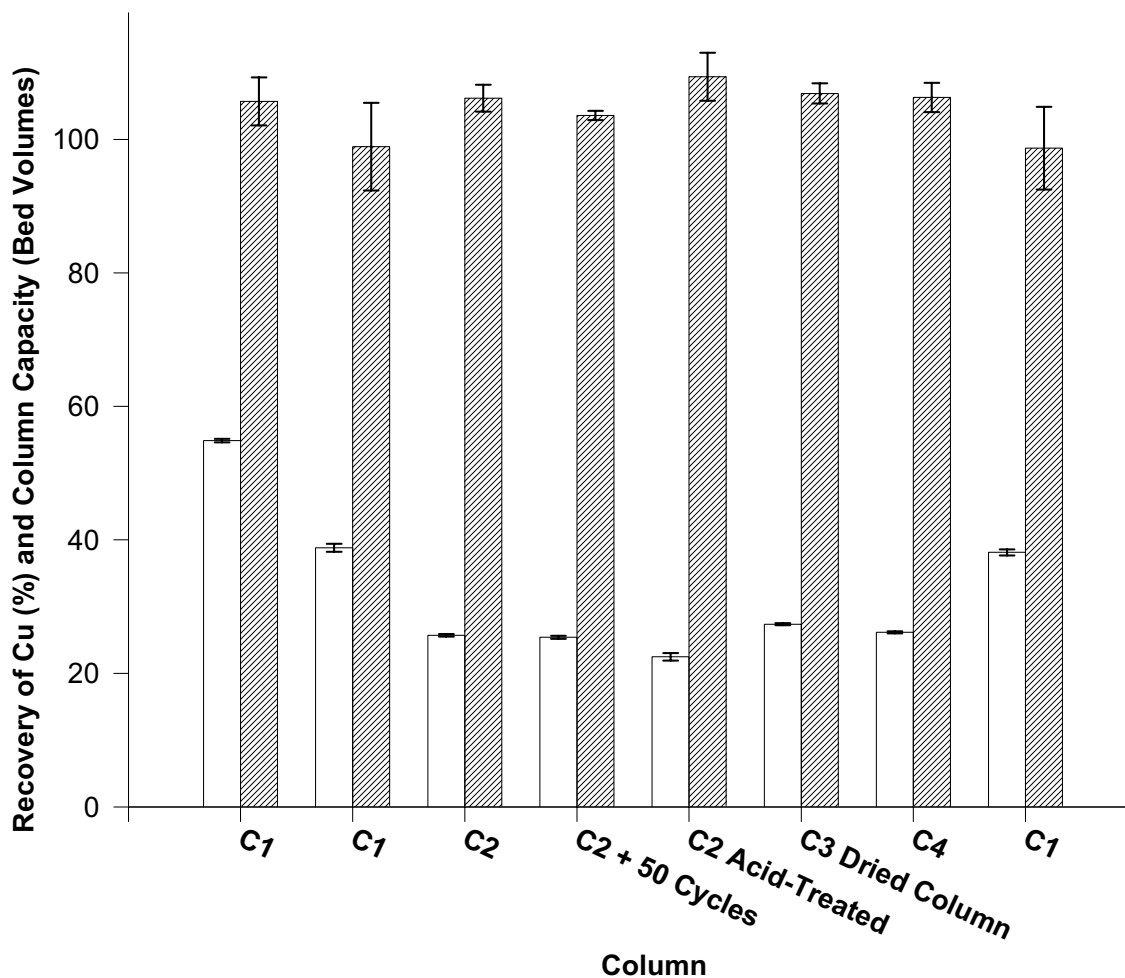
Figure 17. Percentage recovery (± SD) of Cu from column after breakthrough (protocol, see Table 8) and breakthrough bed volumes (± SD) as estimated from amount of Cu leaking through the column in first two fractions (see Table 8). For percentage recovery, variability was due to experimental error, as each measurement was comprised of the sum of several measurements for Cu. C1, C2, C3 and C4 were different batches of the same material (Figs. 10-16). C2+50 cycles was the performance after 50 cycles of 0.012 N HCl and water rinse. C2 (acid-treated) was a column treated for 18 hours with 0.48 N HCl. C3 was dried at 105 $^{\circ}$C and stored desiccated for 1 year. Six months elapsed between the first test of C1 (leftmost bars) and the second and third.
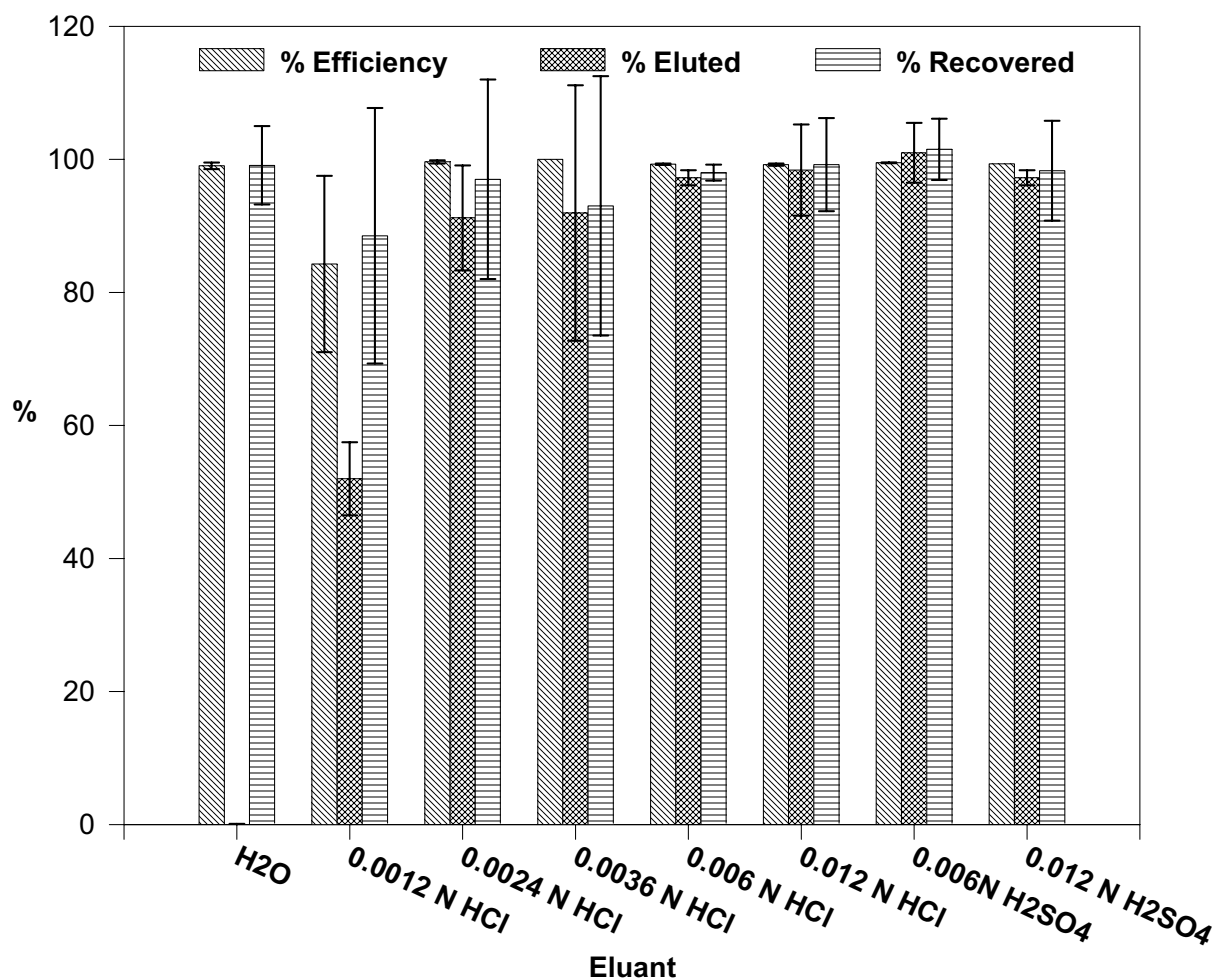
Figure 18. Elution tests with Cu and various eluants (% ± SD, n=3). Protocols for all eluants are given in Tables 6 and 7. For water (pH 5.5), no detectable Cu was eluted from the column in any of the trials. For 0.0012 N HCl, only half of the Cu was eluted indicating that this solution was a marginally effective eluant. Also, efficiency of binding for this eluant was lower and had a higher standard deviations indicating carry-over of Cu between trials. See also these data plotted in Fig. 19 on basis of pH. Column C1 of Fig. 17 was used for this test.
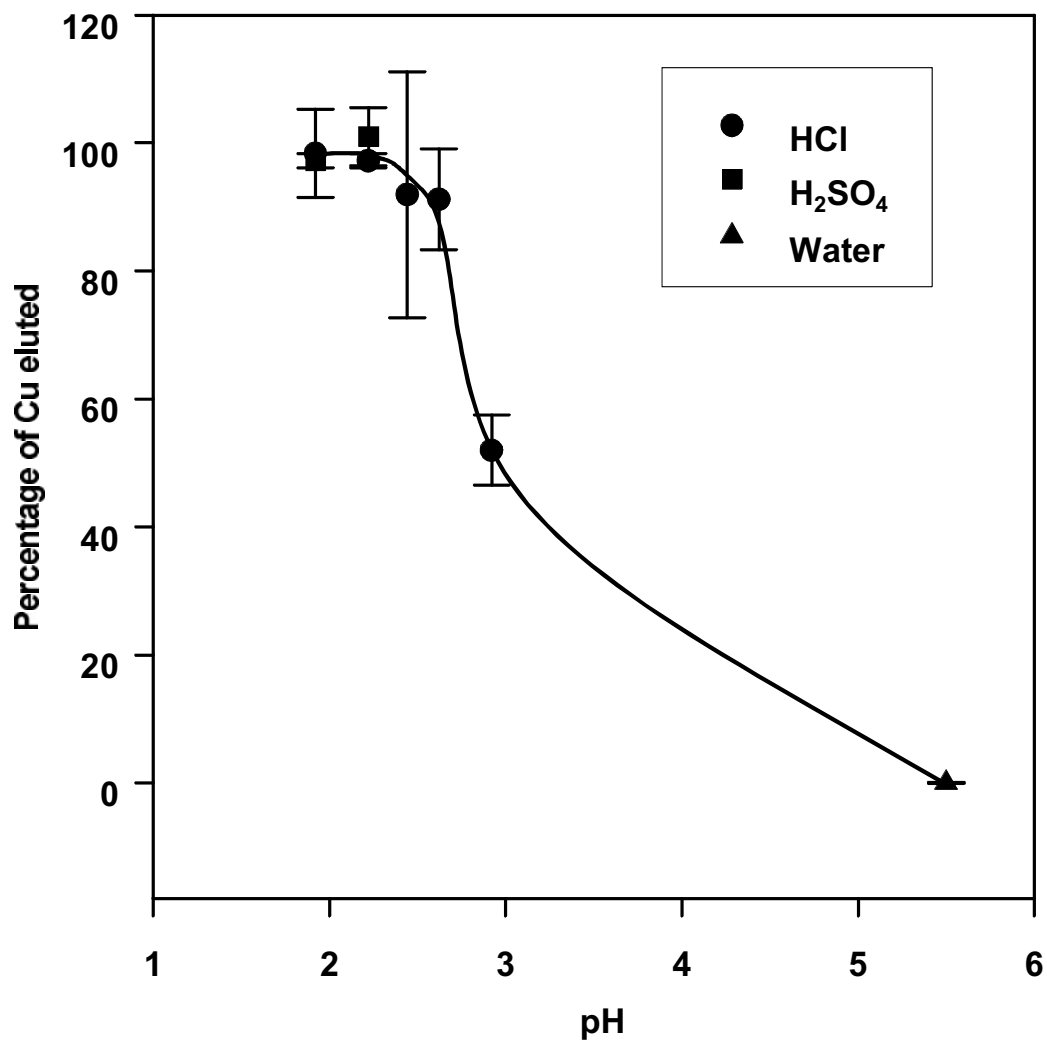
Figure 19. Elution tests for Cu (% ± SD, n=3) (test protocols in Tables 6 and 7). This plot indicates that the pH must be below 2.9 for good elution to occur. It appeared that both HCl and H_2SO_4 were equally good eluants as long as the pH was low enough. Column C1 of Fig. 17 was used for this test.
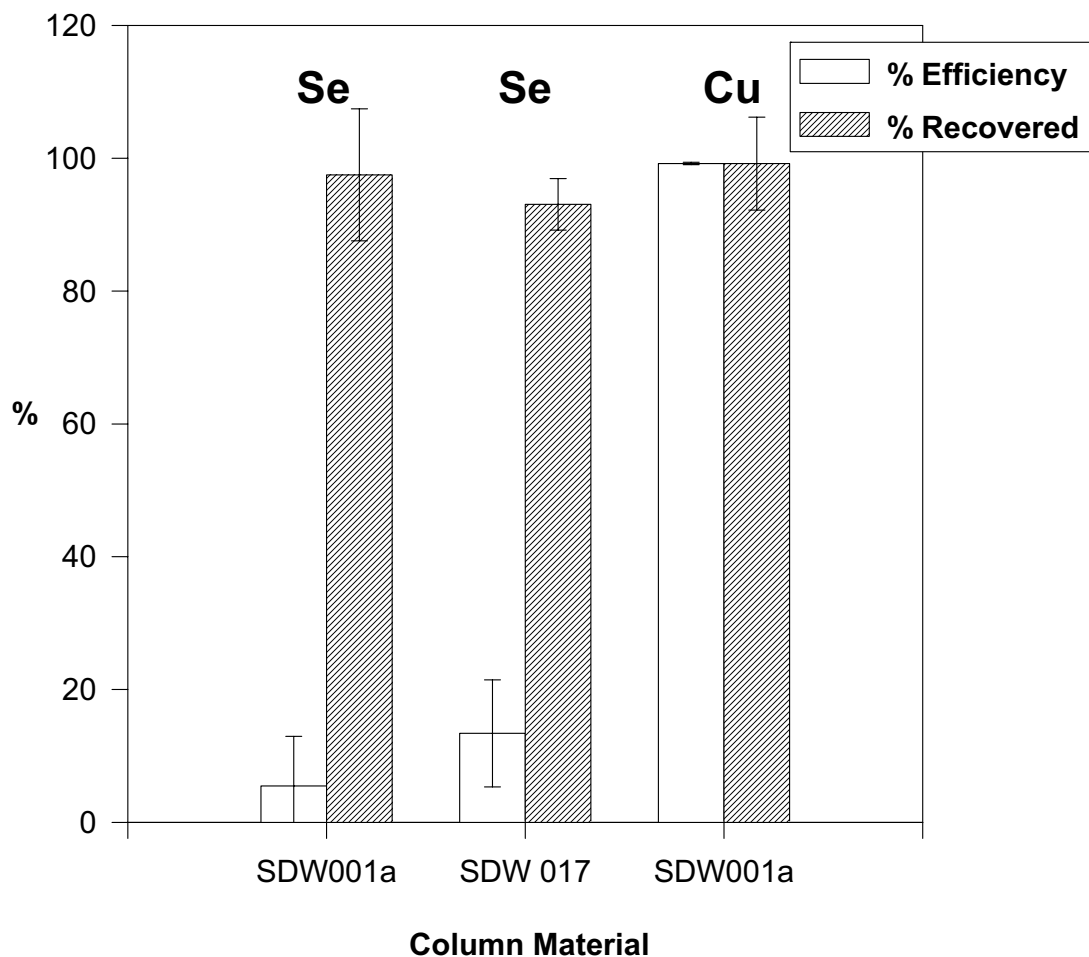
Figure 20. Binding and elution of Se compared to Cu (% ± SD, n=3). Protocol for this experiment is in Table 4. A solution of 10 ppm was added to a bioresin. Aliquots of 6.88 mL were added to the column at a flow rate of 2.5 mL/min. Percentage efficiency refers to the efficiency of binding of the element. Cu was bound with high efficiency to bioresin SDW001a, but Se showed little or no binding to the bioresins SDW001a or SDW017. Overall recovery of Cu was high, and Se recovery was also good, indicating that even though these bioresins were not good binding agents for Se, the experiments successfully followed the fate of Se.
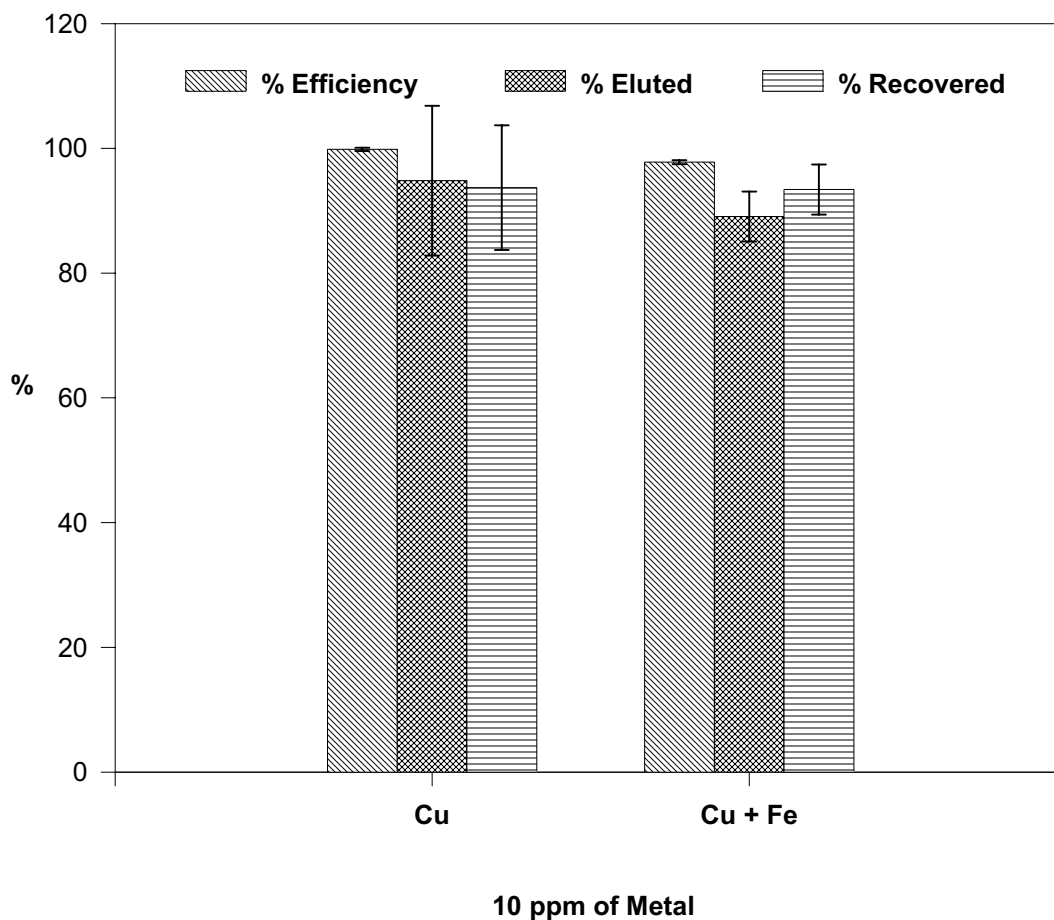
Figure 21. Assessment of efficiency, elution and recovery for Cu^{2+} (% ± SD, n=3) applied to a column at 10 ppm with and without the simultaneous application of 10 ppm Fe^{2+}. Molar ratio Fe:Cu was 1.1:1. A slight decrease in efficiency (~2%) was attributed to the presence of approximately equimolar Fe. See also Figure 22. Protocol is given in Table 12.
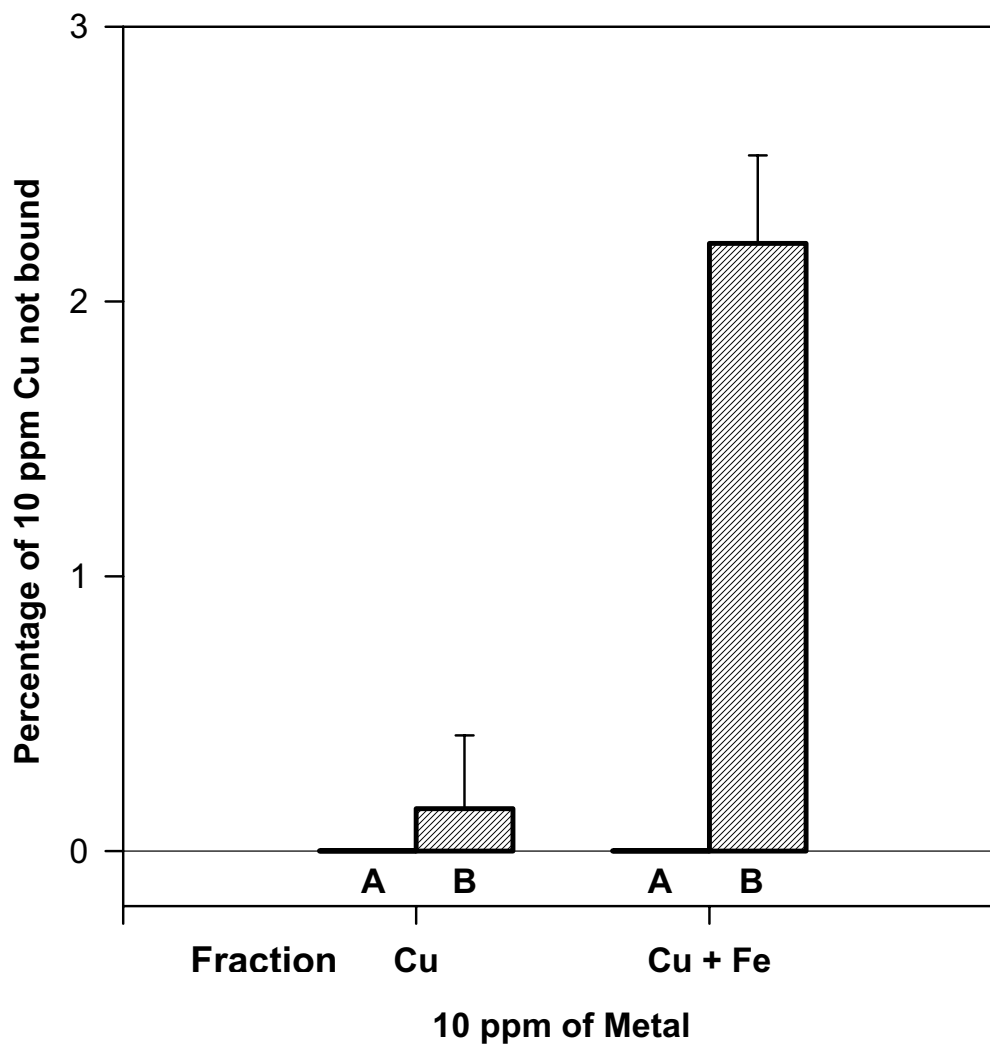
Figure 22. Percentage of Cu^{2+} <u>not</u> bound (% ± SD, n=3) applied to a column at 10 ppm with and without the simultaneous application of 10 ppm Fe^{2+}. Molar ratio Fe:Cu was 1.1:1. Fraction A was the first 10 mL of 10 ppm Cu added, and fraction B was the second 10 mL. A slight increase in leakage of Cu (~2%) was attributed to the presence of approximately equimolar Fe. See also Figure 21. Protocol is given in Table 12.

Effect of Concentration on Cost

Figure 23. Results of application of Excel spreadsheet technoeconomic model. Cost of processing/1000 gal was given as a function of metal concentration in the influent stream. This linear response was also reflected in other plots of costs (Figs. 24-28). Assumptions for this model are given in Table 13.

Effect of Flowrate on Cost

Figure 24. Results of application of Excel spreadsheet technoeconomic model. Cost of processing/1000 gal was given as a function of flowrate of the influent stream. This non-linear response was also reflected in other plots of costs (Figs. 23, 25-28). Assumptions for this model are given in Table 13.

Total Cost
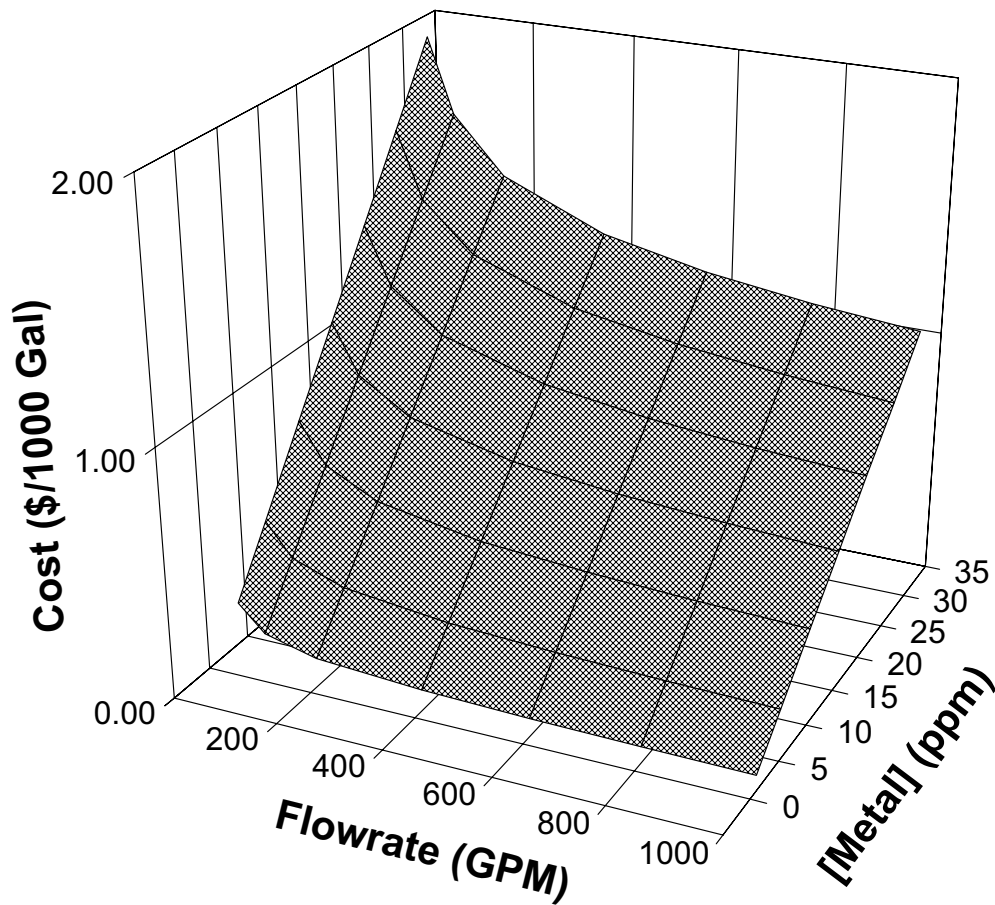
Figure 25. Results of application of Excel spreadsheet technoeconomic model. Cost of processing/1000 gal was given as a function of flowrate of the influent stream and concentration of metals in the influent stream. See also Figs. 23 and 24. Assumptions for this model are given in Table 13. Response to concentration was linear and flowrate was non-linear. Compare to Figs. 26-28.

Capital Cost
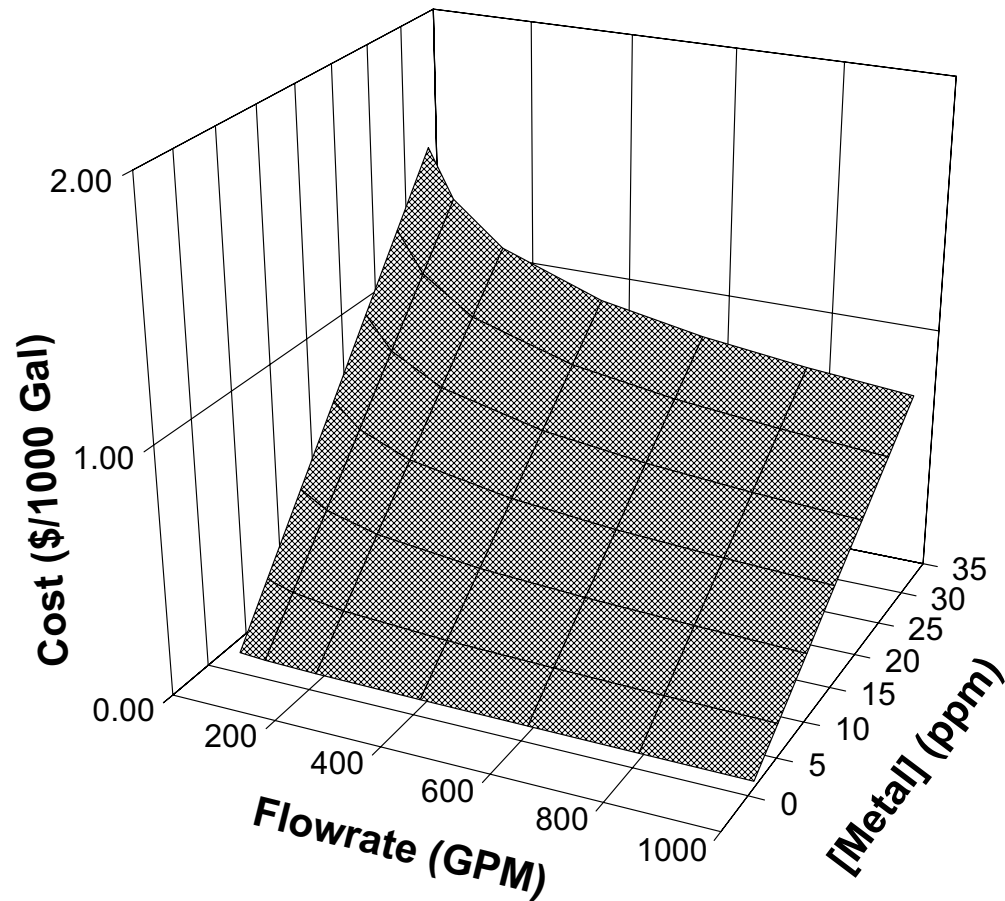
Figure 26. Results of application of Excel spreadsheet technoeconomic model to capital costs. Cost of processing/1000 gal was given as a function of flowrate of the influent stream and concentration of metals in the influent stream. See also Figs. 23 and 24. Assumptions for this model are given in Table 13. Responses to concentration were linear and to flowrate were non-linear. Compare to Figs. 25, 27 and 28. Note that most of the cost of processing arose from capital.
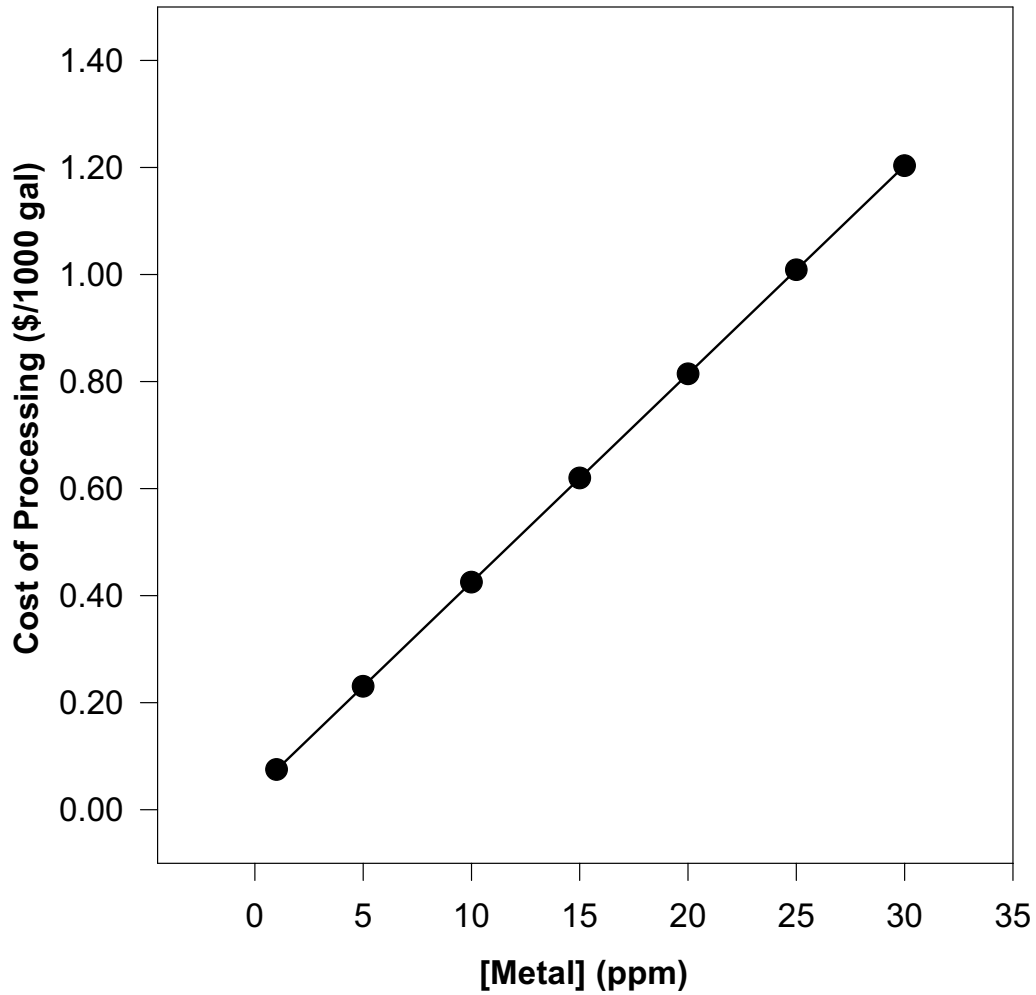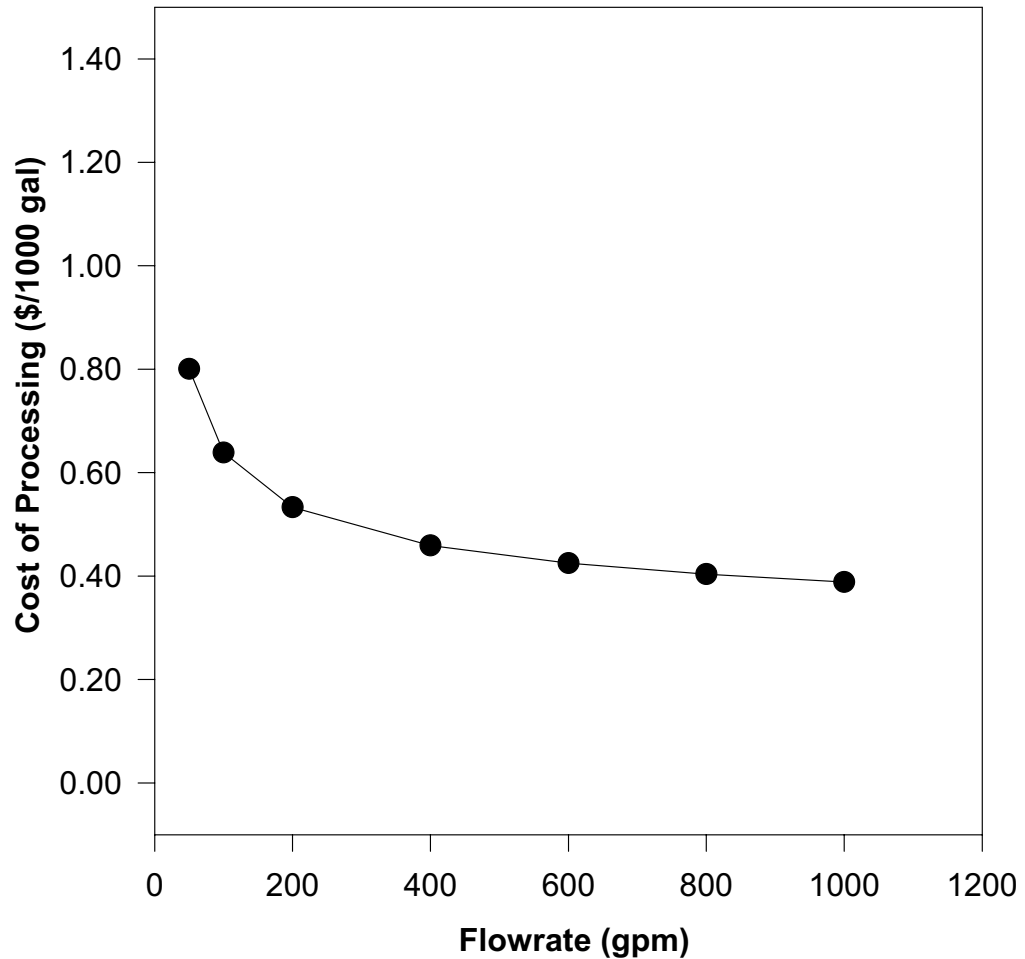
Operating Cost
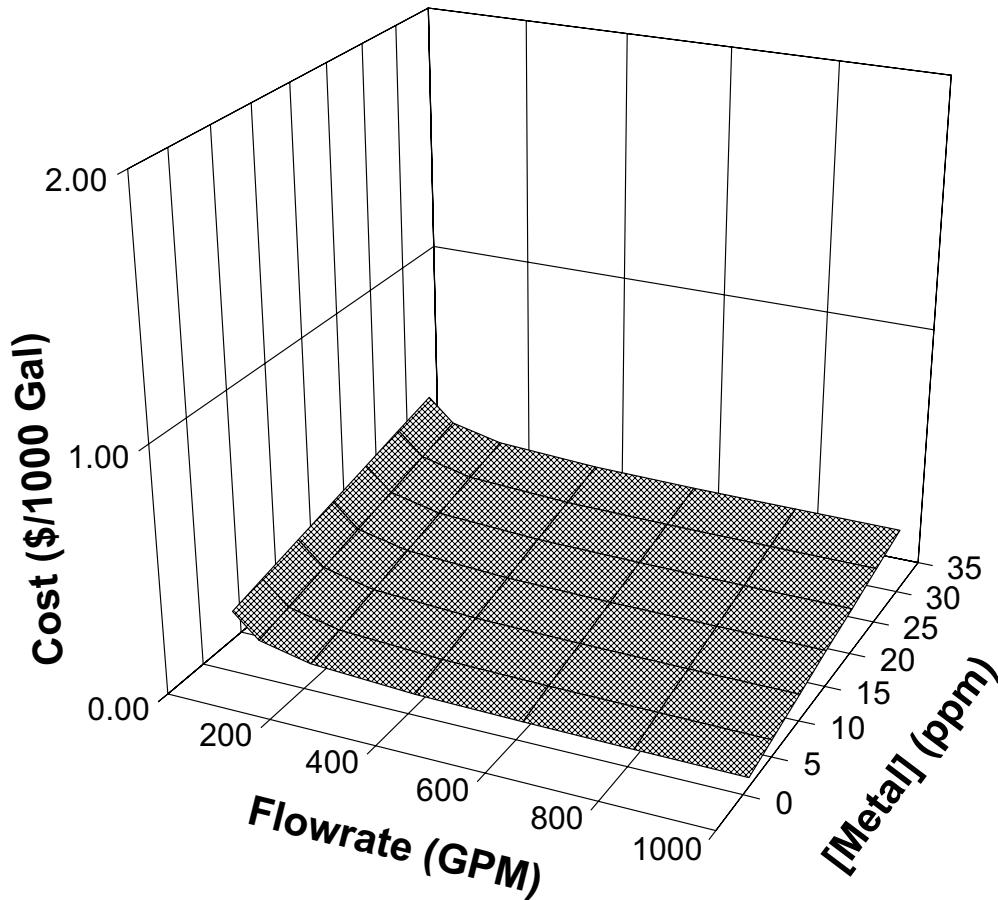
Figure 27. Results of application of Excel spreadsheet technoeconomic model to operating cost. Cost of processing/1000 gal was given as a function of flowrate of the influent stream and concentration of metals in the influent stream. See also Figs. 23 and 24. Assumptions for this model are given in Table 13. Responses to concentration were linear and to flowrate were non-linear. Compare to Figs. 25, 26 and 28. Note that only a minor component of the of the cost of processing arises from operating. Operating cost was further sub-divided in Figure 28.

Operating Costs

Chemicals Cost

Biomass Cost

Labor Cost
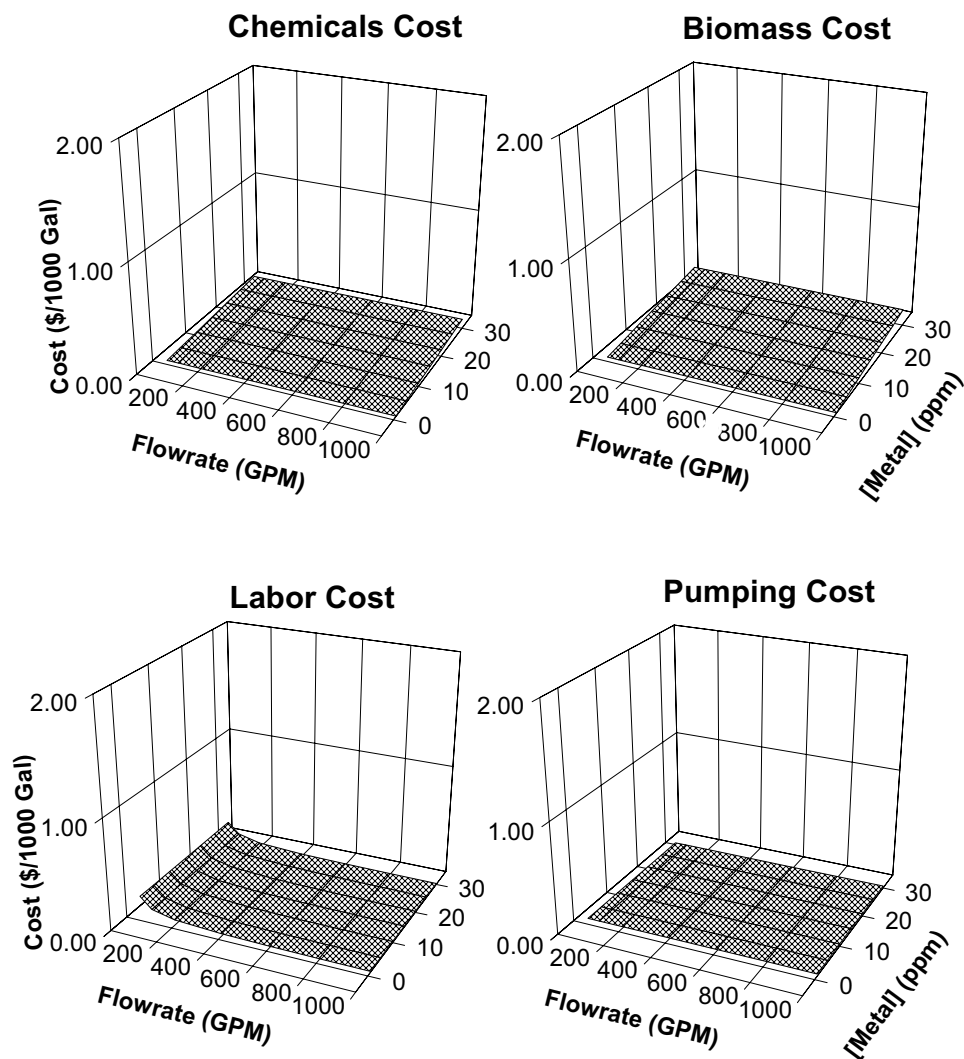
Pumping Cost

Figure 28. Results of application of Excel spreadsheet technoeconomic model to chemicals, biomass, labor and pumping costs. The total of these costs was plotted as total operating cost in Fig. 27. Cost of processing/1000 gal was given as a function of flowrate of the influent stream and concentration of metals in the influent stream. See also Figs. 23 and 24. Assumptions for this model are given in Table 13. Responses to concentration and flowrate were mostly linear. Compare to Figs. 25, 26 and 27. Labor cost/1000 gal was higher at low flowrates.
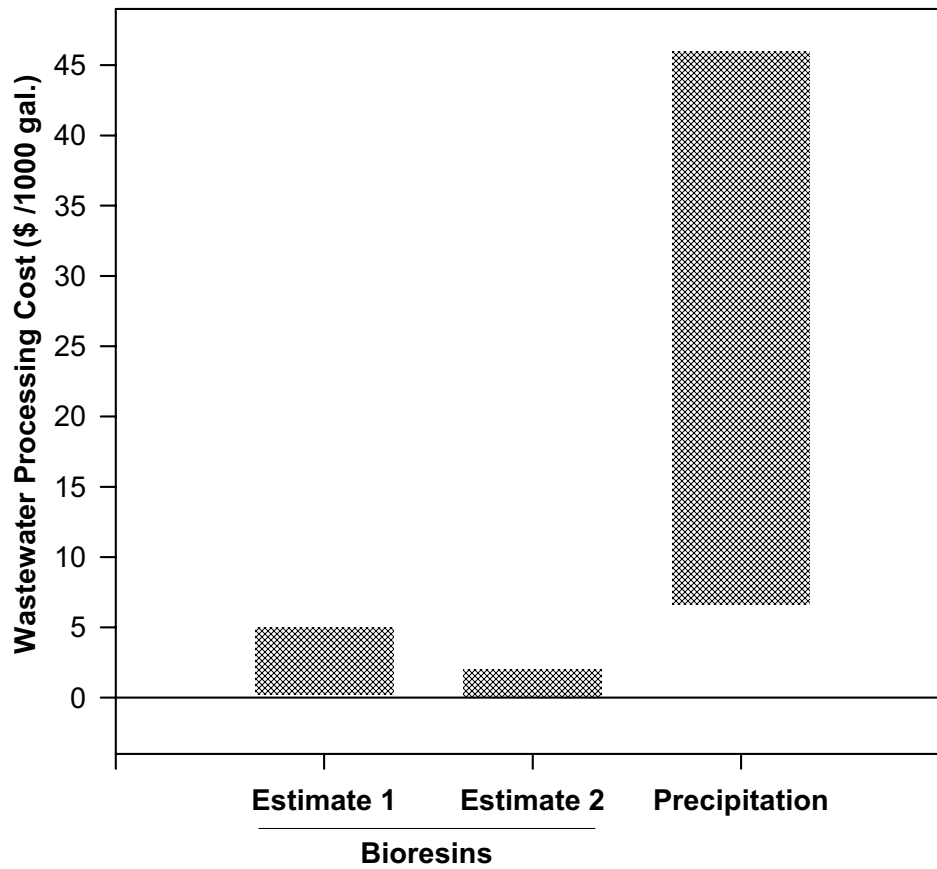
Figure 29. Operating cost ranges for bioresin technology Estimate 1 (Feiler and Darnall 1991) and Estimate 2 (present work, Figs. 23-28) compared to precipitation technology calculated from Leitz et al. (1995) by Brown 1997.

Appendix.   Data Records

The following Tables represent data records used in the report.

Data used to construct Fig. 7	
Sample	µg
1a	0.00
1b	76.63
1c	0.00
2a	0.00
2b	66.63
2c	0.00
3a	0.00
3b	66.44
3c	0.00

Data used to construct Fig. 8			
mL	ppm Cu	mL	ppm Cu
5.00	0.00	5.00	0.00
10.00	0.00	5.00	0.00
15.00	0.00	5.20	0.00
17.50	0.00	10.00	0.00
20.00	0.00	10.00	0.00
22.50	0.12	10.40	1.00e-3
25.00	0.91	15.00	0.00
27.50	2.48	15.00	5.00e-3
30.00	4.01	15.60	0.01
32.50	5.25		
35.00	6.02		
37.50	6.61		
40.00	7.02		
42.50	7.41		
45.00	7.67		
47.50	7.82		
50.00	7.73		
60.00	8.38		
70.00	8.73		
80.00	8.97		
90.00	9.09		
100.00	9.21		

Data used to construct Fig. 9	
Sample #	µg recovered
1a	0.00
1b	0.00
1c	2.30
1d	11.65
1e	22.54
1f	29.75
1g	33.73
1h	36.19
1i	38.64
1jd	428.37
1k	0.00
2a	0.00
2b	0.00
2c	2.91
2d	13.80
2e	24.23
2f	31.28
2g	34.65
2h	36.19
2i	38.33
2jd	446.60
2k	0.00
3a	0.00
3b	0.00
3c	3.37
3d	14.41
3e	24.53
3f	31.28
3g	33.12
3h	36.80
3i	42.93
3jd	455.71
3k	0.00
1a	0.00
1b	0.00
1c	0.00
1d	0.30
1e	4.73
1f	16.70
1g	26.90
1h	31.92
1i	35.47
1jd	390.14

Sample #	µg recovered
1k	0.00
2a	0.00
2b	0.00
2c	0.00
2d	0.30
2e	5.91
2f	18.62
2g	27.78
2h	30.44
2i	33.10
2jd	381.27
2k	0.00
3a	0.00
3b	0.00
3c	0.00
3d	0.30
3e	6.35
3f	18.77
3g	28.96
3h	33.69
3i	36.65
3jd	354.67
3k	0.00
1a	0.00
1b	0.00
1c	0.00
1d	0.30
1e	4.31
1f	15.75
1g	25.56
1h	30.91
1i	33.89
1jd	387.90
1k	0.45
2a	0.00
2b	0.00
2c	0.00
2d	0.15
2e	3.42
2f	14.56
2g	24.97
2h	30.91
2i	33.89
2jd	405.74
2k	0.01
3a	0.00
3b	0.00

3c	0.00
3d	0.00
3e	3.57
3f	15.16
3g	26.16
3h	32.10
3i	35.07
3jd	405.74
3k	0.00
4a	0.00
4b	0.00
4c	0.00
4d	0.30
4e	4.46
4f	16.35
4g	27.35
4h	32.10
4i	35.07
4jd	410.20
4k	0.00

Data used to construct Figs. 10 and 17		
Cycle #	Bed Volumes	% Recovery
1.00	55.20	104.80
2.00	55.20	109.10
3.00	55.20	111.60
4.00	54.63	104.70
5.00	54.75	102.90
6.00	54.78	99.20
7.00	54.57	103.10
8.00	54.81	106.20
9.00	55.20	107.00
10.00	54.59	108.70

Data used to construct Figs. 11 and 17		
Cycle #	Bed Volumes	% Recovery
1.00	38.43	101.24
2.00	38.27	105.98
3.00	39.36	97.93
4.00	39.31	88.73
5.00	39.34	100.62
6.00	39.54	87.00
7.00	39.24	96.86
8.00	38.51	101.64
9.00	38.22	106.32
10.00	38.00	103.03

Data used to construct Figs. 12 and 17		
Cycle #	Bed Volumes	% Recovery
1.00	25.62	102.63
2.00	25.70	107.20
3.00	25.47	106.13
4.00	25.55	104.59
5.00	25.72	106.21
6.00	26.04	104.01
7.00	25.66	107.23
8.00	25.55	107.73
9.00	25.69	106.52
10.00	26.04	109.64
11.00	25.07	103.52
12.00	25.33	102.81
13.00	25.65	104.31
14.00	25.48	102.84
15.00	25.54	104.33

Data used to construct Figs. 13 and 17		
Cycle #	Bed Volumes	% Recovery
1.00	23.45	103.17
2.00	22.48	110.39
3.00	23.51	109.81
4.00	22.95	110.75
5.00	22.27	112.79

Data used to construct Figs. 14 and 17

Cycle #	Bed Volumes	% Recovery
1.00	27.29	104.83
2.00	27.57	108.23
3.00	27.47	105.84
4.00	27.23	108.17
5.00	27.22	107.30

Cycle #	Bed Volumes	% Recovery
1.00	38.16	87.65
2.00	37.93	100.34
3.00	37.75	101.66
4.00	37.97	101.80
5.00	38.92	101.88

Data used to construct Figs. 15 and 17		
Cycle #	Bed Volumes	% Recovery
1.00	26.24	102.57
2.00	26.13	106.78
3.00	25.90	108.16
4.00	26.21	107.47
5.00	26.26	106.50

Data used to construct Figs. 16 and 17						
Data used to construct Figs. 18 and 19						
Eluant	% Elution	Elution SD	% Recovery	Recovery SD	% Efficiency	Efficiency SD
H2O	0.00	0.10	99.10	5.90	99.03	0.48
0.0012 N HCl	51.98	5.49	88.50	19.20	84.27	13.25
0.0024 N HCl	91.21	7.89	97.00	15.00	99.62	0.23
0.0036 N HCl	91.94	19.20	93.00	19.50	100.00	0.00
0.006 N HCl	97.23	1.13	98.00	1.20	99.26	0.11
0.012 N HCl	98.38	6.86	99.20	7.00	99.21	0.18
0.006N H2SO4	100.98	4.50	101.50	4.60	99.48	0.06
0.012 N H2SO4	97.23	1.13	98.30	7.50	99.32	0.00

Data used to construct Fig. 20				
Strain	% Recovered	SD Recovered	% Efficiency	SD Efficiency
SDW001a + Se	97.50	9.93	5.49	7.45
SDW 017 + Se	93.06	3.88	13.40	8.07
SDW001a + Cu	99.20	7.00	99.21	0.18

Data used to construct Fig. 21						
Sample	% Elution	Elution SD	% Recovery	Recovery SD	% Efficiency	Efficiency SD
Cu	94.83	12.00	93.70	10.00	99.85	0.27
Cu + Fe	89.07	4.00	93.40	4.00	97.79	0.32

Data used to construct Fig. 22				
Sample	% Elution	Elution SD	Efficiency	Efficiency SD
Cu	0.15	0.27	0.00	0.00
Cu + Fe	2.21	0.32	0.00	0.00