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Simultaneous multi-element detection of metal ions bound to a *Datura innoxia* material

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Abstract

An on-line detection scheme has been developed for the determination of metal ion affinities for binding to a plant-based substrate. This involves monitoring the effluent of a column packed with cell-wall fragments from the plant *Datura innoxia* for 27 different elements simultaneously by coupling the column to an ICP emission spectrometer. Previously accepted procedures for removing native metal ions from biological materials by washing the material with a pH 2 solution were found to be insufficient for this material. Measurable amounts of Na, Mg, Al, Ca, Mn, Fe, Ni, Cr, Zn, Cd, Pb, Ba, Sr, and Si were all detected in an effluent from the introduction of 1.0 M HCl following washing the material in a pH 2 solution. Metal ion breakthrough curves for Cd^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, and Pb^{2+} were found to exhibit an affinity order of $Pb^{2+} > Cu^{2+} \gg Zn^{2+} \cong Cd^{2+} > Ni^{2+}$ for an equimolar mixture of these metal ions. This configuration also enabled the displacement of metal ions to be detected as the breakthrough curve for a subsequent metal ion was monitored. Comparison of Ni and Zn binding indicates a simple ion exchange model is insufficient to explain sequential binding of these metal ions.

Keywords: Metal binding; Biosorbent; *D. innoxia*; Metal ion removal; Affinity chromatography

1. Introduction

The use of natural materials for the selective removal of toxic heavy metal ions from contaminated water has received increased attention [1–6]. Unfortunately, the chemical heterogeneity of these materials that contribute to their desirability as sorbents hinders their adaptation because of a lack of predictability of their binding properties using simple ion exchange models. In an effort to enhance the utility of these materials, numerous studies

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have been undertaken to elucidate the chemical interactions responsible for the binding of specific metal ions to these biogenic materials [7–10].

These studies have included the analysis of binding isotherms to these materials. Mathematical models have been applied to one-site [11,12], two-site [12,13], and multiple binding site assumptions [12,14,15]. The assumption of the presence of a continuum of binding sites was also described for a material derived from cells of the plant *Datura innoxia* [16]. Through the application of a regularized regression analysis of the binding isotherm data [16], they were able to generate affinity "spectra" for metal ions bound to this material [16,17].

Many of the isotherms studied were derived from data of either equilibrium batch experiments [6,17,18] or aliquots collected from the effluent of a flowing system [16]. These approaches, although useful, have distinct limitations. The use of batch techniques necessitates variations in metal ion binding conditions as equilibrium is established. As the metal ion binds to the substrate, an alternate species is displaced. When this species is a proton, the pH of the solution is necessarily decreased, which can have a profound impact on the ability of the material to bind the metal ion [19]. If the displaced ion is a weakly associated alkali metal ion (e.g. Na^+), its displacement will affect the ionic strength of the solution, thus altering the metal binding conditions [20].

Through the interfacing of the effluent from a column of the biosorbent material to a flame atomic absorption spectrometer, Lin et al. [16] were able to demonstrate variations in the breakthrough curves for metal ions. However, those studies were limited to the monitoring of single metal ions in the effluent stream. Binding isotherms were generated from this variation of frontal affinity chromatography and subsequently processed to yield the corresponding affinity spectra [16].

To address the single metal limitation of this earlier configuration, a frontal affinity chromatographic analysis system has been developed with on-line inductively coupled plasma optical emission detection. This modification has allowed simultaneous, real time, multi-element monitoring of up to 27 different metals by displacement frontal affinity chromatography.

2. Experimental section

2.1. Materials

The biomaterial used for this investigation was derived from cell-wall fragments of cultured anther cells from the plant *D. innoxia*. The conditions used for the culturing of these cells have been detailed elsewhere [18]. Because of the low density, small particle size, and poor mechanical strength of this native biomaterial, it was immobilized within a polysilicate matrix, using the procedure described in detail elsewhere [19]. Only the 40/60 mesh size fraction of the resulting ground material was subsequently used in the columns.

Individual stock solutions of lead, copper, cadmium, nickel, and zinc, and a multi-element solution containing all five of the metals (2.0 mM in each metal ion) were prepared from the respective nitrate salts in distilled, deionized water (18 MΩ by conductivity, Nanopure,

Millipor Corp.). These metals were chosen on the basis of their significance to environmental concerns. All influent solutions were prepared by serial dilution from the stock solutions.

Because the final objective of these studies includes the application of this (or a similar) material for the treatment of contaminated water, all solutions were prepared with a pH determined by the dissolution of ambient species (e.g. CO_2). This resulted in a solution pH between 6.2 and 6.7. Other studies have indicated only minimal pH-dependent metal binding under these conditions [19].

Briefly, the frontal elution method of affinity chromatography, as described by Jaulmes and Vidal-Madjar [21], has been defined as ideally a Dirac step function where the concentration of the solute is instantly elevated at the injection moment and kept at that constant value. The column is packed with an affinity matrix, in this case the immobilized *D. innoxia* cell-wall fragments. As the metal ions interact with the functional groups on the biomaterial, a fraction of them remain on the column. Because the influent solution is continuously supplying metal ions, once the column reaches equilibrium, the concentration of metal in the effluent should be equivalent to that of the influent. By monitoring the effluent directly, an elution profile can be generated. From there the elution volume and the capacity of the biomaterial for the metal, for the conditions of the influent, can be calculated [21,22].

An inductively coupled plasma emission spectrometer equipped with a 1 m Rowland circle polychromator was used to simultaneously monitor 27 different metals (Jarrel Ash, Atom Comp 800 ICAP). This enabled the continuous monitoring of the column effluent composition. The experimental setup used is schematically depicted in Fig. 1. The influent was pumped through the column using a peristaltic pump (Rainin, Minipuls2). The columns were constructed in-house from plastic tubing, 2.5 cm in length with an inner diameter

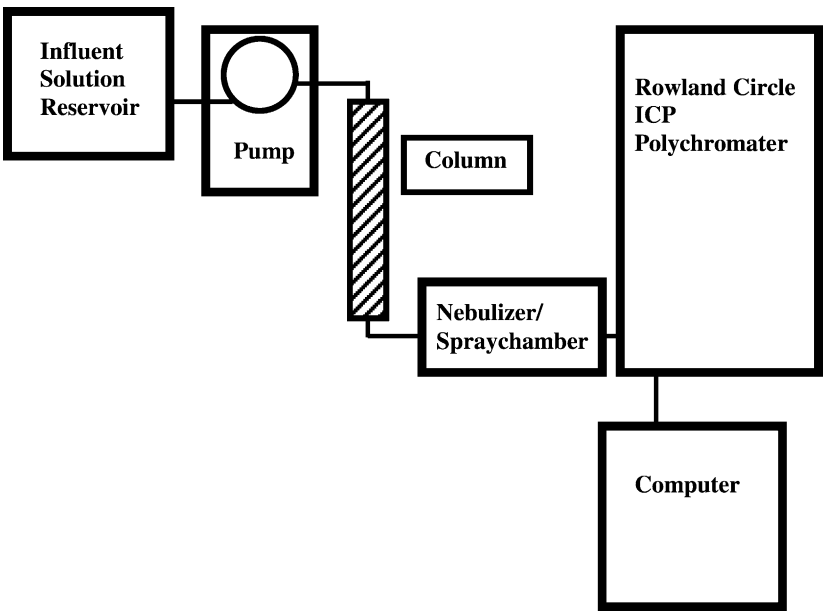

Fig. 1. Experimental configuration.

of 3 mm. Teflon tubing (0.8-mm i.d.) was used for all influent and effluent connections. Interface to the ICP was accomplished by directly connecting the column outlet to the inlet of the cross-flow nebulizer using the minimum length of Teflon tubing (15 cm). Solution flow rates were calibrated by five replicate measurements of the time required to pass 10.0 ml of solution through a packed column.

Each column was packed with 100 mg of immobilized *D. innoxia* and flow tested using distilled deionized water. Measured flow rates were not significantly different from the calibrated flows at a 95% confidence level. Once packed with the 40–60 mesh sized material, the columns were exposed to 20.0 ml of 1.0-M HCl (1.0 ml min^{-1} for 20 min) and the effluent monitored for metals released from the biomaterial. Following the acid rinse, the columns were then exposed to 5.0 ml of distilled deionized water (1.0 ml min^{-1} for 5 min). All experiments were carried out at room temperature.

3. Results and discussion

A procedure has been described previously for the removal of native metal ions from a plant (specifically algae)-based sorbent material [23]. This involved the exposure of the material to a pH 2 solution for approximately 1 h. Unfortunately, those researchers did not report the concentrations of metals removed from the material by this procedure. Because the present instrumentation enables the monitoring of several metal ions that may be present in the effluent, a sample of *D. innoxia* cell material, immobilized in a polysilicate matrix, ground, sieved, and a 40/60 mesh size fraction used to pack a column, was treated by this procedure. After passing 20.0 ml of the distilled, deionized water through it, 3.3 ml of a 1.0 M solution of HCl was pumped through the column (at a rate of 1.0 ml min^{-1}) while monitoring each of the 27 element emission wavelengths from the ICP. Fig. 2 shows the results from those channels exhibiting a discernable signal. Significant amounts of Na, Mg, Al, Ca, Mn, Fe, Ni, Cr, Zn, Cd, Pb, Ba, Sr, and Si were all detected in this effluent. For the purpose of this study, a significant amount was defined as metals that resulting in a maximum signal that was more than 12 times larger than the standard deviation ($n = 15$) of the respective background signals.

It is evident that each of these metal ions either remained on the column after the "washing" procedure or was extracted from the Nanopure water supply. An alternate study in this laboratory has determined the concentrations of Mg, Ca, and Cd, to be 2.6, 3.7, and 2.5 ppb, respectively, in this water supply [24]. It is therefore concluded that the pretreatment of this plant-based material to a pH 2 solution was insufficient to quantitatively remove all native metal ions, as earlier presumed [18–20,23]. The application of a second 20.0-ml aliquot of the acid resulted in no detectable (i.e. $S/N < 3$) eluted species. It can therefore be concluded that all of these metals were quantitatively removed from the material under these conditions. Subsequent studies included the pretreatment of each column with 20.0 ml of a 1.0 HCl solution followed with 5.0 ml of the distilled deionized water.

Metal ion breakthrough curves were then generated for an equimolar solution (0.1 mM) of five metals, Cd, Cu, Ni, Pb, and Zn. Each metal was monitored in the effluent for 75 min as the solution was pumped through the biosorbent column at 1.0 ml min^{-1}. These data are shown in Fig. 3. It is readily apparent under these conditions that the affinity order of

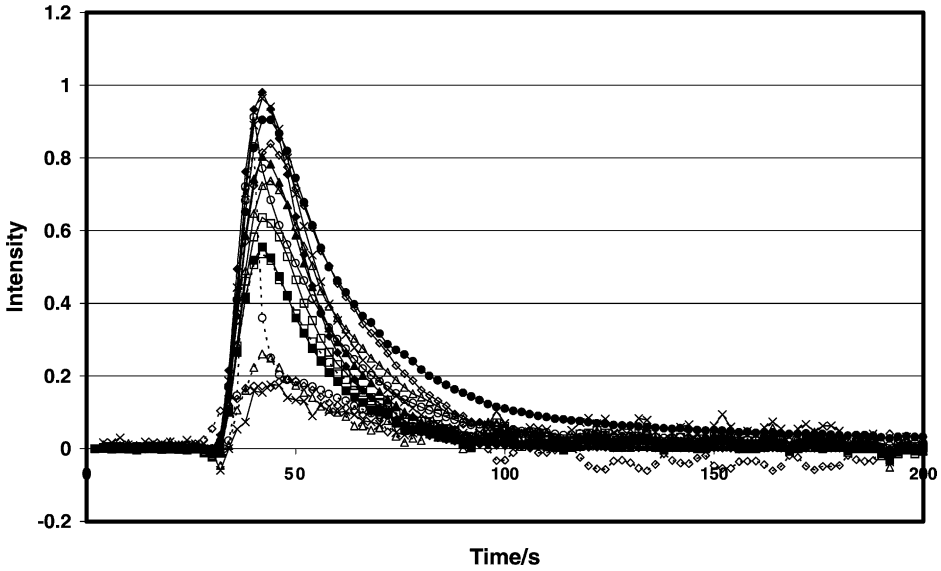

Fig. 2. Emission intensities for each element that showed signals significantly above baseline measurements during elution of 20.0 ml of 1.0 M HCl through column of immobilized *D. innoxia*. Indicated elements include (◆) Na, (■) Mg, (△) Al, (×) Ca, (-△-) Mn, (●) Fe, (×) Ni, (-○-) Cr, (○) Zn, (◇) Cd, (-□-) Pb, (▲) Ba, (□) Sr, and (-◇-) Si.

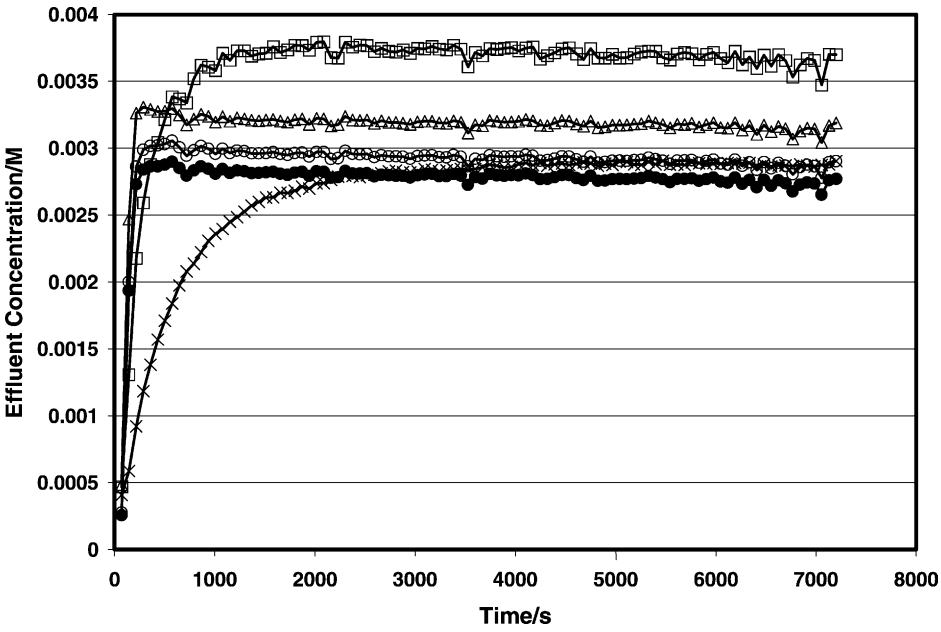

Fig. 3. Breakthrough curves generated from the introduction of a 0.1 mM solution in each of (●) Cd, (□) Cu, (△) Ni, (×) Pb, and (○) Zn.

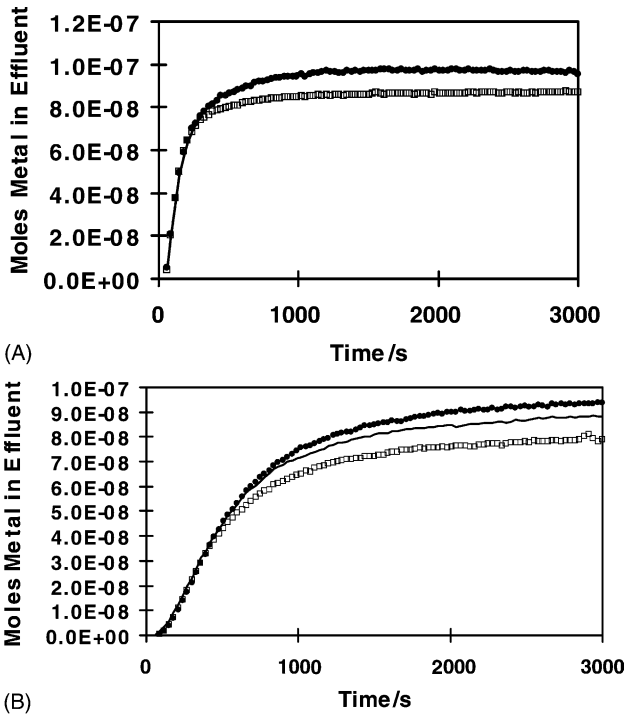

Fig. 4. Three metal exposure of 0.2 mM Cd^{2+} (●), Ni^{2+} (□), and Zn^{2+} (—) for 50 min at a rate of 1.0 ml min^{-1}, simultaneously (A) and individually (B).

these metal ions is $Pb^{2+} > Cu^{2+} \gg Zn^{2+} \cong Cd^{2+} > Ni^{2+}$. Although affinity orders have been determined from the comparison of breakthrough curves for each individual metal ion [6], such data can be misinterpreted. An example of this is shown in Fig. 4. Each set of data is a comparison of the relative affinities of three metal ions, Cd, Ni, and Zn. The data in Fig. 4A were collected from the elution of a single equimolar (0.2 mM) solution of each of the three metal ions while those shown in Fig. 4B resulted from the monitoring of each metal concentration in separate solutions of 0.2 mM. Although each of the elution profiles provides similar information about the binding affinity of the biomaterial towards each metal ion, the shapes of the breakthrough curves are dramatically different. This would infer that the binding of a metal to this material may be dependent on what other metals are present either in the influent solution or previously bound to the material.

In an effort to address this question, a study has been undertaken using the present configuration's ability to monitor both the metal exposed to the material and those metal ions that may be released. This involves the sequential exposure of a column containing the *D. innoxia* material to each of the metal ions Cd^{2+}, Zn^{2+}, and Ni^{2+}. Fig. 5 shows the results of three conditions within that study. Fig. 5A and B shows the impact of sequential exposure of the column to zinc and nickel ions. In Fig. 5A, the sorbent material was first exposed to a 0.2 mM solution of Ni and then to an equimolar solution containing zinc ions. Fig. 5B

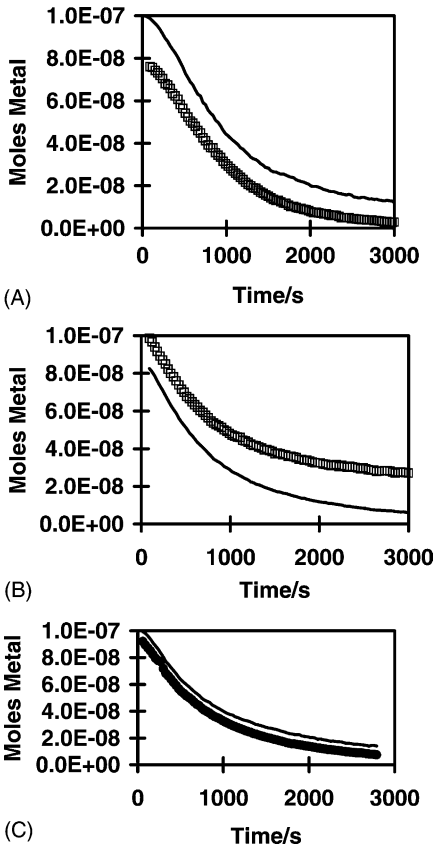

Fig. 5. Sequential exposure of *D. innoxia* sorbent to 0.2 mM solutions of (A) Ni^{2+} (□) followed by Zn^{2+} (—), (B) Zn^{2+} (—) followed by Ni^{2+} (□), and (C) Cd^{2+} (●) followed by Zn^{2+} (—).

shows the results from the same column for which the order of exposure was reversed. Readily apparent from these data is that the amount of metal released was consistently less than the amount of the metal bound. This would argue against a simple exchange mechanism between these first-row transition metal ions. Additionally visible from these data is a significant difference in the amounts of metal continuing to be bound to the material after 5 min of exposure to the influent solution. Conversely, the data shown in Fig. 5C illustrate the condition where the column was first exposed to a 0.2 mM solution of Cd^{2+} and subsequently exposed to the same concentration of Zn^{2+}. Earlier studies have indicated the binding of Cd^{2+} to this material through its association with carboxylate functionalities [25]. Under these conditions, the amount of metal ion released is very similar (although still less) to the amount of metal binding to the sorbent material. A detailed discussion of this study is beyond the scope of the present paper and will be the subject of a future publication. These results have been presented to illustrate the necessity of monitoring multiple metal ions when investigating the interactions of metal ions with biologically

derived sorbent materials. Having the ability to monitor multiple metals, and sequentially expose the biomaterial to those metals allows insights into the types of binding sites on the biomaterial and their affinities towards individual metals.

4. Conclusions

The combination of frontal affinity chromatography with ICPAES detection has been demonstrated to be a valuable method for investigating metal–biomaterial interactions. The major advantage of this technique is the real time multi-element monitoring of the column effluent. This allows for investigation of biomaterial metal interactions in more complex sample matrices. This permits investigators to monitor the interaction of influent solutions with elements present that may not be necessarily target metals (Na, Mg, Ca, etc.), but are likely to be found in a field type situation. Also, as illustrated in Fig. 4, single metal systems behave significantly different from multiple metal systems. That is, the assumption of distinct ion-for-ion relationships as applied towards metal–biomaterial interactions can not be made. When looking at sequential metal exposures to the biomaterial as in Fig. 5, and subsequent quantification of subsequent acid wash effluent following the sequence of metals, it may be possible to assign number densities to metal binding site types on the biomaterial.

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