

# Kinetics of heavy metal uptake by vegetation immobilized in a polysulfone or polycarbonate polymeric matrix

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## Abstract

The ability of four common vegetations – wood, grass, compost, and peat moss – to remove cadmium, chromium, and lead from dilute aqueous solutions is investigated. Dried ground vegetations are immobilized in polysulfone, and poly (bisphenyl A) carbonate to form spherical beads through a phase inversion process. The beads are contacted with a dilute aqueous solution containing metal ions of interest. The removal of metal ions from the solution is monitored over the course of the experiment and the first-order kinetics parameters estimated. The rates of removal as well as the equilibrium bead loadings are shown to be affected by both the choice of vegetation and the choice of polymer. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Heavy metal adsorption; Immobilized vegetation; Cadmium; Chromium; Lead

## 1. Introduction

Metals have become increasingly important in many industries, including battery and power storage, coatings, electroplating, and power industries. These metals inevitably make their way into plant discharge streams in at least dilute concentrations, despite application of remediation technologies [1]. Traditional treatments are often of limited effectiveness in dilute solutions and may be incapable of meeting the decreasing allowable levels specified by regulatory agencies. The limitations and cost of traditional treatment methods has led researchers to search for alternative treatments. One promising area of development is biosorption.

Volesky [1] defines biosorption as a passive process, not reliant upon metabolic activity, by which biomatter uptakes contaminants from a carrier stream. Because this technology is not reliant on the metabolic processes of living biomass, harvested, biologically inactive vegetation or non-living microbes may be investigated as potential adsorbents. The metabolically inactive nature of the biomaterial elim-

inates concerns, such as organism viability and toxicity of solution to the organism.

Although most biosorbents are prepared from algae, moss, fungi, or bacteria [1,2] many different materials have been studied, some of which are not necessarily biosorbents, but are included for completeness. The materials studied include bark or tannin-rich materials, lignin, chitin/chitosan, dead biomass, seaweed, algae, or alginate, xanthate, zeolite, clay, fly ash, peat moss, bone gelatin beads, leaf mould, moss, iron-oxide coated sand, modified wool, and modified cotton. All of the above materials exhibited the ability to remove metals from aqueous solutions to at least some degree with the reported sorption capacities ranging from 1 to 400 mg/g adsorbent, depending on the metal and the adsorbent in question [3].

These materials, although capable of removing metallic species from solutions have, however, been difficult to apply in an industrial setting. This is mainly due to the difficulties in handling and contacting the biomass with the process streams. Biomass tends to be very fragile and is often used in the form of dried powders. This small particle size is necessary to increase the available adsorbent surface area, but also makes handling very difficult, and renders it largely

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inappropriate for existing contact vessels. One method of overcoming these obstacles is to transform the biomass into a form whose physical characteristics are more attractive. Immobilization of the biomass within a polymer matrix is a proven method of achieving this transformation.

Biomass has been successfully immobilized in a variety of media, using a variety of techniques, including mixing with a dissolved polymer, usually polysulfone dissolved in *N,N*-dimethyl-formamide (DMF) and then dropping into water [4–10]. The most common form of immobilization appears to be that developed by Jeffers et al. [4]. In this method, beads are fabricated by mixing biomass (typically peat, algae, bacteria, or fungi) with polysulfone dissolved in DMF. The resulting slurry is atomized over a tank of water. Upon contact with the water, the droplets form solid beads through phase inversion. The authors report that this method produces a wide variety of bead sizes ranging from –100 mesh (1/16 in.) to +8 mesh (1/4 in.) in size [5].

Like unbound biomass, immobilized biomass has been shown to have a strong affinity for binding metals. As would be expected, the extent, and rate of uptake depends on the immobilized biomass, the specific metals present in solution, as well as the specific reaction conditions, such as metal concentration, solution pH, and temperature. The published literature does not address the effect of the immobilizing media other than to state that immobilized biomass is, in general, slower to react than is unbound biomass. This is due to the fact that the rate of uptake is limited by the rate of diffusion throughout the porous bead rather than the rate of binding.

The purpose of this work is to investigate the ability of three commonly available and often discarded vegetations – wood, compost, and grass – to uptake heavy metals from dilute aqueous solutions. The performance of these materials is compared to peat moss, a recognized biosorbent. This work includes the determination of first-order reaction kinetics, and the effect of multiple ions, as well as the effect of the immobilizing polymer upon those parameters.

## 2. Materials and methods

### 2.1. Vegetation preparation

Four vegetative materials were investigated—wood, grass, peat, and compost. Local waste products were used, wherever possible to align with the stated goal of evaluating common waste materials. To that end, the compost and grass were obtained from a local horse boarding facility. The compost used was well-aged and heavily composted material removed from stalls (mostly horse manure). The grass was harvested grass hay of an unknown variety. The wood was purchased hamster bedding (mostly pine), and the peat moss was commercial bedding material purchased from a garden center. All materials were dried in a drying oven and then ground to –80 mesh with a Wiley Mill. The ground material was stored in zip lock bags until used.

### 2.2. Polymers and solvent

Polysulfone and polycarbonate were purchased from Sigma–Aldrich. 1-Methyl-2-pyrrolidinone (NMP) was also purchased from Sigma–Aldrich and used to dissolve the polymers throughout this study. Polymer was dissolved in 1-methyl-2-pyrrolidinone in proportions that resulted in a viable bead being formed without the addition of vegetation. The ratio of polymer to solvent varied from 1 to 1.6 g of polymer per 10 ml of solvent, depending on the specific polymer used. In all cases, the smallest amount of polymer required to achieve physically durable beads was used, as Jeffers et al. [4] showed that porosity decreased as the polymer to solvent ratio increased.

### 2.3. Bead production and preparation

Dried, ground vegetation (–80 mesh) was added to the dissolved polymer in a 1:1 mass ratio with the polymer, resulting in beads that were approximately 50% vegetation and 50% polymer matrix. This slurry was allowed to flow slowly down a wire suspended above a beaker containing clean water. In this manner, the polymer/vegetation slurry was introduced dropwise into standing water. Upon contact with the water, the water-miscible NMP separated from the polymer/vegetation mixture, resulting in the formation of spherical beads. These beads were transferred to a fresh water bath and agitated gently on a shaker table until the wash bath remained clear and did not smell of solvent. The washed beads were dried at room temperature and then screened for odd-shaped and oversized beads using a 1/4 in. mesh screen. This method resulted in a consistent bead size of approximately 3.5 mm diameter. The beads were stored dry in sealed bags until use.

Before use, the desired mass of dry beads was placed in deionized water and agitated until they were clearly saturated with water. The soaked beads were then prepared for metal uptake by washing under agitation with 0.1 M nitric acid to remove any acid-soluble contaminants, rinsing with deionized water, and then washing in 0.1 M sodium hydroxide to place the active sites in a Na-ion form. A final rinse with deionized water completed the wash procedure. The washes were 2 h in duration and consisted 10 ml of wash solution per gram of beads for the vegetation-augmented beads and 20 ml/g for the polymer-only beads. The conditioned beads were stored in clean double-deionized water until use.

Discoloration of the wash water occurred during the early phases of the wash, indicating that some of soluble material was being released from the vegetation, however, free-floating vegetation was not observed in the wash water nor was there any evidence of vegetation being released from the beads during subsequent washes and experiments. Peat moss beads did tend to exhibit further discoloration during the basic washes, but not at any other time.

Polymer-only beads were made as above, omitting the addition of the vegetation.

#### 2.4. Heavy metal uptake

For the single-ion experiments, the conditioned beads were contacted with a solution containing 200 mg/l of a given ion (Cd, Cr, or Pb), at a ratio of 40 ml solution per gram dry beads. In all cases, test solutions were made by dissolving the nitrates salts of the metals in deionized water. This corresponds to 20 ml/g vegetation, as the beads are approximately 50% vegetation and 50% polymer. The polymer-only bead experiments were conducted at a ratio of 20 ml solution per gram dry beads in order to preserve the ion/adsorbent ratio (treating the polymer as the adsorbent in this case). All runs were conducted under agitation on a platform agitator at 150 rpm. Samples were removed at pre-determined times and retained for analysis. Retained samples diluted with deionized water and analyzed using inductively coupled plasma atomic absorption (ICP-AA) to determine the metal ion concentration in the bulk liquid. A simple material balance for a closed system yielded the bead loading as a function of contact time. These data were then used to estimate the first-order reaction rate constant and equilibrium bead loading. The same method was followed for the multiple-ion experiments, using a solution containing 200 mg/l each ion, or 600 mg/l total metal ion concentration. All experiments were performed at room temperature and pH 7 without any buffering or pH control.

### 3. Theory

The mechanism by which non-living vegetation binds metal remains a topic of much discussion with conflicting conclusions being drawn by different studies. It is accepted, however, that the majority uptake occurs in the cell walls rather than within the cell itself. The hypothesized mechanisms for sequestration include chemisorption by ion exchange, surface adsorption, complexation, and adsorption–complexation, chelation, and microprecipitation. Most published literature suggests that the uptake is accomplished through an ion exchange reaction with the polar functional groups – most likely carboxyl groups located within the cell walls of the material [2,3,11–16]. Ion exchange reactions can be appropriately modeled using first-order kinetics. Immobilizing the biosorbent material within a polymer matrix requires the ion containing solution to diffuse through the porous bead to reach the functional groups of the adsorbing material, i.e., the vegetation. It is generally accepted that ion exchange reactions are sufficiently fast as to be considered instantaneous upon contact. It is, therefore, the diffusion process that limits the rate of uptake by these beads.

For diffusion and reaction through a porous material in which the rate of diffusion is very slow compared to the rate of reaction, and in which the surface reaction can be modeled as first-order, the observed reaction rate can be expressed as:

$$r_{\text{obs}} = k_{\text{obs}} c^* \quad (1)$$

where  $c^*$  is a non-dimensionalized concentration given by:

$$c^* = \frac{c - c_f}{c_0 - c_f} \quad (2)$$

where  $c$  is the metal ion concentration in the bulk fluid,  $c_f$  the equilibrium concentration in the bulk, and  $c_0$  is the initial concentration in the bulk. The  $r_{\text{obs}}$  is the observed reaction rate in  $\text{min}^{-1}$ , and  $k_{\text{obs}}$  is the first-order reaction rate constant in  $\text{min}^{-1}$ . In this work, we are primarily concerned with the rate of bead loading, so, it is desirable to transform this expression to be in terms of a non-dimensionalized bead loading,  $l^*$ . A material balance for a closed system shows that the bead loading  $l$  can be determined according to:

$$l = \frac{(c_0 - c) \times V}{W} \quad (3)$$

In this expression,  $l$  is the bead loading, in milligram metal per gram dry vegetation (or milligram metal per gram dry polymer for polymer-only beads),  $c_0$  the initial metal ion concentration in ppm,  $c$  the current metal ion concentration in ppm,  $V$  the volume of the liquid in millilitres, and  $W$  is the weight of the adsorbent (vegetation for the vegetation-augmented beads, and polymer for the polymer-only beads) in grams.  $W$  is estimated based on the amount of vegetation added during bead manufacture, as 50% of the dry weight beads used. The non-dimensionalized bead loading,  $l^*$ , is defined to be:

$$l^* = \frac{l - l_f}{l_0 - l_f} \quad (4)$$

where  $l$  is the bead loading at time  $t$ ,  $l_f$  the final bead loading at equilibrium, and  $l_0$  is the initial bead loading (0 for this study). Combining Eqs. (2) and (3) clearly shows that  $l^* = c^*$ , and the observed reaction rate becomes:

$$r_{\text{obs}} = k_{\text{obs}} \times l^* \quad (5)$$

where  $r_{\text{obs}}$  is defined as the rate at which the lead loading changes over time and can be graphically estimated as the slope of the line tangent to a plot of the non-dimensionalized bead loading versus time. For a reaction that can be modeled using first-order kinetics, a plot of the reaction rate against  $l^*$  will be a straight line with a slope of  $k_{\text{obs}}$  and an intercept approaching zero.

Since the rate-controlling step is the transport of the ions through the pores, the reaction rate constant is a strong function of the effective diffusivity, which is a complex function of the nature of the porous structure as well as many other factors. It is beyond the scope of this work to determine relative effective diffusivities. Instead, we will discuss in broad terms, the effect of the immobilizing polymer on the rate of reaction, the extent of reaction, and the overall performance of the beads.

Once the first-order reaction rate constant has been determined, the predicted bead loading can be calculated from the analytical solution to the reaction rate equation presented as:

$$l_{\text{calc}} = l_f \times (1 - e^{-k_{\text{obs}}^* t}) \quad (6)$$

#### 4. Results

The predicted and observed bead loadings for the overall uptake of metal ions from the multiple-species solutions are presented in Figs. 1 and 2. Similar graphs for single-ion solutions are presented in Appendices A and B. The vegetation-augmented beads showed a high affinity for cadmium, chromium, and lead, efficiently removing these ions

from both single-ion and multiple-ion solutions. In general, the uptake of the metal ions from solution is well-represented by first-order reaction rate kinetics. Peat moss demonstrates superior overall performance, regardless of immobilizing media. Only compost in polysulfone achieves a comparable equilibrium bead loading, but a longer reaction time is required to reach equilibrium, 60 min as compared to 15 min for peat moss. In general, polysulfone appears to

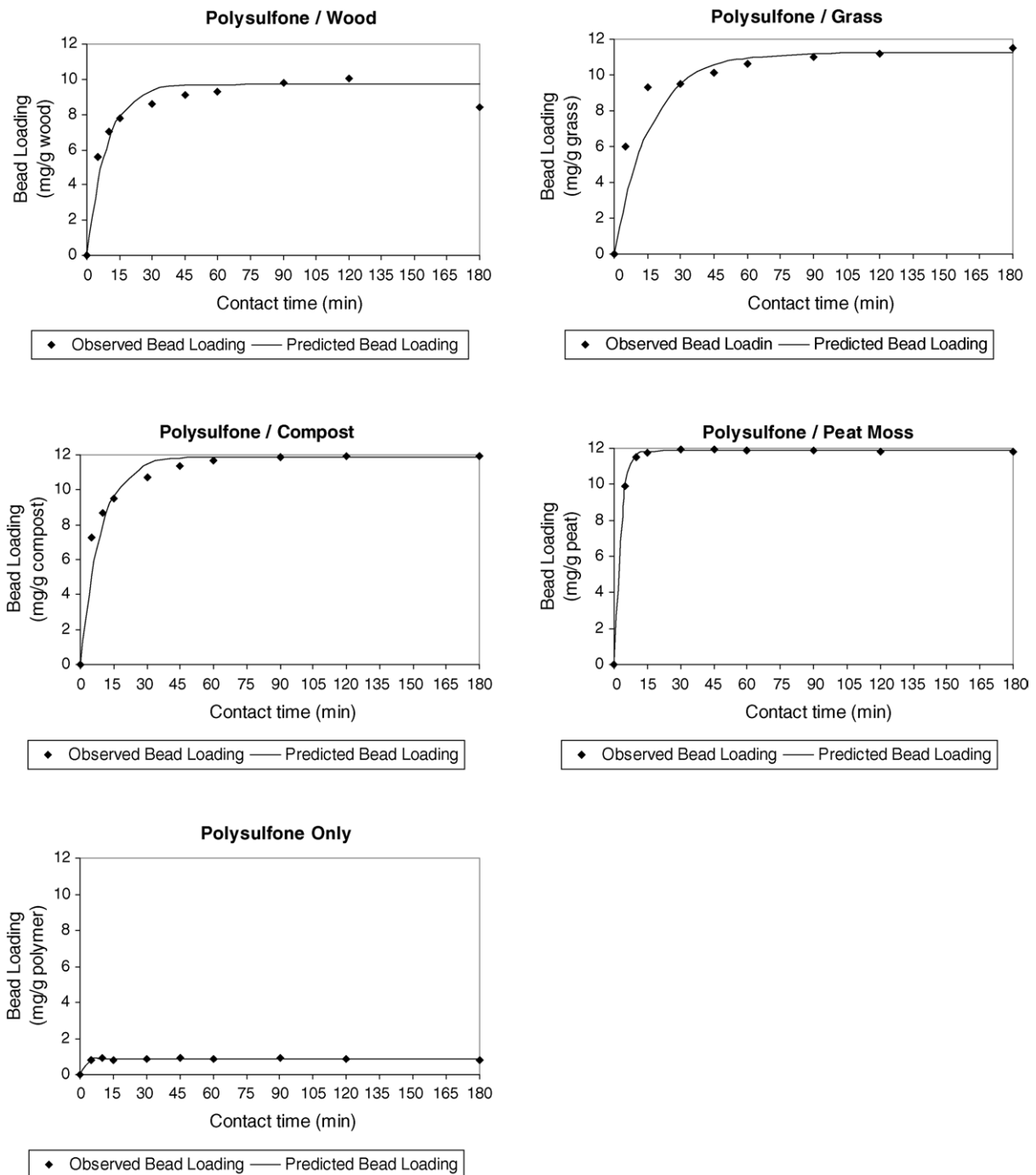


Fig. 1. Polysulfone beads in a solution of 200 mg/l each lead, cadmium, and chromium (600 mg/l total). A bead loading of 12 mg/g corresponds to complete removal of the metal ion.

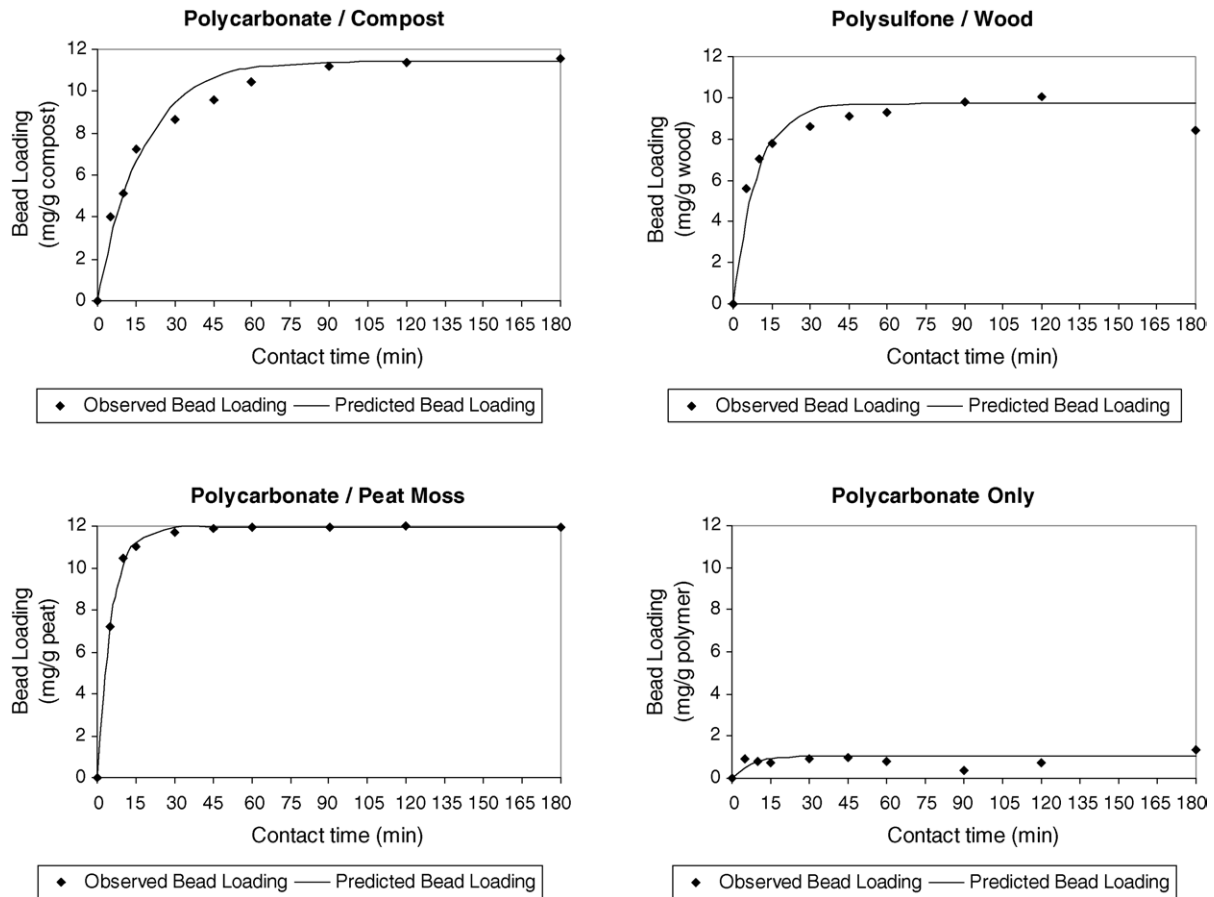


Fig. 2. Polycarbonate beads in a solution of 200 mg/l each lead, cadmium, and chromium (600 mg/l total). A bead loading of 12 mg/g would correspond to complete removal of all metal ions from the solution.

be the preferred immobilizing media. With the exception of the peat moss, all of the vegetations demonstrate a greater equilibrium bead loading when immobilized in polysulfone, despite the fact that polysulfone and polycarbonate in the absence of vegetation demonstrate comparable equilibrium loading.

The observed first-order parameters are presented in Tables 1–4. The performance of a given vegetation depends on the immobilizing material as well as the metal ions present in the solution. Note, however, that the presence of multiple ions does not result in consistent degradation of performance. Consider, for example, compost immobilized in polysulfone. In the presence of single-ion solutions, these beads removed 65% of the cadmium, 100% of the chromium, and 79% of the lead. When exposed to the multiple-ion solution, however, the beads removed essentially all of the metals present in solution. Grass in polysulfone and peat moss in both polysulfone and polycarbonate also demonstrate this behavior. Cadmium appears to be the most challenging ion to remove with only peat and compost in polysulfone achieving complete removal of this ion from multiple-species solution.

## 5. Discussion

The presence of multiple ions in solution as well as the immobilizing media affect both the uptake rate and equilibrium bead loading of all of the vegetations studied with a few exceptions. Polysulfone generally produces more efficient beads than polycarbonate, despite clear evidence that the polymer is not participating in the uptake process directly. It is hypothesized that the polysulfone forms a more porous matrix, resulting in a larger overall surface area per unit volume. It is interesting to note that in some cases the presence of multiple ions actually appears to enhance the performance of the vegetation. Consider, for example, peat moss immobilized in polycarbonate. When exposed to solutions containing only a single ion, the peat removed 75% of the cadmium, 100% of the chromium, and 50% of the chromium. When exposed to the multiple-ion solutions, however, the peat removed essentially all of the ions present, regardless of species. Grass and compost immobilized in polysulfone exhibit similar behavior. Wood does not show a unilateral increase in performance, regardless of immobilizing polymer.

Table 1  
First-order reaction rate constants ( $\text{min}^{-1}$ ) for polysulfone beads

	Cadmium		Chromium		Lead	
	Single-species	Multiple-species	Single-species	Multiple-species	Single-species	Multiple-species
Wood	0.20	0.18	0.08	0.07	0.11	0.18
Grass	0.12	0.07	0.11	0.05	0.09	0.09
Compost	0.12	0.08	0.26	0.11	0.10	0.16
Peat	0.17	0.35	0.58	0.34	0.78	Not determined
None	0.15	0.20	0.10	0.44	0.10	0.63

Table 2  
First-order reaction rate constants ( $\text{min}^{-1}$ ) for polycarbonate beads

	Cadmium		Chromium		Lead	
	Single-species	Multiple-species	Single-species	Multiple-species	Single-species	Multiple-species
Wood	0.21	0.04	0.11	0.03	0.22	0.04
Grass	0.21	0.06	0.10	0.05	0.17	0.08
Compost	0.29	0.04	0.41	0.06	0.28	0.05
Peat	0.16	0.12	0.05	0.28	0.29	0.29
None	0.06	Not determined	0.09	0.18	0.05	0.10

Table 3  
Equilibrium bead loading ( $\text{mg/g}$  adsorbent) for polysulfone beads

	Cadmium		Chromium		Lead	
	Single-species	Multiple-species	Single-species	Multiple-species	Single-species	Multiple-species
Wood	2.73	2.57	3.96	3.76	2.13	3.73
Grass	1.92	3.44	3.98	3.95	3.15	3.95
Compost	2.59	3.97	4.00	4.00	3.17	3.94
Peat	3.00	3.99	3.96	4.00	3.93	3.89
None	0.87	0.28	0.03	0.30	1.37	0.29

Bead loading of 4 mg/g corresponds to complete removal of the ion from solution.

Table 4  
Equilibrium bead loading ( $\text{mg/g}$  adsorbent) for polycarbonate beads

	Cadmium		Chromium		Lead	
	Single-species	Multiple-species	Single-species	Multiple-species	Single-species	Multiple-species
Wood	3.41	2.64	3.98	3.98	1.50	3.94
Grass	3.60	2.82	3.53	3.87	3.64	3.96
Compost	3.90	3.50	3.99	3.98	3.96	3.97
Peat	2.92	3.98	3.99	4.00	1.72	3.97
None	1.33	0.28	1.01	0.31	1.24	0.33

Bead loading of 4 mg/g corresponds to complete removal of the ion from solution.

Although the presence of multiple ions can be seen to, in some cases, increase the equilibrium bead loading, in nearly all cases, the initial rate of reaction decreased in the presence of multiple ions. This is most evident for the polycarbonate beads, where all of the vegetations except peat demonstrated a dramatic decrease in reaction rate constant in the presence of multiple ions. This phenomenon is seen to a slightly lesser extent when the vegetations are immobilized in polysulfone. Peat, by contrast, demonstrated a lower degree of degrada-

tion, and in some cases, even an increase in reaction rate in the presence of multiple ions.

First-order rate constants can be used to estimate the order of removal of the ions from mixed solutions, as the species that is removed the fastest (greatest reaction rate constant) is clearly removed first. This does not, however, necessarily correspond with the order of binding preference. This parameter is more accurately evaluated from the equilibrium composition of the solutions containing multiple species, as the ions

Table 5  
Polysulfone beads binding preference

Bead type	Percent change in equilibrium loading single-species solutions vs. three-metal mixture			Order of preference
	Cd	Cr	Pb	
PS + wood	−6	−5	75	Pb > Cd = Cr
PS + grass	77	−8	23	Cd > Pb > Cr
PS + compost	53	0	24	Cd > Pb > Cr
PS + peat	33	1	−1	Cd > Pb = Cr
PS only	−68	900	−79	Cr ≫ Pb > Cd

Table 6  
Polycarbonate beads binding preference

Bead type	Percent change in equilibrium loading single-species solutions vs. three-metal mixture			Order of preference
	Cd	Cr	Pb	
PC + wood	−22	0	163	Pb ≫ Cr > Cd
PC + grass	−22	12	1	Cr > Pb > Cd
PC + compost	−10	0	0	Pb = Cr > Cd
PC + peat	36	0	99	Pb > Cd > Cr
PC only	−78	−67	−73	Cr > Pb = Cd

that are removed first (fastest) may be displaced by a more preferred ion over time. Thus, the overall performance of a bead is related not only to the rate of reaction, but also to the extent of reaction, or the eventual equilibrium loading that is accomplished.

If we compare the equilibrium bead loading in the presence of multiple ions to that obtained in the presence of only one species, we can get an indication of the binding affinity the vegetations have for a given ion. This can be accom-

plished by calculation the percent change in equilibrium bead loading,  $\Delta l = (l_{a,\text{single}} - l_{a,\text{mixed}}) / l_{a,\text{single}}$ , where  $l_{a,\text{single}}$  and  $l_{a,\text{mixed}}$  are the observed equilibrium loadings for ion a for a single species solution and the multiple-species solution, respectively. The order of preference then is determined by examination of this parameter. A positive value indicates that the uptake of that ion increased when multiple ions were present, and it can thus be inferred that that ion is preferentially bound and may even displace the less preferred ions as the reaction time progresses. This parameter is presented in Tables 5 and 6. Note that the immobilizing media has a noticeable effect on the order of binding preference, despite that fact that the polymers themselves demonstrate similar binding preferences.

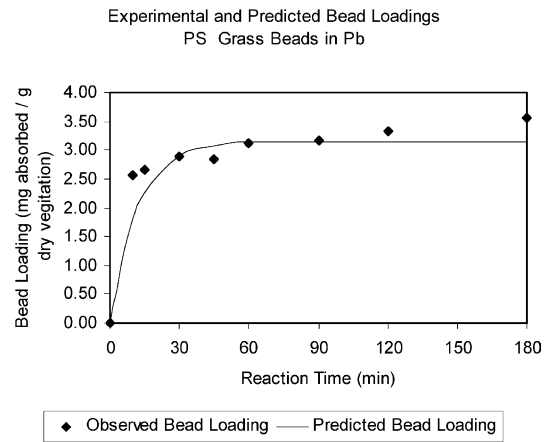
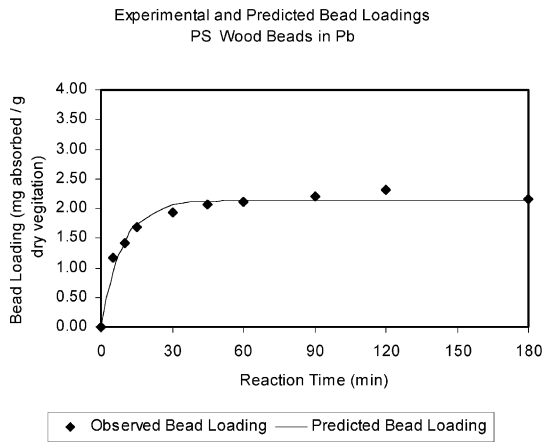
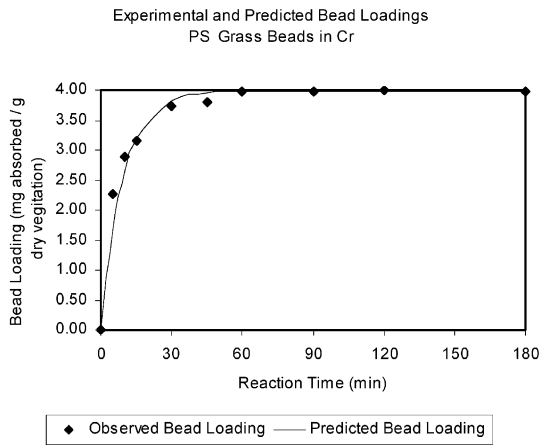
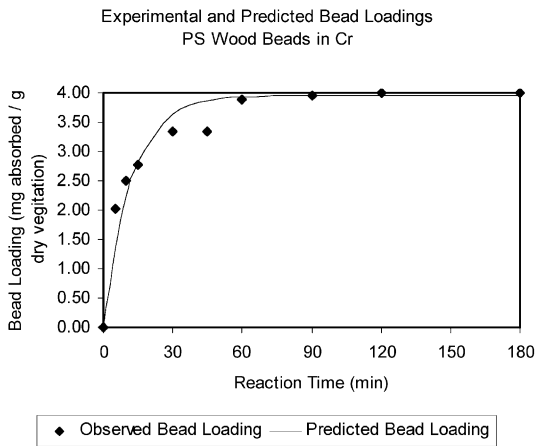
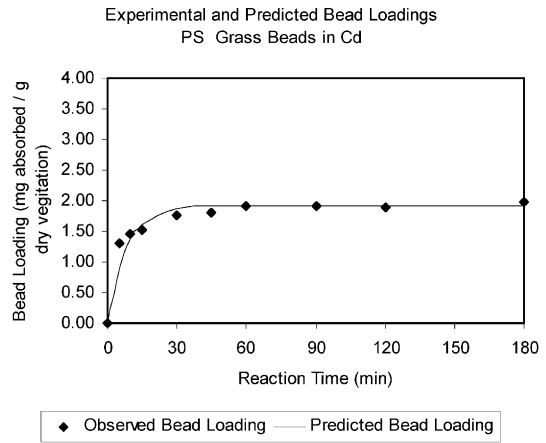
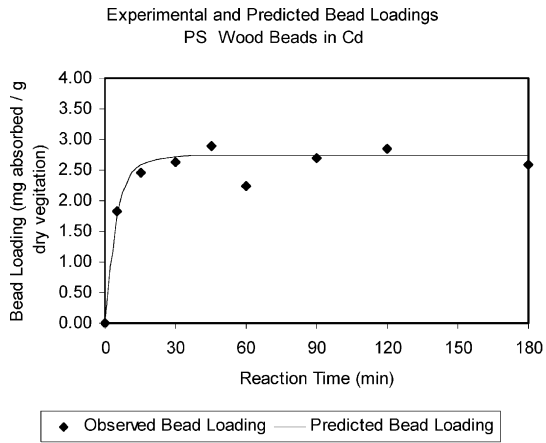
## 6. Conclusions

The common vegetative materials grass and compost are shown to effectively remove heavy metals from aqueous solutions, approaching the equilibrium bead loading of peat moss. Although not performing to the level of the other vegetations studied, herein, wood is shown to also remove heavy metal ions from dilute aqueous solutions. The presence of multiple ions slows the uptake rate, but is seen to in some cases increase the equilibrium loading of the bead.

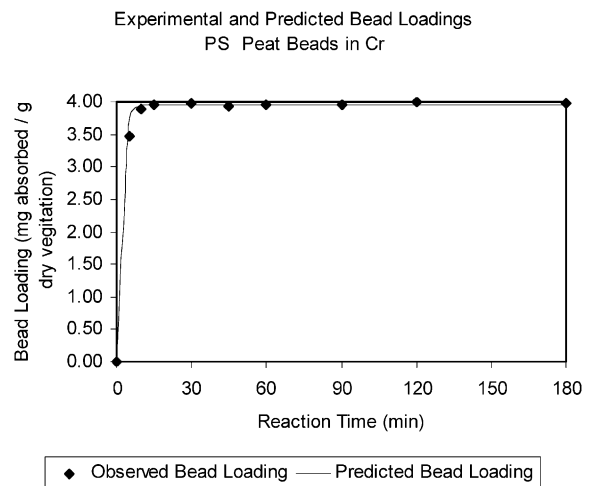
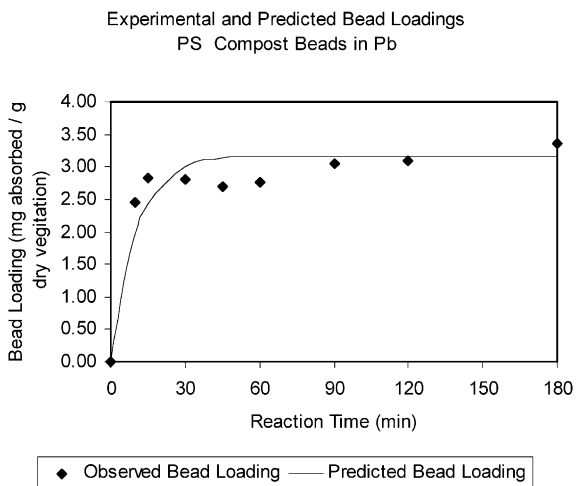
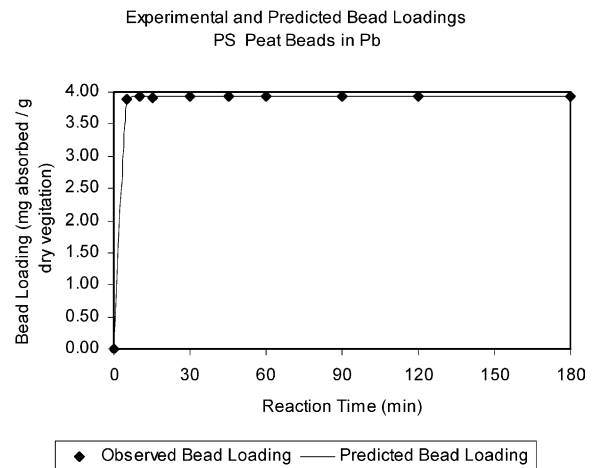
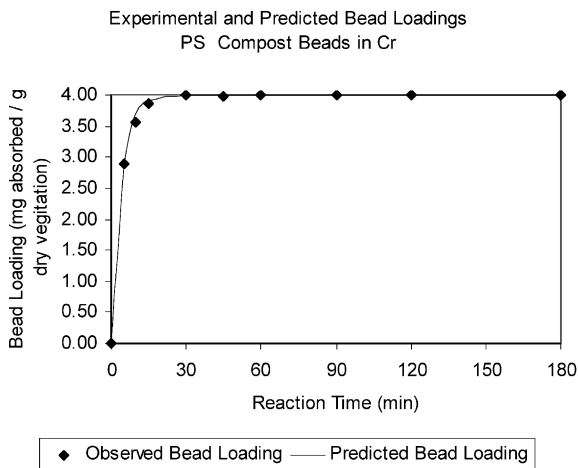
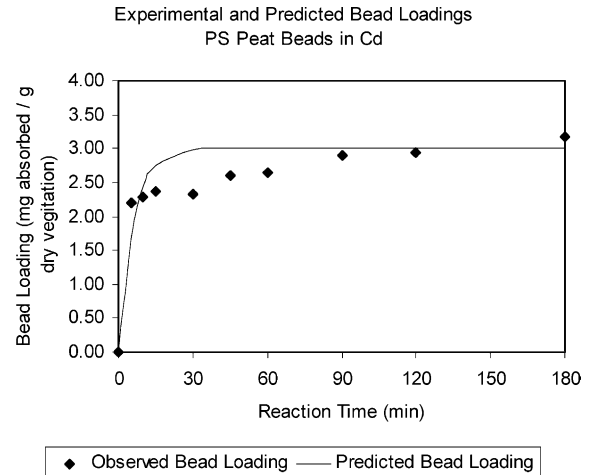
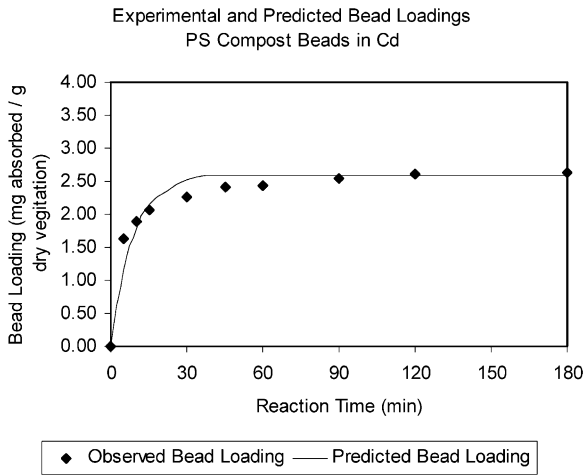
This work clearly demonstrates that the immobilizing polymer significantly affects the performance of a given vegetation, and this effect must be considered in developing biosorbent beads. For applications, where multiple species are likely to present, polysulfone is the preferred polymer, as these beads demonstrated a lower sensitivity to the presence of multiple ions.

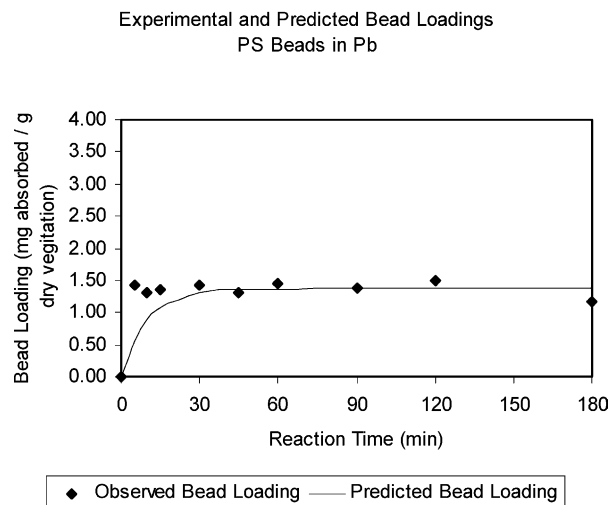
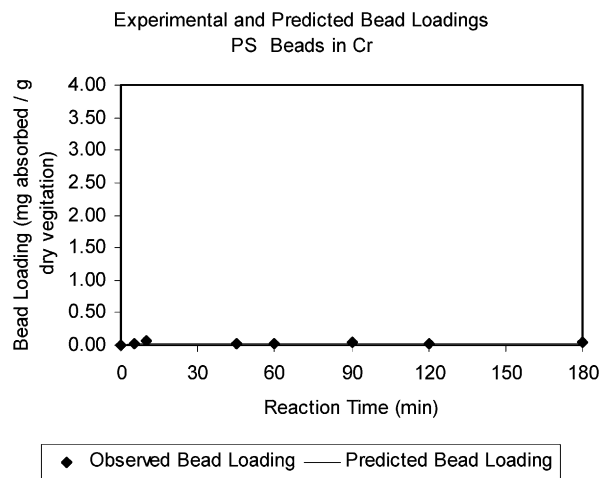
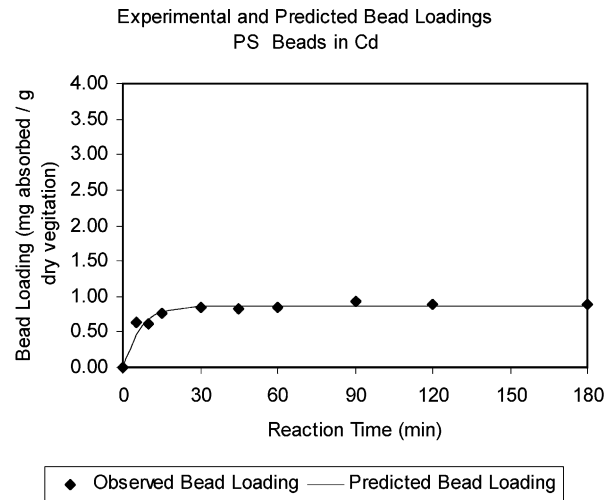


**Appendix A. Polysulfone beads in single-ion solutions**

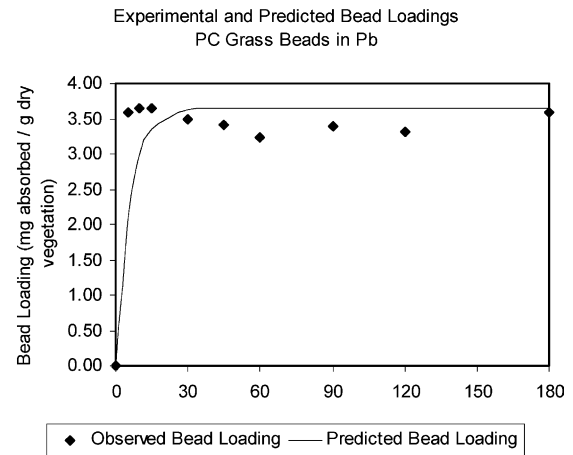
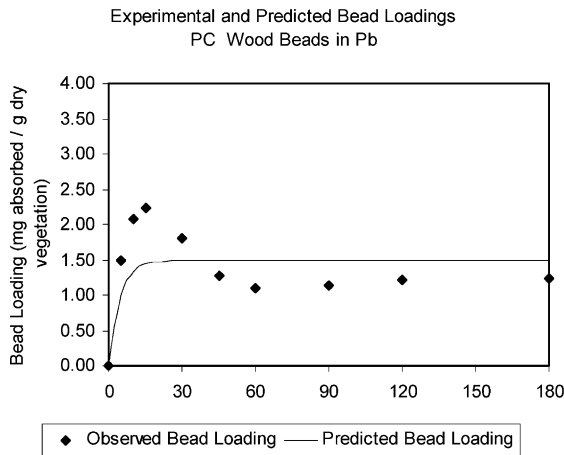
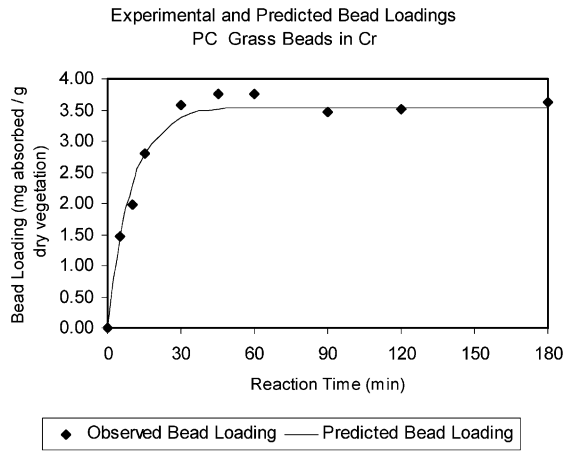
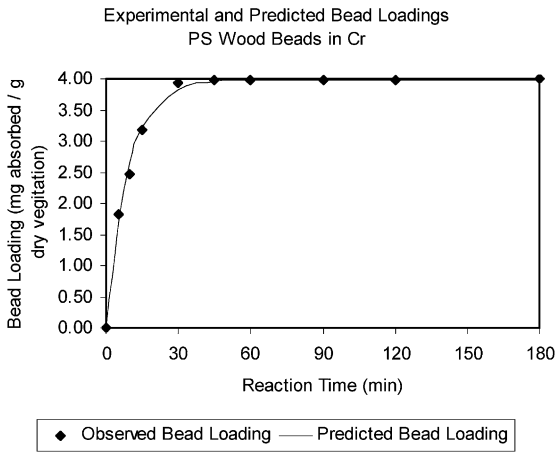
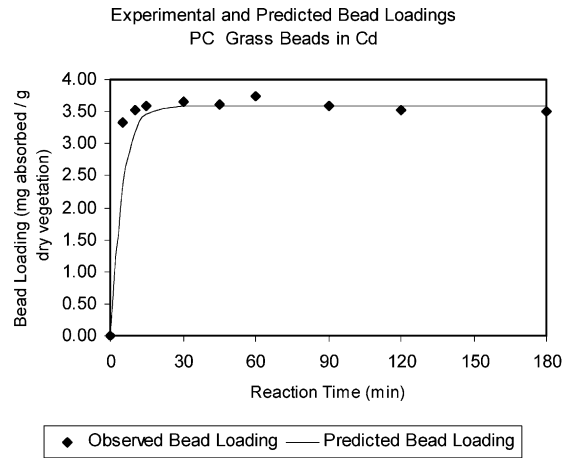
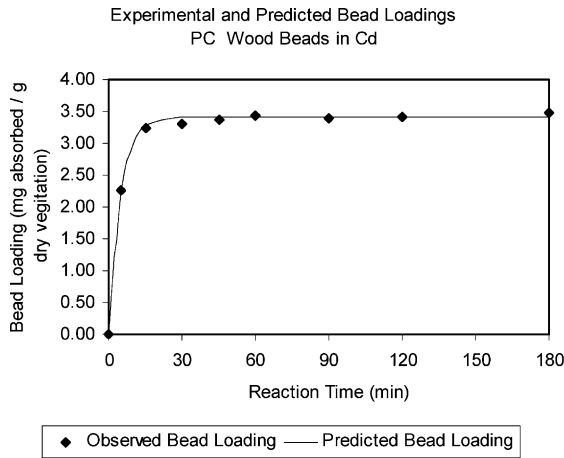


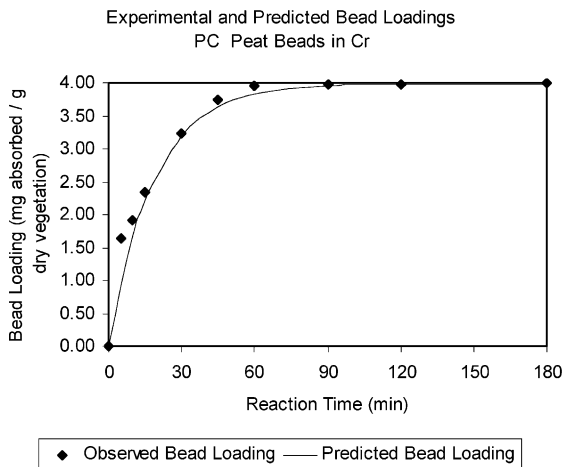
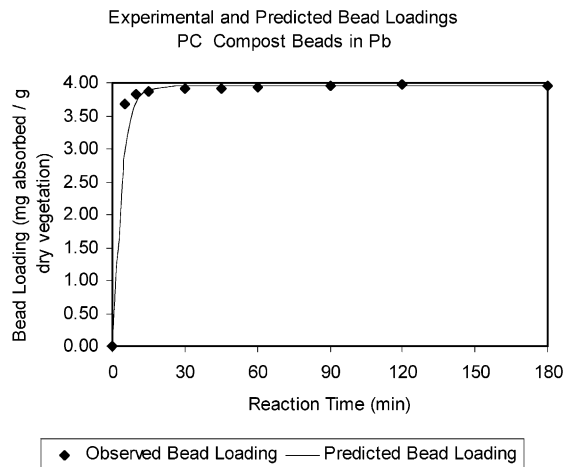
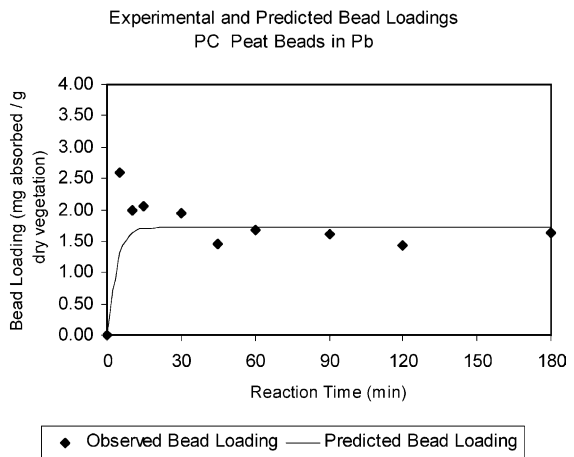
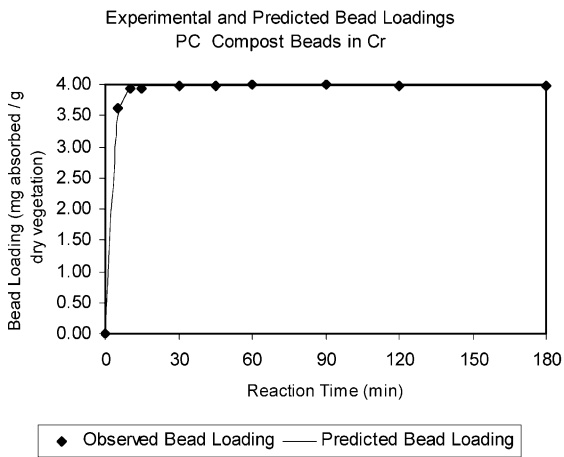
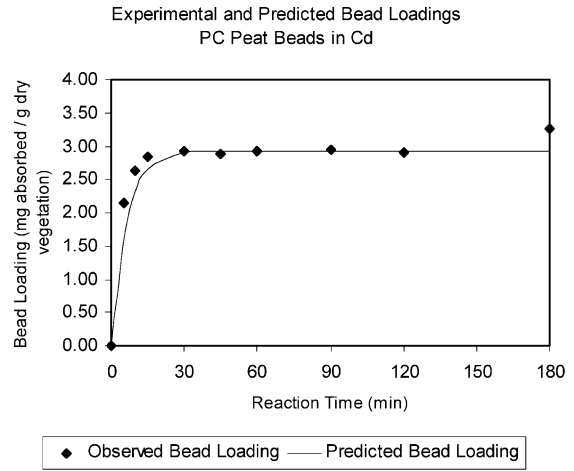
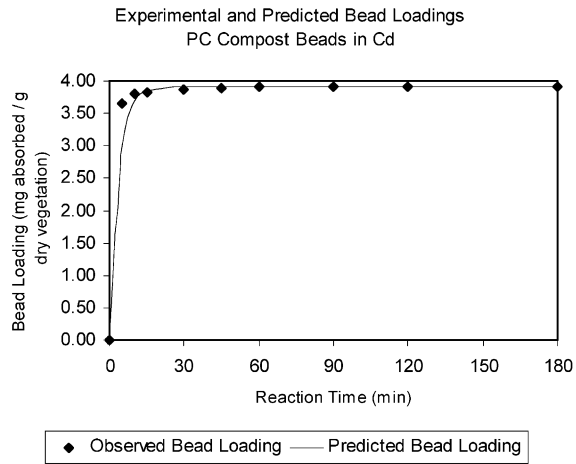


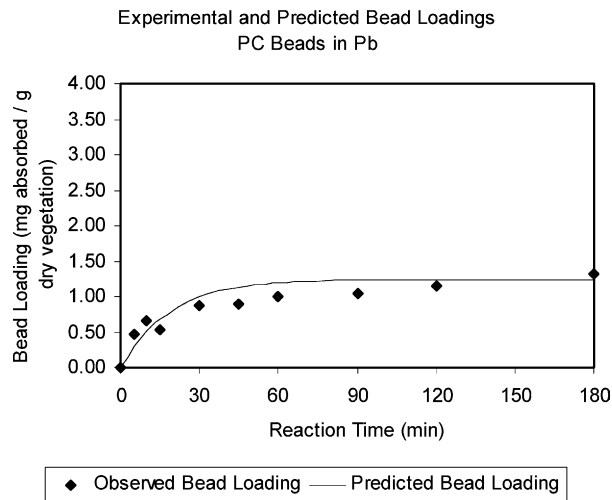
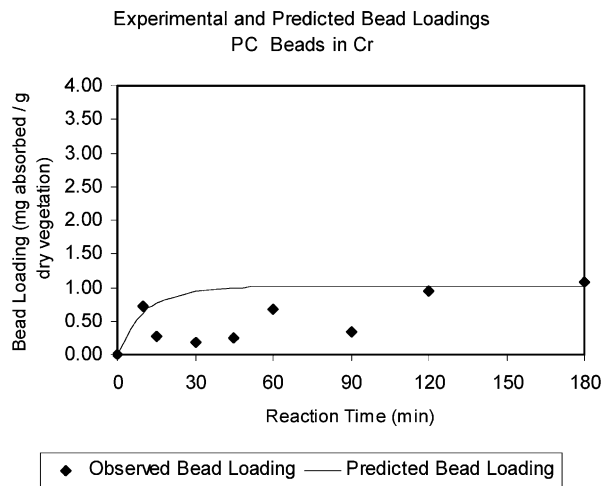
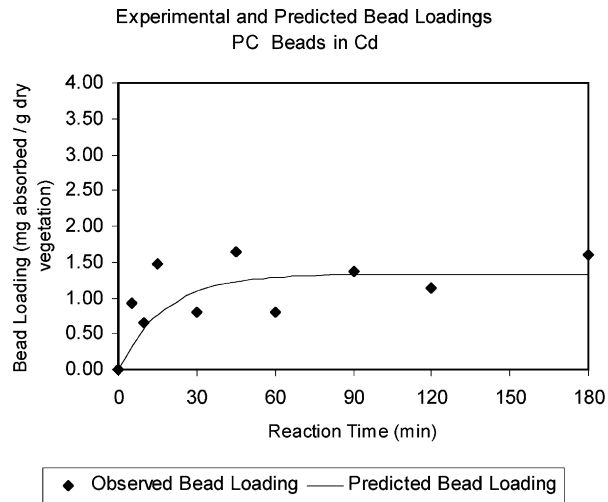




**Appendix B. Polycarbonate beads in single-ion solutions**







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