

ABSTRACT

Title of Document: THE USE OF HATCHERY RESIDUAL
BIOSORBENT FOR REMOVAL OF HEAVY
METALS FROM WASTEWATER

Heloisa Andrade de Paula Tudury, Master of
Science, 2006

Directed By: Assistant Professor Jennifer G. Becker
Department of Biological Resources Engineering
Professor Allen P. Davis
Department of Civil and Environmental
Engineering

The recycling of hatchery wastes could reduce disposal costs for this broiler production residual. Eggshell is abundant in the residual and is composed primarily of calcite, which is known to sorb metals. The uptake of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) from aqueous solutions by the residual was investigated, and the underlying mechanisms were characterized in a series of batch and column experiments. The residual's selectivity decreased according to: $\text{Pb(II)} > \text{Cu(II)} > \text{Zn(II)} > \text{Cd(II)} > \text{Ni(II)}$ and probably can be explained by different removal mechanisms. Compared with a commercial ion exchange resin, treatment columns containing the residual had a relatively low capacity for metals in an electroplating wastewater and regeneration was relatively inefficient. Thus, it may not be practical to use the residual in primary wastewater treatment. Use of the residual in wastewater polishing or as a co-amendment with land-applied biosolids may be more appropriate.

The use of hatchery residual biosorbent for removal of heavy metals from wastewater

By

Heloisa Andrade de Paula Tudury

Thesis submitted to the Faculty of the Graduate School of the
University of Maryland, College Park, in partial fulfillment
of the requirements for the degree of
Master of Science
2006

Advisory Committee:
Professor Jennifer G. Becker, Advisor
Professor Allen P. Davis, co-Advisor
Professor Oliver J. Hao

© Copyright by
Heloisa Andrade de Paula Tudury
2006

Aos meus pais, Lair e Suelly, que sempre me corujaram.

Egghead: Woe is me. My criminal career is now *eggstinct*!

Batman: Foolish, evil man!

Robin: You're going to go where all the broken eggshells end up: in the garbage!

Acknowledgements

First and foremost, I thank my advisor, Dr. Jennifer Becker, and co-advisor, Dr. Allen Davis. They taught me more than they would believe and both were very generous with their time, patience, understanding, and a lot of red ink (in Dr. Becker's case, pencil lead, blue and black ink too).

This work wouldn't be possible without support from the Maryland Industrial Partnerships (MIPS) Program and American Dehydrated Foods, Inc.

My requirements for getting this degree involved having interesting classes with Dr. Torrents, Dr. Hao, Dr. Seagren, Dr. Davis and Dr. Brubaker. I wouldn't mind skipping the exams, but they were all very good teachers.

I am also indebted to my colleagues at the lab, especially Kelly Flint and Roman Hsieh, who taught me how to operate the Atomic Absorption Spectrometer and general lab procedures. Azy Kia is the best lab assistant ever, and also a good friend. Thanks, Azy!

I cannot name each and every friend and family member who was supportive all along, so I won't. You know who you are. Thank you.

Finally, I thank my parents, Lair & Suelly, and my sister Lavinia, whose love can be felt from thousands of miles away.

Table of Contents

Chapter 1. Introduction	1
Chapter 2. Materials and Methods	6
2.1 Chemicals.....	6
2.2 Hatchery Residual.....	6
2.3 Industrial Wastewater	7
2.4 Physical Characterization Methods.....	7
2.5 Experimental Approach	8
2.5.1 Solutions and Sample Storage	8
2.5.2 Batch Equilibrium Experiments.....	9
2.5.3 Column Sorption Experiments (Defined Solutions).....	10
2.5.4 Column Sorption Experiments (Industrial Wastewater).....	13
2.5.5 Analytical Methods.....	14
2.5.6 Metal Speciation Calculations	16
Chapter 3. Characterization of the Uptake of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) by a Hatchery Residual Biosorbent	19
3.1 Introduction.....	19
3.2 Results.....	22
3.2.1 HRB Characteristics.....	22
3.2.2 Batch Sorption Experiments	25
3.2.3 Metal Speciation Calculations	31
3.2.4 Column Experiments	32
3.3 Discussion.....	38

Chapter 4. Comparison of an Ion-Exchange Resin and HRB for Removal of Heavy Metals from Plating Wastewater.....	48
4.1 Introduction.....	48
4.2 Results.....	50
4.2.1 Complexed Metals	50
4.2.2 Industrial Wastewater	53
4.3 Discussion.....	63
Chapter 5. Conclusions	72
References.....	100

List of Tables

Table 2-1. AA operation parameters.....	15
Table 2-2. Stability constants used in chemical speciation calculations for aqueous species (Stumm and Morgan 1996).	17
Table 2-3. Stability constants used for prediction of solids formation (Zachara et al. 1988; Stumm and Morgan 1996)	18
Table 3-1. Capacity of packed HRB column for uncomplexed metals provided as a mixture (10^{-4} M total; pH 5) and recovery of metals using 5 bed volumes of deionized water plus 10 bed volumes of 50 mM EDTA.	35
Table 3-2. Cd(II) uptake and release during repeated column breakthrough and regeneration cycles. 2×10^{-5} M Cd(II); pH 5; 4 ml HRB bed volume (~4.4 mg), regenerated with 10 bed volumes EDTA (9 mM).	38
Table 3-3. Surface complexation reactions for the system $\text{CaCO}_{3(s)}\text{-H}_2\text{O-CO}_2$ and their corresponding homogeneous reactions, and metal speciation in a homogeneous system (adapted from Van Cappellen et al. (1993) and Zachara et al. (1991)).	41
Table 4-1. Capacity of packed HRB column for uncomplexed metals provided as a mixture (10^{-4} M total; pH 5) and a mixture (10^{-4} M total; pH 5) of metals complexed with NH_4Cl (4×10^{-4} M). HRB bed volume = 4 ml (4.4 g). Values for metals without complexing agent are from Chapter 3.....	52
Table 4-2. Final recovery of free metals and metals complexed with NH_4Cl from a 4 cm^3 HRB-packed bed column using 5 bed volumes of deionized water plus 10 bed volumes of 50 mM EDTA.	53
Table 4-3. Concentrations of metals and other inorganic compounds in the electroplating wastewater.....	54

List of Figures

Figure 2-1. Diagram of column breakthrough experimental system.	12
Figure 3-1. X-ray diffraction of HRB (thick line) and calcite (thin line). Insert illustrates X-ray diffraction of eggshells, as reported by Dobiášová et al. (2004).	23
Figure 3-2. SEM image of (a) unused HRB and (b) HRB used in a column experiment, magnified 225x. The bar represents 50 μm	24
Figure 3-3. Effects of pH and initial Cd(II) concentration on sorption of Cd(II) to HRB (1 g/L); I=0.05 M $\text{NaClO}_4\cdot\text{H}_2\text{O}$	26
Figure 3-4. Effects of pH and initial Cr(VI) concentration on sorption of Cu(II) to HRB (1 g/L); I=0.05 M $\text{NaClO}_4\cdot\text{H}_2\text{O}$	26
Figure 3-5. Effects of pH and initial Cu(II) concentration on sorption of Cu(II) to HRB (1 g/L); I=0.05 M $\text{NaClO}_4\cdot\text{H}_2\text{O}$	27
Figure 3-6. Effects of pH and initial Ni(II) concentration on sorption of Ni(II) to HRB (1 g/L); I=0.05 M $\text{NaClO}_4\cdot\text{H}_2\text{O}$	27
Figure 3-7. Effects of pH and initial Zn(II) concentration on sorption of Zn(II) to HRB (1 g/L); I=0.05 M $\text{NaClO}_4\cdot\text{H}_2\text{O}$	28
Figure 3-8. Kinetics of sorption of 2×10^{-5} M Cd(II) onto the HRB (1 g/L) at pH 3, 6.5, and 9 (I = 0.05 M $\text{NaClO}_4\cdot\text{H}_2\text{O}$).	29
Figure 3-9. Effect of pH on sorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) from a solution containing 2×10^{-5} M of each metal onto the HRB (1 g/L) (I = 0.05 M $\text{NaClO}_4\cdot\text{H}_2\text{O}$).	30
Figure 3-10. Effect of influent pH and Cd(II) concentration on Cd(II) breakthrough curves and effluent pH for 4 cm^3 HRB (4.4 g) columns. Cd(II) breakthrough curves for (●) 2×10^{-5} M (2 mg/L) Cd(II), pH 5; (■) 10^{-4} M (10 mg/L) Cd(II), pH 5 ; and (◇) 2×10^{-5} M Cd(II), pH 7.	33
Figure 3-11. Breakthrough curves for uncomplexed metals for a 4 cm^3 HRB packed-bed column. Total influent metals = 10^{-4} M, pH 5, I= 5×10^{-2} M $\text{NaClO}_4\cdot\text{H}_2\text{O}$	34
Figure 3-12. Recovery of uncomplexed metals from a 4 cm^3 HRB packed-bed with 10 bed volumes of EDTA (50 mM). Data for uptake is shown in Table 3-1.	36
Figure 3-13. Cd(II) breakthrough curves and effluent Ca(II) concentrations for a 4 cm^3 HRB packed bed column that was repeatedly loaded with Cd(II) and regenerated with EDTA (10 bed volumes, 9 mM). Influent Cd(II) = 2×10^{-5} M, pH 5, I= 5×10^{-2} M $\text{NaClO}_4\cdot\text{H}_2\text{O}$).	37
Figure 4-1. Breakthrough curves for NH_4Cl complexed metals from a 4 cm^3 HRB packed-bed column. (Influent metals = 2×10^{-5} M each metal, pH 5, I = 5×10^{-2} M $\text{NaClO}_4\cdot\text{H}_2\text{O}$).	51

Figure 4-2. Recovery of metals complexed with NH_4Cl from a 4 cm^3 HRB-packed bed column using 5 bed volumes of deionized water followed by 10 bed volumes of 50 mM EDTA. Adsorbed values are given in Table 4-1.	53
Figure 4-3. Breakthrough of $3.8 \times 10^{-5} \text{ M}$ Pb from the 16 cm^3 Amberlite® IRC748 and HRB packed-bed columns, at pH 5. Other metal concentrations are listed in Table 4-3.	56
Figure 4-4. Breakthrough of $1.3 \times 10^{-4} \text{ M}$ Fe from the 16 cm^3 Amberlite® IRC748 and HRB packed-bed columns, at pH 5. Other metal concentrations are listed in Table 4-3.	56
Figure 4-5. Breakthrough of $5.1 \times 10^{-4} \text{ M}$ Ni from the 16 cm^3 Amberlite® IRC748 and HRB packed-bed columns, at pH 5. Other metal concentrations are listed in Table 4-3.	57
Figure 4-6. Breakthrough of 10^{-5} M Cu from the 16 cm^3 Amberlite® IRC748 and HRB packed-bed columns, at pH 5. Other metal concentrations are listed in Table 4-3. .	57
Figure 4-7. Breakthrough of $2.6 \times 10^{-6} \text{ M}$ Zn from the 16 cm^3 Amberlite® IRC748 and HRB packed-bed columns, at pH 5. Other metal concentrations are listed in Table 4-3.	58
Figure 4-8. Breakthrough of $8.7 \times 10^{-6} \text{ M}$ Ca from the 16 cm^3 Amberlite® IRC748 column and Ca release from the 16 cm^3 HRB packed-bed column, at pH 5. Other metal concentrations are listed in Table 4-3.	58
Figure 4-9. Selectivity coefficients (defined in text) of HRB and Amberlite® IRC748 for metal cations in the industrial wastewater.	60
Figure 4-10. Ca eluted and pH of effluent in breakthrough experiment for NH_4Cl complexed metals from a 4 cm^3 HRB packed-bed column. (Influent metals = $2 \times 10^{-5} \text{ M}$ each metal, pH 5, I = $5 \times 10^{-2} \text{ M}$ $\text{NaClO}_4 \cdot \text{H}_2\text{O}$).	65

Chapter 1. Introduction

Production of broilers is the foremost agricultural activity in the state of Maryland and on the Delmarva Peninsula, the peninsula on the East Coast of the U.S. occupied by Delaware, Maryland, and Virginia, with poultry and eggs accounting for 71%, 32%, and 45%, respectively, of the total sales of agricultural products for DE, MD and VA in 2002 (USDA 2004). These three states produced 790 million broiler chicks in 2004 (Delmarva Poultry Industry Inc. 2005). Thus, hatcheries in this region and other areas within the U.S. produce significant amounts of residuals, and the management and disposal of residuals from hatcheries is a major concern for the U.S. poultry industry. In 1976, production of hatchery residuals in the U.S. was estimated to be 50,900 and 18,200 metric tons for broiler and layer chicks, respectively (Vandepopuliere 1976). Hatchery residuals include infertile eggs, dead embryos, dead chicks, and shells from hatched chicks. By 2000, the amount of byproducts generated annually had increased to more than 90,700 metric tons for broiler chicks alone (Blake 2000). In some cases, it is possible to reduce the volume of hatchery residuals that require disposal by extracting liquid protein, which can be used in animal feed. However, the remaining material still requires disposal. Typical disposal options for this processed material include composting, land application, incineration and burial (Deshmukh and Patterson 1997). Land application is the least expensive alternative, but applying the processed hatchery material to agricultural lands can result in objectionable odors. Unfortunately, composting, incineration and landfilling are not cost effective disposal options. Therefore, an alternative disposal technique is needed. In particular, increasing the

portion of the hatchery residuals that is recycled for use in other applications is an appealing approach.

Thus, it is useful to consider the characteristics of major components of the processed hatchery residuals, which include eggshell and animal fibrous proteins, e.g., in feathers and eggshell membrane. Previously it has been shown that separately, eggshell membrane (Goto and Suyama 2000), and eggshell can sorb a wide variety of dissolved metals from water. As a result, other investigators have proposed that these materials could be used to remove metal contaminants from industrial wastewaters.

Interest in the use of materials derived from biological organisms as sorbents for the removal of dissolved metals and other pollutants from water, termed biosorption (Volesky 1990), is increasing. In addition to eggshells, membranes and feathers derived from poultry, a wide variety of biological materials including algal, fungal, and bacterial biomass, e.g., (Volesky 1990; Huang et al. 1991), seafood processing waste sludge (Lee and Davis 2001), and soybean hulls (Wartelle and Marshall 2001) have been tested for their potential as biosorbents.

Interest in the development of biosorbents is motivated in part by the large volumes of metals-contaminated wastewater that are produced by a variety of industries and require treatment. In 1995, the U.S. Environmental Protection Agency estimated that the metal fabricating and finishing industries (e.g., electroplating) alone transferred more than 34,200 kg/yr of copper, 477,000 kg/yr of nickel, 374,000 kg/yr of chromium, 900,000 kg/yr of zinc and 28,400 kg/yr of cadmium to wastewater for subsequent treatment (U.S. EPA 1995). In addition, contamination of soil and groundwater with heavy metals is a major problem in the U.S.: fifteen percent of Superfund sites are

contaminated solely by heavy metals, and 64% of these sites are impacted by a mixture of heavy metals and organics (Raskin and Ensley 2000). This pollution is often a result of activities involving battery, paint and chemical manufacturing, electroplating, metal finishing and/or mining industries (Raskin and Ensley 2000). Cost effective remediation techniques are needed for cleanup of heavy metal-contaminated soils and groundwater.

Currently, treatment of metals-laden water, wastewater, and groundwater is being accomplished with a variety of treatment technologies, including chemical precipitation, ion exchange, sorption onto metal oxides or activated carbon, and reverse osmosis. Each of these approaches has potential limitations and disadvantages. For example, chemical precipitation is often inadequate for meeting regulatory treatment requirements (Lee and Davis 2001). Other technologies such as sorption and reverse osmosis can be prohibitively expensive if used on a large scale. However, in order for potential users to adopt biosorption in lieu of proven competing technologies, it must be demonstrated that a given biosorbent, in addition to being cost-effective, meets a number of important criteria. First, it must be shown that the biosorbent can achieve satisfactory removal of the metals of interest under the range of conditions that would be experienced in actual treatment scenarios. For example, the effectiveness of the biosorbent at removing metals at a range of concentrations must be known. Further, biosorbents must have physical characteristics that are suitable for process applications. Ideal biosorbents are reusable, inexpensive and easy to handle.

As discussed above, there is a need for a low cost alternative for treating metal-contaminated wastewater, groundwater and soils. Further, approaches for reducing the volume of hatchery residual requiring disposal and associated costs are needed. This

work focused on evaluating whether a processed hatchery residual would exhibit the metal sorbing properties observed for eggshell, eggshell membrane and feathers and could be marketed as a metal biosorbent. Thus, this project was driven by the idea that development of a marketable hatchery residual biosorbent (HRB) could potentially solve two important environmental problems.

Specifically, the objectives of this work were to:

1. Characterize the physical and chemical properties of HRB.
2. Quantify the capacity of HRB for individual metals, and mixtures of uncomplexed metals under batch equilibrium conditions and the effects of pH, initial metal concentration, and contact time on these capacities.
3. Quantify the capacities for HRB for individual metals and mixtures of complexed and uncomplexed metals in a column configuration and characterize the reversibility of sorption.
4. Compare the performance of HRB and a commercially available ion exchange resin during treatment of an industrial wastewater.
5. Calculate the speciation of several metals in a homogeneous aqueous system containing calcite.

In the next chapter, Chapter 2, the experimental materials and methods used in this project are described. Chapter 3 has background information on the use of agricultural residuals for sorbing metals in the treatment of industrial wastewaters. The capacity of unused and regenerated residual to sorb individual metals and mixtures of metals was evaluated in a series of batch and defined-solution column experiments;

results of these assays are presented and discussed also in Chapter 3. Chapter 4 describes defined-solution column experiments that were conducted with mixtures of uncomplexed and NH_3 -complexed metals and treatment of an industrial wastewater obtained from an electroplating facility in columns packed with either the HRB or a commercially-available ion exchange resin. Finally, in Chapter 5, this work's conclusions and recommendations for further work are presented.

Chapter 2. Materials and Methods

2.1 Chemicals

Analytical grade $\text{Cd}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$, $\text{Cu}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$, $\text{Ni}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ and $\text{Zn}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ were obtained from Aldrich (St. Louis, MO). $\text{Pb}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ was obtained from EM Industries, Inc (Hawthorne, NY), and Na_2CrO_4 was obtained from Fisher Chemical (Fairlawn, NJ).

HClO_4 and NH_4Cl were obtained from JT Baker (Phillipsburg, NJ), and EDTA was obtained from EM Industries, Inc (Hawthorne, NY). Reference solutions for Ca, Cd, Fe, Pb, Ni and Zn were obtained from Fisher (Fairlawn, NJ) and Cu reference solution was obtained from Aldrich (St. Louis, MO).

Amberlite® IRC748 (Rohm and Haas Company, Philadelphia, PA) is a commercially-available resin specifically designed to remove heavy metals from wastewater (Brower et al. 1997).

2.2 Hatchery Residual

Processed hatchery residual was provided by American Dehydrated Foods, Inc. (Princess Anne, MD) and was derived from heterogeneous material that included eggs, unhatched chicks, membranes, embryonic fluids and eggshells (personal communication, American Dehydrated Foods Inc., 2002). The raw material was centrifuged by ADF, and protein was extracted from the liquid supernatant for use in pet foods. The remaining fraction was dried through heating and processed with a hammermill, resulting in a product with a dried oatmeal-like appearance.

Preliminary evaluations indicated that hatchery residual particles smaller than 0.5 mm discolored the water and made sample filtration difficult. Particles larger than 2 mm were also discarded because they primarily comprised feathers, which tended to float in the air and complicated handling of the hatchery residual. Hatchery residual particles within the 0.5 mm to 2 mm size fraction were obtained through mechanical sieving for 30 min. The sieved material was stored in airtight polypropylene containers at room temperature until used in experiments. This material is referred to as HRB.

2.3 Industrial Wastewater

Industrial wastewater was obtained from an electroplating plant that plates aircraft parts using nickel and nickel-containing alloys at Perkin-Elmer Fluid Sciences (Beltsville, MD). The wastewater had a pH of 2.7 and contained an unknown mixture of cationic metals. The pH of the wastewater was adjusted to 5 using NaOH and filtered through coffee filters to remove metal precipitates and suspended solids. The heavy metal and calcium content of the wastewater was analyzed using atomic absorption spectrophotometry (AA), and it was stored at room temperature until used in column experiments.

2.4 Physical Characterization Methods

The total surface area of particles in the 0.5-2.0 mm fraction was measured using the Brunauer, Emmett and Teller (BET) method (Nova 1200, QuantaChrome, Boynton Beach, FL). The BET method assumes that multiple layers of molecules can be adsorbed, and that the energy for such adsorption is not homogeneous (McKay 1996). HRB (0.669 g) was placed in a vacuum apparatus, which was evacuated at 80°C for 85 min to

volatilize any adsorbed water or vapor. The vessel was then cooled to 77°K (-196°C) and nitrogen gas was injected until a pressure of 800 mm Hg (P_o) was achieved. The system was then used to automatically obtain a set of relative pressure (P/P_o) measurements that were recorded and used to calculate the total surface area of the sample.

Scanning Electron Microscopy (SEM) was performed using an Electroscan Environmental Scanning Electron Microscope (E-SEM, Electroscan Corp., Wilmington, MA) Samples of unused HRB or HRB removed from a fixed-bed column used in a column experiment supplied with 2 mg/L Cd(II) solution, as described below, were placed in the sample holder and inserted in the E-SEM chamber. After evacuating the chamber to 2 Torr, the filament current was adjusted to 1.83 A, beam voltage was turned on and set to 20 kV. Contrast and brightness were adjusted and pictures were taken with an augmentation of 225x.

X-ray diffraction was conducted using a Siemens D5000 X-ray diffractometer (Bruker AXS, Karlsruhe, Germany). HRB was spread over the sample holder and adhered to double-face adhesive tape. The sample was placed on the goniometer and measurements were taken varying two-theta from 20 to 50 degrees in increments of 0.03 degrees, and at a rate of 1 degree/minute.

2.5 Experimental Approach

2.5.1 Solutions and Sample Storage

Solutions were prepared using deionized water (18 M Ω resistivity), and 5×10^{-2} M NaClO₄ was used to maintain constant ionic strength. Acid-washed (1 N HNO₃) polypropylene sample containers were used for all batch experiments, and polypropylene

centrifuge tubes (15 ml and 50 ml) were used for sample collection during the column experiments.

2.5.2 Batch Equilibrium Experiments

In batch sorption experiments the concentrations of HRB (1 g/L) and of Cd(II), Cu(II), Ni(II) or Zn(II) were kept constant and the pH was varied for each sample bottle. Metal perchlorate solutions at 1.5×10^{-5} M to 2×10^{-4} M were bubbled with N₂ for 20 min to 1 hr in advance to use in experiments in order to minimize the dissolved CO₂ and O₂ concentrations.

100 ml aliquots of solution were added to each 150 ml polypropylene bottle containing 0.1 g of HRB. After the solution was added to HRB, the pH was measured and adjusted within the target range of 5 to 10 by adding HClO₄ or NaOH as 0.1 or 0.01 N solutions. The bottles were then shaken in reciprocating shakers at room temperature (~25°C). The pH was monitored and readjusted for 4 hours, after which equilibration was allowed for at least 12 hours. A final pH measurement was made before filtering (Supor® Membrane Disc Filters, Pore size 0.2 µm, diameter 25 mm., Pall Life Sciences, East Hills, NY), acidifying to pH < 2 using HCl, and analyzing the metal concentrations in the samples, as described below.

The same basic procedure described above for single metal batch experiments was used to analyze the sorption of a mixture of metals in batch experiments. The solution used in the batch metal mixture experiments contained 2×10^{-5} M each of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II).

Batch experiments were also conducted to evaluate the sorption behavior of Cd(II) over time. The procedure described above was used, with a few exceptions.

Experiments were conducted using 200 ml of 2×10^{-5} M solution and 0.2 g of HRB. Bottles were removed from the reciprocating shaker at 60 min intervals starting after the initial 90 min of contact and immediately sampled for analysis of metal concentration. After sampling, the pH of the remaining solution was readjusted as necessary. Shaking was resumed until the next sampling event.

2.5.3 Column Sorption Experiments (Defined Solutions)

Column studies involving a single metal or mixture of metals in solutions of controlled ionic strength were completed using a 2.5 cm (length) x 0.4 cm (dia) polypropylene column that was prepared using the barrel of a 10 cc disposable syringe (Becton, Dickinson and Co, Franklin Lakes, NJ). A small quantity of glass wool was wetted with deionized water and placed in the bottom of the barrel. 4.4 g of HRB (approximately 4 cm^3) were placed on top of the wool. Another piece of glass wool was placed on top of the sorbent. A new column containing glass wool and HRB was prepared for each experiment. The barrel contents were wetted with two to three bed volumes of deionized water (18Ω). The top of the column was then connected to the tubing (described below) and sealed with Parafilm®. The column setup is shown in Figure 2-1. Metal solutions were continuously sparged with N_2 gas and supplied to the column at 1 ml/min using a peristaltic pump and Tygon R-3603 tubing (Saint-Gobain Performance Plastics, Akron, OH). The influent strength was controlled at 5×10^{-2} M using NaClO_4 . Adjustments of pH were made using HClO_4 . The pH of the influent and effluent were monitored during the course of the experiment, and effluent samples were collected at regular intervals (30 min), using an ISCO Retriever II sample collector (Teledyne ISCO Inc, Lincoln, NE) for analysis of metal concentrations until occurrence

of breakthrough. Several experiments were performed using this approach, as described below.

Three experiments were conducted to test the effects of the influent Cd(II) concentration and pH on Cd(II) breakthrough in the HRB column. The following influent conditions were tested: (1) 2×10^{-5} M Cd(II) (2 mg/L), pH 5; (2) 2×10^{-5} M Cd(II) (2 mg/L), pH 7 and (3) 10^{-4} M Cd(II) (10 mg/L), pH 5. The flow rates for these experiments were 1 ml/min.

The efficiencies of four regeneration solutions were compared in this study. The following regeneration solutions were tested: HClO₄ (0.1 N and 1 N), ammonium citrate (36 mM) and ethylenediamine tetraacetic acid (EDTA; 9 mM). After loading the column with Cd(II), 1.25 bed volumes of deionized water were used to flush the column before the regeneration step. Then, 10 bed volumes of a regeneration solution were pumped through the column, and effluent samples were collected, filtered, and analyzed for Cd(II) concentration.

An experiment was also conducted to evaluate the effects of repeated loading regeneration on the capacity of the HRB for Cd(II). The HRB column was loaded with 2×10^{-5} Cd(II) (pH 5) until Cd(II) exhaustion occurred. The column was flushed with five bed volumes of deionized water before pumping 10 bed volumes of 9 mM EDTA, which was found to be the most effective regenerant solution (data not shown), through the column. The EDTA treatment was followed by another five bed volume deionized water rinse. The Cd(II) loading and EDTA regeneration sequence were repeated twice following the same procedures except that the final DI water rinse in cycle 2 involved 3.75 bed volumes. Effluent samples were collected at 12.5 bed volumes intervals during

each Cd(II) loading phase and analyzed for Cd(II) and Ca(II) concentrations. Effluent samples were also collected during the regeneration phases and analyzed for Cd(II).

Two experiments were also conducted to evaluate sorption of mixtures of complexed and uncomplexed metals to the HRB column and regeneration of the HRB using EDTA. In each case, the HRB column was supplied with an influent solution containing 2×10^{-5} M each of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) for a total metal concentration of 10^{-4} M. In the first experiment, the metals were uncomplexed. In the second experiments, 4×10^{-4} M NH_4Cl was added to the influent to complex the metals.

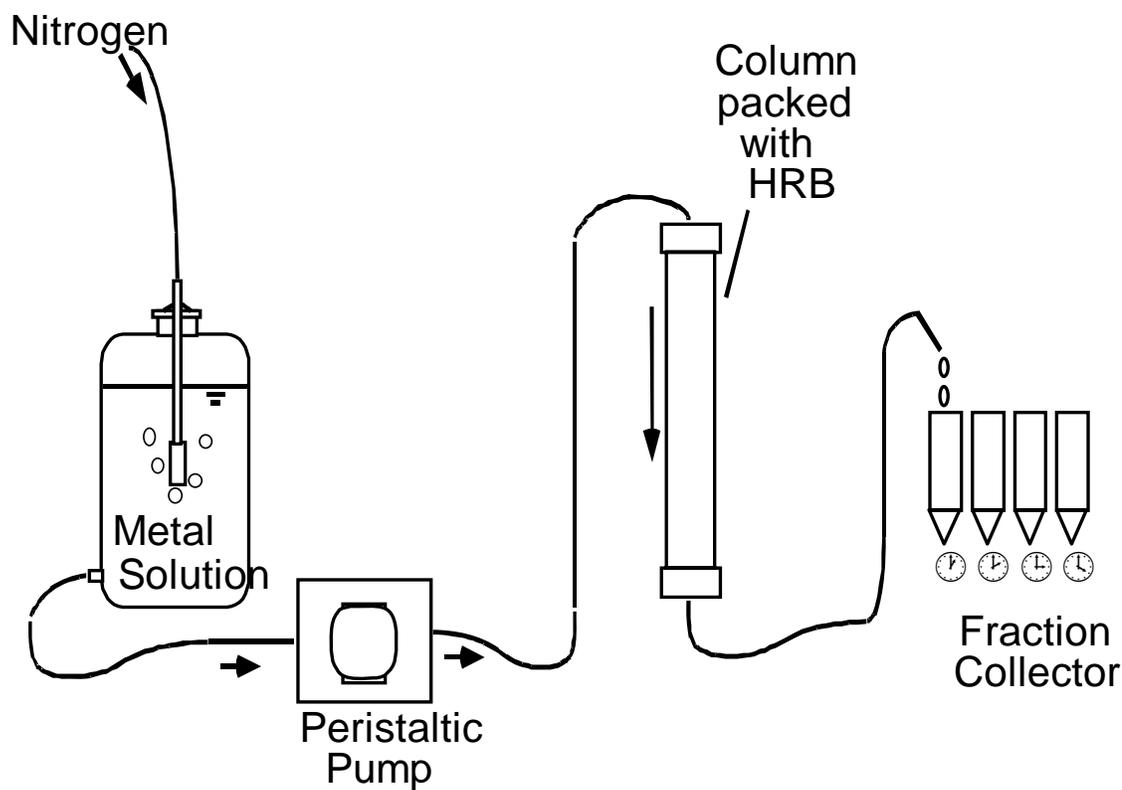


Figure 2-1. Diagram of column breakthrough experimental system.

The flow rate was 1 ml/min, and effluent samples were collected at 12.5 bed volumes intervals for metals analysis. The metal-saturated columns were regenerated as follows: five bed volumes (20 ml) of deionized water were pumped through each column. Then 10 bed volumes (40 ml) of 50 mM EDTA were pumped through each column. Effluent samples were collected during each regeneration phase for metals analysis.

2.5.4 Column Sorption Experiments (Industrial Wastewater)

The columns used in the industrial wastewater treatment experiment were intermediate in scale compared to the columns used in the previous experiments and full-scale treatment columns. The volume of the industrial wastewater treatment columns used in this experiment was restricted by the amount of influent and effluent that could reasonably be collected and stored. The size of the pilot-scale columns was determined using a combination of dimensional and geometric analyses. The former consisted of restricting flowrate (Q) and column bed volume (V), and cross-sectional area (A) values to combinations that would yield the same empty bed contact time (V/Q) and wastewater flux (Q/A) as in the small columns used in the previous experiments. The geometry of the column was selected to yield the desired V and a bed height (h)-to-diameter (D) ratio of 5. An h -to- D ratio of 5 was selected to avoid problems with short-circuiting. This problem was observed in preliminary experiments involving the small columns, which had a smaller h -to- D ratio (2:1).

The volume of the industrial wastewater treatment columns was set at four times the volume of the columns used in the previous experiments, or 16 cm³. Treatment of 2000 bed volumes of a 16 cm³ column corresponds to 32 L of wastewater, a manageable volume to store and treat. In order to achieve the desired h -to- D ration (5:1) with this

volume, a height of 8 cm and a diameter of 1.6 cm were selected. In comparison, the smallest column used in a full-scale treatment system typically has a height of at least 3.75 times larger than that of the column used in the industrial wastewater treatment experiments. Using the geometric constraints selected in this study, this corresponds to a small full-scale column with a diameter of approximately 6 cm and a bed volume of 800 cm³. Approximately 1600 L of wastewater would be treated in 2000 bed volumes with a column of this size.

16 cm³ columns with the desired D and h were constructed from polyethylene drying tubes (ScienceLab.com Inc, Houston, TX). At a Q of 4.9 ml/min, the industrial wastewater treatment columns had the same empty bed contact time (3.27 min) as in the previous column experiments.

2.5.5 Analytical Methods

Aqueous concentrations of Cd(II), Cu(II), Pb(II), Ni(II), Zn(II), and Ca(II) were determined using flame atomic absorption spectrophotometry (AA 5100, Perkin Elmer, Boston, MA). The sample collector was automatically rinsed by the equipment in deionized water between measurements. Atomic absorption metal standards were diluted in deionized water. Standards and a DI water blank were analyzed along with each set of samples.

The AA operating parameters (wavelength, slit width and gas flow rates) are summarized in Table 2-1 along with information on the lamps used for analysis of different metals, the concentration of standards and maximum concentration to achieve a linear calibration for each metal and the instrument noise and sensitivity that were obtained from the instrument manual. For calcium, the standards had higher

concentrations than the linear range; therefore a non-linear calibration curve was used. Whenever the concentration of a metal in a sample was higher than the highest standard used, the sample was diluted. This was often the case for samples collected during column regeneration. Samples and standards were analyzed two or three times and the average result was recorded.

Table 2-1. AA operation parameters.

<i>Element</i>	<i>Lamp brand</i>	<i>λ (nm)</i>	<i>Slit (Å)</i>	<i>Standards concentrations (mg/L)</i>	<i>Linear range (mg/L)</i>	<i>Gas flow (air)</i>	<i>Gas flow (C₂H₂)</i>	<i>Noise</i>	<i>Sensitivity</i>
Ca	Varian (Ca-Mg)	422.7	0.75, 10, 20, 50		5	10	1.9	1	0.092
Cd	Fisher	228.8	0.70.1, 0.5, 1, 2, 5		2	10	1.9	1	0.028
Cr	Varian Techtron	357.9	0.70.5, 1, 2, 5		5	10	1.9	1	0.078
Cu	VWR Scientific	324.8	0.71, 2.5, 5		5	10	1.9	1	0.077
Fe	Fisher Scientific	248.3	0.21, 5, 10		5	10	2	1	0.1
Ni	VWR Scientific	341.5	0.21, 2, 5, 10		10	9	1.9	0.55	0.4
Pb	VWR Scientific	283.3	0.71, 2, 4, 10, 20		20	9.9	1.9	0.43	0.45
Zn	Perkin Elmer Intensitron	213.9	0.70.3, 0.5, 1, 2.5		1	10	1.9	1	0.018

The amount of metal sorbed to HRB was determined by the equation:

$$\%_{\text{sorbed}} = \frac{C_i - C_f}{C_i} \times 100\% \quad (2-1)$$

where C_i is the initial aqueous metal concentration and C_f is the final aqueous metal concentration, in batch equilibrium experiments. In column experiments, C_i and C_f are the aqueous influent and effluent metal concentrations, respectively.

The moisture content of the HRB was determined by desiccating the adsorbent at 105°C for 80 min and comparing the weight of the HRB sample before and after desiccation. Volatile solids and total dissolved solids (TDS) were measured essentially according to Standard Methods (American Public Health Association et al. 1989).

2.5.6 Metal Speciation Calculations

Metal speciation calculations were performed using the program MINEQL+ (Version 4.0, Environmental Research Software, Hallowell, ME). In performing the calculations, it was assumed that the system was homogeneous and closed. The initial concentration of each metal was set to 2×10^{-5} M. Ca(II) and CO_3^{-2} were set to 9×10^{-5} M, the average concentration of Ca(II) in the column experiment effluent. For calculation of complexed metal speciation, NH_4^+ and Cl^- concentrations were set at 4×10^{-4} M. In all cases, the ionic strength was fixed at 5×10^{-2} M, and calculations were performed for 25°C and pH values ranging from 4 to 10. Key stability constants that were not provided in the MINEQL+ database were obtained from Stumm and Morgan (1996). The stability constants used for aqueous species are summarized in Table 2-2, and the stability constants used to predict the formation of solids are in Table 2-3.

Table 2-2. Stability constants used in chemical speciation calculations for aqueous species (Stumm and Morgan 1996).

<i>Species</i>	<i>Log K</i>	<i>Species</i>	<i>Log K</i>
$\text{Ca}(\text{NH}_3)_2^{+2}$	-18.79	$\text{Ni}(\text{NH}_3)_3^{+2}$	-21.132
CaCO_3 (aq)	3.2	$\text{Ni}(\text{NH}_3)_4^{+2}$	-29.276
CaHCO_3^+	11.599	$\text{Ni}(\text{NH}_3)_5^{+2}$	-37.92
CaOH^+	-12.7	$\text{Ni}(\text{OH})_2$ (aq)	-18.994
$\text{Cd}(\text{CO}_3)_2^{-2}$	7.228	$\text{Ni}(\text{OH})_3^{3-}$	-29.991
$\text{Cd}(\text{NH}_3)_2^{+2}$	-13.89	NiCO_3 (aq)	4.572
$\text{Cd}(\text{NH}_3)_3^{+2}$	-21.83	NiHCO_3^+	12.42
$\text{Cd}(\text{NH}_3)_4^{+2}$	-30.28	NiNH_3^{+2}	-6.514
$\text{Cd}(\text{OH})_2$ (aq)	-20.29	NiOH^+	-9.897
$\text{Cd}(\text{OH})_3^-$	-32.51	OH^-	-13.997
$\text{Cd}(\text{OH})_4^{-2}$	-47.29	$\text{Pb}(\text{CO}_3)_2^{-2}$	9.938
$\text{Cd}_2\text{OH}^{+3}$	-9.397	$\text{Pb}(\text{OH})_2$ (aq)	-17.094
CdCO_3 (aq)	4.358	$\text{Pb}(\text{OH})_3^-$	-28.091
CdHCO_3^+	10.686	$\text{Pb}(\text{OH})_4^{-2}$	-39.699
CdNH_3^{+2}	-6.644	$\text{Pb}_2\text{OH}^{+3}$	-6.397
CdOH^+	-10.1	$\text{Pb}_3(\text{OH})_4^{+2}$	-23.888
$\text{Cu}(\text{CO}_3)_2^{-2}$	10.2	$\text{Pb}_4(\text{OH})_4^{+4}$	-19.988
$\text{Cu}(\text{NH}_3)_2^{+2}$	-10.99	PbCO_3 (aq)	6.478
$\text{Cu}(\text{NH}_3)_3^{+2}$	-17.43	PbHCO_3^+	13.2
$\text{Cu}(\text{NH}_3)_4^{+2}$	-25.18	PbOH^+	-7.597
$\text{Cu}(\text{OH})_2$ (aq)	-16.19	$\text{Zn}(\text{NH}_3)_2^{+2}$	-13.988
$\text{Cu}(\text{OH})_3^-$	-26.88	$\text{Zn}(\text{NH}_3)_3^{+2}$	-20.832
$\text{Cu}(\text{OH})_4^{-2}$	-39.98	$\text{Zn}(\text{NH}_3)_4^{+2}$	-28.076
$\text{Cu}_2(\text{OH})_2^{+2}$	-10.59	$\text{Zn}(\text{NH}_3)_5^{+2}$	-46.22
CuCO_3 (aq)	6.77	$\text{Zn}(\text{OH})_2$ (aq)	-17.794
CuHCO_3^+	12.129	$\text{Zn}(\text{OH})_3^-$	-28.091
CuNH_3^{+2}	-5.234	$\text{Zn}(\text{OH})_4^{-2}$	-40.488
CuOH^+	-7.497	ZnCO_3 (aq)	4.76
H_2CO_3 (aq)	16.681	ZnHCO_3^+	11.829
HCO_3^-	10.329	ZnNH_3^{+2}	-7.044
$\text{Ni}(\text{NH}_3)_2^{+2}$	-13.6	ZnOH^+	-8.997

Table 2-3. Stability constants used for prediction of solids formation (Zachara et al. 1988; Stumm and Morgan 1996)

<i>Solid</i>	<i>LogK</i>	<i>Solid</i>	<i>LogK</i>
Ca(OH) ₂ (Portlandite)	-22.804	Pb ₂ O(OH) ₂	-26.188
CaCO ₃ (Aragonite)	8.300	Pb ₂ OCO ₃	.558
CaCO ₃ (Calcite)	8.480	Pb ₃ (CO ₃) ₂ (OH) ₂ (Hydrocerussite)	18.770
CaO (Lime)	-32.699	Pb ₃ O ₂ CO ₃	-11.020
Cd(OH) ₂	-13.644	PbCO ₃ (Cerrusite)	13.130
Cd(OH) ₂ (am)	-13.730	PbO (Litharge)	-12.694
CdCO ₃ (Otavite)	12.000	PbO (Massicot)	-12.894
CdO (Monteponite)	-15.103	PbO:0.3H ₂ O	-12.980
Cu(OH) ₂	-8.674	Zn(OH) ₂	-12.200
Cu ₂ (CO ₃)(OH) ₂ (Malachite)	5.306	Zn(OH) ₂ (am)	-12.474
Cu ₃ (CO ₃) ₂ (OH) ₂ (Azurite)	16.906	Zn(OH) ₂ (beta)	-11.754
CuCO ₃	11.500	Zn(OH) ₂ (epsilon)	-11.534
CuO (Tenorite)	-7.644	Zn(OH) ₂ (gamma)	-11.734
Ni(OH) ₂	-12.794	Zn ₅ (OH) ₆ (CO ₃) ₂ (Hydrozincite)	-9.650
NiCO ₃	6.870	ZnCO ₃ (Smithsonite)	10.000
NiO (Bunsenite)	-12.446	ZnCO ₃ :1H ₂ O	10.260
Pb(OH) ₂	-8.150	ZnO (active)	-11.188
Pb ₁₀ (OH) ₆ O(CO ₃) ₆ (Plumbonacrite)	8.760	ZnO (Zincite)	-11.334

Chapter 3. Characterization of the Uptake of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) by a Hatchery Residual Biosorbent

3.1 Introduction

Large volumes of heavy metal-contaminated wastewater must be treated each year to protect human health and environmental quality. Increasingly the use of a wide variety of materials of biological origin as metal sorbents, i.e., biosorption, is promoted as a way of reducing the cost of treating metal-contaminated wastewater by eliminating the need for expensive, synthetic sorbents or resins (Volesky and Holan 1995; Wase and Forster 1997; Volesky 2003; Gavrilescu 2004). At the same time, implementation of biosorption also poses several technological and practical challenges. For example, while ion exchange resins are relatively expensive, they are highly selective and the removal mechanisms involved in the exchange of ions with a given resin are reasonably well understood, making application of ion exchange to wastewater treatment relatively straightforward. In contrast, while generally available at modest cost, biosorbents are inherently heterogeneous materials, and the metal-removing capacity that a given material displays likely occurs via a complex combination of mechanisms. Without some reasonable understanding of the possible underlying removal mechanisms, systematic design and operation of a biosorbent-based treatment system will be difficult and inefficient.

In particular, utilization of residuals generated during agricultural animal production and processing is appealing because consolidation within these industries typically results in regional surpluses of these materials that cannot be disposed of using

conventional approaches, e.g., land application. For example, poultry production is an important agricultural activity in the U.S. Mid-Atlantic region. The disposal of residuals generated by hatcheries is a major concern for the poultry industry in this and other regions in the United States (Das et al. 2002). In 1999, it was estimated that more than 90,000 metric tons of hatchery residuals were produced yearly in the United States for broiler chicks alone (Blake 2000). Hatchery residuals can include eggshells and unhatched eggs from broiler hatcheries and inedible eggs from layer hatcheries. These large numbers and the increasing difficulty in disposing of the residuals through land application make recovery or recycling an attractive management approach.

In some cases, liquid protein can be extracted from hatchery residual and subsequently recycled as an ingredient of animal feed. Major components of the resulting processed hatchery residual material include eggshell and animal fibrous proteins, such as feathers and eggshell membrane (Das et al. 2002). Eggshells, in turn, are composed of calcium carbonate (95.1%), proteins (3.3%) and moisture (1.6%) (Kuh and Kim 2000). Several of these hatchery-derived materials have separately been shown to remove dissolved metals from water. Eggshells provided at 10 to 70 g/L removed 79-99.4% of 4.5×10^{-5} M Cd(II) after 5 hr of contact in batch experiments (Kuh and Kim 2000). Eggshell membranes and chicken feathers exhibited gold uptake capacities of 4.35 mol/g and 2.6 mol/g, respectively, when gold was provided at 3.4×10^{-3} M (Ishikawa and Suyama 1998). The ability of chicken feathers to remove Cu(II) and Zn(II) at concentrations ranging from 1.6×10^{-5} M to 1.7×10^{-4} M was also evaluated, and uptake ranged from 3×10^{-5} mol/g to 1.7×10^{-4} mol/g (Al-Asheh et al. 2003). Other animal

fibrous proteins were also reported as good sorbents (Goto and Suyama 2000; Ishikawa et al. 2002).

The calcium carbonate in eggshells is calcite with embedded proteins that provide it with more resistance to weathering and dissolution than calcite alone (Solomon 1999). Sorption of metals to carbonate minerals, including calcium carbonate (calcite), has been observed in numerous studies, including evaluation of the mechanisms of adsorption of divalent ions (Zachara et al. 1988; Stipp and Hochella 1992; Kobayashi et al. 2004), the use of models to describe and understand the adsorption of metals (Zachara et al. 1991; Van Cappellen et al. 1993) and spectroscopic evaluation of adsorption mechanisms and complexes (Elzinga and Reeder 2002; Rouff et al. 2004; Chada et al. 2005; Shahwan et al. 2005). We hypothesized that a hatchery-derived biosorbent (HRB) could be employed for the removal of metals from aqueous solutions, and, because of the complexity of metal interactions with carbonate materials and the heterogeneity of processed hatchery residuals, that this removal could conceivably occur via a complex combination of mechanisms possibly including ion exchange, precipitation, co-precipitation and/or solid-solution diffusion. This work focuses on demonstrating that HRB can effectively remove several common divalent metal cations (Cd, Cu, Ni, Pb, Zn) from dilute aqueous solutions and evaluating the mechanisms by which this uptake occurs. These goals were addressed by conducting batch equilibrium experiments over a range of pH conditions and initial metal concentrations, and performing column breakthrough and regeneration experiments for individual metals and metal mixtures. Concurrently, the HRB physical properties were investigated. The theoretical chemical

speciation of metals in homogeneous solutions containing HRB dissolution products is also provided as supporting information.

3.2 Results

3.2.1 HRB Characteristics

The apparent density and moisture content of the HRB were 1.1 g/cm³ and 0.9% (w/w), respectively. Volatile solids made up 7.4% (w/w) of the HRB. Presumably, the volatile solids primarily comprise proteins derived from feathers, membranes and other organic matter that was not extracted by ADF.

The average BET surface area of the HRB was 0.74 m²/g, which is consistent with the surface areas of 0.8 m²/g and 0.2 to 0.46 m²/g reported for coral sand (Suzuki and Takeuchi 1994), which is primarily calcite, and pure calcite (Martin-Garin et al. 2003; del Rio et al. 2004), respectively.

The X-ray diffraction patterns for the HRB and calcite (Kontoyannis and Vagenas 2000) are shown in Figure 3-1, along with a typical diffraction pattern for eggshells (Dobiášová et al. 2004). Patterns obtained from eggshells correspond very well to standard calcite patterns (Dobiášová et al. 2004), and the HRB X-ray diffraction pattern is also very similar to that of calcite. This is an important finding, because it demonstrates that calcite comprises a large fraction of the HRB and thus results obtained in studies of metal uptake by calcite are relevant to metal uptake by the HRB.

To evaluate changes in HRB particle characteristics resulting from treatment of wastewater flows in column configurations, unused particles and particles obtained from

a column after a breakthrough experiment were compared using SEM. SEM images of the unused and spent HRB are shown in Figure 3-2. In the unused material, a feather is clearly visible. Eggshells and other structures are difficult to specifically identify in either image. One significant observation that can be made by comparing the two SEM images is that the numerous small particles that were present in the unused material are no longer visible in the sample obtained from the column used in the treatment process. Presumably these particles either dissolved or were washed out of the column.

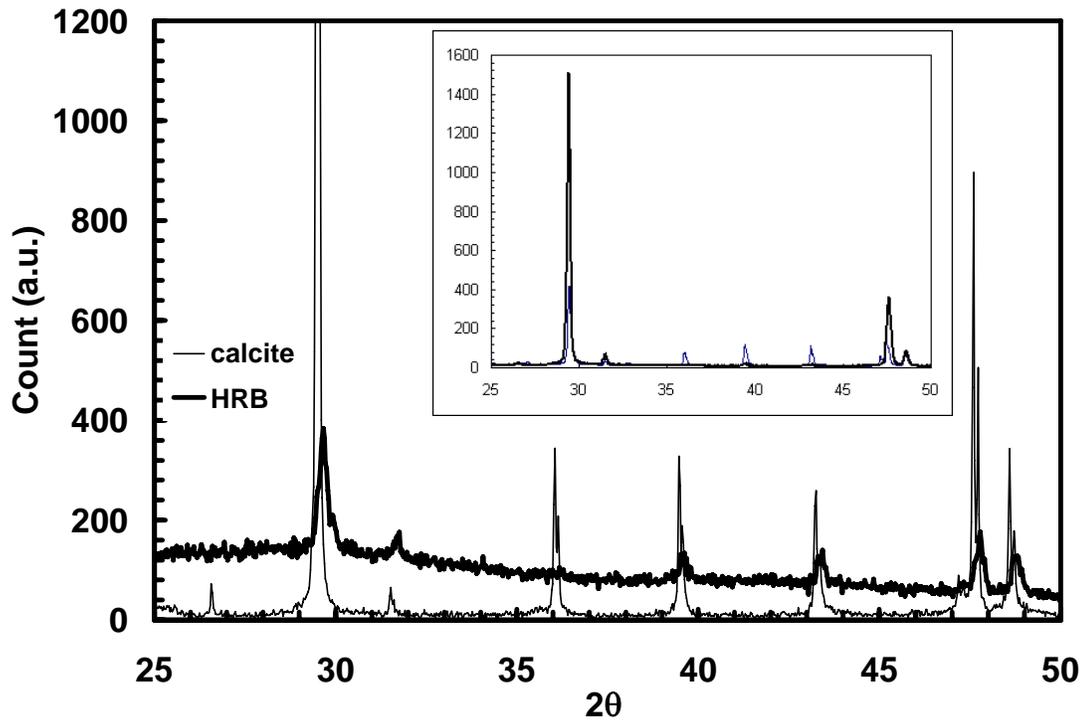


Figure 3-1. X-ray diffraction of HRB (thick line) and calcite (thin line). Insert illustrates X-ray diffraction of eggshells, as reported by Dobiášová et al. (2004).

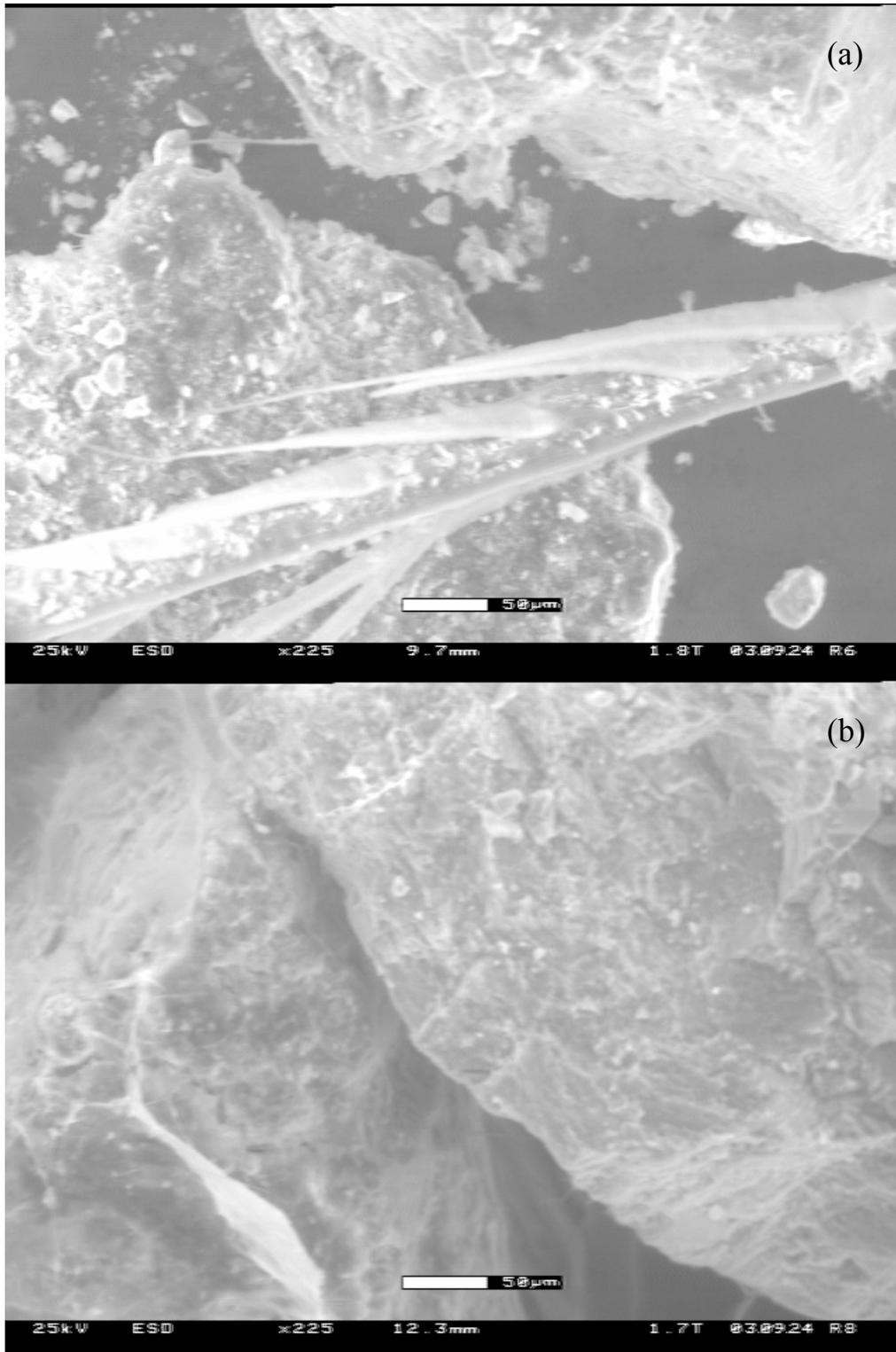
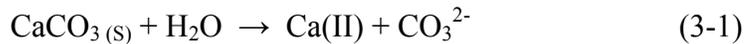


Figure 3-2. SEM image of (a) unused HRB and (b) HRB used in a column experiment, magnified 225x. The bar represents 50 μm.

3.2.2 Batch Sorption Experiments

The effect of solution pH on the removal of individual metal sorbates (Cd(II), Cu(II), Ni(II) and Zn(II)) and a metal mixture by HRB was evaluated in a series of batch equilibrium experiments. To obtain the experimental adsorption-pH curves shown for individual metals in Figures 3-3 through 3-7, different pH values had to be established and maintained in sample vials throughout a sorption experiment. For a given metal, the targeted pH values varied from around 5 to 8 at the low end to around 10 at the upper end. However, in all cases, the low pH values proved difficult to maintain experimentally, presumably because of the dissolution of calcite in the HRB, which added alkalinity to the solutions according to:



As discussed below, the strong dependence of metal uptake by the HRB on pH and the tendency of the HRB to neutralize the acidic samples may have led to errors in the estimation of metal removal at relatively low pH values.

For each metal, the effect of pH on metal uptake was evaluated at three different initial metal concentrations. In general, the percentage of metal sorbed decreased with increasing initial concentration. For example, at pH 8, 80% of Cd(II) was removed when it was provided at an initial concentration of 2×10^{-5} M, compared with removal of only 30% at 2×10^{-4} M Cd(II) (Figure 3-3). Similar trends were observed for Ni(II) and Zn(II) (Figures 3-6 and 3-7). However, this trend was reversed for Cu(II) (Figure 3-5). The most effective removal was observed for the highest initial Cu(II) concentration. As expected, removal of each metal by HRB increased abruptly with increasing pH over a

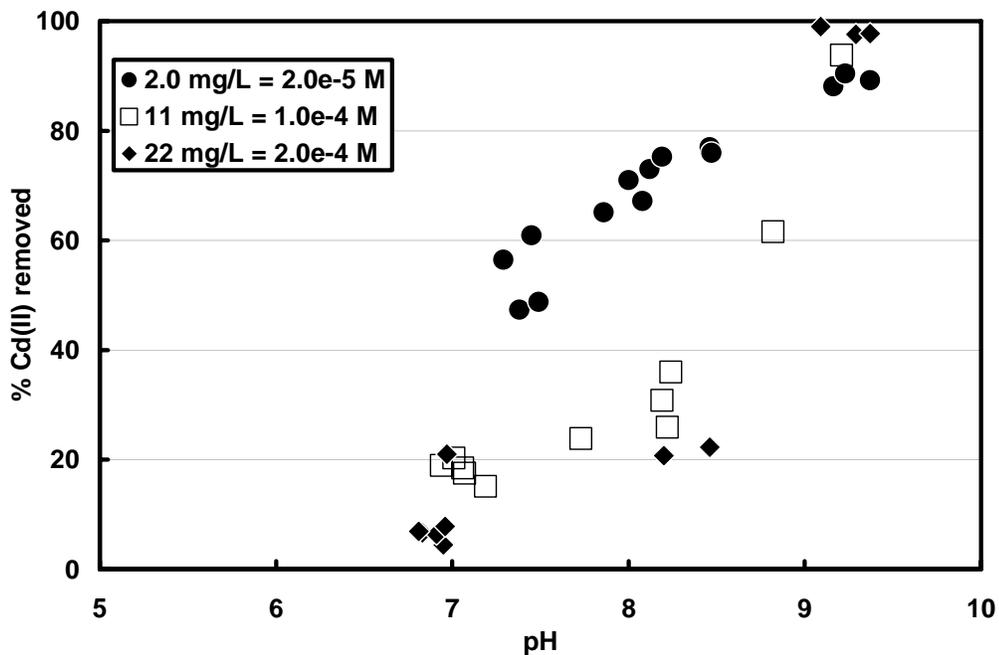


Figure 3-3. Effects of pH and initial Cd(II) concentration on sorption of Cd(II) to HRB (1 g/L); I=0.05 M NaClO₄·H₂O.

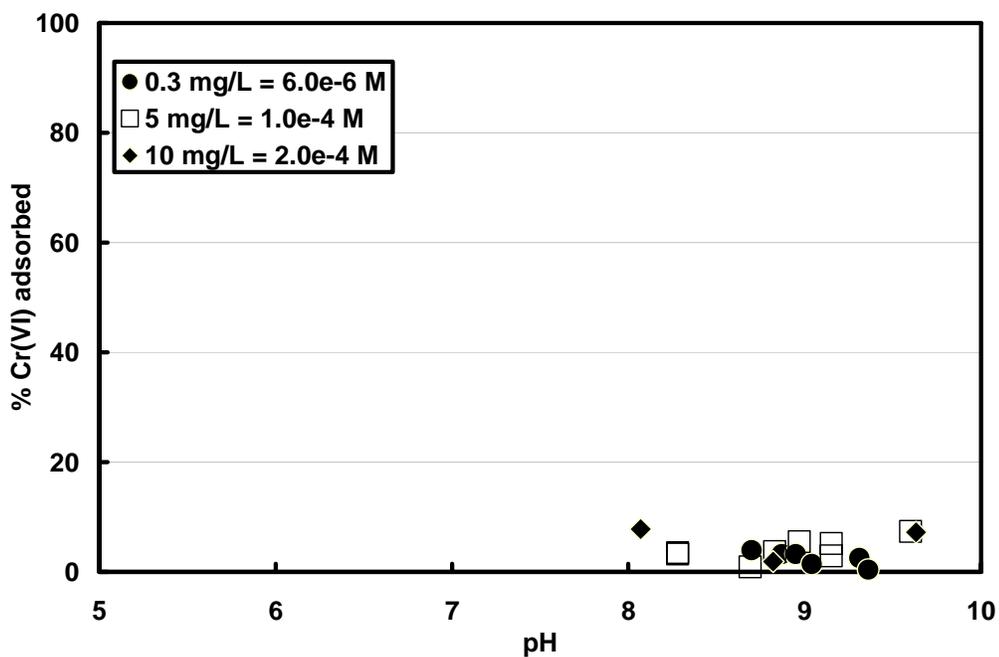


Figure 3-4. Effects of pH and initial Cr(VI) concentration on sorption of Cu(II) to HRB (1 g/L); I=0.05 M NaClO₄·H₂O.

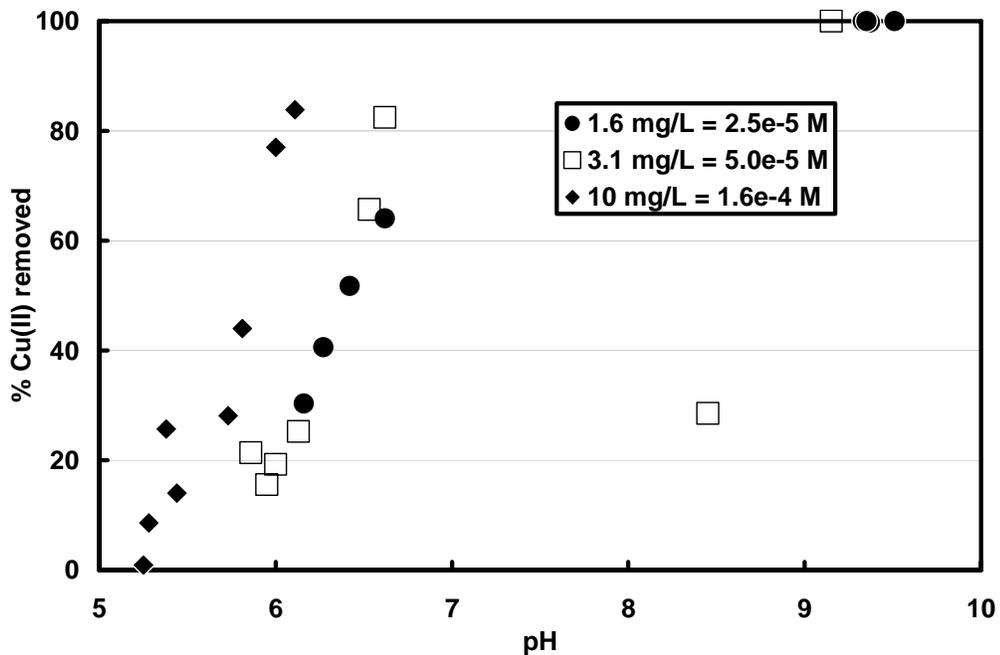


Figure 3-5. Effects of pH and initial Cu(II) concentration on sorption of Cu(II) to HRB (1 g/L); I=0.05 M NaClO₄·H₂O.

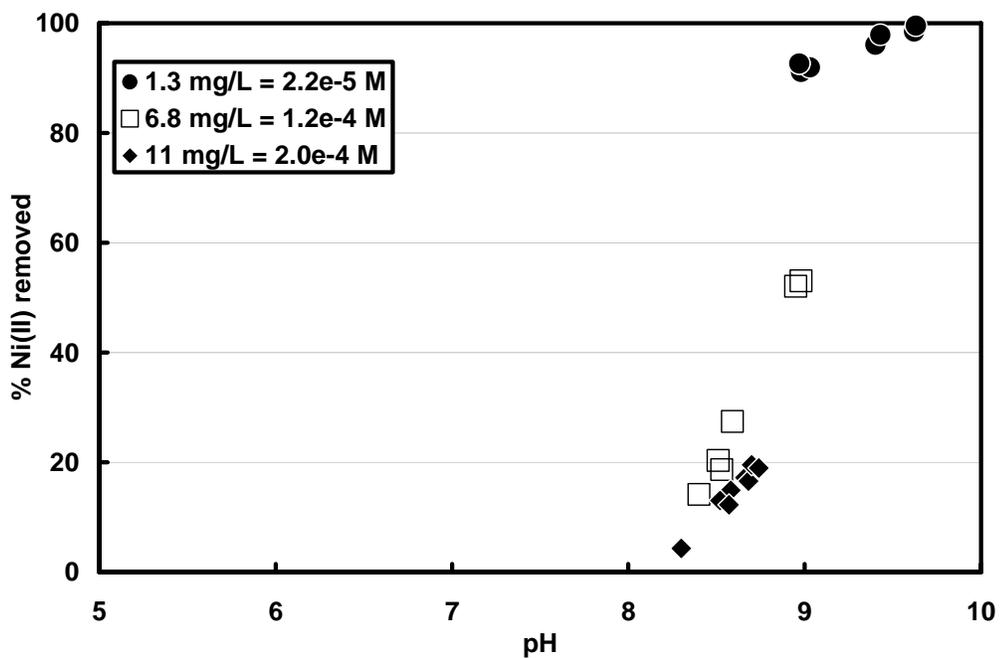


Figure 3-6. Effects of pH and initial Ni(II) concentration on sorption of Ni(II) to HRB (1 g/L); I=0.05 M NaClO₄·H₂O.

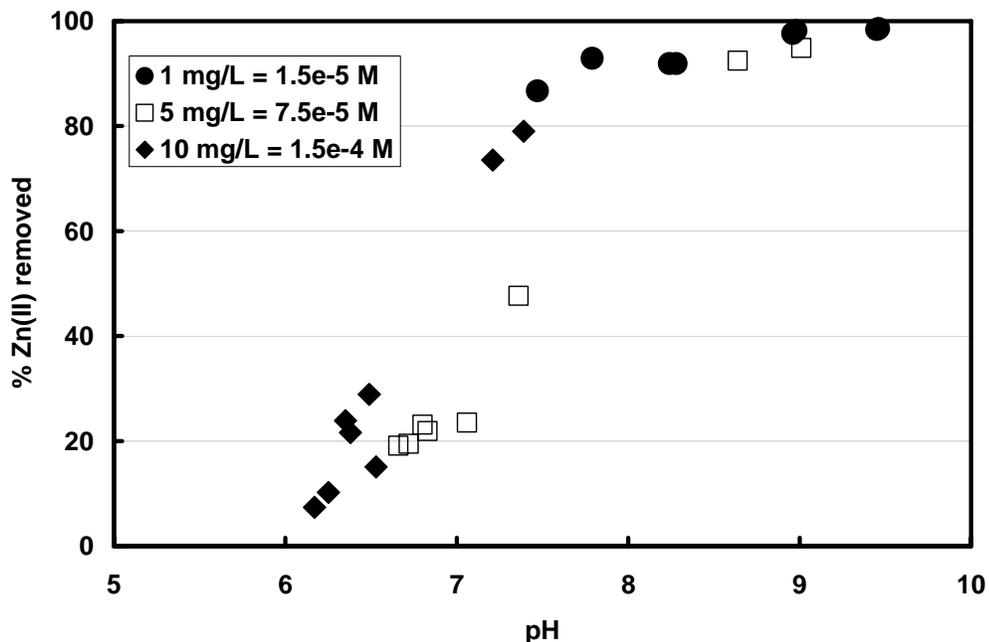


Figure 3-7. Effects of pH and initial Zn(II) concentration on sorption of Zn(II) to HRB (1 g/L); I=0.05 M NaClO₄·H₂O.

narrow pH range (Figures 3-3 to 3-7). In contrast to the effective sorption of the positively-charged metals by the HRB, no significant uptake of Cr(VI) by the HRB was noted at relatively high pH values, as shown in Figure 3-4. This is not completely surprising because Cr(VI) is negatively charged in the form of HCrO₄⁻ and CrO₄²⁻. HCrO₄⁻ will dominate in solutions below pH 6.5 and CrO₄²⁻ is the major Cr(VI) species under basic conditions.

The uptake of Cd(II) by HRB at three different pH values (3, 6.5 and 9) was also monitored as a function of time, and the results are shown in Figure 3-8. At pH 3, dynamic sorption and desorption of Cd(II) was observed and presumably was the result of problems with maintaining very low pH values in the presence of HRB. Specifically, the data suggest that the amount of Cd(II) that sorbed to the HRB decreased when the pH was measured and acid was added to the sample to restore the pH to 3. At pH 9, the

amount of sorption increased significantly for up to 4 h, and then leveled off between 4 and 7 hr. Similar trends were observed at pH 6.5. The results obtained at pH 6.5 and 9 suggest that sorption of Cd(II) is largely complete within 4 h. However, some additional sorption of Cd(II) to HRB occurred between 7 and 24 h.

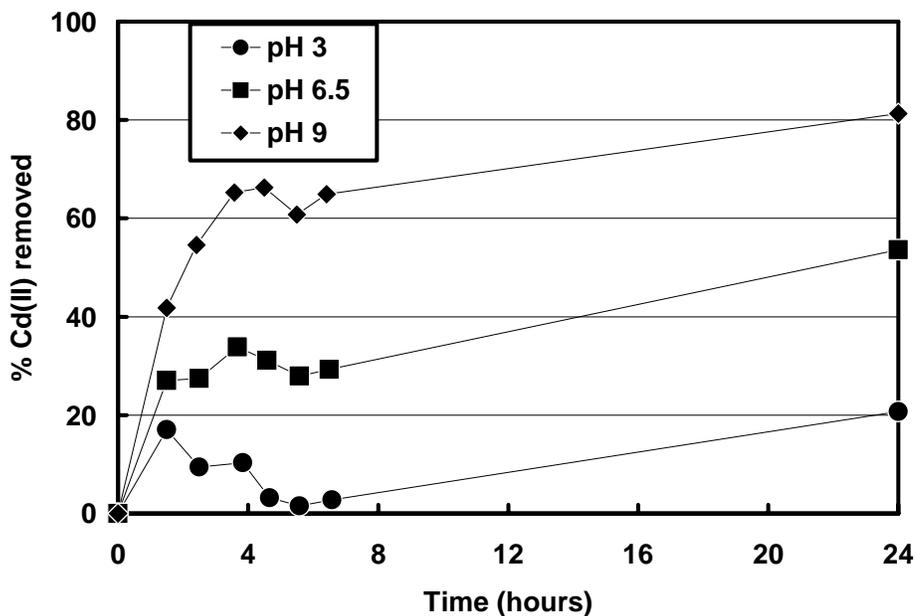


Figure 3-8. Kinetics of sorption of 2×10^{-5} M Cd(II) onto the HRB (1 g/L) at pH 3, 6.5, and 9 ($I = 0.05$ M NaClO₄·H₂O).

Figure 3-9 shows the effect of pH on HRB uptake of a mixture of metals containing Pb(II), Cd(II), Cu(II), Ni(II), and Zn(II) at a concentration of 2×10^{-5} M each. The percent removal of Cd(II), Cu(II), Ni(II), and Zn(II) present in the mixture was reduced as compared with the removal of the individual metals at 2×10^{-5} M (Figures 3-3 to 3-7) because of the increase in the initial total metal concentration to 10^{-4} M.

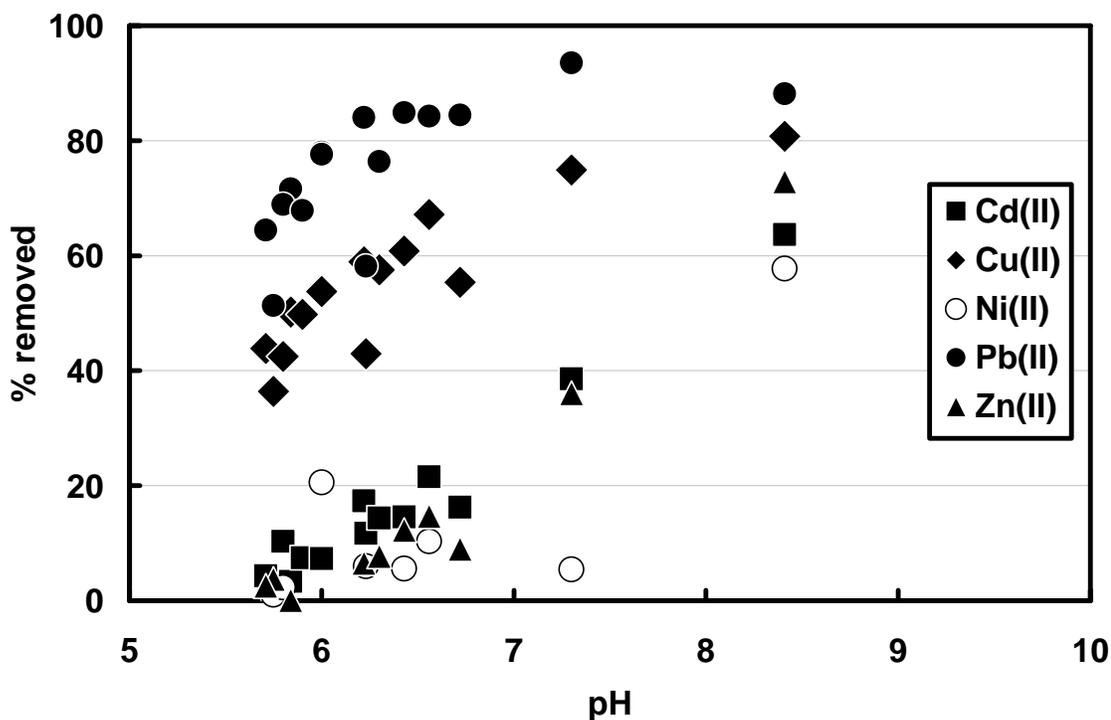


Figure 3-9. Effect of pH on sorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) from a solution containing 2×10^{-5} M of each metal onto the HRB (1 g/L) ($I = 0.05$ M $\text{NaClO}_4 \cdot \text{H}_2\text{O}$).

To assess the affinity of the HRB for the different metals, the pH values at which sorption is 50% complete (pH_{50}) in batch systems can be compared (Kinniburgh and Jackson 1981). Thus, the batch experiments conducted with individual metals suggest that the selectivity of the HRB decreases in the order: Cu(II) ($\text{pH}_{50} \approx 6$) > Zn(II) ($\text{pH}_{50} \approx 7$) > Cd(II) ($\text{pH}_{50} \approx 7.5-8$) > Ni(II) ($\text{pH}_{50} \approx 9$). The pH_{50} value for Pb(II) in the mixture was 5.5–6. The pH_{50} values observed for Cu(II) (≈ 6) and Cd(II) (≈ 7.5) in the mixture were the same as in the individual metal sorption experiments. In contrast, the pH_{50} for Zn(II) shifted from pH 7 when HRB was exposed to Zn(II) alone to nearly 8 when Zn(II) was provided in the mixture, and the pH_{50} for Ni(II) alone was pH 9 and seems to have decreased to pH 8 in the presence of other metals. The shift in the apparent pH_{50} value for

Ni(II) and the lack of change in the pH_{50} for Cd(II) in the mixture were somewhat surprising. Specifically, if it is assumed that the metals affiliated with the HRB primarily through surface interactions (e.g., surface complexation or ion exchange reactions), then it is expected that the strongly affiliated metals would be minimally affected by competition from other metals for the HRB surface, while weakly affiliated metals would be negatively affected by the presence of other metals.

Comparison of the pH_{50} values obtained with the metal mixture and the percent removal of each metal at a given pH (e.g., 8.5) in Figure 3-9 suggests that the selectivity of the HRB for the five metals decreased in the following order: Pb(II) > Cu(II) > Zn(II) = Cd(II) > Ni(II), which is consistent with the selectivity sequence determined from the individual metal batch experiments.

3.2.3 Metal Speciation Calculations

The homogeneous speciation of each metal (2×10^{-5} M) was calculated for Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) in an aqueous system containing Ca and CO_3^{-2} (9×10^{-5} M), over a pH range of 4 to 10. These values were selected from average $CaCO_3$ release in column experiment effluents (Section 4.3).

Speciation calculations were performed and analyzed for total metals in solution and the possible formation of carbonates and/or hydroxycarbonates precipitates (due to the dissolution of calcite according to Eq. 3-1 and 3-2), as well as for precipitation of metal hydroxides. The equilibrium speciation calculations predicted the formation of several solids. The solids and the lowest pH or range of pH values at which they formed were as follows: tenorite ($CuO_{(s)}$, pH 6.2), hydrocerussite ($Pb_3(CO_3)_2(OH)_{2(s)}$, pH 6.3–7), lead hydroxide ($Pb(OH)_{2(s)}$, pH 6.9), otavite ($CdCO_{3(s)}$, pH 7.4), zinc oxide ($ZnO_{(s)}$, pH

8.4), hydrozincite ($Zn_5(OH)_6(CO_3)_2(s)$, pH 7.9–8.5), and bunsenite ($NiO_{(s)}$, pH 8.6). Based on the predicted precipitation processes, metal removal by the HRB should decrease in the order: $Cu(II) > Pb(II) > Cd(II) > Zn(II) > Ni(II)$.

The similarity of this precipitation sequence with the selectivity sequence of the various metals in the batch experiments suggests that the observed HRB selectivity may be due in part to precipitation. In fact, the pH_{50} values for Ni(II) and Cd(II) reported above fall within or near the pH values at which precipitation is predicted. However, it is important to note that some uptake of Cu(II), Pb(II), and, to a greater extent, Zn(II) occurred at pH values lower than those for which precipitation was predicted (Figures 3-5, 3-7 and 3-9). Further, although calculations of metal speciation in a homogeneous system have previously been applied to evaluate the mechanisms of removal by calcite (e.g., Stipp et al. 1992), it is important to recognize that a system containing a sorbent surface is much more complex than a homogeneous solution. In particular, the addition of a solid sorbent, like calcite inherently alters several homogeneous system properties. For example, aqueous metal ions are sorbed, thus decreasing the aqueous metal concentration. Calcite also dissolves according to Eq. (3-1) and (2), which increases the number of Ca(II) ions in solution, and a “local atmosphere”, rather than the overall system properties like pH, can control the reactions close to the calcite surface.

3.2.4 Column Experiments

The breakthrough curves of Cd(II) exiting the columns for the three conditions tested are shown in Figure 3-10. Approximately 1500 bed volumes could be treated before complete exhaustion for Cd(II) supplied at 2×10^{-5} M occurred at pH 5 or 7. For an influent concentration of 10^{-4} M Cd(II), exhaustion occurred at 500 bed volumes.

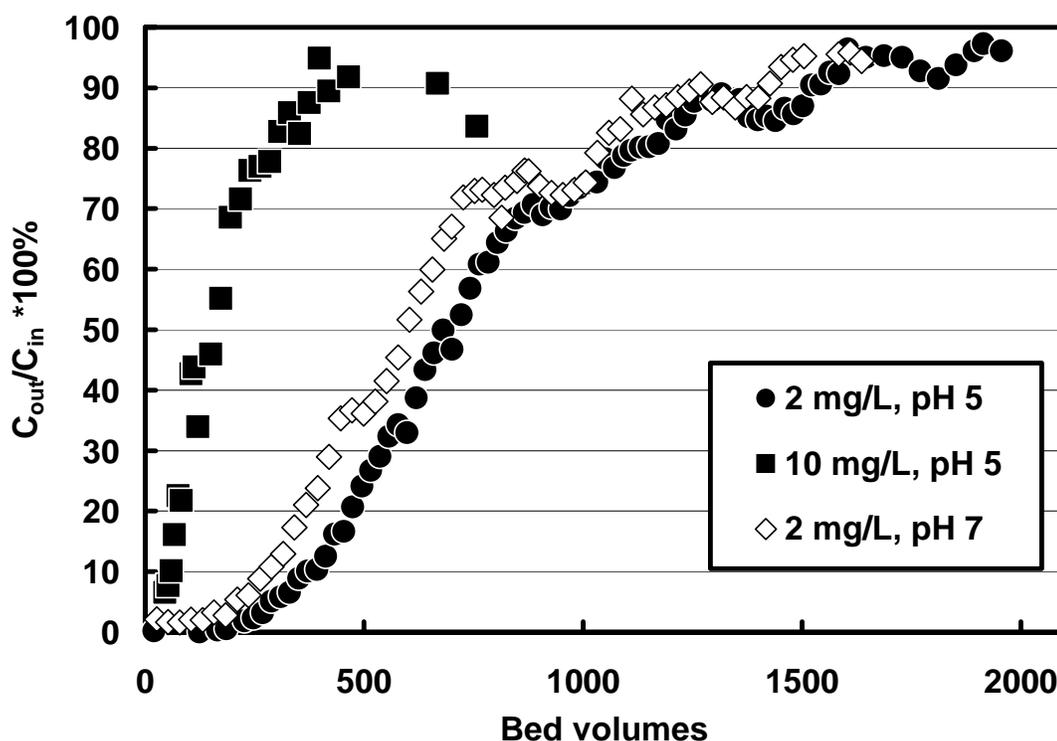


Figure 3-10. Effect of influent pH and Cd(II) concentration on Cd(II) breakthrough curves and effluent pH for 4 cm³ HRB (4.4 g) columns. Cd(II) breakthrough curves for (●) 2 x 10⁻⁵ M (2 mg/L) Cd(II), pH 5; (■) 10⁻⁴ M (10 mg/L) Cd(II), pH 5; and (◇) 2 x 10⁻⁵ M Cd(II), pH 7.

Column studies were conducted with HRB supplied with a mixture of uncomplexed salts of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) at pH 5. The breakthrough curves are shown in Figure 3-11. The effluent pH typically ranged from 6 to 7. Ni(II), Cd(II) and Zn(II) broke through much sooner than Pb(II) and Cu(II). Exhaustion for Cd(II) and Zn(II) was complete within just over 200 bed volumes. Removal of Pb(II) and Cu(II) by the HRB appeared to displace Cd(II), Ni(II) and Zn(II), resulting in effluent Ni(II) and, to a greater extent, Cd(II) and Zn(II) concentrations that exceeded the influent levels. Thus, the selectivity of the HRB for uncomplexed metals based on the breakthrough curves decreased in the order: Pb(II) > Cu(II) > Zn(II) ≈ Cd(II) > Ni(II),

which is consistent with the results of the batch HRB sorption experiments.

The total capacities of the HRB column for the free metals provided in a mixture were calculated according to:

$$capacity = \int_0^{t_D} \frac{(C_o - C) Q}{m} dt \quad (3-3)$$

where C_o is the influent metal concentration [$M L^{-3}$], C is the effluent concentration [$M L^{-3}$], Q is the flow rate [$L^3 T^{-1}$], m is the mass of HRB in the column [M], and t_D is the duration of the experiment [T]. The capacity data are presented in Table 4-1. The integration was done using the rectangle rule, and using at least 70 rectangles in each calculation.

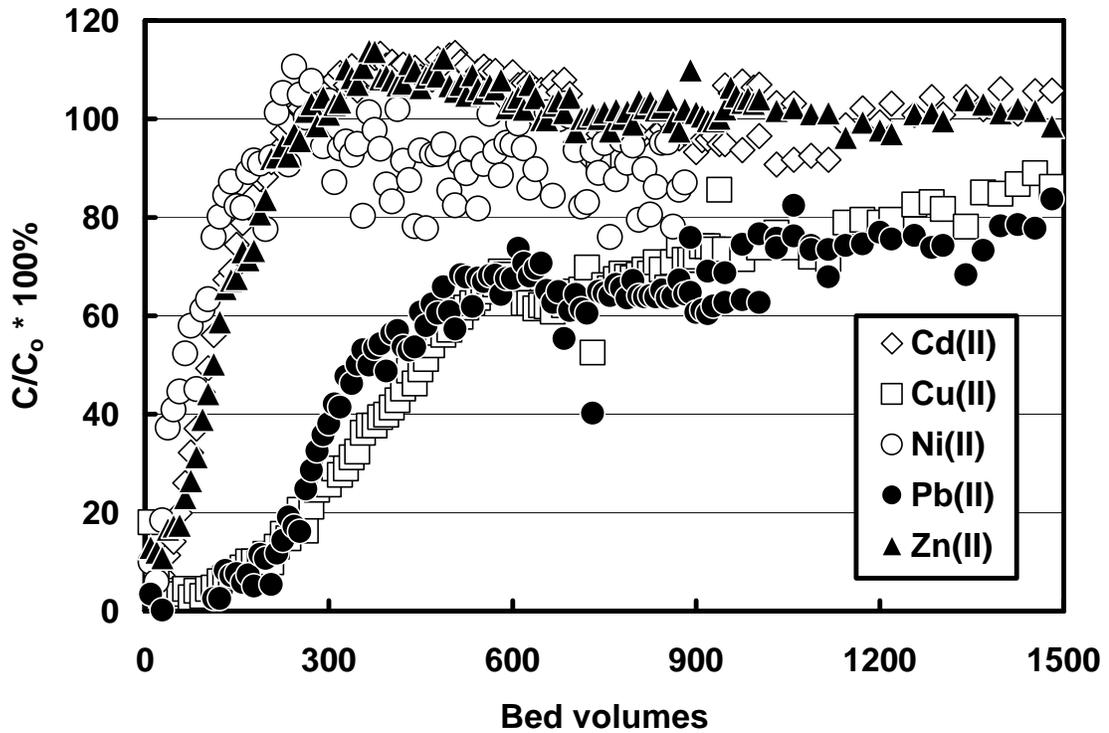


Figure 3-11. Breakthrough curves for uncomplexed metals for a 4 cm³ HRB packed-bed column. Total influent metals = 10⁻⁴ M, pH 5, I= 5 x 10⁻² M NaClO₄·H₂O.

Table 3-1. Capacity of packed HRB column for uncomplexed metals provided as a mixture (10^{-4} M total; pH 5) and recovery of metals using 5 bed volumes of deionized water plus 10 bed volumes of 50 mM EDTA.

	<i>Removal (meq/g)</i>	<i>Recovery (%)</i>
Cd(II)	2.18×10^{-3}	32.0
Cu(II)	8.56×10^{-3}	79.7
Ni(II)	4.88×10^{-3}	11.1
Pb(II)	1.96×10^{-2}	80.0
Zn(II)	3.20×10^{-3}	65.1

The breakthrough capacities of the metals follow the same trend as the selectivity sequence. The capacity of the HRB was significantly higher for Pb(II) than for the other metals.

The column loaded with the mixture of metals was regenerated with 50 mM EDTA at pH 4.7 and the results are shown in Figure 3-12. The trend in the recovery of the metals was essentially opposite of the selectivity sequence. The metals for which the HRB had the highest selectivity and capacity were recovered the most efficiently using EDTA. Approximately 80% of the removed Pb(II) and Cu(II) were recovered. In comparison, recoveries of 65%, 30% and 10% were observed for removed Zn(II), Cd(II) and Ni(II), respectively.

The effectiveness of EDTA as a regenerant was further evaluated in a column experiment in which an HRB packed column was loaded with Cd(II) supplied at 2×10^{-5} M (pH 5, 5×10^{-2} M NaClO₄) and then regenerated with 10 bed volumes of EDTA (9 mM) three times in sequence. Cd(II) and Ca(II) were measured in the effluent during the loading phases. The results are presented in Figure 3-13. The Cd(II) breakthrough curve showed effective removal through approximately 200 bed volumes, followed by increasing effluent Cd(II) concentrations. Exhaustion was essentially complete after

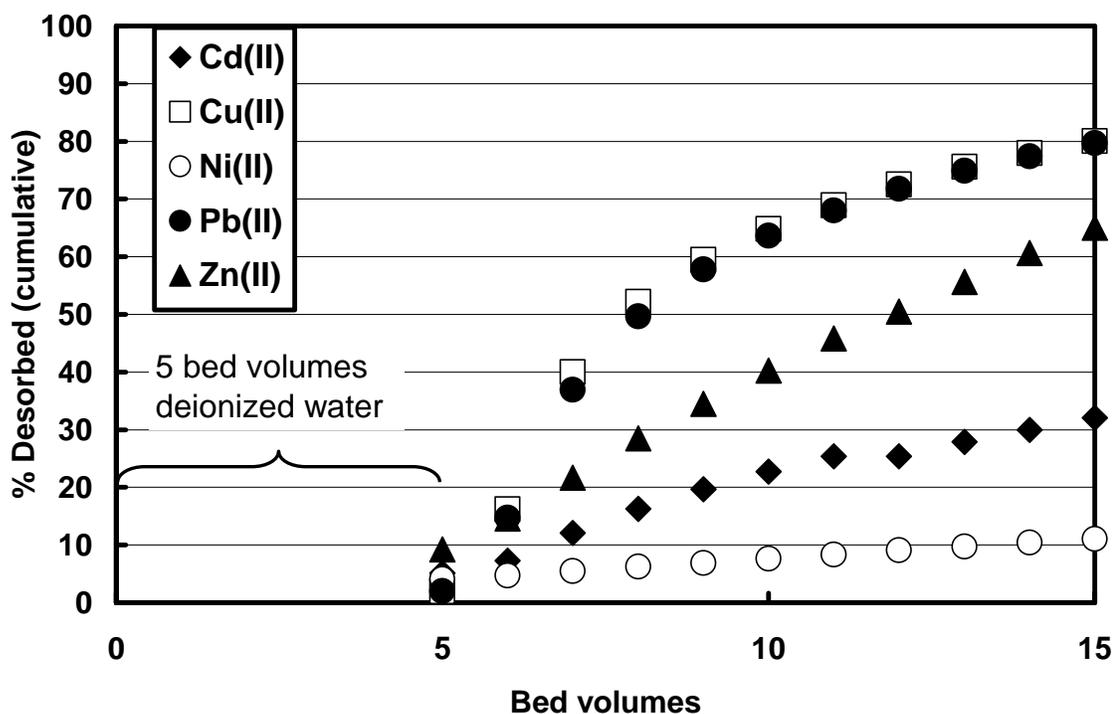


Figure 3-12. Recovery of uncomplexed metals from a 4 cm³ HRB packed-bed with 10 bed volumes of EDTA (50 mM). Data for uptake is shown in Table 3-1.

1500 bed volumes had been treated. In contrast, when Cd(II) was provided at the same concentration in the metal mixture (Figure 3-11), complete exhaustion was observed within 200 bed volumes, as noted above. Presumably, the competition from Pb(II) and Cu(II) with Cd(II) (and Zn(II) and Ni(II)) for reaction sites on the HRB surface discussed above caused Cd(II) to exhaust more rapidly when it was provided in a metal mixture than when it was provided as the sole sorbate.

During the first loading cycle, Ca(II) was released from the HRB continuously. Initially levels were relatively high (> 5 mg/L or 1.2 x 10⁻⁴ M), but gradually decreased to around 1 mg/L (2.5 x 10⁻⁵ M). The results were quite different for the second and third loading cycles. In both cases, Cd(II) exhaustion occurred much more quickly compared

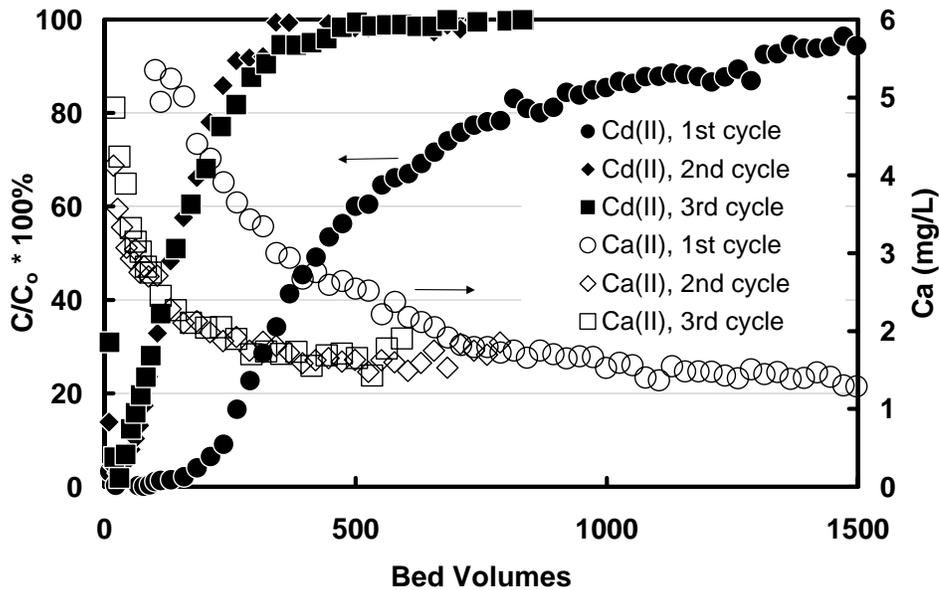


Figure 3-13. Cd(II) breakthrough curves and effluent Ca(II) concentrations for a 4 cm³ HRB packed bed column that was repeatedly loaded with Cd(II) and regenerated with EDTA (10 bed volumes, 9 mM). Influent Cd(II) = 2 x 10⁻⁵ M, pH 5, I=5 x 10⁻² M NaClO₄·H₂O).

with the first cycle, and much less Ca(II) was released.

The total amount of Cd(II) sorbed and Ca(II) released in each of the loading stages was calculated according to Eq. (3-3), and the Cd(II) recovery in each regeneration stage was calculated as

$$recovery = C \cdot V \quad (3-4)$$

where V is the amount of eluent used and C is the concentration of Cd(II) in the effluent from the regeneration stage. The Cd(II) sorption/desorption and Ca(II) release data are summarized in Table 3-2. Only 27.6% of the relatively large amount of Cd(II) removed from the column feed during the first loading cycle was recovered during the first regeneration cycle. The amount of Cd(II) removed was lower during the next two loading

cycles; however, the amount of Cd(II) recovered represented a slight decrease of percentage relative to the net amount of metal present in the sorbent, that is, 25.9 and 23%, for the second and third cycles, respectively.

Table 3-2. Cd(II) uptake and release during repeated column breakthrough and regeneration cycles. 2×10^{-5} M Cd(II); pH 5; 4 ml HRB bed volume (~4.4 mg), regenerated with 10 bed volumes EDTA (9 mM).

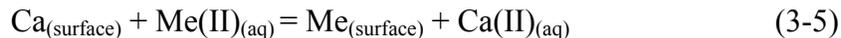
<i>Cycle</i>	<i>Mass Cd(II) adsorbed (mol)</i>	<i>Mass Cd(II) desorbed (mol)</i>	<i>% Desorbed (cycle)</i>	<i>% Desorbed (net)</i>	<i>Mass Ca(II) released (mol)</i>	<i>Cd(II) sorbed /Ca(II) released ratio (mol/mol)</i>	<i>Cd(II) sorption capacity (meq/g HRB)</i>
1	5.7×10^{-5}	1.6×10^{-5}	27.6	27.6	3.4×10^{-4}	0.17	2.6×10^{-2}
2	1.3×10^{-5}	1.4×10^{-5}	110.5	25.9	1.5×10^{-4}	0.09	5.8×10^{-3}
3	1.4×10^{-5}	1.3×10^{-5}	88.1	23.0	1.2×10^{-4}	0.12	6.5×10^{-3}
Total	8.4×10^{-5}	4.2×10^{-5}			6.1×10^{-4}	0.14	--

3.3 Discussion

The HRB had a significantly higher affinity for Pb(II) and Cu(II) than for Zn(II) and Cd(II), and its capacity for Ni(II) was much lower than for the other metals tested, as clearly demonstrated by the results of the batch equilibrium and column breakthrough experiments. The experimentally-determined HRB selectivity sequence is also supported by the speciation calculations and compares well to results obtained in previous studies conducted with calcite materials (Zachara et al. 1991).

The selectivity of the HRB sorbent for metal cations can arise due to several factors. For example, Zachara et al. (1991) studied the sorption of several metals onto calcite, including Cd(II), Ni(II) and Zn(II) and found that the selectivity of calcite decreased in the order: Cd(II) > Zn(II) > Ni(II). The authors interpreted the results in

terms of an ion exchange mechanism according to:



It was found that among metals smaller than Ca(II), the selectivity was greatest for Cd(II), which has an ionic radius only 2% smaller than that of Ca(II) (Stipp et al. 1992), and decreased as the ionic radius of the metal sorbate decreased.

Exchange of Ca(II) at the HRB surface for Cd(II) could have also contributed to the release of Ca(II) during the Cd(II) loading and regeneration experiment (Figure 3-13). However, Cd(II) uptake can account for only a small fraction of the Ca(II) released (Table 3-2). Therefore, it is likely that a significant amount of Ca(II) was released by the dissolution of CaCO₃ (Eq. 3-1). This explains why periods of high Ca(II) release (Figure 3-13) and high effluent pH (data not shown) both occurred during treatment of the first several hundred bed volumes in HRB columns. It also explains why Ca(II) release decreased over time and with repeated loading and regeneration (Figure 3-13). Another possibility is that some of the CaCO₃ present in the HRB consisted of smaller particles that readily dissolved upon contact with the metal solution and, therefore, could not have contributed to Ca(II) release during the second and third treatment cycles. These particles were no longer visible in SEM images of the HRB after one treatment cycle (Figure 3-2).

Additionally, the sorption of Cd(II) (Martin-Garin et al. 2003) and other metals (Pokrovsky and Schott 2002) has been shown to inhibit CaCO₃ dissolution, even after the metals are desorbed, and a similar mechanism could explain the Ca(II) behavior during the sorption phases of the column regeneration experiment. Removal of adsorbed Cd(II) from the HRB using EDTA may have allowed some additional CaCO₃ dissolution to occur after regeneration, but not to the same extent as in unused HRB. It is also likely

that the amount of Ca(II) released after the first treatment cycle decreased because EDTA used to regenerate the HRB dissolved some of the CaCO₃ leaving less to leach out during the next loading cycle. Similarly, other complexing agents such as citrate and polyphosphates have been shown to dissolve CaCO₃ (Stumm and Morgan 1996).

Finally, it should be noted that the data shown in Table 3-2 suggest that while most (>70%) of the adsorbed Cd(II) remains strongly bound to the sorbent, another fraction is readily desorbable. This might explain why the HRB Cd(II) uptake capacity in the first cycle could not be completely restored in the second cycle. Conceivably, the CaCO₃ surface sites that may have played a key role in adsorbing Cd(II) simply may not have been available after the first cycle.

The pH dependence of divalent metal uptake by calcite also could be attributable to surface complexation at the carbonate mineral-aqueous solution interface (Van Cappellen et al. 1993). Metal adsorption is pH dependent, increasing at higher pH, as can be seen in Eqs. 3-7 and 3-12 in Table 3-3.

Because dissolution of calcite occurred via Eqs. 3-1 and 3-2, the HRB increased the experimental system pH, as discussed above, and thus it is likely that some metal removal occurred via heterogeneous or even homogeneous precipitation of the influent metals in the form of hydroxides, carbonates, or hydroxycarbonate composites, as noted by Zachara et al (1991) for calcite. However, the amount of precipitation that occurred in the column experiments may have been somewhat limited because the pH measured in the effluent generally was below 7. Thus, formation of several solids that the speciation

Table 3-3. Surface complexation reactions for the system $\text{CaCO}_3(\text{s})\text{-H}_2\text{O-CO}_2$ and their corresponding homogeneous reactions, and metal speciation in a homogeneous system (adapted from Van Cappellen et al. (1993) and Zachara et al. (1991)).

	<i>Homogeneous reactions (Ca(II))</i>	<i>Surface reactions</i>
(3-6)	$\text{H}_2\text{CO}_3(\text{aq}) \Leftrightarrow \text{HCO}_3^- + \text{H}^+$	$>\text{CO}_3\text{H} \Leftrightarrow >\text{CO}_3^- + \text{H}^+$
(3-7)	$\text{H}_2\text{CO}_3(\text{aq}) + \text{Me}^{2+} \Leftrightarrow \text{MeHCO}_3^+ + \text{H}^+$	$>\text{CO}_3\text{H} + \text{Me}^{2+} \Leftrightarrow >\text{CO}_3\text{Me}^+ + \text{H}^+$
(3-8)	$\text{CaOH}^+ + \text{H}_2\text{O} \Leftrightarrow \text{Ca}(\text{OH})_2 + \text{H}^+$	$>\text{CaOH}_2^+ \Leftrightarrow >\text{CaOH} + \text{H}^+$
(3-9)	$\text{Ca}(\text{OH})_2 + \text{H}_2\text{O} \Leftrightarrow \text{Ca}(\text{OH})_3^- + \text{H}^+$	$>\text{CaOH} \Leftrightarrow >\text{CaO}^- + \text{H}^+$
(3-10)	$\text{CaOH}^+ + \text{CO}_2 \Leftrightarrow \text{CaHCO}_3^+$	$>\text{CaOH} + \text{CO}_2 \Leftrightarrow >\text{CaHCO}_3$
(3-11)	$\text{CaOH}^+ + \text{CO}_2 \Leftrightarrow \text{CaCO}_3 + \text{H}^+$	$>\text{CaOH} + \text{CO}_2 \Leftrightarrow >\text{CaCO}_3^- + \text{H}^+$
(3-12)		$>\text{CaOH} + \text{Me}^{2+} \Leftrightarrow >\text{CaOMe}^+ + \text{H}^+$

calculations predicted would be important at higher concentrations was not likely in the columns except, perhaps, in local high pH environments. Further, the data shown in Figure 3-11 - separate breakthrough curves for different metals and displacement desorption of the weakly affiliated metals - argues for an adsorption-like metal removal mechanism as opposed to a gross precipitation process. Presumably, only metals that accumulated at the interface of the HRB and the aqueous phase could be displaced by adsorption of metals that were higher in the HRB selectivity sequence. It seems less likely that metals that were removed and incorporated into a three-dimensional structure during formation of a precipitate or solid-solution could themselves be desorbed or displace adsorbed metals. Thus, the displacement of a portion of the Cd(II) and Zn(II) removed from solution by metals that were higher in the HRB selectivity sequence (Pb(II) and Cu(II), Figure 3-11) suggests that adsorption contributed to the removal of these four metals by HRB. In addition, adsorption of each of the metals examined in this study to calcite has previously been reported, particularly from solutions that were undersaturated with respect to solid phases of the sorbates (Zachara et al. 1991; Stipp et

al. 1992; Elzinga and Reeder 2002; Rouff et al. 2004).

The macroscopic measurements of metal uptake from solution performed in this study do not allow full discrimination between adsorption, precipitation, and other possible interactions between the HRB and metal sorbates such as formation of solid solutions. However, as discussed below, it seems likely that the mechanisms by which the various metals were removed by the HRB varied and contributed to the observed differences in the magnitude and reversibility of uptake among the metals.

Several pieces of evidence obtained in this study suggest that removal of Cd(II) by the HRB occurred in two phases and involved two distinct mechanisms. First, in the batch evaluation of Cd(II) uptake by the HRB over time, removal at pH 6.5 and 9 appeared to be biphasic, with a relatively large fraction of Cd(II) taken up rather rapidly, followed by slower uptake of a smaller fraction of Cd(II) (Figure 3-8). Although the possibility that the increase in the percentage of aqueous Cd(II) removed by the HRB after 4 h was the result of an increase in solution pH due to calcite dissolution cannot be ruled out, another explanation is that the Cd(II) removal that occurred before and after 4 h involved different mechanisms.

The two-phase, fast-slow, biphasic Cd(II) removal pattern exhibited by the HRB has been observed in previous studies of calcite-based sorbents (Zachara et al. 1991; Martin-Garin et al. 2002; Martin-Garin et al. 2003). As noted by Stipp et al (1992), the initial "fast" uptake phase is usually presumed to reflect adsorption due to surface complexation or ion exchange, and the period of slow uptake that follows is often attributed to precipitation or co-precipitation. In addition, Stipp et al. (1992) provided strong evidence that solid-state diffusion, the migration of Cd(II) (or other metal) ions

from the surface into the bulk lattice of calcite, can play a role in the removal of metals from solution. Martin-Garin et al.(2003) demonstrated that the rapid uptake of Cd(II) onto calcite was almost completely reversible, whereas the Cd(II) taken up through a slower process was irreversibly bound.

The Cd(II) uptake model of adsorption to the calcite surface followed by incorporation into a three-dimensional structure through precipitation, co-precipitation, or solid-state diffusion is consistent with the results of the column experiment evaluating the effects of repeated loading and regeneration on Cd(II) uptake by the HRB. Specifically, it appears that a relatively small amount of the Cd(II) loaded onto the column (27.6% or approximately 1.4 to 1.8 mg in this experiment) was adsorbed to the HRB surface via either surface complexation or ion exchange reactions and thus could be recovered using EDTA (Figure 3-12). Cd(II) that could not be recovered during the first treatment cycle and was irreversibly associated with the HRB could conceivably have been taken up via several different mechanisms (Martin-Garin et al. 2003). However, precipitation of Cd(II) was not predicted by the speciation calculations within the range of pH values measured in the HRB column effluent. Therefore, it is possible that Cd(II) that was not mobilized by EDTA may have diffused into the CaCO₃ lattice and formed a solid-solution, as observed by Stipp et al. (1992).

In contrast to Cd(II), the majority of the Pb(II) and Cu(II) taken up by the HRB could be recovered by EDTA (Figure 3-12). This suggests that compared with Cd(II), a greater portion of the removed Pb(II) and Cu(II) remained available for complexation with EDTA at the HRB surface either in an adsorbed state or in the form of a precipitate. In fact, the speciation calculations suggest that precipitation of Pb(II) solids may have

occurred within the range of pH values (6-7) typically measured in the HRB column effluent. In particular, formation of hydrocerrusite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_{2(s)}$) was predicted at pH 6.5-7. Precipitation of lead hydroxide ($\text{Pb}(\text{OH})_{2(s)}$) was predicted at pH 7.1 and therefore was probably less important in the HRB column. The idea that precipitation of Pb(II) contributed to its removal by HRB is supported by the results of Rouff et al. (2004). The authors observed that removal of Pb(II) at low concentrations ($<1 \times 10^{-6}$ M) resulted from the formation of strongly adsorbed inner-sphere complexes at the calcite surface, which is consistent with the displacement of Cd(II) and Zn(II) from HRB by Pb(II) observed in this study. However, at concentrations of 2×10^{-5} M or higher, removal of Pb(II) by calcite was dominated by precipitation of hydrocerrusite and cerrusite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_{2(s)}$). In addition, Chada et al. (2005) summarized the results of several studies that demonstrated that Pb(II) taken up by calcite resides primarily in disordered surface layers and calcite uptake of Pb(II) is largely reversible.

Dilute Cu-calcite solid solutions have been formed from Cu(II)-doped calcite crystals in co-precipitation experiments; however, incorporation of Cu distorted the calcite lattice structure (Elzinga and Reeder 2002). Like Pb(II), Cu(II) has been shown to form strong inner-sphere sorption complexes at the calcite surface (Elzinga and Reeder 2002), which is consistent with the displacement of Cd(II) and Zn(II) by Cu(II) and Pb(II) in the column experiment (Figure 3-11). In fact, adsorption of Cu(II) to calcite prevented precipitation of Cu(II) from an oversaturated solution. Presumably, the distorted geometries needed to form complexes with Cu(II) limits diffusion of adsorbed Cu(II) into the calcite lattice and the formation of solid-solutions that have been observed with Cd(II). Although formation of a CuCO_3 precipitate is not suggested, the speciation

calculations indicated that $\text{CuO}_{(s)}$ would form in the HRB column. As discussed above for Pb(II) , it seems likely that Cu present in surface layers (either in adsorbed complexes or a CuO solid layer) would be available for complexation and release with EDTA, and this could explain the effective recovery of Cu(II) during the column regeneration experiment (Figure 3-12).

Thus, based on the results of this study and previous investigations, it appears that Pb(II) and Cu(II) interact with calcite-based materials in a fundamentally different way compared with Cd(II) . That is, a portion of the Pb(II) and Cu(II) appear to adsorb to the calcite or HRB surface through the formation of strong complexes, and in the process, may displace Cd(II) that has associated with the sorbent surface through ion exchange reactions or other interactions. Cd(II) that is not displaced by Pb(II) and Cu(II) or recovered using EDTA apparently migrates into the CaCO_3 lattice structure to form a solid-state solution. Precipitation, rather than formation of a solid-state solution, likely contributes more to the removal of Pb(II) and Cu(II) by HRB.

When compared to the data obtained for Cu(II) and Cd(II) , the capacity of HRB for Zn(II) and recovery of Zn(II) using EDTA were intermediate in nature (Figure 3-11). It is not surprising that the HRB had a higher capacity for Zn(II) than for Cd(II) because an earlier study showed that sorption of cations with ionic radii smaller than Ca(II) generally increased with ionic size and could be described by an Me(II)-Ca(II) exchange at surface sites (Eq. 3-4, Zachara et al. (1989; 1991)). The exception to this trend was Zn(II) , which showed a higher affinity for the calcite surface than predicted based on its ionic radius. As noted above, the high capacity of HRB for Pb(II) and Cu(II) can probably be explained in part by precipitation of these metals. In contrast, no formation

of zinc carbonate/hydroxide precipitates was observed when Zn(II) provided at concentrations of up to $10^{-1.8}$ M was sorbed to calcite (Shahwan et al. 2005). Similarly, hydrozincite did not form in zinc/calcite suspensions that were oversaturated with respect to hydrozincite due to adsorption of zinc on the calcite surface (Elzinga and Reeder 2002). On the other hand, formation of a thin layer of hydrozincite ($Zn_5(CO_3)_2(OH)_6$) was observed in an earlier study of zinc precipitates on calcite when Zn(II) was provided at a concentration of 10^{-4} M (Zachara et al. 1988). In this study, formation of ZnO was not predicted below pH 8.2. Shahwan et al. (2005) noted that the formation of zinc carbonate species occurs within time periods on the order of days or weeks, compared with the formation of Pb(II) carbonate precipitates within hours. Because of the relatively slow formation of zinc carbonates, it is unlikely that significant amounts of hydrozincite would have formed in the HRB column during the breakthrough experiment. Moreover, the pH for the formation of hydrozincite (7.9) predicted in the speciation calculations is well above the typical pH values measured in the column effluent (6–7). If precipitation did not play an important role in the removal of Zn(II) in the HRB column, it is possible that a solid-state diffusion process similar to that observed for Cd(II) took place, as observed by Zachara et al. (1991). In that study, approximately 20% of the Zn(II) removed by calcite was not desorbable and was incorporated into the calcite lattice.

Recovery of the relatively small amount of Ni(II) sorbed to the HRB column using EDTA was poor compared to the other metals studied here (Figure 3-12). Ni(II) also occupied an unfavorable position in the calcite selectivity sequence for divalent metal cations in the study of Zachara et al. (1991). However, in contrast to our results, Ni(II) was among the most readily desorbable metals in the earlier study. It is not clear why the

desorption results obtained in the two investigations differ so much. However, the desorbable nature of Ni(II) observed by Zachara et al. (1991) suggests that the formation of a Ni(II) solid-solution was not important, and the speciation calculations performed in this study indicate that precipitation of nickel carbonate/hydroxide species did not occur in the HRB column. Thus, although only a relatively small amount of Ni(II) was taken up by the HRB, it seems likely that Ni(II) formed strong complexes with the surface of calcite or perhaps was bound by a minor constituent of the HRB, e.g., proteins.

.

Chapter 4. Comparison of an Ion-Exchange Resin and HRB for Removal of Heavy Metals from Plating Wastewater.

4.1 Introduction

The use of a wide variety of materials of biological origin as metal sorbents, i.e., biosorption, is increasingly being promoted as a way of reducing the cost of treating metal-contaminated wastewater by eliminating the need for expensive, synthetic sorbents or resins (Volesky and Holan 1995; Wase and Forster 1997; Volesky 2003; Gavrilesco 2004). Residuals generated during agricultural animal production and processing are potential candidates for use in biosorption. The regional surpluses resulting from consolidation within these industries create a problem due to the increasing difficulty of disposing of such residuals, which, at the same time, makes recovery or recycling of residuals an attractive management approach. The abundance of agricultural residuals also makes these materials available free of charge or at a modest cost. Of course, before an agricultural residual can be used as a biosorbent, its metal-removing capacity must first be characterized and, if metal uptake by an agricultural residual is observed, ideally the removal mechanisms should be characterized to facilitate the design and operation of a biosorbent-based treatment system.

In this study, the potential for use of hatchery residual as a biosorbent was evaluated. Major components of HRB include eggshell and animal fibrous proteins, e.g., feathers and eggshell membrane. Eggshells, in turn, are composed of layers of calcite (CaCO_3), containing embedded proteins that make eggshells less prone to dissolution compared with calcite alone (Solomon 1999; Dobiášová et al. 2004). X-ray diffraction

analysis of the HRB confirmed that calcite was a major component of the residual (Section 3.2.1). HRB was shown to remove several divalent cations (Cd(II), Cu(II), Ni(II), Pb(II), Zn(II)) from aqueous solutions containing individual metals or a mixture of the metals, as discussed in Chapter 3. Comparison of the batch and column sorption experiment results with those obtained in previous studies of metal uptake by calcite (Zachara et al. 1988; Stipp and Hochella 1992; Elzinga and Reeder 2002; Kobayashi et al. 2004; Rouff et al. 2004; Chada et al. 2005; Shahwan et al. 2005) suggest that the underlying removal mechanisms vary for the different metals and occur via a complex combination of mechanisms that may include adsorption, precipitation, co-precipitation and/or solid-solution diffusion.

In Chapter 4, the results of experiments that examined the feasibility of using HRB for treatment of several common divalent metal cations (Cd(II), Cu(II), Fe(II), Ni(II), Pb(II), Zn(II)) from industrial wastewaters are presented. Two different approaches were used to evaluate HRB uptake of metals from industrial wastewater.

First, because industrial wastewaters and contaminated groundwaters often contain organic and inorganic complexing agents in addition to heavy metals (Benjamin et al. 1996; Sedlak et al. 1997; Raskin and Ensley 2000), the ability of the HRB to sorb a mixture of metals was tested in the presence of a complexing agent (NH₄Cl). Studies conducted using ferrous oxide-coated sand as an adsorbent showed that weak ligands like ammonia interfere with adsorption, although to a lesser extent than a strong ligand such as EDTA (Benjamin et al. 1996; Mustafa et al. 1998). Second, columns that were scaled up in size compared with the HRB packed columns used to evaluate metal uptake from defined solutions were used to compare the performance of the HRB to a commercially

available ion exchange resin, Amberlite® IRC748 when treating a real industrial wastewater obtained from an electroplating operation. Based on the results of these two sets of experiments, technical recommendations for the use of HRB in the treatment of industrial wastewaters are made along with suggestions for alternative uses of HRB.

4.2 Results

4.2.1 Complexed Metals

The results obtained when the HRB column was loaded with a mixture of metals complexed with NH_4Cl are shown in Figure 4-1. In general, the results are fairly similar to those obtained with the uncomplexed metals (Chapter 3). Cd(II) , Zn(II) , and Ni(II) broke through the column before Pb(II) and Cu(II) . This is consistent with the selectivity sequence predicted on the basis of the batch experiments when an uncomplexed mixture of metals was provided simultaneously (Chapter 3) ($\text{Pb(II)} > \text{Cu(II)} > \text{Zn(II)} = \text{Cd(II)} > \text{Ni(II)}$). However, exhaustion for all of the complexed metals occurred significantly earlier compared with their behavior in the uncomplexed form. For example, the effluent concentrations of Zn(II) and Cd(II) were equal to 50% of their influent concentrations within approximately 60 bed volumes when complexed with NH_4Cl (Figure 4-1). 125 bed volumes were required to reach the same effluent concentrations for uncomplexed Zn(II) and Cd(II) (Chapter 3).

The overall capacities of the HRB for uncomplexed and metals complexed with NH_4Cl were calculated based on the column experiment results according to Eq. 3-3 and are presented in Table 4-1. The capacity of the HRB for complexed Cd(II) was within 3% of the HRB's capacity for the uncomplexed forms of this metals, and the recovery of

Cd(II) did not appear to be affected by complexation. Zn(II) uptake decreased three-fold when complexed, and only 49% of the complexed Zn(II) could be recovered with EDTA, which is less than the 65% recovery of uncomplexed Zn(II). The capacity of the HRB for complexed Cu(II) was 8.6×10^{-3} meq/g, close to its capacity for free Cu(II) (7.2×10^{-3} meq/g, Table 4-1).

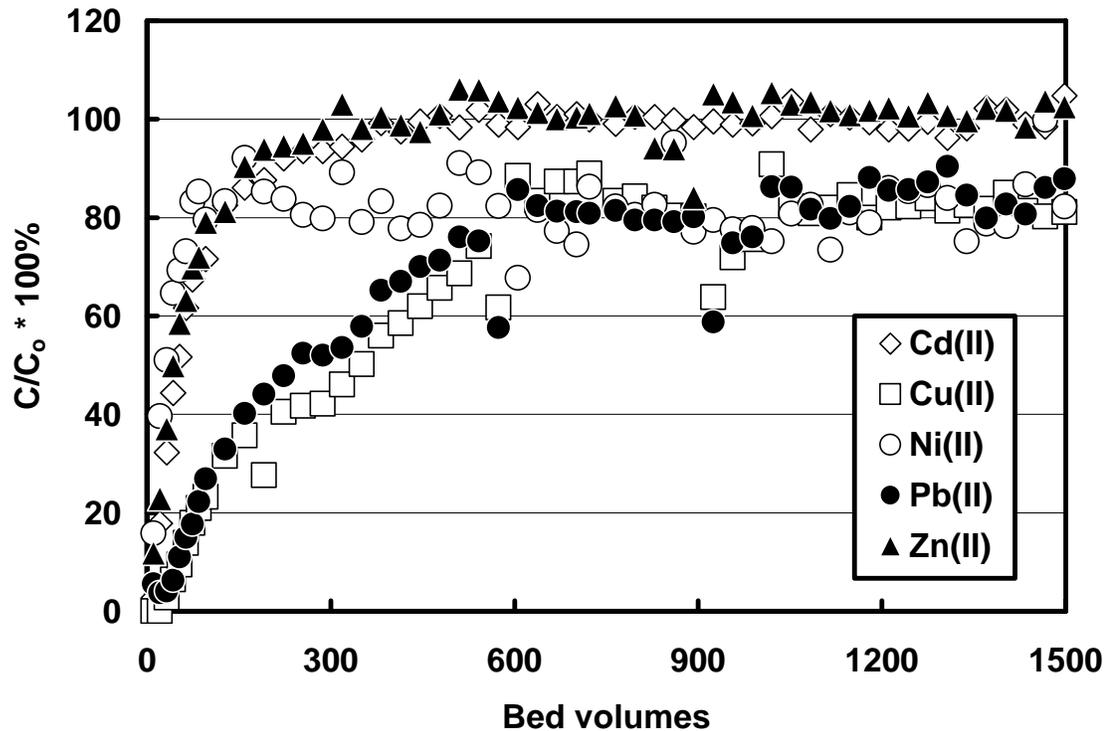


Figure 4-1. Breakthrough curves for NH_4Cl -complexed metals from a 4 cm^3 HRB packed-bed column. (Influent metals = 2×10^{-5} M each metal, pH 5, $I = 5 \times 10^{-2}$ M $\text{NaClO}_4 \cdot \text{H}_2\text{O}$).

The recovery of metals from the column using EDTA is shown in Figure 4-2 and Table 4-2. Recovery of Cu(II) decreased from 80% for the uncomplexed metal (Table 4-2) to 25% for the complexed form (Figure 4-2). For Pb(II), the adsorption capacity for

both mixtures was similar; however, 80% of uncomplexed Pb(II) was recovered using EDTA, compared with recovery of only around 46% of NH₃-complexed Pb(II).

The removal of Ni(II) increased four-fold in the presence of NH₃, and desorption of Ni(II) decreased from 11% for uncomplexed Ni(II) to ~3% for complexed Ni(II).

Table 4-1. Capacity of packed HRB column for uncomplexed metals provided as a mixture (10⁻⁴ M total; pH 5) and a mixture (10⁻⁴ M total; pH 5) of metals complexed with NH₄Cl (4 x 10⁻⁴ M). HRB bed volume = 4 ml (4.4 g). Values for metals without complexing agent are from Chapter 3.

<i>Metal</i>	<i>Without complexing agent (meq/g)</i>	<i>Complexed with NH₄Cl (meq/g)</i>
Cd(II)	2.18 x 10 ⁻³	2.14 x 10 ⁻³
Cu(II)	8.56 x 10 ⁻³	7.15 x 10 ⁻³
Ni(II)	4.88 x 10 ⁻³	1.86 x 10 ⁻²
Pb(II)	1.96 x 10 ⁻²	2.07 x 10 ⁻²
Zn(II)	3.20 x 10 ⁻³	1.13 x 10 ⁻³
Total	3.84 x 10⁻²	4.97 x 10⁻²

Table 4-2. Final recovery of free metals and metals complexed with NH₄Cl from a 4 cm³ HRB-packed bed column using 5 bed volumes of deionized water plus 10 bed volumes of 50 mM EDTA.

<i>Metal</i>	<i>Without complexing agent (% of removed)</i>	<i>Complexed with NH₄Cl (% of removed)</i>
Cd(II)	32	29
Cu(II)	80	25
Ni(II)	11	2.7
Pb(II)	80	46
Zn(II)	65	49

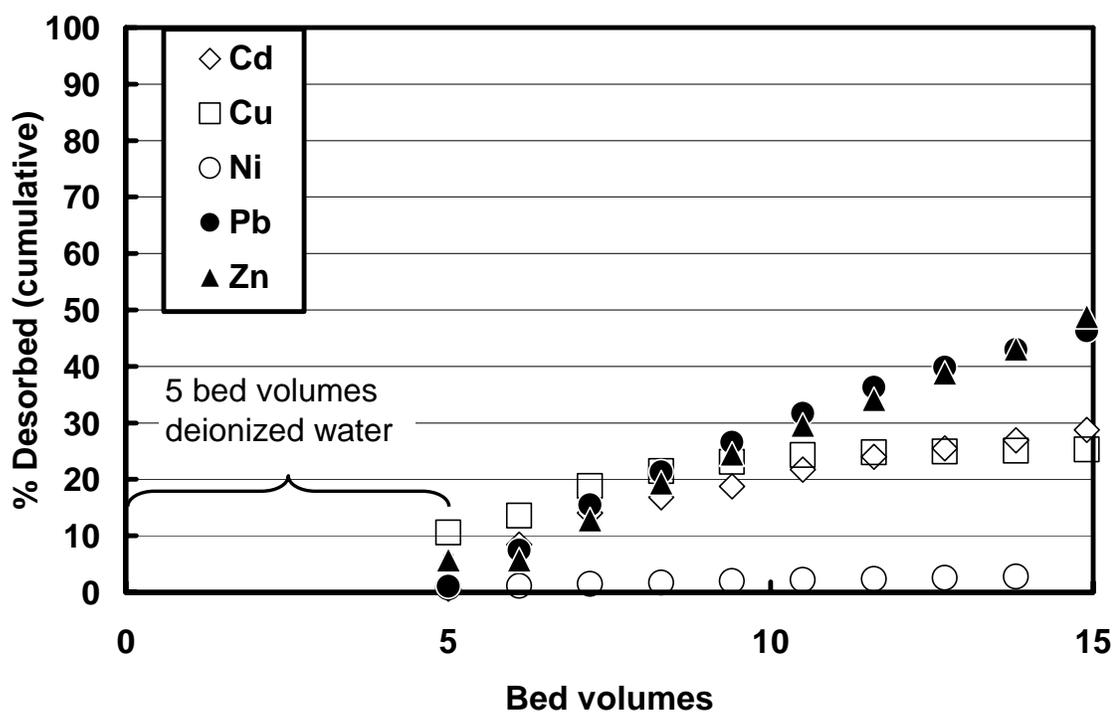


Figure 4-2. Recovery of metals complexed with NH_4Cl from a 4 cm^3 HRB-packed bed column using 5 bed volumes of deionized water followed by 10 bed volumes of 50 mM EDTA. Adsorbed values are given in Table 4-1.

4.2.2 Industrial Wastewater

Treatment of an electroplating wastewater using HRB and ion exchange resin (Amberlite IRC748) columns was compared. The wastewater was first characterized following the pH adjustment and filtration pretreatment steps, and key characteristics of the wastewater are summarized in Table 4-3. Ni(II) was much more abundant in the wastewater compared to other metals. It is also noteworthy that the wastewater contained a significant amount of iron, which was not evaluated in any of the other sorption experiments reported in this chapter or in Chapter 3. The analytical technique for iron did not distinguish between Fe(II) and Fe(III), but based on the apparent selectivity of the

resin for the dissolved iron in the wastewater and the selectivity sequence for the resin reported by the manufacturer (discussed below), it seems like that most iron was in the form of Fe(II). Conversely, the wastewater did not contain significant amounts of Cd(II), which was previously used to evaluate the effects of many factors on sorption by HRB. The wastewater had a relatively high TDS concentration of 1400 mg/L. Dissolved metals and other inorganic ions like calcium contribute to TDS. However, the concentrations of the measured metal ions and calcium constituted only a small fraction (~3%) of the measured TDS. The presence of a significant amount of TDS is important, in part, because the presence of the "background ions" can affect the quality of water treated in ion exchange processes (Clifford 1990). In fact, ion exchange is usually not feasible in the presence of high TDS levels. The addition of NaOH to the original wastewater for pH adjustment contributed to the TDS measured in the filtered wastewater.

Table 4-3. Concentrations of metals and other inorganic compounds in the electroplating wastewater.

<i>Constituent</i>	<i>Concentration</i>	
	<i>(mg/L)</i>	<i>(M)</i>
TDS ¹	1404	
Cr ²	0.40	7.7 x 10 ⁻⁶
Cu	0.65	1.0 x 10 ⁻⁵
Ni	30	5.1 x 10 ⁻⁴
Fe	7.39	1.3 x 10 ⁻⁴
Pb	7.95	3.8 x 10 ⁻⁵
Zn	0.17	2.6 x 10 ⁻⁶
Ca	0.35	8.7 x 10 ⁻⁶
Tot. metals	46.34	7.1 x 10 ⁻⁴

¹After adjustment to pH and filtration.

²The concentration of Cr was at least this high. AA response for Cr is suppressed by the presence of Ni and/or Fe. (Perkin-Elmer 1996)

³Iron was presumed to be in predominantly in the Fe(II) form, as described in the text.

The breakthrough of individual metals through the HRB and ion exchange columns are compared in Figures 4-3 through 4-8. Pb and Fe broke through the resin more quickly than through the HRB (Figures 4-3 and 4-4), although the difference in the performances of the two adsorbents is more dramatic for Pb (Figure 4-3). In effect, full exhaustion of the capacity of the HRB for Pb(II) was not noted after 1100 bed volumes.

The opposite trend was observed when sorption of Ni, the most abundant wastewater metal, and Cu by the two sorbents was compared (Figures 4-5 and 4-6). In fact, the concentration of Ni was not significantly affected by the HRB. Almost immediately, the effluent Ni concentration was only 20% lower than in the influent, and within less than 200 bed volumes, the effluent and influent Ni concentrations were equal. In comparison, the ion exchange resin approached saturation with respect to Ni only after approximately 1300 bed volumes had been treated. The concentration of Cu in the wastewater was almost two orders of magnitude lower than that of Ni. Thus, it is not surprising that Cu exhaustion did not approach 100% until more than 1000 bed volumes were treated (Figure 4-6), compared with the almost immediate Ni exhaustion. Uptake of Cu by the resin was even more effective. The ion exchange resin column effluent never contained more than 20% of the influent Cu concentration. In contrast, Zn was detected in the effluents of both columns almost immediately (Figure 4-7), despite the fact that it was present in the wastewater at only 2.6×10^{-6} M, which was lower than the Zn concentration used in the previous column experiments. The ion exchange resin removed Zn only slightly better than the HRB.

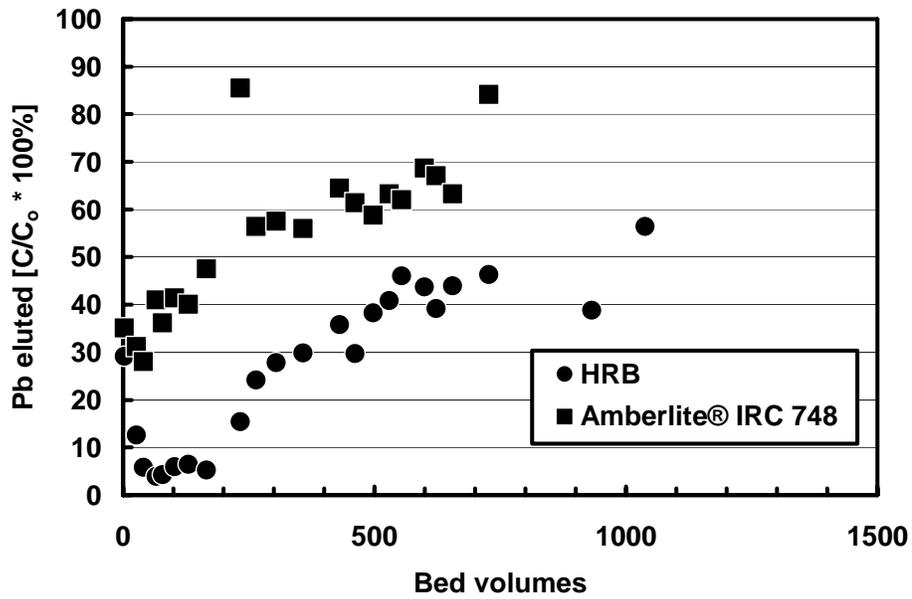


Figure 4-3. Breakthrough of 3.8×10^{-5} M Pb from the 16 cm^3 Amberlite® IRC748 and HRB packed-bed columns, at pH 5. Other metal concentrations are listed in Table 4-3.

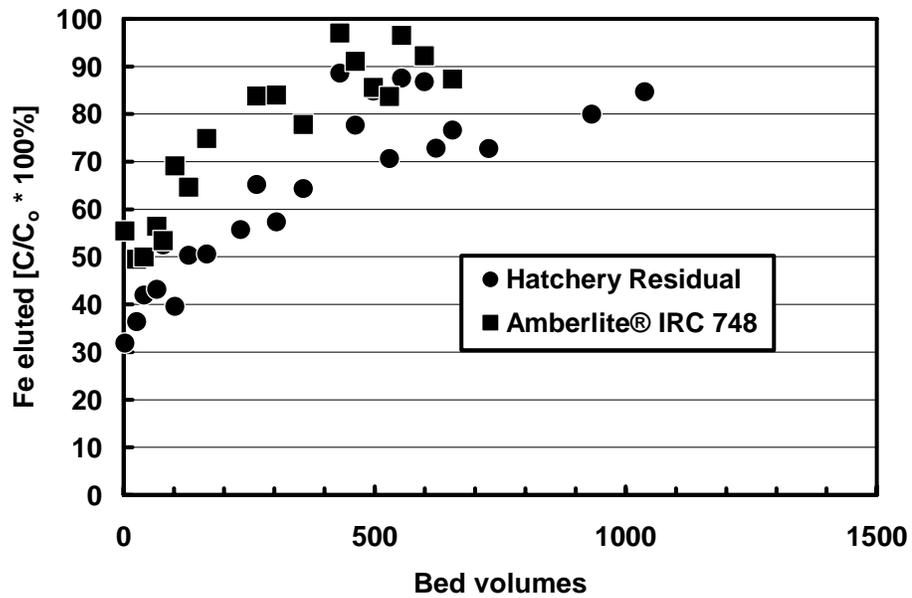


Figure 4-4. Breakthrough of 1.3×10^{-4} M Fe from the 16 cm^3 Amberlite® IRC748 and HRB packed-bed columns, at pH 5. Other metal concentrations are listed in Table 4-3.

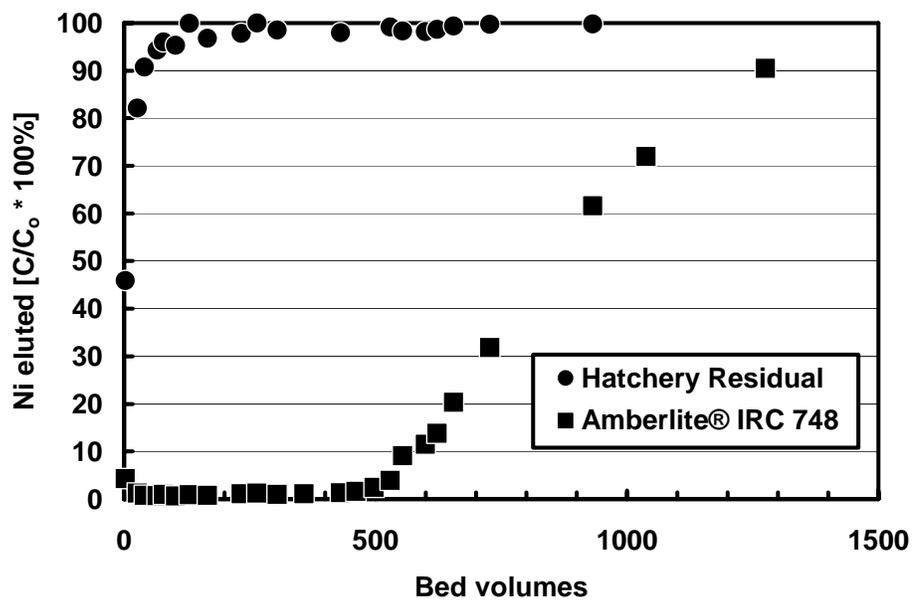


Figure 4-5. Breakthrough of 5.1×10^{-4} M Ni from the 16 cm^3 Amberlite® IRC748 and HRB packed-bed columns, at pH 5. Other metal concentrations are listed in Table 4-3.

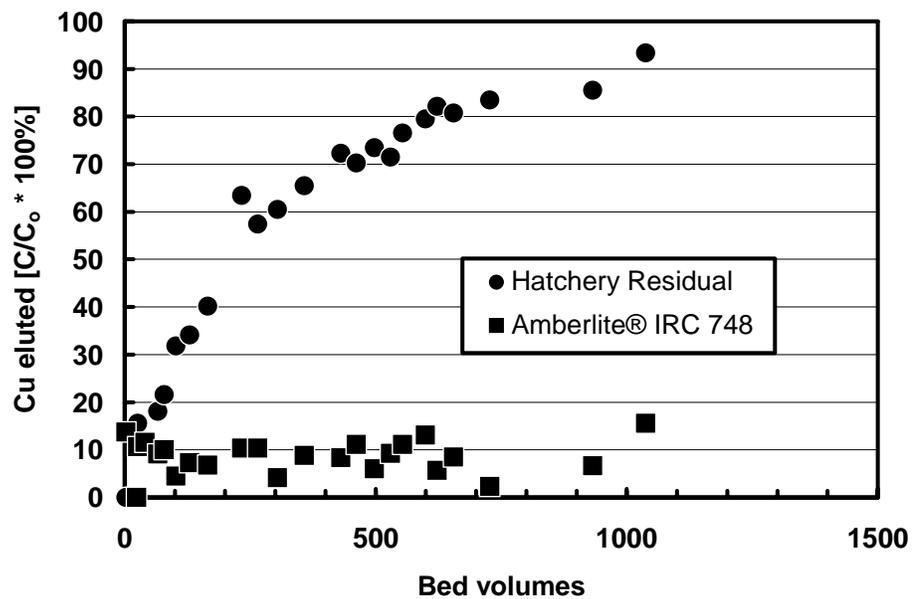


Figure 4-6. Breakthrough of 10^{-5} M Cu from the 16 cm^3 Amberlite® IRC748 and HRB packed-bed columns, at pH 5. Other metal concentrations are listed in Table 4-3.

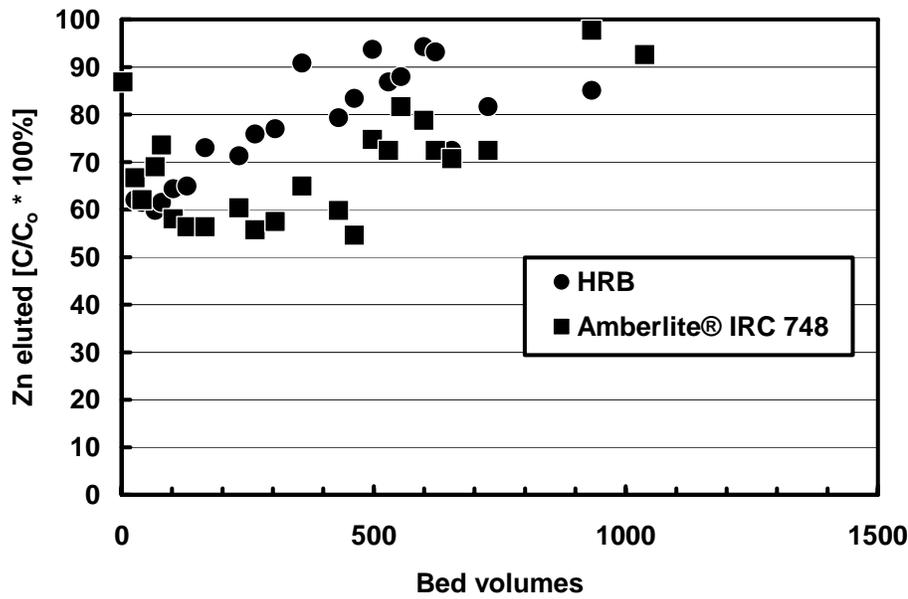


Figure 4-7. Breakthrough of 2.6×10^{-6} M Zn from the 16 cm^3 Amberlite® IRC748 and HRB packed-bed columns, at pH 5. Other metal concentrations are listed in Table 4-3.

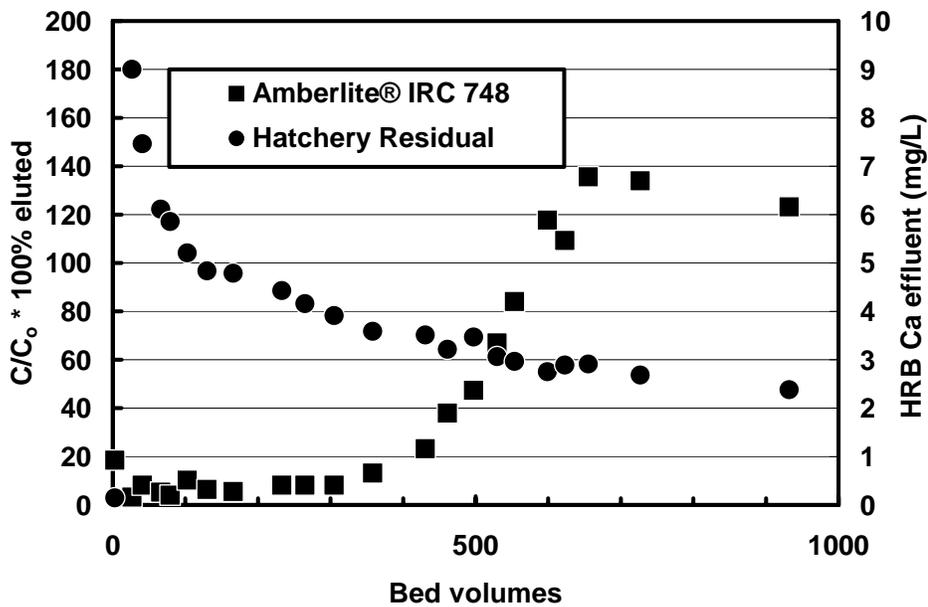


Figure 4-8. Breakthrough of 8.7×10^{-6} M Ca from the 16 cm^3 Amberlite® IRC748 column and Ca release from the 16 cm^3 HRB packed-bed column, at pH 5. Other metal concentrations are listed in Table 4-3.

Ca was present in the wastewater (Table 4-3), and additional Ca was released by the HRB during the loading phase (Figure 4-8), as was observed in previous column experiments (Chapter 3). In contrast, Ca in the wastewater was removed by the ion exchange column until the resin became saturated with respect to Ca after approximately 600 bed volumes had been treated. Not surprisingly, Ca was displaced from the resin by a preferred metal after 600 bed volumes, resulting in effluent concentrations that exceeded the influent Ca concentrations. Ni began breaking through the resin at around this time and was present in the influent in high concentrations. Therefore, it is likely that Ni contributed to the displacement of Ca. This suggests that the resin had a higher selectivity for Ni compared to Ca.

Comparing the affinity of the HRB for the different metals was relatively straightforward for the previous column experiments because all of the metals were present at approximately the same concentration in the feed. Therefore, metal concentrations did not affect the selectivity sequence of the HRB, which was determined simply by comparing the time until exhaustion occurred. In contrast, metal concentrations varied by several orders of magnitude in the electroplating wastewater. Thus, in order to assess the selectivity sequences of the HRB and ion exchange resin for the metals in the wastewater, removal of each metal was normalized to the amount of metal present in the wastewater by calculating a selectivity coefficient (K) for each metal and sorbent, according to:

$$K = \frac{q}{C_o} \quad (4-1)$$

where q is the mass of metal accumulated on the sorbent at exhaustion, and C_o is the influent concentration of the same metal. Thus, K values are reported in terms of

volumes, and can be conceptualized as the amount of wastewater that can be treated until exhaustion of a metal occurs. Higher K values correspond to higher positions in a selectivity sequence. This selectivity coefficient is analogous to, but slightly different than, the one used by Brower et al. (1997) for batch experiments.

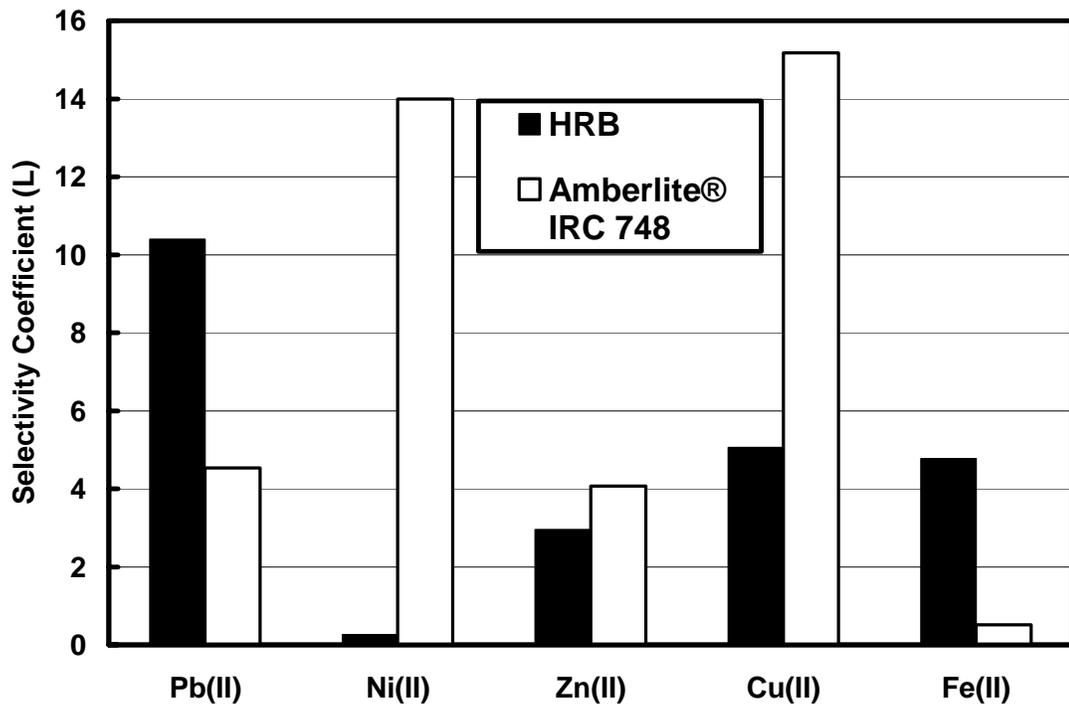


Figure 4-9. Selectivity coefficients (defined in text) of HRB and Amberlite® IRC748 for metal cations in the industrial wastewater.

The selectivity coefficients of the HRB and ion exchange resin for the different metals are presented graphically in Figure 4-9. As suggested by comparing individual breakthrough curves, the resin has a much higher affinity for Cu and Ni compared with the HRB, but the HRB is more selective for Pb and Fe as compared to the resin. Based on the selectivity coefficients, the experimentally-determined selectivity sequence of the

resin for the different metals in decreasing order is: $\text{Cu} > \text{Ni} > \text{Pb} > \text{Zn} > \text{Fe}$. The selectivity reported by the resin manufacturer is similar except that the positions of Ni and Pb in the sequence are switched: $\text{Fe (II)} > \text{Cu(II)} > \text{Pb(II)} > \text{Ni(II)} > \text{Zn(II)} > \text{Fe(III)} > \text{Ca(II)}$. In comparison, the industrial wastewater experiment suggests that the selectivity sequence of the HRB decreases in the order: $\text{Pb} > \text{Cu} \approx \text{Fe} > \text{Zn} > \text{Ni}$, which is consistent with the results of the previous column and batch experiments conducted with metals presented in equimolar metal concentrations.

Key physical and chemical characteristics of the HRB and its capacities for the metals tested in this study are compared to the characteristics and properties of the Amberlite® IRC748 in Table 4-4. The capacities for metals were calculated according to Eq. 4-1. The HRB and resin breakthrough curves suggested that the HRB had a higher affinity for Fe and Pb compared to the resin, and, as shown in Table 4-4, the HRB also had higher capacities for these two metals than the resin. In contrast, the HRB had little affinity for Cu, Ni, or Zn, and it also had lower capacities for these metals compared with the capacities of the resin for the same metals. It is important to note though that despite the HRB's low affinity for Ni and the rapid HRB column exhaustion for this metal, a significant amount of Ni was taken up by the HRB (Table 4-4). The rapid exhaustion occurred because Ni was present at a very high concentration in the feed. The ion exchange resin took up even more Ni compared to the HRB. In fact, the resin's capacity for Ni was over 100 times greater than that of the HRB. This contributed to the much higher total capacity measured for the resin compared to the HRB.

Table 4-4. Comparison of capacities and physical and chemical characteristics of the HRB and ion exchange resin evaluated in this study (Amberlite® IRC748).

	<i>HRB</i>	<i>Amberlite® IRC748 Resin¹</i>
<i>Capacity (meq/g)</i>		
Ca	-1.5×10^{-1}	8.5×10^{-3}
Cu	5.7×10^{-3}	3.5×10^{-2}
Fe	7.2×10^{-2}	1.5×10^{-2}
Ni	1.5×10^{-2}	1.6
Pb	4.5×10^{-2}	4.0×10^{-2}
Zn	9.1×10^{-4}	2.5×10^{-3}
Total capacity	0.14 ²	1.7
Total exchange capacity (eq/L)	0.15	1.28 ³ (≥ 1.35)
Moisture holding capacity (%)		60.0-65.0
Moisture content (%)	0.9	
Volatile organics (%)	8.4	
Shipping weight/apparent density (g/L)	1100	750
Particle size range (mm)	0.5-2.0	
Harmonic mean size (mm)	0.5-1.0	0.50-0.65
Uniformity coefficient		≤ 1.7
Fines (≤ 0.300 mm) content (%)		1.0
Coarse (≥ 1.100 mm) bead content (%)		5.0
Surface area (cm ² /g)	0.74	
<i>Suggested operating conditions</i>		
Maximum temperature (°C)		90
pH range	5-14	1.5-14
Service flow rate (bed volumes/h)	15-20	19 ³ (6-32)
Regenerant	EDTA	HCl or H ₂ SO ₄
Regenerant concentration	36 mM	5 to 10%
Regenerant flow rate (bed volumes/h)	15-20	2 to 4

¹Information obtained from manufacturer's product sheet unless otherwise noted.

²Total capacity of HRB does not include loss of Ca.

³Determined during this study.

The HRB and resin particles are similar in size. The surface area of Amberlite® IRC748 particles was not available. The specific surface area of the HRB was 0.74 m²/g, which, as discussed in Chapter 3, is comparable with other calcite-based materials. However, the HRB surface area is small compared to the surface areas of some commercially available adsorbents. Most carbonaceous materials are fairly porous and have surface areas on the order of 10 m²/g (Allen 1996). Surface areas of activated carbons typically range from 500 to 1500 m²/g (Cooney 1999). On the other hand,

adsorbent characteristics other than surface area, including surface charge, the nature of surface functional groups, and the density of surface sites, play a role in determining how effective an adsorbent will be at removing a given pollutant. For example, the net surface charge on activated carbon is typically very low, and consequently, it is not very effective for sorbing some uncomplexed metal ions (Kinniburgh and Jackson 1981). It should be noted though that metals are frequently complexed by organic molecules in natural and wastewaters, and complexed forms of metals may be sorbed to a greater extent by activated carbon compared with the free metal forms. Activated alumina is an adsorbent that is frequently used in metal removal applications. Typical surface areas of activated alumina range from 50 to 300 m²/g (Clifford 1990). Thus, the surface areas of these materials are also higher than the surface area of the HRB, but they are much lower than the activated carbon surface areas.

4.3 Discussion

It is not surprising that exhaustion of metals in a mixture complexed with NH₄Cl from the HRB occurred more rapidly compared with uncomplexed metals because the concentrations of NH₄Cl and total metals were added to the column feed in a 4:1 ratio. In theory, this gave the free metals in solution the possibility of binding to NH₃ as an alternative to sorbing to the HRB surface (Stumm and Morgan 1996), which could have contributed to the rapid exhaustion of the metals. However, speciation calculations suggest that metals were complexed incompletely (less than 4% for Ni and less than 1% for other metals within the 4-10 pH range), and the complexed metals were present mostly as monoamines. Coordination of the metal with NH₃ could conceivably have resulted in the adsorption of metal-amine complexes to the HRB surface (Stumm and

Morgan 1996). On the other hand, the $\text{NH}_4^+/\text{NH}_3$ couple, like the HRB surface and metal ion speciation, is affected by pH. The effluent pH typically varied between pH 6 and 6.5. It is conceivable that at these pH values, NH_4^+ may have competed with metal ions for the HRB sorption sites and/or incomplete metal coordination with NH_3 may have occurred.

The HRB effectively sorbs a number of metals that are of environmental concern and commonly found in waste streams. Nevertheless, the specific surface area of the HRB is at least two orders of magnitude smaller than that of other metal adsorbents, and, more importantly, its sorption capacity for metals is also significantly lower than the capacities of ion exchange resins and metal oxides. This is not surprising because commercially-available resins and inorganic adsorbents are designed and synthesized specifically to remove metals and other targeted pollutants from wastewater. Production of these materials requires considerable investment in terms of research and product development, raw materials, manufacturing equipment, and marketing. These investments are reflected in the relatively high cost of resins and other adsorbents. In contrast, the metal-sorbing properties of the HRB are fortuitous. As a result, this waste material could presumably be sold at a relatively low cost and still generate a net revenue.

In addition, the HRB offers at least two potential advantages that a resin like Amberlite® IRC748 does not offer. First, the HRB acts as an acid-neutralizing agent. As a result, the pH of acidic wastewater being treated in an HRB column increases. This is beneficial because highly acidic wastewaters cannot be discharged (either as a point source or to a municipal sewer system) and because uptake of metals by the HRB

improves dramatically with pH. Second, there may be economic or public relations benefits for a company that uses a recycled waste product in its operations.

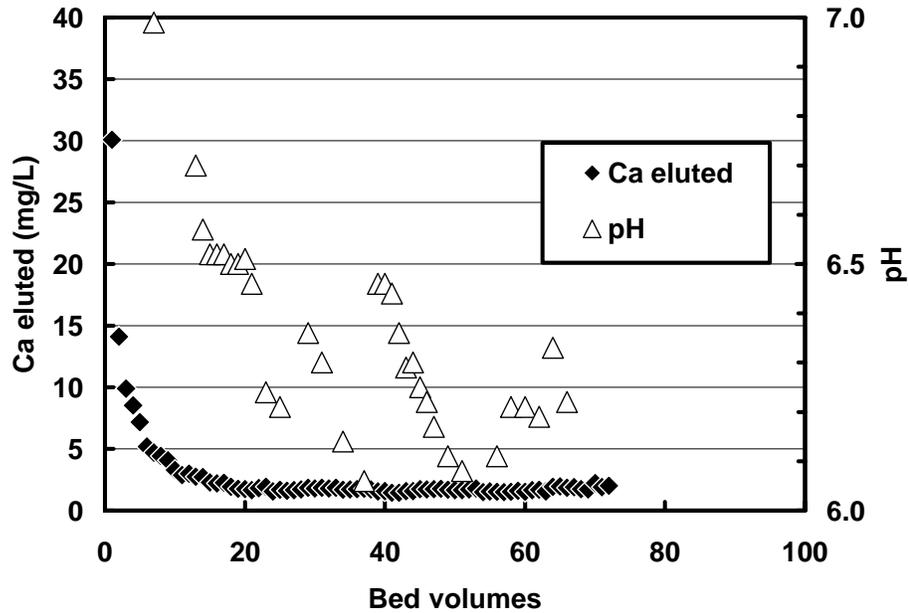


Figure 4-10. Ca eluted and pH of effluent in breakthrough experiment for NH_4Cl complexed metals from a 4 cm^3 HRB packed-bed column. (Influent metals = 2×10^{-5} M each metal, pH 5, $I = 5 \times 10^{-2}$ M $\text{NaClO}_4 \cdot \text{H}_2\text{O}$).

Nonetheless, utilization of the HRB in the treatment of metal wastewaters could pose some real challenges as well as the advantages described above. First, significant amounts of Ca were released by the HRB during the loading and regeneration stages, which indicates that a significant portion of the HRB dissolved during treatment. This is important because the loss of HRB mass means that the total capacity of the material will be reduced. In fact, the capacity of the HRB for Cd sorption decreased significantly after a single loading and regeneration cycle (Chapter 3).

Second, the loss of CaCO_3 reduces the acid neutralizing capacity of the material. Column experiments indicated that the acid neutralizing capacity of HRB columns, and

consequently the effluent pH, was highest during treatment of the first several hundred bed volumes of wastewater. This corresponded to the period of highest Ca loss during the treatment or loading phase (Figure 4-10). During a typical breakthrough and regeneration cycle, approximately 28 mg Ca were eluted by the HRB (7×10^{-4} mol), which would correspond to a 2% reduction in HRB mass due to assumed loss of CaCO_3 .

Approximately one-half of this loss occurred during the loading phase. It is possible that along with CaCO_3 , other components of the HRB were dissolved during treatment and regeneration but were not quantified in the treated effluent. Consequently, the loss of HRB was likely higher than that estimated on the basis of CaCO_3 alone.

In this study, all of the column experiments were conducted using defined aqueous metal solutions or industrial wastewaters that had been adjusted to $\text{pH} \geq 5$. Significantly more than 2% of the HRB presumably would be lost if it were used to treat wastewaters with $\text{pH} < 5$ because of the greatly increased dissolution of CaCO_3 expected under highly acidic conditions. Therefore, the use of the HRB to treat highly acidic wastewaters ($\text{pH} < 5$) is not recommended. In contrast, based on manufacturer information, the Amberlite® IRC748 resin can be used to treat even highly acidic wastewaters ($\text{pH} 1.5$).

The relatively low capacity of the HRB and rapid exhaustion of metals through the HRB columns, coupled with its poor regenerability, pose an additional challenge. That is, very large volumes of HRB would be needed to treat a typical high-strength wastewater using sorption to HRB as a stand-alone treatment process. This probably would not be practical for an industrial user. Instead, a more likely scenario would be to use HRB columns as a polishing step in conjunction with another upstream treatment

technology, such as alkaline precipitation.

The use of the HRB as a metal adsorbent may be appropriate for some industrial wastewater treatment applications. However, it is not appropriate for use in pharmaceutical, food processing, or potable water treatment systems because of its tendency to release calcium. Although the HRB was not tested for the presence of pathogens, the possibility that *Salmonella* and/or *E. coli* contamination is present is generally a concern when working with poultry by-products (Das et al. 2002).

In addition, the low selectivities and capacities of the HRB for Ni, Cd, and Zn may make it difficult to reliably treat these metals using the HRB. This may preclude use of HRB in electroplating wastewater treatment applications. Instead, HRB is best suited for use in industries that generate wastewaters containing primarily Pb, Fe, and/or Cu. Pb is present in wastewaters produced by the following industries: pulp and paper, organic and petrochemicals, inorganic chemicals, fertilizer, petroleum refining, steel works and foundries, and non-ferrous metal works and foundries (Wase and Forster 1997). However, it should be noted that the wastewaters listed above all contain a suite of metals in addition to Pb. Some of the metals, like iron and Cu, are well-suited for treatment using HRB because of their relatively high positions in the selectivity sequences of the HRB. However, the wastewaters also typically contain metals like Ni, Zn, and chromium that are not effectively sorbed by the HRB and/or metals like mercury and arsenic that were not evaluated in this study. Other wastewaters that contain high concentrations of Pb and may be better suited for treatment through sorption to HRB include those generated by the power-storage-battery industry, mining operations, and primary and

secondary smelters, which process ore material and scrap derived from old batteries, cable sheathing and other materials, respectively (Volesky 1990).

Regardless of the specific application, sorption to HRB should be done in conjunction with another metal pretreatment step, as mentioned above. A number of different treatment schemes are feasible, and the one most appropriate for a given application depends on the nature of the wastewater and the regulations that apply. In the U.S., industries that discharge wastewater flows to the sanitary sewer must meet specific pretreatment standards or new source performance standards. In many cases, the regulatory requirements for discharging to sanitary sewers may be met by precipitating the metals, and additional treatment of metals-laden wastewater via adsorption, ion exchange, or other methods is not required. Wastewater generators that discharge directly to surface waters, however, must have a National Pollutant Discharge Elimination System (NPDES) permit. To discharge wastewater to surface water, the metal concentrations typically must be significantly lower than required for sanitary sewer discharge. Thus, industrial operations that discharge directly to surface waters may represent the most likely potential users of the HRB because in most cases, these operations will not be able to meet the necessary effluent metal concentrations using precipitation alone (Lee and Davis 2001). In fact, metal precipitation followed by additional metal uptake in HRB packed-bed columns is an ideal treatment scenario. Precipitation significantly reduces metal concentrations by increasing the pH so that the solubility limit of the metal is exceeded. The removal of large amounts of metals through precipitation minimizes the volume of HRB that would be needed to polish the wastewater and reduce metal concentrations to regulated levels. Further, if precipitation

is used upstream of an HRB polishing step, an additional acid-neutralization pretreatment step is not needed to raise the pH to an acceptable level (≥ 5). The increase in wastewater pH caused by precipitation will also minimize dissolution of the HRB and improve metal removal efficiency. It may also be possible to couple HRB treatment with other metal removal technologies.

A number of different configurations can be used to treat wastewater using fixed-bed packed columns. For example, they can be operated as single or multiple units, and multiple units can be operated in series, parallel, or a combined series and parallel system. The column(s) can also be operated in upflow or downflow mode. A single column configuration is not appropriate in this case because of the frequency with which the HRB would have to be replaced. In parallel columns, the feed is split and distributed through a manifold to different columns that are brought online in evenly spaced intervals. The effluents from parallel columns are combined. One advantage of operating columns in parallel is that the pressure drop across a given column is smaller than for columns operated in series, and, as a result, smaller pumps are required and other equipment costs may be reduced. However, the adsorbents used in parallel columns usually are not completely spent to prevent excessively high effluent concentrations. This means that an adsorbent's maximum sorption capacity is not attained. Therefore, to minimize the amount of adsorbent that is "wasted" in a parallel column system, it is usually recommended that they be used in systems that exhibit steep breakthrough curves. In general, the HRB columns exhibited gradual breakthrough curves. For this reason, the HRB is probably better suited for use in a series of columns in which the effluent of one column serves as the influent of the next column. When the adsorbent in

the first column is completely spent, it is taken off-line for regeneration or replacement. The second column becomes the lead column and another column is added at the end of the series. Operating HRB packed bed columns in series offers at least two advantages. First, the HRB will be used until its relative sorbent capacity is reached. This is desirable because the HRB has a relatively low capacity, and so it is especially important to operate HRB columns to the point of saturation so that the volume of HRB needed is not larger than necessary. Because the adsorbent material is completely saturated in series columns, operating costs are lower than for single columns or multiple columns operated in parallel. Columns in series are also ideally suited for treatment of waste streams containing multiple metals (Wase and Forster 1997). The lead column removes the metals that are highest in the selectivity sequence. Metals that are lower in the selectivity sequence may be displaced from the lead column as it becomes saturated, but will be captured by downstream columns. Changes in effluent characteristics, indicative of column exhaustion, can ideally be monitored using a simple probe or combination of probes, such as pH and/or conductivity.

Another possible application of the HRB would be to use it as a co-amendment with biosolids that are land-applied. Presumably, the capacity of the HRB for metal uptake would reduce the bioavailability of metals in biosolids, while at the same time increasing the buffering capacity of the amended soils. Similarly, the use of other industrial residuals with properties like those of the HRB as soil amendments has been suggested by other researchers (Bolan and Duraisamy 2003; Rodriguez-Rubio et al. 2003). Specifically, the sorption and/or co-precipitation of uncomplexed aqueous metals to the HRB mixed with biosolids would reduce their bioavailability to plants. Biosolids,

by themselves, have been known to reduce phytoavailability of metals in solids, although the reason for that is not completely understood. However, it is possible that the organic phase of biosolids is responsible for the reduction of phytoavailability (Hettiarachchi et al. 2006). In this case, the degradation of the organic phase will eventually release free metals to the soil again. Eggshells are more resistant to weathering than calcite (Solomon 1999), and metal sorption further prevents dissolution of calcite (Pokrovsky and Schott 2002; Martin-Garin et al. 2003). Thus, the addition of HRB to biosolids could conceivably reduce the phytoavailability of metals in land-applied biosolids over time. It would be of interest to evaluate this idea in future studies.

Chapter 5. Conclusions

Systematic design and operation of biosorbent-based treatment systems requires a reasonable understanding of the possible complex removal mechanisms through which inherently heterogeneous materials uptake heavy metals. The main goal of this work was to characterize hatchery residual-derived biosorbent, HRB, as a sorbent for divalent heavy metals (mainly Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II)), in defined aqueous metal solutions and industrial wastewaters.

HRB contains eggshells and animal fibrous proteins, e.g., feathers and eggshell membrane. Eggshells, in turn, are composed of more than 95% calcite (Kuh and Kim 2000). Indeed, X-ray diffraction patterns of HRB are comparable with those of eggshells and calcite. Moreover, the average BET surface area of the HRB was $0.74 \text{ m}^2/\text{g}$, which is consistent with pure calcite and calcite-based materials (Suzuki and Takeuchi 1994; Martin-Garin et al. 2003; del Rio et al. 2004). Thus, calcite was a major component of the HRB and probably played a significant role in metal uptake.

Batch experiments showed a strong pH dependence for the adsorption of cations in single-metal solutions. The adsorption edges, characterized by the pH_{50} values, suggest a selectivity for individual metals in the order Cu(II) ($\text{pH}_{50} \approx 6$) > Zn(II) ($\text{pH}_{50} \approx 7$) > Cd(II) ($\text{pH}_{50} \approx 7.5-8$) > Ni(II) ($\text{pH}_{50} \approx 9$) at $2 \times 10^{-5} \text{ M}$. When metals were provided within a mixed solution (10^{-4} M total metals), the selectivity decreased in the order Pb(II) > Cu(II) > Zn(II) = Cd(II) > Ni(II). The percentage of individual metals removed generally decreased with increasing initial concentration. Batch kinetic experiments conducted with Cd(II) showed that most of the metal uptake took place within the first four hours of

HRB-solution contact. A slight increase in Cd(II) uptake was observed between 4 and 24 hours.

Column breakthrough experiments were conducted with 2×10^{-5} M Cd(II) solutions. Approximately 1500 bed volumes were treated before exhaustion occurred, with a slight difference between pH 5 and pH 7 influent solutions. Exhaustion of the HRB with a 10^{-4} M Cd(II) solution occurred within 500 bed volumes. An additional column experiment was performed in which an HRB packed column was loaded with Cd(II) supplied at 2×10^{-5} M (pH 5, 5×10^{-2} M NaClO₄) and then regenerated with 10 bed volumes of EDTA (9 mM) three times in sequence. The results suggest that a portion of the metal (~73%) is strongly or irreversibly associated with HRB, approximately 27% of the metal is reversibly bound to HRB and can be recovered using EDTA.

Column studies were also conducted with HRB supplied with a mixture of uncomplexed salts of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) at pH 5. The selectivity of the HRB for the mixture uncomplexed metals decreased in the order: Pb(II) > Cu(II) > Zn(II) \approx Cd(II) > Ni(II), which was consistent with the results of the batch HRB sorption experiments. The trend of the recovery of metals from this column using 50 mM EDTA was opposite of the selectivity sequence. Metals for which the HRB had the highest selectivity and capacity were recovered most efficiently

Similar column studies were performed with the addition of 4×10^{-4} M NH₄Cl to the influent as a complexing agent for the mixture of metals. In this case, exhaustion of all of the complexed metals occurred significantly earlier and the recovery of all metals was not as efficient compared with the behavior of the uncomplexed metals.

In all experiments performed, calcium was released. This is important for two reasons. In batch equilibrium experiments, dissolution of HRB made attempts to control sample pH at low values difficult because it increased alkalinity of the solutions. The same problem was evident in the kinetic experiment, in which dynamic sorption and desorption repeatedly occurred, especially at pH 3. When the HRB was repeatedly loaded with Cd(II) and regenerated with EDTA, the Ca(II) released to effluent during Cd(II) loading was monitored, and ranged from 1.2×10^{-4} M in the first few bed volumes to 2.5×10^{-5} M towards the end of a treatment cycle. For the column experiments conducted with a mixture of metals, CaCO₃ dissolution (and associated alkalinity) resulted in pH values varying from 6 to 7 in the effluent solution.

Speciation calculations were performed for conditions occurring in metal mixture column experiments. The equilibrium speciation calculations predicted the formation of several solids. The solids and the lowest pH or range of pH values at which they formed were as follows: tenorite (CuO_(s), pH 6.2), hydrocerussite (Pb₃(CO₃)₂(OH)_{2(s)}, pH 6.3–7), lead hydroxide (Pb(OH)_{2(s)}, pH 6.9), otavite (CdCO_{3(s)}, pH 7.4), zinc oxide (ZnO_(s), pH 8.4), hydrozincite (Zn₅(OH)₆(CO₃)_{2(s)}, pH 7.9–8.5), and bunsenite (NiO_(s), pH 8.6). Based on the predicted precipitation processes, metal removal by the HRB should decrease in the order: Cu(II) > Pb(II) > Cd(II) > Zn(II) > Ni(II). The similarity of this sequence with the selectivity sequences observed in the sorption experiments suggests that precipitation may have contributed to metal uptake by the HRB.

Adsorption also appeared to play an important role in the uptake of metals by HRB. Most importantly, the separation of the breakthrough curves for metal mixtures is

consistent with adsorption, as is displacement desorption of Cd(II) and Zn(II) by Pb(II) and Cu(II).

The differences in the selectivity of the HRB for various metals and the reversibility of uptake suggest that different removal mechanisms were involved in the uptake of the various metals tested in this study. For example, Cd(II) uptake apparently occurred via adsorption to the calcite surface followed by incorporation of a portion of the sorbed Cd(II) into a three-dimensional structure through precipitation, co-precipitation, or solid-state diffusion. Pb(II) taken up by the HRB could mostly be recovered by EDTA, suggesting a greater role of adsorption and/or precipitation in Pb(II) uptake compared with Cd(II) removal. It seems likely that Cu(II) formed $\text{CuO}_{(s)}$ as well as surface complexes. As for Zn(II), precipitation can be ruled out as a removal mechanism, and it is possible that a solid-state diffusion process contributed to Zn(II) uptake. Uptake by the HRB and recovery of Ni(II) were poor compared to the other metals studied here. It seems likely that Ni(II) formed strong complexes with the surface of calcite or perhaps was bound by a minor constituent of the HRB, e.g., proteins.

This study also compared the performance of the HRB and Amberlite® IRC748 ion exchange resin during treatment of an industrial wastewater. The wastewater used was generated at a local metal plating facility and contained Ni (5.1×10^{-4} M), Fe (1.3×10^{-4} M), Pb (3.8×10^{-5} M), Cu (1.0×10^{-5} M), Ca (8.7×10^{-6} M), Cr (7.7×10^{-6} M) and Zn (2.6×10^{-6} M). Selectivity coefficients were calculated as the ratio between the mass of metal adsorbed and the influent metal concentration, for each metal. Although the performance of the ion-exchange resin was better than that of HRB for Cu and Ni and, to a lesser extent, for Zn, HRB was a better adsorbent for Pb and Fe. The selectivity

sequence for HRB during treatment of the plating wastewater was $Pb > Cu \approx Fe > Zn > Ni$. HRB also has an acid-neutralizing effect. This is an advantage when treating metallic wastewaters, which tend to be acidic, and also enhances uptake of metals. However, the acid-neutralizing capacity of the HRB is due to dissolution of $CaCO_3$ during treatment, which reduces the potential for reutilization of the HRB.

Nevertheless, the low regenerability of HRB and the large volumes of HRB that would be needed to treat full-strength metal wastewaters probably limit its use to wastewater polishing treatments, e.g., downstream of a chemical precipitation step. In fact, this would be the ideal scenario, since the pH adjustments required for metal precipitation would minimize HRB dissolution and increase its efficiency.

As a suggestion for further work, HRB may be a good co-amendment with biosolids that are land-applied. The HRB metal uptake capacity presumably would reduce metal bioavailability, and, at the same time, could increase the pH of acidic soils (Bolan and Duraisamy 2003; Rodriguez-Rubio et al. 2003). Free ions are the most phytoavailable forms of metals in soil; however, sorption and/or co-precipitation of metal ions to HRB incorporated into biosolids would help immobilize and prevent these metals from reaching biota. Before this approach could be implemented, it would be necessary to test the resistance of HRB to weathering in a field setting and examine the ability of HRB to retain the sorbed metal. If these requirements are met, the addition of HRB to biosolids could conceivably reduce the risk of release of metals in the long term.

Appendix. Raw Data

Cd(II) uptake (batch)								
22 mg/L = 2.0e-4 M			11 mg/L = 1.0e-4 M			2.0 mg/L = 2.0e-5 M		
Final	C _f	SD	Final	C _f	SD	Final	C _f	SD
pH	(mg/L)		pH	(mg/L)		pH	(mg/L)	
(control)	22.37	0.097	(control)	11.05	0.077	(control)	2.018	0.006
(control)	22.16	0.649	6.94	8.96	0.099	7.5	0.789	0.009
6.95	21.38	0.140	7.01	8.81	0.098	7.9	0.704	0.013
6.83	20.88	0.225	7.06	9.01	0.066	8.0	0.586	
6.91	20.94	0.067	7.07	9.12	0.169	8.1	0.545	0.014
6.81	20.83	0.425	7.19	9.38	0.056	8.2	0.500	0.007
6.97	17.67	0.279	7.73	8.42	0.096	8.1	0.662	0.009
6.96	20.62	0.236	8.19	7.64	0.092	8.5	0.464	0.010
8.46	17.39	0.262	(control)	11.19	0.085	8.5	0.485	0.011
8.2	17.73	0.277	8.22	8.19	0.040	(control)	2.109	0.033
9.09	0.22	0.013	8.24	7.16	0.124	7.3	0.918	0.001
9.29	0.53	0.010	8.82	4.30	0.115	7.4	1.111	0.010
9.37	0.51	0.007	9.21	0.69	0.042	7.5	1.080	0.003
						9.2	0.251	0.009
						9.2	0.201	0.004
						9.4	0.228	0.005

Cu(II) uptake (batch)								
10 mg/L = 1.6e-4 M			3.1 mg/L = 5.0e-5 M			1.6 mg/L = 2.5e-5 M		
Final	C _f	SD	Final	C _f	SD	Final	C _f	SD
pH	(mg/L)		pH	(mg/L)		pH	(mg/L)	
(control)	10.12	0.062	(control)	3.13	0.029	(control)	1.618	0.019
5.3	9.25	0.035	6.0	2.64	0.015	6.2	1.127	0.015
5.3	10.03	0.140	6.0	2.53	0.014	6.3	0.961	0.013
5.4	7.52	0.037	6.1	2.34	0.002	6.4	0.781	0.008
5.4	8.70	0.028	5.9	2.46	0.012	6.6	0.581	0.007
5.7	7.27	0.043	6.6	0.55	0.003	9.4	0.004	0.001
5.8	5.67	0.007	8.5	2.24	0.014	9.5	-0.022	0.003
6.0	2.32	0.016	9.2	-0.01	0.002	9.3	-0.011	0.001
6.1	1.64	0.008	6.5	1.07	0.003	9.4	-0.003	0.002

Cr(VI) uptake (batch)								
10 mg/L = 2.0e-4 M			5 mg/L = 1.0e-4 M			0.3 mg/L = 6.0e-6 M		
Final	C _f	SD	Final	C _f	SD	Final	C _f	SD
pH	(mg/L)		pH	(mg/L)		pH	(mg/L)	
(control)	9.731	0.502	(control)	4.625	0.128	(control)	0.280	0.017
7.9	9.959	0.261	8.3	4.464	0.092	8.7	0.269	0.009
8.1	8.971	0.160	8.3	4.477	0.206	8.8	0.286	0.006
8.2	10.46	0.410	8.7	4.584	0.212	8.9	0.271	0.018
8.6	9.929	0.251	8.8	4.455	0.135	8.7	0.292	0.020
8.9	9.798	0.194	9.0	4.372	0.234	9.0	0.271	0.003
8.8	9.552	0.322	9.2	4.385	0.062	9.0	0.276	0.019
9.4	9.851	0.025	9.2	4.492	0.072	9.3	0.273	0.037
9.6	9.030	0.402	9.6	4.285	0.092	9.4	0.279	0.035

Ni(II) uptake (batch)								
6.8 mg/L = 1.2e-4 M			11 mg/L = 2.0e-4 M			1.3 mg/L = 2.2e-5 M		
Final pH	C _f (mg/L)	SD	Final pH	C _f (mg/L)	SD	Final pH	C _f (mg/L)	SD
(control)	6.790	0.240	(control)	11.52	0.502	(control)	1.339	0.062
8.51	5.410	0.235	8.58	9.801	0.277	8.98	1.029	0.016
8.40	5.830	0.055	8.30	11.02	0.254	9.03	0.927	0.063
8.53	5.525	0.265	8.52	10.02	0.299	8.97	0.845	0.017
8.59	4.930	0.220	8.57	10.11	0.172	8.97	0.845	0.046
8.95	3.255	0.125	8.66	9.539	0.131	9.40	0.453	0.015
8.98	3.190	0.270	8.68	9.611	0.074	9.43	0.244	0.025
			8.70	9.266	0.199	9.62	0.181	0.027
			8.74	9.334	0.135	9.63	0.054	0.032

Zn(II) uptake (batch)								
10 mg/L = 1.5e-4 M			4.8 mg/L = 7.4e-5 M			1.2 mg/L = 1.9e-5 M		
Final pH	C _f (mg/L)	SD	Final pH	C _f (mg/L)	SD	Final pH	C _f (mg/L)	SD
(control)	9.871	0.060	(control)	4.207	0.041	(control)	1.236	0.043
6.17	9.147	0.357	6.66	3.405	0.066	7.47	0.558	0.002
6.25	8.867	0.096	6.72	3.389	0.081	7.79	0.366	0.009
6.35	7.511	0.082	6.8	3.237	0.049	8.28	0.297	0.010
6.38	7.739	0.082	6.83	3.287	0.045	8.24	0.342	0.010
6.49	7.022	0.095	7.36	2.203	0.011	8.98	0.077	0.009
6.53	8.383	0.082	7.06	3.220	0.023	8.96	0.099	0.016
7.21	2.613	0.051	8.64	0.317	0.005	9.46	0.060	0.001
7.39	2.072	0.032	9.01	0.217	0.009	9.45	0.068	0.010

Mixture of metals (batch)						
Final pH	Ca(II)		Cu(II)		Pb(II)	
	C _f (mg/L)	SD	C _f (mg/L)	SD	C _f (mg/L)	SD
(control)	-	-	0.426	0.002	3.533	0.010
5.75	3.099	0.039	0.271	0.006	1.719	0.053
5.71	2.827	0.031	0.239	0.003	1.256	0.079
5.84	1.736	0.141	0.212	0.001	1.003	0.071
5.80	4.990	0.104	0.245	0.01	1.100	0.139
5.90	3.024	0.007	0.214	0.002	1.137	0.081
6.00	2.127	0.044	0.197	0.001	0.778	0.124
6.22	1.681	0.005	0.175	0.006	0.564	0.048
6.23	3.728	0.180	0.243	0.001	1.478	0.147
6.30	2.562	0.046	0.181	0.011	0.836	0.103
6.56	2.522	0.023	0.14	0.011	0.558	0.122
6.43	2.114	0.103	0.167	0.012	0.535	0.011
8.41	1.964	0.128	0.082	0.006	0.420	0.146
7.30	1.788	0.053	0.107	0.002	0.229	0.092
6.72	2.366	0.008	0.19	0.004	0.550	0.069

Mixture of metals (batch)					
Final pH	Cd(II)	Zn(II)		Ni(II)	
	C _f (mg/L)	C _f (mg/L)	SD	C _f (mg/L)	SD
(control)	1.891	1.278	0.006	1.034	0.076
5.75	1.85	1.230	0.035	1.023	0.079
5.71	1.809	1.245	0.004	1.063	0.129
5.84	1.828	1.277	0.004	1.059	0.009
5.80	1.696	1.298	0.046	1.01	0.057
5.90	1.75	1.293	0.004	1.041	0.021
6.00	1.753	1.518	0.008	0.821	0.233
6.22	1.563	1.194	0.019		
6.23	1.669	1.342	0.011	0.972	0.078
6.30	1.619	1.179	0.002		
6.56	1.484	1.090	0.005	0.927	0.044
6.43	1.615	1.121	0.023	0.976	0.093
8.41	0.687	0.347	0.014	0.437	0.068
7.30	1.162	0.817	0.006	0.978	0.07
6.72	1.584	1.163	0.031		

Kinetics				
Delta Time (hours)	Cd conc. (mg/L)	SD	pH before taking sample	pH adjusted to
0.00	2.259	0.110		3.6
1.50	1.874	0.034	6.2	3.9
2.50	2.045	0.067	6.2	3.9
3.83	2.026	0.032	6.2	3.9
4.67	2.187	0.113	6.0	3.9
5.58	2.223	0.018	6.1	4.0
6.58	2.196	0.100	5.6	3.9
24.00	1.790	0.034	6.9	
Delta Time (hours)	Cd conc. (mg/L)	SD	pH before taking sample	pH adjusted to
0.00	2.259	0.110		5.4
1.50	1.647	0.044	6.9	5.2
2.50	1.639	0.038	7.0	4.8
3.67	1.494	0.026	6.7	5.7
4.58	1.555	0.046	6.4	5.2
5.58	1.628	0.023	6.7	5.3
6.50	1.597	0.024	6.6	5.1
24.00	1.048	0.012	7.4	
Delta Time (hrs)	Cd conc. (mg/L)	SD	pH before taking sample	pH adjusted to
0.00	2.259	0.110		9.0
1.50	1.314	0.028		9.2
2.42	1.026	0.041	8.4	9.2

Kinetics				
3.58	0.785	0.117	8.9	8.9
4.50	0.762	0.057	8.6	8.7
5.50	0.886	0.012	8.3	8.8
6.42	0.793	0.009	8.7	8.7
24.00	0.422	0.025	8.6	

Column Cd(II), pH 5, 2 mg/L					
volume (mL)	pH	Cd (mg/L)	SD	Ca (mg/L)	SD
influent	5.1	1.959	0.011	0.384	0.006
influent		2.004	0.032		
82.5	7.18	0.004	0.005	13.42	0.185
165.0	7.35	-0.004	0.008		
247.5	7.46	-0.014	0.007		
330.0	7.74				
412.5	7.8	-0.010	0.008	8.108	0.126
495.0	7.56	0.000	0.015		
577.5	7.76	-0.005	0.005		
660.0	8.04	0.007	0.008		
742.5	8.24	0.010	0.010		
825.0	8.65	-0.001	0.015	6.992	0.151
907.5	8.39	0.037	0.012		
990.0	8.53	0.045	0.001		
1072.5	8.92	0.062	0.004	6.496	0.43
1155.0	8.97	0.100	0.014		
1237.5	7.33	0.114	0.003		
1320.0	7.34	0.129	0.015		
1402.5	7.45	0.174	0.005	5.856	0.062
1485.0	7.35	0.197	0.008		
1567.5	7.37	0.203	0.015		
1650.0	7.38	0.246	0.004		
1732.5	7.18	0.317	0.005	5.174	0.185
1815.0	7.23	0.326	0.019		
1897.5		0.405	0.007		
1980.0		0.473	0.012		
2062.5		0.524	0.015	4.385	0.112
2145.0		0.569	0.013		
2227.5		0.634	0.013		
2310.0		0.672	0.008		
2392.5		0.645	0.005		
2475.0		0.759	0.009		
2557.5	7.31	0.850	0.006	4.093	0.082
2640.0	7.33	0.904	0.013		
2722.5	7.18	0.978	0.010		
2805.0		0.916	0.002		
2887.5	7.14	1.027	0.007		
2970.0		1.113	0.005		
3052.5		1.191	0.003	3.128	0.045
3135.0	6.96	1.198	0.015		
3217.5		1.261	0.011		

Column Cd(II), pH 5, 2 mg/L					
3300.0	7.01	1.299	0.011		
3382.5		1.340	0.031		
3465.0	7.06	1.359	0.013		
3547.5		1.385	0.023		
3630.0	7.05	1.351	0.019		
3712.5		1.376	0.024		
3795.0	7.04	1.371	0.004	2.969	0.053
3877.5		1.413	0.025		
3960.0	6.91	1.438	0.019		
4042.5		1.455	0.014		
4125.0		1.457	0.021		
4207.5		1.568	0.030		
4290.0		1.539	0.006	2.478	0.047
4372.5		1.579	0.049		
4439.5		1.596	0.036		
4522.0		1.606	0.032		
4604.5		1.608	0.053		
4687.0		1.618	0.009		
4769.5		1.698	0.029		
4852.0		1.666	0.037		
4934.5	6.77	1.713	0.022		
5017.0	6.76	1.719	0.063		
5099.5		1.683	0.028		
5182.0		1.721	0.017		
5264.5		1.743	0.020	2.16	0.032
5429.5		1.725	0.027		
5512.0		1.669	0.033		
5594.5		1.659	0.025		
5677.0		1.670	0.059		
5759.5		1.656	0.019		
5842.0		1.697	0.063		
5924.5		1.679	0.030		
6007.0		1.705	0.041	2.048	0.074
6089.5		1.772	0.038		
6172.0		1.774	0.033		
6254.5		1.813	0.029		
6337.0		1.808	0.024		
6419.5		1.889	0.040		
6584.5		1.862	0.013		
6667.0	6.59				
6749.5	6.76	1.867	0.019		
6914.5		1.862	0.019	2.506	0.026
6997.0	6.79				
7079.5		1.818	0.005		
7244.5	6.77	1.793	0.035		
7409.5	6.79	1.837	0.034		
7574.5		1.882	0.031		
7657.0		1.906	0.019	2.372	0.077
7822.0		1.883	0.005		

Column Cd(II), pH 7, 2 mg/L					
volum e (mL) influen t	pH	Conc. (mg/L)	SD	Calcium (mg/L)	SD
		2.328	0.088	0.442	0.002
70.0	6.45				
105.0		0.049	0.007	13.010	0.294
175.0	6.6				
210.0		0.039	0.009	9.544	0.199
280.0	6.67				
315.0		0.037	0.005		
385.0	6.76				
420.0		0.048	0.009		
490.0	6.83				
525.0		0.047	0.015	7.349	0.232
595.0	6.95				
630.0		0.075	0.015		
700.0	6.9				
735.0		0.065	0.015		
840.0		0.125	0.016		
910.0	7.39				
945.0		0.142	0.012	5.636	0.006
1050.0		0.205	0.024		
1120.0	7.41				
1155.0		0.251	0.005		
1260.0		0.301	0.002		
1330.0	7.94				
1365.0		0.403	0.012	4.301	0.067
1470.0		0.489	0.003		
1540.0	8.09				
1575.0		0.554			
1680.0		0.675			
1750.0	6.96				
1785.0		0.823		3.200	0.085
1890.0		0.853			
1960.0	6.82				
1995.0		0.841			
2100.0		0.887			
2170.0	6.87				
2205.0		0.966	0.018	3.085	0.104
2310.0		1.057	0.015		
2380.0	6.79				
2415.0		1.203			
2520.0		1.310			
2590.0	6.81				
2625.0		1.396			
2730.0		1.515			
2765.0	6.71				
2800.0		1.560			

Column Cd(II), pH 7, 2 mg/L				
2905.0		1.673		
2975.0	6.74			
3010.0		1.698		
3080.0		1.703	1.784	0.01
3150.0	6.64			
3185.0		1.683		
3255.0		1.594	0.072	
3290.0	6.56	1.711		
3395.0		1.736		
3465.0		1.777	0.013	
3500.0		1.774		
3605.0		1.717	1.848	0.071
3675.0	6.61			
3710.0		1.691		
3815.0		1.682		
3885.0	6.64			
3920.0		1.701		
4025.0		1.731	0.019	1.693
4095.0	6.66			0.027
4130.0		1.845		
4235.0		1.922	0.025	
4305.0	6.7			
4340.0		1.936		
4445.0		2.053	1.351	0.086
4515.0	6.6			
4550.0		1.993		
4655.0		2.019		
4725.0	6.8			
4760.0		2.028		
4865.0		2.059	1.243	0.047
4935.0	6.72			
4970.0		2.081		
5075.0		2.109		
5145.0	6.64			
5180.0		2.041		
5285.0		2.058		
5355.0	6.55			
5390.0		2.020		
5495.0		2.060	1.264	0.03
5565.0	6.49			
5600.0		2.054		
5705.0		2.112		
5775.0	6.43			
5810.0		2.175		
5915.0		2.203		
5985.0	6.5			
6020.0		2.217		
6125.0		2.391	1.249	0.021
6195.0	6.74			

Column Cd(II), pH 7, 2 mg/L			
6230.0	2.354		
6335.0	2.225		
6440.0	2.230		
6545.0	2.198	1.245	0.016

**Column Cd(II), pH 5,
10 mg/L**

Volume (mL)	Conc. (mg/L)
influent	10.30
180	0.67
210	0.79
240	1.05
270	1.66
300	2.32
330	2.24
420	4.40
450	4.52
480	3.50
600	4.73
690	5.68
780	7.06
870	7.38
960	7.86
1050	7.93
1140	8.01
1230	8.52
1320	8.84
1410	8.49
1500	9.02
1590	9.78
1680	9.21
1860	9.45
2670	9.34
3030	8.61

**Cd(II) column
1st treatment cycle**

Sample size (mL)	Cd(mg/L)	Ca(mg/L)
influent	2.862	
45	0.090	
45	0.009	
45	-0.005	
45	-0.009	
45	-0.002	

45	0.006	
45	0.003	
45	0.010	
45	0.031	5.348
45	0.038	4.940
80	0.042	5.240
105	0.060	5.011
105	0.114	4.403
105	0.181	4.211
105	0.256	3.911
105	0.467	3.648
105	0.640	3.430
105	0.806	3.342
105	0.965	2.998
105	1.166	2.940
105	1.280	2.670
105	1.386	2.753
105	1.508	2.590
105	1.589	2.638
105	1.693	2.543
105	1.706	2.516
105	1.822	2.215
105	1.866	2.373
105	1.891	2.180
105	1.953	2.111
105	2.020	2.047
105	2.089	1.916
105	2.141	1.817
105	2.184	1.794
105	2.205	1.794
105	2.211	1.724
105	2.344	1.749
105	2.284	1.654
105	2.258	1.746
105	2.356	1.701
105	2.448	1.647
105	2.431	1.673
105	2.463	1.666
105	2.478	1.526
105	2.517	1.588
105	2.504	1.560
105	2.547	1.401
105	2.548	1.366
105	2.568	1.546
105	2.560	1.481
105	2.546	1.482
105	2.512	1.475
105	2.544	1.428
105	2.592	1.394
105	2.520	1.506

105	2.684	1.447
105	2.616	1.473
105	2.672	1.385
105	2.648	1.395
105	2.649	1.468
105	2.659	1.412
105	2.720	1.301
105	2.663	1.285
105	2.709	1.380
105	2.682	1.284
105	2.748	1.412
105	2.680	1.318
105	2.729	1.366
105	2.766	3.479
105		1.339

2nd treatment cycle			3rd treatment cycle		
Sample size (mL)	Cd(mg/L)	Ca(mg/L)	Sample size (mL)	Cd(mg/L)	Ca(mg/L)
influent	2.485		Influent	2.601	
35	0.344		40	0.802	
35	0.107	4.124	40	0.164	4.865
35	0.072	3.571	40	0.048	4.238
35	0.101	3.334	50	0.179	3.891
35	0.132	3.071	40	0.322	3.321
35	0.198	2.929	40	0.411	3.145
35	0.256	3.048	40	0.510	3.016
35	0.326	2.754	40	0.608	2.826
35	0.431	2.835	40	0.728	2.751
35	0.586	2.702	80	0.961	2.452
70	0.816	2.711	120	1.323	2.266
105	1.201	2.283	120	1.570	2.106
105	1.432	2.105	120	1.766	2.042
105	1.645	2.126	120	2.000	2.046
105	1.940	1.986	120	2.122	1.897
105	2.133	1.870	120	2.274	1.699
105	2.267	1.925	120	2.348	1.736
105	2.282	1.746	120	2.454	1.704
105	2.288	1.864	120	2.452	1.729
105	2.470	1.809	120	2.466	1.551
105	2.469	1.724	120	2.488	1.686
105	2.495	1.584	120	2.564	1.708
105	2.498	1.627	120	2.591	1.653
105	2.465	1.653	120	2.571	1.428
105	2.439	1.606	120	2.577	1.774
105	2.442	1.630	120	2.578	1.902
105	2.439	1.475	120	2.568	
105	2.459	1.625	120	2.569	
105	2.486	1.600	120	2.606	

105	2.493	1.488	120	2.621
105	2.457	1.589	120	2.594
105	2.420	1.747	120	2.624
105	2.456	1.528	120	2.600
105	2.434	1.836	120	2.605
105	2.483	1.750	120	2.636
105		1.695		
105		1.855		

1st regeneration cycle			
	bed volumes	Cd accumulated (mg)	Ca accumulated (mg)
water	5	0.015	0.220
EDTA	1.11	0.401	0.723
EDTA	1.11	0.819	2.703
EDTA	1.11	1.067	4.378
EDTA	1.11	1.238	6.179
EDTA	1.11	1.374	7.942
EDTA	1.11	1.484	9.674
EDTA	1.11	1.566	11.132
EDTA	1.11	1.637	12.574
EDTA	1.11	1.700	13.879
water	5	1.781	14.755

2nd regeneration cycle				3rd regeneration cycle		
	bed volumes	Cd accumulated (mg)	Ca accumulated (mg)	bed volumes	Cd accumulated (mg)	Ca accumulated (mg)
water	5	0.012	0.196	5	0.026	0.123
EDTA	1.11	0.288	0.692	1	0.310	0.893
EDTA	1.11	0.634	2.368	1	0.594	2.191
EDTA	1.11	0.850	4.388	1	0.771	3.435
EDTA	1.11	1.004	6.335	1	0.918	4.475
EDTA	1.11	1.129	8.341	1	1.033	8.239
EDTA	1.11	1.234	10.383	1	1.140	9.605
EDTA	1.11	1.326	12.398	1	1.233	10.910
EDTA	1.11	1.407	14.338	1	1.280	11.988
EDTA	1.11	1.485	16.407	1	1.348	12.839
EDTA				1	1.402	13.561
water	3.75	1.581	18.036	5		19.801

Column experiment, mixture of uncomplexed metals								
Volume through (mL)	Cd(II)	Stdev	Volume through (mL)	Pb(II)	Stdev	Volume through (mL)	Zn(II)	Stdev
influent	1.887	0.075	influent	3.736	0.214	influent	1.360	0.082
37.5	0.068	0.013	37.5	0.141	0.520	37.5	0.179	0.000
75.0	0.071	0.004	75.0	-0.119	0.189	75.0	0.166	0.009
112.5	0.141	0.022	112.5	0.006	0.154	112.5	0.150	0.023

<i>Column experiment, mixture of uncomplexed metals</i>								
Volume through (mL)	Cd(II)	Stdev	Volume through (mL)	Pb(II)	Stdev	Volume through (mL)	Zn(II)	Stdev
150.0	0.222	0.018	150.0	-0.238	0.116	150.0	0.230	0.033
187.5	0.276	0.039	187.5	-0.243	0.096	187.5	0.239	0.013
225.0	0.388	0.002	225.0	-0.241	0.067	225.0	0.242	0.051
262.5	0.508	0.020	262.5	-0.111	0.225	262.5	0.319	0.012
300.0	0.630	0.024	300.0	-0.126	0.074	300.0	0.367	0.015
337.5	0.725	0.013	337.5	-0.088	0.083	337.5	0.435	0.028
375.0	0.868	0.000	375.0	-0.120	0.064	375.0	0.540	0.002
412.5	0.964	0.036	412.5	-0.086	0.020	412.5	0.612	0.004
450.0	1.096	0.024	450.0	0.106	0.111	450.0	0.696	0.034
487.5	0.120	0.006	487.5	0.105	0.191	487.5	0.814	0.029
525.0	1.316	0.033	525.0	0.342	0.216	525.0	0.908	0.037
562.5	1.347	0.003	562.5	0.297	0.177	562.5	0.931	0.024
600.0	1.455	0.027	600.0	0.313	0.055	600.0	0.936	0.002
637.5	1.540	0.082	637.5	0.238	0.127	637.5	1.012	0.043
675.0	1.603	0.006	675.0	0.303	0.234	675.0	0.989	0.030
712.5	1.649	0.056	712.5	0.210	0.134	712.5	1.015	0.010
750.0	1.715	0.084	750.0	0.477	0.186	750.0	1.118	0.017
787.5	1.723	0.053	787.5	0.441	0.127	787.5	1.158	0.052
825.0	1.782	0.042	825.0	0.223	0.274	825.0	1.274	0.025
862.5	1.826	0.018	862.5	0.486	0.109	862.5	1.278	0.015
900.0	1.901	0.036	900.0	0.593	0.058	900.0	1.310	0.012
937.5	1.936	0.025	937.5	0.790	0.129	937.5	1.280	0.017
975.0	2.017	0.007	975.0	0.711	0.265	975.0	1.344	0.024
1012.5	1.997	0.010	1012.5	0.667	0.074	1012.5	1.324	0.025
1050.0	2.059	0.086	1050.0	1.027	0.142	1050.0	1.407	0.015
1087.5	1.988	0.023	1087.5	1.185	0.228	1087.5	1.428	0.039
1125.0	2.036	0.001	1125.0	1.347	0.289	1125.0	1.366	0.006
1162.5	2.074	0.088	1162.5	1.482	0.124	1162.5	1.446	0.031
1200.0	2.067	0.011	1200.0	1.576	0.109	1200.0	1.399	0.003
1237.5	2.110	0.022	1237.5	1.741	0.501	1237.5	1.426	0.048
1275.0	2.136	0.032	1275.0	1.715	0.073	1275.0	1.433	0.008
1312.5	2.089	0.091	1312.5	1.973	0.119	1312.5	1.527	0.064
1350.0	2.164	0.010	1350.0	1.913	0.087	1350.0	1.502	0.023
1387.5	2.067	0.037	1387.5	2.075	0.092	1387.5	1.483	0.069
1425.0	2.121	0.055	1425.0	2.196	0.110	1425.0	1.530	0.058
1462.5	2.131	0.054	1462.5	2.068	0.137	1462.5	1.577	0.029
1500.0	2.196	0.007	1500.0	2.211	0.095	1500.0	1.575	0.045
1537.5	2.212	0.056	1537.5	2.247	0.164	1537.5	1.498	0.052
1575.0	2.166	0.038	1575.0	2.018	0.382	1575.0	1.506	0.012
1612.5	2.180	0.098	1612.5	2.335	0.243	1612.5	1.495	0.002
1650.0	2.153	0.024	1650.0	2.358	0.138	1650.0	1.481	0.019
1687.5	2.169	0.025	1687.5	2.222	0.159	1687.5	1.486	0.047
1725.0	2.085	0.085	1725.0	2.193	0.198	1725.0	1.541	0.034
1762.5	2.157	0.011	1762.5	2.221	0.128	1762.5	1.521	0.076
1800.0	2.120	0.055	1800.0	2.512	0.135	1800.0	1.473	0.062
1837.5	2.121	0.023	1837.5	2.399	0.094	1837.5	1.503	0.044
1875.0	2.111	0.048	1875.0	2.580	0.171	1875.0	1.516	0.004
1912.5	2.192	0.069	1912.5	2.504	0.188	1912.5	1.506	0.021
1950.0	2.171	0.005	1950.0	2.726	0.217	1950.0	1.557	0.056
1987.5	2.207	0.022	1987.5	2.516	0.325	1987.5	1.479	0.057
2025.0	2.216	0.075	2025.0	2.372	0.395	2025.0	1.463	0.010
2062.5	2.181	0.063	2062.5	2.828	0.130	2062.5	1.482	0.026

<i>Column experiment, mixture of uncomplexed metals</i>								
Volume through h (mL)	Cd(II)	Stdev	Volume through h (mL)	Pb(II)	Stdev	Volume through h (mL)	Zn(II)	Stdev
2100.0	2.162	0.069	2100.0	2.807	0.215	2100.0	1.452	0.001
2137.5	2.104	0.005	2137.5	2.559	0.211	2137.5	1.510	0.018
2175.0	2.142	0.055	2175.0	2.801	0.386	2175.0	1.470	0.048
2212.5	2.162	0.040	2212.5	2.771	0.233	2212.5	1.458	0.061
2250.0	2.143	0.046	2250.0	2.820	0.074	2250.0	1.480	0.024
2287.5	2.144	0.046	2287.5	2.822	0.402	2287.5	1.470	0.053
2325.0	2.047	0.068	2325.0	2.661	0.124	2325.0	1.495	0.014
2362.5	2.084	0.052	2362.5	2.795	0.245	2362.5	1.417	0.038
2400.0	2.139	0.048	2400.0	2.796	0.102	2400.0	1.435	0.000
2437.5	2.088	0.142	2437.5	3.049	0.049	2437.5	1.446	0.019
2475.0	2.096	0.054	2475.0	2.925	0.465	2475.0	1.412	0.016
2512.5	2.095	0.077	2512.5	2.818	0.257	2512.5	1.482	0.062
2550.0	2.071	0.012	2550.0	2.880	0.099	2550.0	1.445	0.001
2587.5	2.070	0.035	2587.5	2.925	0.223	2587.5	1.383	0.036
2625.0	2.062	0.053	2625.0	2.695	0.377	2625.0	1.383	0.042
2662.5	2.098	0.073	2662.5	2.593	0.164	2662.5	1.424	0.004
2700.0	2.060	0.010	2700.0	2.684	0.123	2700.0	1.436	0.015
2737.5	2.109	0.022	2737.5	2.292	0.250	2737.5	1.403	0.087
2775.0	2.054	0.051	2775.0	2.528	0.289	2775.0	1.446	0.040
2812.5	1.860	0.007	2812.5	2.661	0.081	2812.5	1.349	0.006
2850.0	1.845	0.020	2850.0	2.541	0.102	2850.0	1.387	0.001
2887.5	1.913	0.018	2887.5	2.503	0.051	2887.5	1.388	0.027
2925.0	1.786	0.010	2925.0	1.664	0.087	2925.0	1.398	0.051
2962.5	1.894	0.032	2962.5	2.690	0.074	2962.5	1.387	0.001
3000.0	1.923	0.114	3000.0	2.671	0.060	3000.0	1.405	0.051
3037.5	1.902	0.103	3037.5	2.651	0.155	3037.5	1.351	0.019
3075.0	1.902	0.023	3075.0	2.746	0.125	3075.0	1.411	0.007
3112.5	1.894	0.019	3112.5	2.715	0.039	3112.5	1.387	0.017
3150.0	1.917	0.032	3150.0	2.630	0.049	3150.0	1.407	0.007
3187.5	1.946	0.041	3187.5	2.780	0.158	3187.5	1.371	0.035
3225.0	1.869	0.043	3225.0	2.653	0.091	3225.0	1.436	0.031
3262.5	1.918	0.013	3262.5	2.643	0.049	3262.5	1.417	0.019
3300.0	1.944	0.102	3300.0	2.652	0.133	3300.0	1.433	0.016
3337.5	1.894	0.007	3337.5	2.643	0.070	3337.5	1.410	0.009
3375.0	1.912	0.005	3375.0	2.698	0.100	3375.0	1.418	0.005
3412.5	1.947	0.035	3412.5	2.635	0.064	3412.5	1.440	0.038
3450.0	1.916	0.008	3450.0	2.646	0.116	3450.0	1.378	0.022
3487.5	1.876	0.053	3487.5	2.784	0.119	3487.5	1.351	0.016
3525.0	1.897	0.012	3525.0	2.665	0.152	3525.0	1.413	0.019
3562.5	1.908	0.028	3562.5	2.750	0.313	3562.5	1.523	0.012
3600.0	1.822	0.003	3562.5	2.679	0.029	3600.0	1.404	0.009
3637.5	1.870	0.026	3600.0	2.511	0.112	3637.5	1.393	0.047
3675.0	1.873	0.030	3637.5	2.529	0.184	3675.0	1.381	0.029
3712.5	1.887	0.125	3675.0	2.502	0.28	3712.5	1.380	0.000
3750.0	1.854	0.020	3675.0	2.500	0.025	3750.0	1.388	0.004
3787.5	1.854	0.020	3712.5	2.563	0.03	3787.5	1.414	0.009
3787.5	1.942	0.029	3787.5	2.490	0.124	3825.0	1.439	0.01
3825.0	1.915	0.017	3787.5	2.595	0.044	3862.5	1.415	0.009
3862.5	1.928	0.078	3900.0	2.700	0.262	3900.0	1.398	0.029
3900.0	1.831	0.031	3900.0	2.619	0.028	3937.5	1.409	0.013
3900.0	1.957	0.057	4012.5	2.775	0.254	3975.0	1.395	0.019
3937.5	1.891	0.011	4012.5	2.595	0.044	4012.5	1.407	0.013

<i>Column experiment, mixture of uncomplexed metals</i>								
Volume through h (mL)	Cd(II)	Stdev	Volume through h (mL)	Pb(II)	Stdev	Volume through h (mL)	Zn(II)	Stdev
3975.0	1.935	0.000	4125.0	2.744	0.328	4125.0	1.376	0.006
4012.5	1.886	0.016	4125.0	3.052	0.076	4237.5	1.383	0.017
4012.5	1.945	0.002	4237.5	2.985	0.272	4350.0	1.367	0.049
4125.0	1.773	0.010	4237.5	3.153	0.088	4462.5	1.369	0.004
4125.0	1.877	0.055	4350.0	2.690	0.158	4575.0	1.302	0.015
4237.5	1.792	0.028	4350.0	3.038	0.179	4687.5	1.344	0.012
4237.5	1.876	0.034	4462.5	2.661	0.096	4800.0	1.321	0.001
4350.0	1.808	0.068	4462.5	2.810	0.196	4875.0	1.312	0.033
4462.5	1.792	0.038	4575.0	2.840	0.125	5025.0	1.367	0.008
4575.0	1.796	0.022	4687.5	2.853	0.067	5137.5	1.369	0.014
4687.5	1.858	0.011	4800.0	2.943	0.121	5212.5	1.347	0.001
4800.0	1.806	0.024	4875.0	2.891	0.037	5362.5	1.405	0.041
4875.0	1.876	0.019	5025.0	2.918	0.11	5475.0	1.393	0.011
5025.0	1.835	0.066	5137.5	2.826	0.083	5587.5	1.369	0.037
5137.5	1.900	0.019	5212.5	2.842	0.053	5700.0	1.381	0.037
5212.5	1.835	0.066	5362.5	2.615	0.03	5812.5	1.376	0.022
5362.5	1.900	0.019	5475.0	2.805	0.063	5925.0	1.333	0
5475.0	1.855	0.015	5587.5	2.993	0.041	6037.5	1.363	0.007
5587.5	1.929	0.064	5700.0	3.005	0.039	6150.0	1.375	0.026
5700.0	1.839	0.042	5812.5	2.976	0.045	6262.5	1.367	0.013
5812.5	1.922	0.060	5925.0	3.202	0.114	6375.0	1.401	0.038
5925.0	1.924	0.060	6037.5	3.251	0.067	6487.5	1.39	0.049
6037.5	1.876	0.015	6150.0	3.130	0.123	6615.0	1.398	0.005
6150.0	1.889	0.025	6262.5	3.246	0.049	6727.5	1.411	0.025
6262.5	1.932	0.027	6375.0	3.202	0.006	6840.0	1.432	0.01
6375.0	1.899	0.011	6487.5	3.226	0.053	6952.5	1.398	0.007
6487.5	1.945	0.032	6615.0	3.291	0.04	7065.0	1.43	0.021
6615.0	1.876	0.015	6727.5	3.325	0.057	7177.5	1.406	0.025
6727.5	1.899	0.011	6840.0	3.079	0.042	7290.0	1.402	0.028
6840.0	1.863	0.082	6952.5	3.240	0.021	7402.5	1.371	0.006
6952.5	1.913	0.018	7065.0	3.213	0.125	7515.0	1.434	0.043
7065.0	1.853	0.028	7177.5	3.103	0.06	7627.5	1.416	0.015
7177.5	1.893	0.025	7290.0	3.220	0.041	7740.0	1.437	0.01
7290.0	1.926	0.073	7402.5	3.068	0.103	7852.5	1.389	0.059
7402.5	1.845	0.040	7515.0	3.223	0.217	7965.0	1.438	0.026
7515.0	1.808	0.009	7627.5	3.220	0.096			
7627.5	1.812	0.070	7740.0	3.514	0.036			
7740.0	1.846	0.042	7852.5	3.336	0.038			
7852.5	1.864	0.040	7965.0	3.423	0.107			
7965.0	1.826	0.039						

<i>Column experiment, mixture of uncomplexed metals</i>								
Volume through h (mL)	Cu(II)	Stdev	Volume through h (mL)	Ni(II)	Stdev	Volume through h (mL)	Ca(II)	Stdev
influent	0.467	0.021	influent	1.135	0.071	influent	0.144	0.029
37.5	0.084	0.049	37.5	0.132	0.048	37.5	50.960	0.223
75.0	0.027	0.006	75.0	0.079	0.044	75.0	21.350	0.834
112.5	0.019	0.000	112.5	0.244	0.137	112.5	11.230	0.048
225.0	0.016	0.003	150.0	0.492	0.105	150.0	9.577	0.449

<i>Column experiment, mixture of uncomplexed metals</i>								
<i>Volum e throug h (mL)</i>	<i>Cu(II)</i>	<i>Stdev</i>	<i>Volum e throug h (mL)</i>	<i>Ni(II)</i>	<i>Stdev</i>	<i>Volum e throug h (mL)</i>	<i>Ca(II)</i>	<i>Stdev</i>
262.5	0.021	0.001	187.5	0.541	0.103	187.5	8.932	0.557
300.0	0.013	0.007	225.0	0.589	0.124	225.0	7.501	0.337
337.5	0.019	0.002	262.5	0.692	0.113	262.5	7.683	0.258
375.0	0.014	0.005	300.0	0.766	0.111	300.0	5.022	0.113
412.5	0.021	0.002	337.5	0.596	0.012	337.5	4.641	0.157
450.0	0.022	0.000	375.0	0.809	0.069	375.0	4.863	0.141
487.5	0.028	0.003	412.5	0.837	0.063	412.5	4.730	0.013
525.0	0.031	0.010	450.0	1.004	0.045	450.0	4.006	0.086
562.5	0.033	0.001	487.5	1.059	0.054	487.5	4.239	0.025
600.0	0.036	0.004	525.0	1.116	0.091	525.0	4.113	0.245
637.5	0.041	0.011	562.5	1.153	0.179	562.5	3.747	0.173
675.0	0.047	0.009	600.0	1.087	0.133	600.0	3.745	0.037
712.5	0.047	0.008	637.5	1.083	0.031	637.5	3.642	0.051
750.0	0.045	0.007	675.0	1.179	0.053	712.5	3.552	0.000
787.5	0.054	0.003	712.5	1.210	0.076	750.0	6.990	0.024
825.0	0.046	0.061	750.0	1.202	0.132	787.5	3.314	0.183
862.5	0.061	0.011	787.5	1.026	0.002	862.5	3.009	0.019
900.0	0.073	0.007	825.0	1.219	0.085	975.0	2.674	0.041
937.5	0.069	0.007	862.5	1.338	0.221	1087.5	2.623	0.046
975.0	0.080	0.010	900.0	1.391	0.062	1200.0	2.447	0.014
1012.5	0.096	0.000	937.5	1.199	0.122	1312.5	2.266	0.006
1050.0	0.076	0.008	975.0	1.463	0.112	1387.5	2.157	0.025
1087.5	0.099	0.014	1012.5	1.387	0.125	1425.0	2.170	0.028
1125.0	0.115	0.008	1050.0	1.326	0.222	1500.0	2.085	0.098
1162.5	0.124	0.006	1087.5	1.424	0.107	1612.5	2.000	0.086
1200.0	0.120	0.012	1125.0	1.267	0.095	1725.0	2.004	0.100
1237.5	0.135	0.017	1162.5	1.248	0.039	1762.5	1.830	0.062
1275.0	0.129	0.017	1200.0	1.371	0.163	1800.0	1.791	0.038
1312.5	0.135	0.016	1237.5	1.152	0.142	1837.5	1.750	0.032
1350.0	0.146	0.011	1275.0	1.243	0.008	1875.0	1.704	0.008
1387.5	0.151	0.016	1312.5	1.261	0.143	1912.5	1.531	0.049
1425.0	0.169	0.022	1350.0	1.225	0.003	1950.0	1.521	0.075
1462.5	0.176	0.015	1387.5	1.255	0.094	2062.5	1.679	0.088
1500.0	0.176	0.011	1425.0	1.062	0.181	2175.0	1.772	0.023
1537.5	0.184	0.015	1462.5	1.340	0.105	2287.5	1.500	0.087
1575.0	0.186	0.015	1500.0	1.292	0.071	2400.0	1.800	0.060
1612.5	0.193	0.023	1537.5	1.241	0.089	2512.5	1.846	0.031
1650.0	0.200	0.025	1575.0	1.146	0.039	2625.0	1.869	0.025
1687.5	0.211	0.016	1612.5	1.100	0.115	2737.5	1.908	0.036
1725.0	0.228	0.002	1650.0	1.348	0.019	2850.0	1.889	0.049
1762.5	0.216	0.020	1687.5	1.209	0.023	2962.5	1.746	0.246
1800.0	0.229	0.016	1725.0	1.158	0.041	3075.0	1.850	0.011
1837.5	0.239	0.022	1762.5	1.034	0.067	3187.5	1.822	0.037
1875.0	0.252	0.032	1800.0	1.237	0.085	3300.0	1.730	0.064
1912.5	0.264	0.019	1837.5	1.028	0.094	3412.5	1.682	0.073
1950.0	0.262	0.012	1875.0	1.226	0.122	3525.0	1.649	0.046
1987.5	0.267	0.034	1912.5	1.227	0.122	3562.5	2.032	0.019
2025.0	0.285	0.022	1950.0	1.253	0.205	3675.0	1.583	0.045
2062.5	0.279	0.021	1987.5	1.129	0.029	3787.5	1.566	0.017
2100.0	0.288	0.028	2025.0	1.090	0.035	3900.0	1.568	0.121

<i>Column experiment, mixture of uncomplexed metals</i>								
<i>Volum e throug h (mL)</i>	<i>Cu(II)</i>	<i>Stdev</i>	<i>Volum e throug h (mL)</i>	<i>Ni(II)</i>	<i>Stdev</i>	<i>Volum e throug h (mL)</i>	<i>Ca(II)</i>	<i>Stdev</i>
2137.5	0.292	0.010	2062.5	1.203	0.016	4012.5	1.514	0.030
2175.0	0.297	0.030	2100.0	1.176	0.007	4125.0	1.453	0.021
2212.5	0.303	0.044	2137.5	1.242	0.065	4237.5	1.976	0.001
2250.0	0.313	0.015	2175.0	1.081	0.042	4350.0	2.006	0.087
2287.5	0.310	0.025	2212.5	1.201	0.108	4462.5	1.997	0.008
2325.0	0.322	0.007	2250.0	1.335	0.100	4575.0	1.908	0.035
2362.5	0.319	0.015	2287.5	1.234	0.027	4800.0	1.815	0.006
2400.0	0.307	0.026	2325.0	1.170	0.146	5025.0	1.648	0.052
2437.5	0.308	0.025	2362.5	1.258	0.095	5212.5	1.573	0.042
2475.0	0.292	0.029	2400.0	1.252	0.130	5475.0	1.175	0.058
2512.5	0.292	0.028	2437.5	1.309	0.169	5700.0	1.036	0.052
2550.0	0.287	0.030	2475.0	1.243	0.096	5925.0	1.279	0.017
2587.5	0.290	0.004	2512.5	1.137	0.003	6150.0	1.200	0.019
2625.0	0.289	0.013	2550.0	1.187	0.000	6375.0	1.233	0.114
2662.5	0.284	0.039	2587.5	1.326	0.019	6615.0	1.205	0.034
2700.0	0.299	0.025	2625.0	1.340	0.126	6840.0	1.183	0.068
2737.5	0.290	0.021	2662.5	1.115	0.005	7065.0	1.023	0.097
2775.0	0.295	0.030	2700.0	1.320	0.178	7290.0	1.144	0.395
2812.5	0.303	0.003	2737.5	1.363	0.168	7515.0	0.970	0.065
2850.0	0.305	0.017	2775.0	1.329	0.100	7740.0	1.089	0.009
2887.5	0.326	0.004	2812.5	1.238	0.059	7965.0	1.183	0.006
2925.0	0.245	0.035	2850.0	1.086	0.011			
2962.5	0.426	0.058	2887.5	1.098	0.000			
3000.0	0.309	0.007	2925.0	1.236	0.056			
3037.5	0.306	0.033	2962.5	1.177	0.006			
3075.0	0.315	0.012	3000.0	1.257	0.083			
3112.5	0.320	0.014	3037.5	1.004	0.123			
3150.0	0.317	0.029	3075.0	1.160	0.148			
3187.5	0.316	0.005	3112.5	1.265	0.044			
3225.0	0.319	0.013	3150.0	1.204	0.012			
3262.5	0.324	0.039	3187.5	1.250	0.051			
3300.0	0.320	0.013	3225.0	1.051	0.051			
3337.5	0.331	0.023	3262.5	1.187	0.001			
3375.0	0.324	0.005	3300.0	1.065	0.036			
3412.5	0.307	0.030	3337.5	1.139	0.075			
3450.0	0.331	0.031	3375.0	1.258	0.051			
3487.5	0.347	0.001	3412.5	1.259	0.052			
3525.0	0.333	0.017	3450.0	1.032	0.111			
3562.5	0.333	0.017	3487.5	1.132	0.255			
3600.0	0.336	0.022	3525.0	1.151	0.052			
3637.5	0.346	0.016						
3675.0	0.346	0.018						
3712.5	0.343	0.026						
3750.0	0.309	0.010						
3787.5	0.343	0.011						
3900.0	0.334	0.024						
4012.5	0.345	0.035						
4125.0	0.359	0.034						
4237.5	0.345	0.017						
4350.0	0.336	0.022						

Column experiment, mixture of uncomplexed metals								
Volum e throug h (mL)	Cu(II)	Stdev	Volum e throug h (mL)	Ni(II)	Stdev	Volum e throug h (mL)	Ca(II)	Stdev
4462.5	0.334	0.007						
influent	0.361	0.013						
4575.0	0.285	0.003						
4687.5	0.287	0.003						
4800.0	0.285	0.002						
4875.0	0.287	0.002						
5025.0	0.298	0.000						
5137.5	0.300	0.009						
5212.5	0.295	0.012						
5362.5	0.282	0.001						
5475.0	0.307	0.001						
5587.5	0.306	0.010						
5700.0	0.313	0.000						
5812.5	0.321	0.006						
5925.0	0.311	0.012						
6037.5	0.305	0.002						
6150.0	0.315	0.005						
6262.5	0.311	0.012						
6375.0	0.313	0.001						
6487.5	0.325	0.002						
6615.0	0.327	0.005						
6727.5	0.325	0.007						
6840.0	0.320	0.001						
6952.5	0.318	0.008						
7065.0	0.318	0.002						
7177.5	0.321	0.002						
7290.0	0.332	0.005						
7402.5	0.338	0.001						
7515.0	0.351	0.007						
7627.5	0.354	0.001						
7740.0	0.341	0.019						
7852.5	0.330	0.000						
7965.0	0.332	0.001						

Column experiment, mixture of complexed metals							
Volume throug h (mL)	Pb(II)	Stdev	Volume throug h (mL)	Cu(II)	Stdev	Volume throug h (mL)	Cd(II)
influent	3.783	0.155	influent	0.434	0.005	influent	2.057
42.5	0.196	0.016	42.5	0.000	0.002	42.5	0.055
85.0	0.133	0.064	85.0	0.000	0.008	85.0	0.361
127.5	0.142	0.074	127.5	0.012	0.002	127.5	0.653
170.0	0.221	0.077	170.0	0.028	0.009	170.0	0.898
212.5	0.386	0.079	212.5	0.041	0.002	212.5	1.047
255.0	0.528	0.047	255.0	0.060	0.004	255.0	1.248
297.5	0.623	0.071	297.5	0.078	0.000	297.5	1.365
340.0	0.782	0.023	340.0	0.091	0.002	340.0	1.443
382.5	0.947	0.034	382.5	0.101	0.006	382.5	1.450
510.0	1.157	0.088	510.0	0.137	0.004	510.0	1.670
637.5	1.413	0.090	637.5	0.155	0.002	637.5	1.744

Column experiment, mixture of complexed metals							
Volume through (mL)	Pb(II)	Stdev	Volume through (mL)	Cu(II)	Stdev	Volume through (mL)	Cd(II)
765.0	1.550	0.180	765.0	0.120	0.002	765.0	1.775
892.5	1.684	0.086	892.5	0.176	0.003	892.5	1.863
1020.0	1.843	0.102	1020.0	0.181	0.008	1020.0	1.894
1147.5	1.830	0.077	1147.5	0.183	0.008	1147.5	1.893
1275.0	1.883	0.103	1275.0	0.200	0.009	1275.0	1.912
1402.5	2.035	0.045	1402.5	0.218	0.014	1402.5	1.942
1530.0	2.295	0.053	1530.0	0.243	0.002	1530.0	2.009
1657.5	2.358	0.115	1657.5	0.254	0.003	1657.5	1.974
1785.0	2.463	0.062	1785.0	0.269	0.003	1785.0	2.015
1912.5	2.510	0.122	1912.5	0.285	0.013	1912.5	2.038
2040.0	2.676	0.179	2040.0	0.298	0.001	2040.0	1.991
2167.5	2.646	0.066	2167.5	0.322	0.002	2167.5	2.063
2295.0	2.027	0.386	2295.0	0.268	0.003	2295.0	2.003
2422.5	3.013	0.137	2422.5	0.384	0.026	2422.5	1.993
2550.0	2.900	0.022	2550.0	0.362	0.004	2550.0	2.087
2677.5	2.859	0.031	2677.5	0.379	0.000	2677.5	2.034
2805.0	2.857	0.085	2805.0	0.379	0.005	2805.0	2.045
2890.0	2.845	0.175	2890.0	0.386	0.001	2890.0	2.024
3060.0	2.864	0.178	3060.0	0.362	0.007	3060.0	2.005
3187.5	2.795	0.138	3187.5	0.366	0.004	3187.5	2.036
3315.0	2.795	0.049	3315.0	0.356	0.001	3315.0	2.033
3442.5	2.784	0.170	3442.5	0.349	0.003	3442.5	2.020
3570.0	2.818	0.011	3570.0	0.348	0.007	3570.0	1.992
3697.5	2.066	0.054	3697.5	0.277	0.010	3697.5	2.015
3825.0	2.632	0.179	3825.0	0.312	0.015	3825.0	2.003
3952.5	2.674	0.079	3952.5	0.328	0.013	3952.5	2.008
4080.0	3.034	0.281	4080.0	0.394	0.042	4080.0	2.037
4207.5	3.031	0.160	4207.5	0.357	0.001	4207.5	2.098
4335.0	2.874	0.048	4335.0	0.351	0.004	4335.0	1.983
4462.5	2.806	0.051	4462.5	0.356	0.017	4462.5	2.046
4590.0	2.894	0.189	4590.0	0.367	0.007	4590.0	2.032
4717.5	3.099	0.094	4717.5	0.347	0.009	4717.5	2.013
4845.0	3.009	0.165	4845.0	0.356	0.009	4845.0	1.982
4972.5	3.012	0.042	4972.5	0.357	0.013	4972.5	1.986
5100.0	3.068	0.266	5100.0	0.364	0.007	5100.0	2.014
5227.5	3.181	0.189	5227.5	0.353	0.001	5227.5	1.948
5355.0	2.974	0.120	5355.0	0.358	0.002	5355.0	1.988
5482.5	2.811	0.060	5482.5	0.355	0.000	5482.5	2.070
5610.0	2.909	0.252	5610.0	0.369	0.006	5610.0	2.063
5737.5	2.838	0.146	5737.5	0.353	0.004	5737.5	2.004
5865.0	3.028	0.062	5865.0	0.348	0.003	5865.0	1.995
5992.5	3.092	0.060	5992.5	0.352	0.006	5992.5	2.122
6120.0	3.000	0.110	6120.0	0.362	0.015	6120.0	2.070
6247.5	2.931	0.137	6247.5	0.365	0.004	6247.5	2.023
6375.0	3.011	0.081	6375.0	0.364	0.008	6375.0	2.061
6502.5	3.205	0.113	6502.5	0.360	0.002	6502.5	2.022
6630.0	3.151	0.137	6630.0	0.360	0.010	6630.0	2.042
6757.5	3.139	0.228	6757.5	0.363	0.008	6757.5	2.038
6885.0	3.204	0.144	6885.0	0.361	0.014	6885.0	1.964
7012.5	3.252	0.097	7012.5	0.364	0.014	7012.5	2.022
7140.0	3.210	0.261	7140.0	0.355	0.005	7140.0	1.940
7267.5	3.235	0.029	7267.5	0.367	0.008	7267.5	2.034

Column experiment, mixture of complexed metals							
Volume through (mL)	Pb(II)	Stdev	Volume through (mL)	Cu(II)	Stdev	Volume through (mL)	Cd(II)
7395.0	3.188	0.073	7395.0	0.375	0.003	7395.0	2.094
7522.5	3.161	0.025	7522.5	0.371	0.001	7522.5	2.076
7650.0	3.139	0.123	7650.0	0.376	0.004	7650.0	2.064
7777.5	3.355	0.167	7777.5	0.365	0.003	7777.5	2.126
7905.0	3.288	0.173	7905.0	0.366	0.007	7905.0	2.153
8032.5	3.265	0.294	8032.5	0.363	0.000	8032.5	2.150
8160.0	3.107	0.018	8160.0	0.374	0.004	8160.0	2.061
8287.5	3.277	0.032	8287.5	0.380	0.002	8287.5	2.175
8415.0	3.309	0.089	8415.0	0.376	0.003	8415.0	2.110

Column experiment, mixture of complexed metals						
Volume through (mL)	Zn(II)	Volume through (mL)	Ni(II)	Volume through (mL)	Ca(II)	Stdev
influent	1.433		1.874	influent	0.34	0.044
42.5	0.169	85.0	0.743	42.5	30.09	1.606
85.0	0.328	127.5	0.956	85.0	14.09	0.75
127.5	0.532	170.0	1.211	127.5	9.894	0.006
170.0	0.715	212.5	1.298	170.0	8.537	0.382
212.5	0.839	255.0	1.37	212.5	7.178	0.698
255.0	0.905	297.5	1.56	255.0	5.178	0.027
297.5	1.000	340.0	1.598	297.5	4.689	0.099
340.0	1.031	382.5	1.491	340.0	4.439	0.035
382.5	1.133	510.0	1.561	382.5	4.079	0.001
510.0	1.165	637.5	1.727	510.0	3.285	0.141
637.5	1.295	765.0	1.598	637.5	2.875	0.092
765.0	1.346	892.5	1.571	765.0	2.993	0.067
892.5	1.355	1020.0	1.509	892.5	2.735	0.103
1020.0	1.363	1147.5	1.496	1020.0	2.708	0.112
1147.5	1.404	1275.0	1.672	1147.5	2.289	0.05
1275.0	1.477	1402.5	1.482	1275.0	2.19	0.015
1402.5	1.406	1530.0	1.561	1402.5	2.266	0.049
1530.0	1.439	1657.5	1.458	1530.0	1.918	0.085
1657.5	1.416	1785.0	1.471	1657.5	1.768	0.128
1785.0	1.397	1912.5	1.544	1785.0	1.746	0.129
1912.5	1.449	2040.0	1.706	1912.5	1.669	0.022
2040.0	1.521	2167.5	1.671	2040.0	1.81	0.003
2167.5	1.519	2295.0	1.543	2167.5	1.921	0.12
2295.0	1.486	2422.5	1.27	2295.0	1.562	0.027
2422.5	1.467	2550.0	1.528	2422.5	1.675	0.055
2550.0	1.453	2677.5	1.448	2550.0	1.604	0.031
2677.5	1.435	2805.0	1.397	2677.5	1.668	0.032
2805.0	1.439	2890.0	1.616	2805.0	1.713	0.049
2890.0	1.450	3060.0	1.541	2890.0	1.853	0.096
3060.0	1.472	3187.5	1.509	3060.0	1.785	0.158
3187.5	1.445	3315.0	1.548	3187.5	1.839	0
3315.0	1.349	3442.5	1.784	3315.0	1.804	0.071
3442.5	1.347	3570.0	1.445	3442.5	1.841	0.138
3570.0	1.206	3697.5	1.489	3570.0	1.677	0.054
3697.5	1.507	3825.0	1.455	3697.5	1.713	0.082
3825.0	1.484	3952.5	1.459	3825.0	1.734	0.046

Column experiment, mixture of complexed metals						
Volume through (mL)	Zn(II)	Volume through (mL)	Ni(II)	Volume through (mL)	Ca(II)	Stdev
3952.5	1.444	4080.0	1.409	3952.5	1.759	0.056
4080.0	1.511	4207.5	1.514	4080.0	1.724	0.035
4207.5	1.477	4335.0	1.547	4207.5	1.556	0.041
4335.0	1.484	4462.5	1.376	4335.0	1.587	0.069
4462.5	1.458	4590.0	1.518	4462.5	1.44	0.089
4590.0	1.446	4717.5	1.48	4590.0	1.435	0.141
4717.5	1.459	4845.0	1.611	4717.5	1.575	0.104
4845.0	1.466	4972.5	1.6	4845.0	1.574	0.178
4972.5	1.443	5100.0	1.623	4972.5	1.747	0.009
5100.0	1.481	5227.5	1.574	5100.0	1.704	0.103
5227.5	1.444	5355.0	1.409	5227.5	1.734	0.064
5355.0	1.429	5482.5	1.476	5355.0	1.755	0.129
5482.5	1.465	5610.0	1.466	5482.5	1.68	0.101
5610.0	1.459	5737.5	1.625	5610.0	1.662	0.044
5737.5	1.410	5865.0	1.872	5737.5	1.655	0.045
5865.0	1.486	5992.5	1.542	5865.0	1.715	0.174
5992.5	1.470	6120.0	1.897	5992.5	1.801	0.103
6120.0	1.467	6247.5	1.635	6120.0	1.497	0.043
6247.5	1.449	6375.0	1.607	6247.5	1.562	0.048
6375.0	1.469	6502.5	1.501	6375.0	1.528	0.075
6502.5	1.500	6630.0	1.557	6502.5	1.5	0.087
6630.0	1.465	6757.5	1.515	6630.0	1.516	0.028
6757.5	1.464	6885.0	1.506	6757.5	1.594	0.006
6885.0	1.477	7012.5	1.549	6885.0	1.517	0.003
7012.5	1.491	7140.0	1.886	7012.5	1.652	0.046
7140.0	1.464	7267.5	1.856	7140.0	1.686	0.082
7267.5	1.483	7395.0	1.876	7267.5	1.548	0.041
7395.0	2.047	7522.5	1.791	7395.0	1.936	0.067
7522.5	1.497	7650.0	2.449	7522.5	1.961	0.033
7650.0	1.512	7777.5	1.708	7650.0	1.848	0.073
7777.5	1.499	7905.0	1.677	7777.5	1.89	0.008
7905.0	1.566	8032.5	1.911	7905.0	1.736	0.19
8032.5	1.529	8160.0	2.088	8032.5	1.71	0.088
8160.0	1.506			8160.0	2.232	0.019
8287.5	1.536			8287.5	1.903	0.062
8415.0	1.538			8415.0	2.009	0.13

bed volumes	Industrial wastewater							
	Pb(II)				Ni(II)			
	HRB		Amberlite® IRC 748		HRB		Amberlite® IRC 748	
	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev
influent	7.953	0.144	7.953	0.144	29.77		29.77	
2.81	2.317	0.855	2.791	0.044	13.66	0.256	1.274	0.011
26.38	1.004	0.464	2.481	0.057	24.44	0.803	0.375	0.05
40.87	0.462	0.139	2.229	0.101	27.02	0.035	0.225	0.029
66.25	0.313	0.049	3.263	0.068	28.07	0.625	0.212	0.013
78.94	0.34	0.116	2.878	0.217	28.58	0.058	0.282	0.031

Industrial wastewater								
bed volum es	Pb(II)				Ni(II)			
	HRB		Amberlite® IRC 748		HRB		Amberlite® IRC 748	
	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev
102.5	0.473	0.105	3.296	0.097	28.37	0.189	0.19	0.001
129.7	0.512	0.143	3.186	0.101	29.74	0.099	0.27	0.089
165.9	0.42	0.037	3.779	0.038	28.81	0.455	0.231	0.054
233	1.228	0.061	6.798	0.26	29.12	0.121	0.34	0.079
264.9	1.92	0.035	4.486	0.304	29.77	0.253	0.383	0.015
304.8	2.211	0.127	4.575	0.154	29.33	0.023	0.291	0.02
358.1	2.372	0.078	4.454	0.041	29.92	0.396	0.343	0.082
430.6	2.846	0.141	5.128	0.156	29.17	0.112	0.386	0.023
461.4	2.365	0.213	4.884	0.043	30.53	0.055	0.475	0.137
497.3	3.041	0.092	4.675	0.119	30.11	0.14	0.739	0.036
529.5	3.249	0.127	5.032	0.091	29.52	0.403	1.176	0.048
553.8	3.662	0.043	4.933	0.2	29.27	0.235	2.717	0.553
599.1	3.476	0.059	5.462	0.068	29.22	0.073	3.419	0.079
622.7	3.118	0.047	5.331	0.058	29.37	0.238	4.115	0.077
655.3	3.494	0.086	5.03	0.14	29.58	0.31	6.055	0.101
727.1	3.683	0.019	6.692	0.057	29.68	0.596	9.479	0.438
932.3	3.087	0.161			29.7	0.308	18.33	0.357
1037.8	4.486	0.337	9.543	0.639			21.42	0.388
							22.92	0.429
							26.93	0.487

Industrial wastewater								
bed volum es	Zn(II)				Cu(II)			
	HRB		Amberlite® IRC 748		HRB		Amberlite® IRC 748	
	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev
	Zn(II) HRB		Amberlite® IRC 748		Cu(II) HRB		Amberlite® IRC 748	
Bed volum es influen t	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev
	0.174		0.174		0.648		0.648	
2.81	0.205	0.025	0.151	0.020		0.186	0.089	0.029
26.38	0.108	0.012	0.116	0.030	0.101	0.006	0.069	0.02
40.87	0.107	0.011	0.108	0.005	0.074	0.029	0.075	0.025
66.25	0.104	0.004	0.120	0.012	0.117	0.032	0.059	0.001
78.94	0.107	0.003	0.128	0.008	0.14	0.024	0.065	0.003
102.5	0.112	0.011	0.101	0.012	0.206	0.007	0.029	0.024
129.7	0.113	0.027	0.098	0.005	0.221	0.02	0.047	0.006

Industrial wastewater								
bed volum es	Zn(II)				Cu(II)			
	HRB		Amberlite® IRC 748		HRB		Amberlite® IRC 748	
	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev
165.9	0.127	0.001	0.098	0.005	0.26	0.007	0.044	0.007
233	0.124	0.001	0.105	0.019	0.411	0.033	0.067	0.008
264.9	0.132	0.000	0.097	0.022	0.372	0.008	0.067	0.002
304.8	0.134	0.001	0.100	0.026	0.392	0.018	0.027	0.005
358.1	0.158	0.004	0.113	0.019	0.424	0.017	0.057	0.029
430.6	0.138	0.014	0.104	0.013	0.468	0.004	0.054	0.011
461.4	0.145	0.004	0.095	0.014	0.455	0.033	0.072	0.004
497.3	0.163	0.003	0.130	0.032	0.476	0.005	0.039	0.027
529.5	0.151	0.004	0.126	0.010	0.463	0.022	0.06	0.031
553.8	0.153	0.012	0.142	0.042	0.496	0.009	0.072	0
599.1	0.164	0.015	0.137	0.006	0.515	0.024	0.085	0.028
622.7	0.162	0.002	0.126	0.013	0.532	0.059	0.037	0.005
655.3	0.126	0.006	0.123	0.036	0.523	0.022	0.055	0.016
727.1	0.142	0.003	0.126	0.017	0.541	0.027	0.015	0.018
932.3					0.554	0.005	0.043	0.002
1037.8					0.605	0.019	0.101	0.017

Industrial wastewater								
bed volum es influen t	Fe(II)				Ca(II)			
	HRB		Amberlite® IRC 748		HRB		Amberlite® IRC 748	
	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev
	7.39		7.39		0.345	0.006	0.345	0.006
2.81	2.354	0.527	4.096	0.573	0.147	0.046	0.064	0.013
26.38	2.686	0.18	3.656	0.572	8.999	0.293	0.011	0.025
40.87	3.1	0.833	3.693	0.182	7.462	0.054	0.028	0.016
66.25	3.191	0.092	4.169	0.657	6.111	0.038	0.018	0.025
78.94	3.877	0.14	3.946	0.876	5.852	0.292	0.014	0.01
102.5	2.924	0.23	5.106	0.399	5.21	0.088	0.035	0.013
129.7	3.716	0.741	4.777	0.484	4.834	0.12	0.022	0.001
165.9	3.74	0.966	5.53	0.773	4.786	0.04	0.019	0.022
233	4.118	0.331	7.748	0.184	4.425	0.026	0.028	0.006
264.9	4.817	0.129	6.188	0.391	4.159	0.131	0.028	0.004
304.8	4.235	0.202	6.205	0.183	3.913	0.144	0.028	0.003
358.1	4.754	0.362	5.748	0.42	3.583	0.105	0.045	0.002
430.6	6.548	0.768	7.169	0.85	3.513	0.025	0.08	0.008
461.4	5.738	0.48	6.729	0.576	3.215	0.001	0.131	0.016
497.3	6.265	0.591	6.322	0.317	3.467	0.036	0.163	0.005
529.5	5.222	0.691	6.183	0.244	3.059	0.172	0.231	0.003
553.8	6.469	0.539	7.129	0.517	2.963	0.073	0.29	0.02
599.1	6.409	0.327	6.817	0.585	2.752	0.013	0.406	0.012

bed volum es	Industrial wastewater							
	Fe(II)				Ca(II)			
	HRB		Amberlite® IRC 748		HRB		Amberlite® IRC 748	
	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev	C (mg/L)	Stdev
622.7	5.382	0.707	7.475	0.321	2.893	0.022	0.377	0.019
655.3	5.66	0.699	6.454	0.493	2.913	0.068	0.468	0.033
727.1	5.375	0.202	7.911	0.703	2.683	0.019	0.462	0.001
932.3	5.91	0.363	8.735	0.452	2.379	0.062	0.425	0.017
1037.8	6.254	0.948	9.696	0.27	2.342	0.043	0.576	0.022

References

- Al-Asheh, S., Banat, F., and Al-Rousan, D. (2003). "Beneficial Reuse of Chicken Feathers in Removal of Heavy Metals from Wastewater." *J Clean Prod*, 11(3), 321-326.
- Allen, S. J. (1996). "Types of Adsorbent Materials." *Use of Adsorbents for the Removal of Pollutants from Wastewaters*, G. McKay, ed., CRC Press, Inc., Boca Raton, FL.
- American Public Health Association, American Water Works Association, and Water Pollution Control Federation. (1989). *Standard Methods for the Examination of Water and Wastewater*, 17th, American Public Health Association, Washington, D.C.
- Benjamin, M. M., Sletten, R. S., Bailey, R. P., and Bennett, T. (1996). "Sorption and Filtration of Metals Using Iron-Oxide-Coated Sand." *Water Research*, 30(11), 2609-2620.
- Blake, J. P. (2000). "Hatchery by-Product Disposal." *Curr Concept Broiler Prod*, 2000(Winter), 2-3.
- Bolan, N. S., and Duraisamy, V. P. (2003). "Role of Inorganic and Organic Soil Amendments on Immobilisation and Phytoavailability of Heavy Metals: A Review Involving Specific Case Studies." *Australian Journal of Soil Research*, 41(3), 533-555.
- Brower, J. B., Ryan, R. L., and Pazirandeh, M. (1997). "Comparison of Ion-Exchange Resins and Biosorbents for the Removal of Heavy Metals from Plating Factory Wastewater." *Environ Sci Technol*, 31(10), 2910-2914.
- Chada, V. G. R., Hausner, D. B., Strongin, D. R., Rouff, A. A., and Reeder, R. J. (2005). "Divalent Cd and Pb Uptake on Calcite {1014} Cleavage Faces: An XPS and Afm Study." *J Colloid Interf Sci*, 288(2), 350-360.
- Clifford, D. A. (1990). "Ion Exchange and Inorganic Adsorption." *Water Quality and Treatment : A Handbook of Community Water Supplies*, American Water Works Association, ed., McGraw-Hill, New York.
- Cooney, D. O. (1999). *Adsorption Design for Wastewater Treatment*, Lewis Publishers, Boca Raton, FL.
- Das, K. C., Minkara, M. Y., Melear, N. D., and Tollner, E. W. (2002). "Effect of Poultry Litter Amendment on Hatchery Waste Composting." *J Appl Poultry Res*, 11(3), 282-290.

- del Rio, J. A. G., Morando, P. J., and Cicerone, D. S. (2004). "Natural Materials for Treatment of Industrial Effluents: Comparative Study of the Retention of Cd, Zn and Co by Calcite and Hydroxyapatite. Part 1: Batch Experiments." *J Environ Manage*, 71(2), 169-177.
- Delmarva Poultry Industry Inc. (2005). "Delmarva and U.S. Facts." Delmarva Poultry Industry Inc., <http://www.dpichicken.org/index.cfm?content=facts>.
- Deshmukh, A. C., and Patterson, P. H. (1997). "Preservation of Hatchery Waste by Lactic Acid Fermentation. Large-Scale Fermentation and Feeding Trial to Evaluate Feeding Value." *Poult Sci*, 76(9), 1220-1226.
- Dobiášová, L., Kužel, R., Šichová, H., and Kopecek, J. "The Egg-Shell Microstructure Studied by Powder Diffraction." *European Powder Diffraction Conference, 2004*, Prague, <http://www.xray.cz/epdic/abstracts/293.htm>.
- Elzinga, E. J., and Reeder, R. J. (2002). "X-Ray Absorption Spectroscopy Study of Cu²⁺ and Zn²⁺ Adsorption Complexes at the Calcite Surface: Implications for Site-Specific Metal Incorporation Preferences During Calcite Crystal Growth." *Geochim Cosmochim Acta*, 66(22), 3943-3954.
- Gavrilescu, M. (2004). "Removal of Heavy Metals from the Environment by Biosorption." *Eng Life Sci*, 4(3), 219-232.
- Goto, M., and Suyama, K. (2000). "Occlusion of Transition Metal Ions by New Adsorbents Synthesized from Plant Polyphenols and Animal Fibrous Proteins." *Appl Biochem Biotechnol*, 84-6, 1021-1038.
- Hettiarachchi, G. M., Scheckel, K. G., Ryan, J. A., Sutton, S. R., and Newville, M. (2006). "Mu-Xanes and Mu-Xrf Investigations of Metal Binding Mechanisms in Biosolids." *Journal of Environmental Quality*, 35(1), 342-351.
- Huang, C. P., Huang, C. P., and Morehart, A. L. (1991). "Proton Competition in Cu(I) Adsorption by Fungal Mycelia." *Water Res*, 25(11), 1365-1375.
- Ishikawa, S., and Suyama, K. (1998). "Recovery and Refining of Au by Gold-Cyanide Ion Biosorption Using Animal Fibrous Proteins." *Appl Biochem Biotechnol*, 70-72, 719-728.
- Ishikawa, S., Suyama, K., Arihara, K., and Itoh, M. (2002). "Uptake and Recovery of Gold Ions from Electroplating Wastes Using Eggshell Membrane." *Bioresour Technol*, 81(3), 201-206.
- Kinniburgh, D. G., and Jackson, M. L. (1981). "Cation Adsorption by Hydrous Metal Oxides and Clay." *Adsorption of Inorganics at Solid-Liquid Interfaces*, M. A. Anderson and A. J. Rubin, eds., Ann Arbor Science, Ann Arbor, Mich.

- Kobayashi, H., Satoh, K., and Sawada, K. (2004). "Adsorption of Divalent Heavy Metal Ions on Calcium Carbonate (Calcite)." *Bunseki Kagaku*, 53(2), 101-107.
- Kontoyannis, C. G., and Vagenas, N. V. (2000). "Calcium Carbonate Phase Analysis Using Xrd and Ft-Raman Spectroscopy." *Analyst*, 125(2), 251-255.
- Kuh, S. E., and Kim, D. S. (2000). "Removal Characteristics of Cadmium Ion by Waste Egg Shell." *Environ Technol*, 21(8), 883-890.
- Lee, S. M., and Davis, A. P. (2001). "Removal of Cu(Ii) and Cd(Ii) from Aqueous Solution by Seafood Processing Waste Sludge." *Water Res*, 35(2), 534-540.
- Martin-Garin, A., Gaudet, J. P., Charlet, L., and Vitart, X. (2002). "A Dynamic Study of the Sorption and the Transport Processes of Cadmium in Calcareous Sandy Soils." *Waste Manage*, 22(2), 201-207.
- Martin-Garin, A., Van Cappellen, P., and Charlet, L. (2003). "Aqueous Cadmium Uptake by Calcite: A Stirred Flow-through Reactor Study." *Geochim Cosmochim Acta*, 67(15), 2763-2774.
- McKay, G. (1996). *Use of Adsorbents for the Removal of Pollutants from Wastewaters*, CRC Press, Boca Raton, Fla.
- Mustafa, S., Nadia, L. H., Rehana, N., Naeem, A., and Samad, H. Y. (1998). "Ligands Sorption Studies on Transition Metal Ion Loaded Amberlite Irc-50." *Langmuir*, 14(9), 2378-2384.
- Perkin-Elmer. (1996). *Analytical Methods for Atomic Absorption Spectroscopy*, Manual part 0303-0152, Release D, Norwalk, Conn.
- Pokrovsky, O. S., and Schott, J. (2002). "Surface Chemistry and Dissolution Kinetics of Divalent Metal Carbonates." *Environ Sci Technol*, 36(3), 426-432.
- Raskin, I., and Ensley, B. D. (2000). *Phytoremediation of Toxic Metals: Using Plants to Clean up the Environment*, John Wiley, New York.
- Rodriguez-Rubio, P., Morillo, E., Madrid, L., Undabeytia, T., and Maqueda, C. (2003). "Retention of Copper by a Calcareous Soil and Its Textural Fractions: Influence of Amendment with Two Agroindustrial Residues." *Eur J Soil Sci*, 54(2), 401-409.
- Rouff, A. A., Elzinga, E. J., Reeder, R. J., and Fisher, N. S. (2004). "X-Ray Absorption Spectroscopic Evidence for the Formation of Pb(Ii) Inner-Sphere Adsorption Complexes and Precipitates at the Calcite-Water Interface." *Environ Sci Technol*, 38(6), 1700-1707.

- Sedlak, D. L., Phinney, J. T., and Bedsworth, W. W. (1997). "Strongly Complexed Cu and Ni in Wastewater Effluents and Surface Runoff." *Environmental Science & Technology*, 31(10), 3010-3016.
- Shahwan, T., Zunbul, B., Tunusoglu, O., and Eroglu, A. E. (2005). "AAS, XRPD, SEM/EDS, and FTIR Characterization of Zn²⁺ Retention by Calcite, Calcite-Kaolinite, and Calcite-Clinoptilolite Minerals." *J Colloid Interf Sci*, 286(2), 471-478.
- Solomon, S. E. (1999). "An Egg Ist Ein Ei, Es Un Huevo, Est Un Oeuf." *Brit Poultry Sci*, 40(1), 5-11.
- Stipp, S. L., and Hochella, M. F. (1992). "Uptake of Cd²⁺ and Other Divalent-Cations by Calcite, Solid-State Diffusion and Solid-Solution Formation." *Abstr Pap Am Chem S*, 203, 178-Geoc.
- Stipp, S. L., Hochella, M. F., Parks, G. A., and Leckie, J. O. (1992). "Cd²⁺ Uptake by Calcite, Solid-State Diffusion, and the Formation of Solid-Solution - Interface Processes Observed with near-Surface Sensitive Techniques (XPS, LEED, and AES)." *Geochim Cosmochim Acta*, 56(5), 1941-1954.
- Stumm, W., and Morgan, J. J. (1996). *Aquatic Chemistry : Chemical Equilibria and Rates in Natural Waters*, 3rd ed., Wiley, New York.
- Suzuki, Y., and Takeuchi, Y. (1994). "Uptake of a Few Divalent Heavy-Metal Ion Species from Their Aqueous-Solutions by Coral Sand Heat-Treated at Various Temperatures." *J Chem Eng Jpn*, 27(2), 165-170.
- U.S. EPA. (1995). *Profile of the Fabricated Metal Products Industry*, Office of Compliance, Office of Enforcement and Compliance Assurance, Washington, D.C.
- USDA. (2004). "2002 Census of Agriculture. 1, Geographic Area Series." U.S. Dept. of Agriculture, National Agricultural Statistics Services, Washington, D.C.
- Van Cappellen, P., Charlet, L., Stumm, W., and Wersin, P. (1993). "A Surface Complexation Model of the Carbonate Mineral-Aqueous Solution Interface." *Geochim Cosmochim Acta*, 57(15), 3505-3518.
- Vandepopuliere, J. M. (1976). "Convert Hatchery Waste into Feedstuff." *Pout Digest*, 35, 247-248.
- Volesky, B. (1990). *Biosorption of Heavy Metals*, CRC Press, Boca Raton, Fla.
- Volesky, B. (2003). *Sorption and Biosorption*, BV Sorbex, St. Lambert, Québec.
- Volesky, B., and Holan, Z. R. (1995). "Biosorption of Heavy-Metals." *Biotechnol Prog*, 11(3), 235-250.

- Wartelle, L. H., and Marshall, W. E. (2001). "Nutshells as Granular Activated Carbons: Physical, Chemical and Adsorptive Properties." *J Chem Technol Biot*, 76(5), 451-455.
- Wase, D. A. J., and Forster, C. F. (1997). *Biosorbents for Metal Ions*, Taylor & Francis, London.
- Zachara, J. M., Cowan, C. E., and Resch, C. T. (1991). "Sorption of Divalent Metals on Calcite." *Geochim Cosmochim Acta*, 55(6), 1549-1562.
- Zachara, J. M., Kittrick, J. A., Dake, L. S., and Harsh, J. B. (1989). "Solubility and Surface Spectroscopy of Zinc Precipitates on Calcite." *Geochim Cosmochim Acta*, 53(1), 9-19.
- Zachara, J. M., Kittrick, J. A., and Harsh, J. B. (1988). "The Mechanism of Zn²⁺ Adsorption on Calcite." *Geochim Cosmochim Acta*, 52(9), 2281-2291.