Published in final edited form as:

Biometals. 2013 October ; 26(5): 755–762. doi:10.1007/s10534-013-9651-1.

Thermodynamic Parameters for Eu(III) Binding to *Datura innoxia* Root Material

Jessica L. Moore[†] and Gary D. Rayson^{*}

Department of Chemistry and Biochemistry, Box 30001 MSC 3C, New Mexico State University, Las Cruces, NM 88003

Abstract

Plants offer the potential for selective removal and sequestration of toxic heavy metals from contaminated soil. Phytoextraction of metal ions involve their transport through the plant's root system and into its shoots and leaves. This study investigates the thermodynamics of Eu(III) ion chemical interactions with *Datura innoxia* plant root materials under solution conditions of pH 4.0 and 5.0. Both changes in enthalpies (ΔH) and entropies (ΔS) of metal binding were elucidated from isotherms collected under varied temperature conditions using regularized regression data analysis and conditional affinity spectra. ΔH values for binding to root materials at pH 4.0 and 5.0 were each calculated to be +30 kJ/mol. Values of ΔS for these same materials were found to be +170 and +153 J/mol K for solution conditions of pH 4.0 and 5.0, respectively. These results suggest binding to the root material to be entropically driven ($\Delta S^\circ > 0$ and $\Delta H > 0$) through possible displacement of waters of solvation.

1.0 Introduction

Cold war activities generated large quantities of hazardous and radioactive waste that resulted in the contamination of large volumes of soil [Sas-Nowosielske, et al., 2008]. One approach to remediation of these areas is phytoextraction, the use of plants to remove toxic metals from soil and water [Nakajime and Sadaguchi, 1990]. A limited understanding of the metal ion phytoextraction chemical interactions presents a barrier to the general implementation of this remediation methodology [Doran, 2009; Igwe and Abia, 2007].

Considerable effort has been made to understand the chemical processes responsible for metal ion binding of to non-viable biomaterials, i.e., biosorption [Diniz and Volesky, 2005; Sawalha, et al., 2008; Drake and Rayson, 1996]. These have involved both direct spectroscopic determinations of metal binding environments [Drake, et al., 1996; Gardea-Torresdey, et al., 2001] and analysis of binding isotherms [Gardea-Torresdey, et al., 2001; Lin, et al., 1996; Drake, et al., 1997; Basha and Jha, 2008; Benhammou, et al., 2007; Babarinde, et al., 2007; Sawalha, et al., 2007; Sawalha et al., 2006]. Many biosorbents are

^{*} garayson@nmsu.edu, Telephone (575) 646-5832, Fax (575) 646-2649.

[†] Present address: Department of Chemistry, University of California at Davis, Davis, CA 95616

Disclaimer

Any opinions, findings, conclusions or recommendations expressed in this paper are those of the authors and do not necessarily reflect the views of the National Science Foundation.

reported to involve oxygen-containing chemical moieties in passive binding of metal ions [Drake and Rayson, 1996; Drake, et al., 1997]. The majority of these binding sites include carboxylates [Gardea-Torresdey, et al., 2001; Lin, et al., 1996; Drake, et al., 1997; Akther, et al., 1996].

Biosorption inherently involves the adsorption of metal ions onto a chemically heterogeneous surface. Such a surface can involve collections of binding sites with varied chemical interactions. These sites can differ in either the chemical functionalities involved or the form of those interaction (e.g., electrostatic attraction or surface complex formation. [Serna, et al., 2012]

When adsorption involves binding to a homogeneous surface where each adsorbate can be treated as an isolated species, the amount bound, q , can be described using the equation derived by Langmuir [Basha and Jha, 2008; Igwe and Abia, 2007],

$$q = KC_{eq} / (1 + KC_{eq}) \quad \text{eq. 1}$$

where C_{eq} is the equilibrium concentration of the adsorbate in solution and K is the corresponding equilibrium constant for the interaction. While biosorbents may appear to approximate this homogeneity assumption with higher concentrations, the presence of multiple binding sites and chemical inactions has been clearly indicated for biosorbents. Such heterogeneity in the binding surface would then suggest the application of the relationship describe by Freundlich with the equation [Tsai, et al., 2005]

$$q = K_f C_{eq}^n \quad \text{eq. 2}$$

where the parameters K_f and n are the Freundlich constant and exponent, respectively, while C_{eq} and q denote similar quantities as described above. Binding isotherms under low concentration conditions may exhibit values of the parameter, n , greater than 1.0.

A combination of the models of Langmuir and Freundlich is found in the model proposed by Sips [Sips, 1948].

$$q = [M(KC_{eq})^\beta] / [1 + (KC_{eq})^\beta] \quad \text{eq. 3}$$

where q represents the amount adsorbed, M the maximum adsorption, and C_{eq} the adsorbate's equilibrium concentration [Aquino, et al., 2003]. K_m represents the equilibrium constant and β is then the Langmuir-Freundlich coefficient [Aquino, et al., 2003]. Because of the presence of three separate parameters, numerical methods are typically required for extraction of M , K , and β .

One interesting point regarding the Sips model is its flexibility. Based on the model's equation, the denominator goes to one at low adsorbate concentrations; which causes the model to reduce to the Freundlich isotherm model [Graces, et al., 2004; Koopal and Vos,

1993]. At high adsorbate concentrations (β approaches unity), however, the model transforms to the Langmuir isotherm model; suggesting monolayer adsorption [Graces, et al., 2004; Koopal and Vos, 1993].

Binding can be described as a continuum function of the conditional affinity constant, K , as $\log K$, using the following equation

$$q = \int K_c C_{eq} / (1 + K_c C_{eq}) f(\log K_c) d \log K_c \quad \text{eq. 4}$$

q is the total material adsorbed with solution concentration, C_{eq} , and continuous variation in conditional affinity constant, K_c , and affinity distribution of $f(\log K_c) = S_i / \Delta \log K_c$, where $\Delta \log K_c = \log K_{c,i+1} - \log K_{c,i}$, the grid spacing. The solution of the inverse of equation 2 yields the density of binding sites, S_i , as a function of $\log K_c$. The solution of this ill-posed problem was first reported in Sip's landmark paper for heterogeneous surfaces [Sips, 1948] and determined using regularized least-squares methods, as described by Chernik, et al., [1995]. Because of the conditional nature of the affinities, the resulting distributions of site densities have been more recently described by Gracés, et al., as conditional affinity spectra (CAS) [Rey-Castro, et al., 2009; Graces, et al., 2006].

Energetic and thermodynamic parameters governing metal ion biosorption have been specifically investigated [Sawalha, et al., 2007; Sawalha, et al., 2006]. Those researchers reported values of ΔG° for the binding of Cd(II), Cr(III), Cr(VI), Pb(II), Zn(II), and Cu(II) to leaves from saltbush (*Atriplex canescens*) at room temperature. They applied both Langmuir and Freundlich binding models to isotherms for each metal species. They reported ΔG° values of less than 7 kJ/mole for each species with Pb(II), Cd(II), and Cr(III) binding indicated as thermodynamically favorable process (i.e., $\Delta G^\circ < 0$). Interestingly, values of $\Delta G^\circ > 0$ were reported for the remaining metal ion species. Their reported binding suggested the additional involvement of other thermodynamically favorable processes.

In the present study, thermodynamic parameters governing Eu(III) binding to root materials from the plant *Datura innoxia* were investigated at pH 4.0 and 5.0. These solution pH conditions were selected because earlier studies [Lin, et al., 1996] indicated favorable binding under these conditions. The metal ion, Eu(III) was selected because of both its chemical similarities to Am(III) and our previous investigations of its biosorption to the heterogeneous surface of cultured cells of the same plant species [Drake and Rayson, 1996; Drake, et al., 1996; Lin, et al., 1996; Drake, et al., 1997; Serna, et al., 2010]. This perennial plant was selected for potential phytoextraction applications because of its 1) tolerance to toxic metals, 2) natural occurrence in arid regions, and 3) native resistance to herbivory [Allison, 1991]. This last attribute can be attributed to the presence of toxic alkaloids (e.g., atropine, hyocine, hysyamine, and scopolamine) in its leaves and stems [Kaushik and Goyal, 2008].

2.0 Experimental Methods

D. innoxia plant materials were collected from wild plants growing on the New Mexico State University campus in Las Cruces, New Mexico. Briefly, *D. innoxia* samples were

segregated by tissue type (root, stem, leaves, flowers, and seed pods) and placed in separate brown paper bags for drying to constant weight at 50–55°C.

Each plant component was then ground separately a fine powder in a kitchen-style blender (Oster, Osterizer). Each material was then sieved and the 100/200 mesh fraction collected and washed with 1.0 M HCl and freeze dried to remove any indigenous contaminant metal ions [Williams and Rayson, 2003]. Because any remediation scheme would involve initial metal ion interactions with the plant roots, only root materials were used in the present study.

A stock solution of 0.10 M Eu (III) was prepared by dissolution of europium oxide (MolyCorp) in a minimum volume of concentrated HNO₃ and diluted with double deionized water (18 MΩ, Millipore, Milli-Q UV Plus). A separate stock solution of 0.10 M 2-N-[morpholino] ethanesulfonic acid (MES) was also prepared by dissolution of the sodium salt (Sigma-Aldrich) in double deionized water. MES was used throughout as a non-complexing reagent to control the ionic strength of all solutions [Good, et al., 1966]. The pH of each solution concentration (i.e., 1.0 to 200. μM) was iteratively adjusted to either 4.0 or 5.0 using concentrated HCl and saturated NaOH. Metal solutions were prepared by dilution of the Eu (III) stock using the MES stock solution. Each final solution was also adjusted to the respective pH.

2.1 Isotherm Preparation

All measurements, including controls, were conducted with five replicates. Binding isotherms were generated at each temperature. Specifically, pH 4.0 samples were thermally equilibrated to conditions of 5, 15, 25, 35, and 45 °C and pH 5.0 samples to 5, 20, and 50°C. A water bath was prepared at each temperature using a constant temperature bath (Fisher, model Versa-Bath). The Eu (III) solutions were placed in 50 mL centrifuge tubes and again thermally equilibrated in the water bath.

Each sample consisted of 30 mg of the washed 100/200 mesh *D. innoxia* tissue material in a 3 mL plastic test tube (Sarstedt). Samples were also equilibrated to each respective temperature. A 2.5 mL aliquot of the appropriate Eu (III) solution was then added to each tube. They were then capped, sealed, and returned to the water bath. This procedure was repeated for each of the five control samples in the absence of the *D. innoxia* sorbent.

All samples were manually agitated in the bath for 20 minutes by inversion of the sealed tubes until metal binding equilibrium was achieved [Serna, et al., 2010]. Although this procedure differed from that previously described [Serna, et al., 2010], the amount of metal bound did not differ significantly from that earlier room temperature work using a Student-t test (at a 95% confidence level) under conditions of 25°C. The resulting binding isotherms are shown in Figure 1A and B for pH 4 and 5, respectively. Because uncertainty was present in the determination of both the equilibrium solution concentration, C_{eq} , and the amount bound, q , error bars have been included for both parameters (Figure 1). Readily apparent is the absence of a “plateau” region for each temperature and pH condition. This indicates the lack of an achieved condition of saturation of the biomaterial’s ability to bind the metal ion.

2.2 ICP-OES Analysis

The concentration of the Eu in each solution (supernatant and control) was determined using inductively coupled plasma – optical emission spectrometry (ICP-OES). Sample preparation required all solutions to be filtered to prevent nebulizer clogging by the plant materials. Syringes (BD 10 mL, Luer-Lok) fitted with nylon filters (20 μm pore size, 15 mm diameter, Minisart SRP) were used to remove any biomaterial. Control samples were similarly processed. The resulting filtrate was transferred to 15 mL tubes. Standards, samples, and controls were then analyzed for Eu(III) content using ICP-OES (381.967 nm, Perkin Elmer, Optima 2100DV). Operational parameters of the spectrometer included gas flows (i.e., plasma, auxiliary, and sample) of 15.0, 0.2, and 0.8 L min^{-1} , respectively, a sample solution flow rate of 1.5 mL min^{-1} , with 1.3 kW applied rf power.

Either a pH 4.0 or pH 5.0 0.10 M MES blank was used for respective sample solutions. Additionally, a midrange standard (5.0 μM Eu (III)) was analyzed between each sample set for quality control purposes. All ICP intensity readings were made in triplicate with a 60 second delay time.

3.0 Results and Discussion

The amount of Eu (III) bound to each plant material, q , in mol/g, was calculated as the difference between the average concentration of the five controls, $\overline{C}_{ctl}$, and the equilibrium supernatant concentration of each sample, C_{eq} . The value was multiplied by the volume of metal solution used (v) and then divided by the mass of plant material, m , according to the equation:

$$q = (\overline{C}_{ctl} - C_{eq})v/m \quad \text{eq. 5}$$

3.1 Thermodynamic Parameters

Regularized regression analysis of each isotherm (Figure 1) yielded each corresponding affinity spectrum [Rey-Castro, et al., 2009]. A program developed by erník et al. [1995], QUASI, was used for data analysis. The operational parameters used in the data analysis included a spectral window of $\log K = -5.0$ to 10.0, grid spacing of 0.07, a regularization parameter of 1, and smoothing of the regularization function [erník et al., 1995].

Figures 2 and 3 show the resulting affinity spectra for metal ion binding at each temperature for the root materials at pH 4 and 5, respectively. Binding-site densities (s , mol/g) are shown as a function of the conditional affinity constant of each site (K_c , presented as $\log K_c$). An conditional affinity constant is computed because of this model's limited ability to account for variations in solution pH or ionic strength [Lin, et al., 1996; erník et al., 1995]. Rather than a few distinct sites, the model assumes the presence of a continuum of sites, with varied affinities, with each independent site exhibiting Langmuir-Freundlick binding behavior (equation 3) [Graces, et al., 2006]. Each computed distribution of sites was then defined by the mean conditional affinity and the computed variance with that collection of binding sites indicated by the width of the resulting peaks.

Conditional affinities (i.e., peak values of K_c) were found to vary generally from approximately $10^{3.1}$ to about $10^{4.5}$ for pH 4.0 and $10^{2.5}$ to $10^{3.4}$ for pH 5.0 (Figures 2 and 3, respectively). These are in general agreement with those reported by Serna, et al. for this same metal species bound to a cultured anther cell biosorbent [18]. Variations with those earlier results arise from differences in the nature of the respective isotherm data. Specifically, their work involved binding isotherms associated with each of the chemically distinct binding environments found on that material while data from the present study describe the total amount of metal ion bound to the material. This is suggested in the asymmetry observed in the affinity distributions (Figures 2 and 3) compared to the Gaussian peaks reported earlier [Serna, et al., 2010].

Earlier studies of metal ion affinity spectra have suggested large apparent affinities to be indicative of surface complex formation [Serna, et al., 2010]. Conversely very small constants were interpreted to suggest more Coulombic attractions of metal cations to a negatively charged biosorbent surface [Sawalha, et al., 2007]. This electrostatic metal-ion binding mechanism can be describe by the general reaction

Where n is the charge on the solvated metal ion, M, and m is the effective charge on at the surface of the biosorbent, B.

Variation in temperature was observed to result in measurable changes in the apparent affinity constants (Figures 2 and 3). Coulombic interactions would be expected to be governed by charge densities of the metal ion and the sorbent surface (n and m, respectively, in equation 6). Under conditions of constant pH and ionic strength, these parameters would be predicted to exhibit temperature independence. Purely electrostatic interactions would be, therefore, not predicted to display significant temperature dependence.

Alternately, formation of surface metal complexes would be predicted to follow the general reaction

Where x indicates the coordination number of the metal (initially occupied by coordinating water molecules) and y is the number of solvated binding moieties at a given site on the biosorbent surface. The apparent affinity constant would reflect this equilibrium condition. This interaction would then be thermodynamically controlled by an associated change in Gibb's free energy, G° , according to the equation

$$\Delta G^\circ = -RT \ln K \quad \text{eq. 8}$$

where R and T are the gas constant and absolute temperature of the system, respectively.

Alternately, the associated G° can be written in terms of changes in enthalpy, H° , and entropy, S° , by the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{eq. 9}$$

Combining equations 8 and 9 yields the familiar expressions

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ \quad \text{eq. 10}$$

or

$$\ln K = -\Delta H^\circ / R (1/T) + \Delta S^\circ / R \quad \text{eq. 11}$$

or

$$\log K = -\Delta H^\circ / (2.303R) \times (1/T) + \Delta S^\circ / (2.303R) \quad \text{eq. 12}$$

The present study involved elucidation of conditional affinity constants, K_c , and did not utilize standard state conditions. Equation 12 can then be rewritten to reflect this.

$$\log K_c = -(\Delta H / (2.303R) \times (1/T) + \Delta S / (2.303R)) \quad \text{eq. 12}$$

Therefore, it is possible to extract values of both H and S for metal ion binding under the ambient conditions of these studies (i.e., ambient pressure of ~660 Torr) to this plant tissue material by plotting $\log K_c$ as a function of $1/T$ for metal binding governed by surface complex formation at each solution pH.

Figure 4 and Table 1 indicate the results of this treatment of the affinity spectra shown in Figures 2 and 3. Affinity constants corresponding to those with maximum site density (i.e., peak maxima) were plotted as a function of each binding temperature, in Kelvin. The corresponding values of H and S have been listed in Table 1 with the corresponding values of G at 298 K (i.e., room temperature). For each solution pH condition, metal ion binding was found to be endothermic, i.e. $H > 0$, with an increase in system entropy, $S > 0$. When typical room temperature conditions are assumed, $T = 25^\circ\text{C}$, the binding process was indicated to be thermodynamically favorable with $G^\circ < 0$. Uncertainties shown in Figure 4 were derived from the widths of corresponding binding distributions shown in Figure 2 and 3 (full widths at half maximum) as an approximation of the variance in the conditional affinities. It should be emphasized that although the temperature range used in the present study was relatively small ($5\text{--}50^\circ\text{C}$) and temperature conditions for pH 5 involved only three values, the presence of a negative slope ($H > 0$) and a positive y-intercept ($S > 0$) shown in Figure 4 are significant in the understanding of the mechanisms of biosorption of Eu^{3+} ions to this material.

Although a positive ΔH for binding is inconsistent with enthalpies of metal ion complexation [Portanova, et al., 2003], association of the metal ion with a negatively charged surface (equation 6) would require removal of one or more waters of solvation, an endothermic process. Such a loss of waters is supported by a positive change in entropy (Table 1). A binding mechanism dominated by electrostatic interactions is consistent with the findings of Serna et al., [2010] for independent binding environments on a biosorbents derived from cultured anther cells from *D. innoxia*. A positive change in enthalpy is also consistent with the temperature dependent binding data shown in Figure 1 where metal ion binding was observed to increase with increased temperature, suggesting endothermic processes.

4.0 Conclusion

The binding observed in this study were determined to be the result of electrostatic attraction between the metal ion and the negatively charged biomaterial surface. This is coupled with removal of waters of solvation from the aqua complex of the Eu^{3+} ion prior to its association with deprotonated negatively charged sites. This results in an endothermic process which is entropically driven.

Acknowledgments

The authors wish to acknowledge the financial support of the National Institutes of Health through the MBRS-RISE program (#R25GM061222) and the National Science Foundation under a NSF Graduate Research Fellowship (JLM).

Literature Cited

- Akthar, MdN, Sastry, KS., Mohan, PM. Mechanism of Metal Ion Biosorption by Fungal Biomass. *BioMetals*. 1996; 9:21–28.
- Allison, C. Cooperative extension Service Circular 531. New Mexico State University; Las Cruces, NM: 1991. Livestock-Poisoning Plants of New Mexico Rangelands.
- Aquino LCL, Miranda EA, Duarte IS, Rosa PTV, Bueno SMA. Adsorption of human immunoglobulin G onto ethacrylate and histidine-linked methacrylate, *Braz. J Chem Eng*. 2003; 20:251–262.
- Babarinde NAA, Oyesiku OO, Dairo OF. Isotherm and Thermodynamic Studies of the Biosorption of Copper (II) by *Erythrodontium barteri*. *Int J Phys Sci*. 2007; 2:300–304.
- Basha S, Jha B. Estimation of Isotherm Parameters for Biosorption of Cd(II) and Pb(II) onto Brown Seaweed, *Lobophora variegata*. *J Chem Eng Data*. 2008; 53:449–455.
- Benhammou A, Yaacoubi A, Nibou L, Tanouti B. Adsorption of metal ions onto Moroccan Stevensite: kinetic and isotherm studies. *J Colloid Interface Sci*. 2005; 282:320–326. [PubMed: 15589536]
- Bieerkens J, Simkiss K. The use of chemical analogues such as Eu/Am in ecotoxicological studies. *Funct Ecol*. 1990; 4:445–447.
- ernik M, Borkovec M, Westall J. Regularized Least-Squares Methods for the Calculation of Discrete and Continuous Affinity Distributions for Heterogeneous Sorbents. *Environ Sci Technol*. 1995; 29:413–425. [PubMed: 22201388]
- Diniz V, Volesky B. Biosorption of La, Eu and Yb using *Sargassum* biomass. *Water Res*. 2005; 39:239–247. [PubMed: 15607182]
- Doran P. Application of Plant Tissue Cultures in Phytoremediation Research: Incentives and Limitations. *Biotechnol Bioeng*. 2009; 103:60–76. [PubMed: 19309741]
- Drake L, Rayson G. Plant-Derived Materials for Metal Ion-Selective Binding and Preconcentration. *Anal Chem*. 1996; 68:22 A–27 A.
- Drake LR, Lin S, Rayson GD. Chemical Modification and Metal Binding Studies of *Datura innoxia*. *Environ Sci Technol*. 1996; 30:110–114.

- Drake LR, Hensman CE, Lin S, Rayson GD, Jackson PJ. Characterization of Metal Ion Binding Sites on *Datura innoxia* by Using Lanthanide Ion Probe Spectroscopy. *Appl Spectrosc*. 1997; 51:1476–1483.
- Gardea-Torresdey JL, Arteaga S, Tiemann KJ, Chinaelli R, Pingatore N, Mackay W. Absorption of Copper(II) by Creosote Bush (*Larrea tridentata*): Use of Atomic and X-ray Absorption Spectroscopy. *Environ Tox Chem*. 2001; 20:2572–2579.
- Gracés JL, Mas F, Puy J. Conditional Equilibrium Constants in Multicomponent Heterogeneous Adsorption: The Conditional Affinity Spectrum. *J Chem Phys*. 2006; 124
- Gracés JL, Mas F, Puy J. Affinity distribution functions in multicomponent heterogeneous adsorption. Analytical inversion of isotherms to obtain affinity spectra. *J Chem Phys*. 2004; 120:9266–9276. [PubMed: 15267863]
- Good E, Winget GD, Winter W, Connolly TN, Izawa S, Singh RMM. Hydrogen Ion Buffers for Biological Research. *Biochemistry*. 1966; 5:467. [PubMed: 5942950]
- Igwe JC, Abia AA. Equilibrium sorption isotherm studies of Cd(II), Pb(II) and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize husk. *Electron J Biotechnol*. 2007; 10:536–548.
- Kaushik P, Goyal P. *In vitro* evaluation of *Datura innoxia* (thorn-apple) for potential antibacterial activity. *Indian J Microbiol*. 2008; 48:353–357. [PubMed: 23100734]
- Koopal LK, Vos CHW. Adsorption on Heterogeneous Surfaces. Calculation of the Adsorption Energy Distribution Function or the Affinity Spectrum. *Lanmuir*. 1993; 9:2593–2605.
- Lehto J. Americium in the Finnish Environment. *Boreal Environ Res*. 2009; 14:427–437.
- Lin S, Drake L, Rayson G. Chemical Modification and Metal Binding Studies of *Datura innoxia*. *Environ Sci Technol*. 1996; 30:110–114.
- Nakajima A, Sakaguchi T. Recovery and Removal of Uranium by Using Plant Wastes. *Biomass*. 1990; 21:55–63.
- Portanova R, Lajunen LH, Tolazzi M, Piispänen J. Critical Evaluation of Stability Constants for α -hydroxycarboxylic acid Complexes with Protons and Metal Ions and the Accompanying Enthalpy Changes Part II. Aliphatic 2-hydroxycarboxylic acids. *Pure Appl Chem*. 2003; 75:495–540.
- Rey-Castro C, Mongin S, Huidobro C, David C, Salvador J, Barces JL, Galceran J, Mas F, Puy J. Effective Affinity Distribution for the Binding of Metal Ions to a Generic Fulvic Acid in Natural Water. *Environ Sci Technol*. 2009; 43:7184–7191. [PubMed: 19848120]
- Sas-Nowosielska A, Kucharski R, Pogrzeba M, Malkowski E. Soil Remediation Scenarios for Heavy Metal Contaminated Soil. Soil Chemical Pollution, risk assessment, remediation and security; proceedings of the NATO Advanced Research Workshop on Soil Pollution. 2008:301–307. Ri.
- Sawalha MF, Peralta-Videa JR, Romero-Gonzalez J, Gardea-Torresdey JL. Biosorption of Cd(II), Cr(III), and Cr(VI) by Saltbush (*Atriplex canescens*) biomass: Thermodynamic and Isotherm Studies. *J Colloid Interface Sci*. 2006; 300:100–104. [PubMed: 16600278]
- Sawalha MF, Peralta-Videa JR, Romero-González; D-DM, Gardea-Torresdey JL. Thermodynamic and Isotherm Studies of the Biosorption of Cu (II), Pb (II), and Zn (II) by Leaves of Saltbush (*Atriplex canescens*). *J Chem Thermodyn*. 2007; 39:488–492.
- Sawalha M, Peralta-Videa J, Duarte-Gardea M, Gardea-Torresdey J. Removal of copper, lead, and zinc from contaminated water by saltbush biomass: Analysis of the optimum binding, stripping, and binding mechanism. *Bioresour Technol*. 2008; 99:4438–4444. [PubMed: 17931861]
- Serna D, Moore J, Rayson G. Site-specific Eu(III) binding affinities to a *Datura innoxia* biosorbent. *J Hazard Mater*. 2010; 173:409–414. [PubMed: 19836885]
- Sips R. On the Structure of a Catalyst Surface. *J Chem Phys*. 1948; 16:490–495.
- Tsai SC, Juang KW, Jan YL. Sorption of cesium on rocks using heterogeneity-based isotherm models. *J Radioanal Nucl Chem*. 2005; 266:101–105.
- Williams PA, Rayson GD. Simultaneous Multi-element Detection of Metal Ions Bound to a *Datura innoxia* Material. *J Hazard Mater*. 2003; 99:277–285. [PubMed: 12758012]

Figure 1.

Metal binding isotherms for Eu(III) bound to *Datura innoxia* root material at (A) pH 4.0 at temperatures of (◆) 5°C, (■) 15°C, (○) 25°C, (▲) 35°C, and (△) 45°C and at (B) pH 5.0 at temperatures of (▲) 5°C, (◆) 20°C, and (■) 50°C. Error bars denote ± 1 standard deviation of five replicates. Points without error bars exhibited uncertainties less than the marker size.

Figure 2.
Conditional affinity spectra for Eu(III) binding to *D. inoxia* root biomaterial at solution pH= 4.0 under temperature conditions of (◆) 5°C, (□) 15°C, (○) 25°C, (▲) 35°C, and (■) 45°C using regularized regression analysis of isotherm data shown in Figure 1A.

Figure 3. Conditional affinity spectra for Eu(III) binding to *D. innoxia* root biomaterial at solution pH= 5.0 under temperature conditions of (■) 5°C, (◆) 20°C, and (▲) 50°C using regularized regression analysis of isotherm data shown in Figure 1B

Figure 4. Thermodynamics of Eu(III) binding to *D. innoxia* root biomaterial based on log K (from QUASI results) and corresponding temperatures for (■) pH 4.0 and (▲) pH 5.0.

Thermodynamic parameters for Eu(III) binding to *D.innoxia* root biosorbents under varied solution pH.

Table 1

Solution pH	Slope	H° (kJ/mol K)	y-intercept	S° (J/mol)	R ²	G° at 25°C (kJ/mol)
4.0	-1560	30	8.9	170	0.770	-21
5.0	-1550	30	8.0	153	0.990	-16