Competitive metal binding to a silicate-immobilized humic material

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Abstract

The investigation of the competitive binding of metal ions to a biogenic material comprised of organic peat immobilized in a polysilicate matrix was undertaken. This material was packed into 5.0 mL bed-volume columns using 40–60 mesh size particles. Two separate mixtures of metal ions were studied by monitoring the solution pH and the concentration of each metal in the effluent as a function of the volume of influent introduced to the material. These mixtures contained either the metal ions Ca^{2+}, Mg^{2+}, and Cu^{2+} or the ions Cu^{2+}, Hg^{2+}, and Pb^{2+}. A general order of binding affinities was determined to be $Mg^{2+} < Ca^{2+} \ll Cu^{2+} < Pb^{2+} < Hg^{2+}$. Comparisons of amounts of metal ions bound and protons released indicated the initial release of two protons for each divalent metal ion bound. However, prolonged exposure of the material to the metal solutions yielded a molar ratio of 1:1. This suggests the involvement of ion exchange sites followed by that of sites using an alternate binding mechanism. The presence of binding sites with varied mechanisms and metal ion affinities was further illustrated through the initial binding and subsequent release of lower affinity metal ions (e.g., Mg^{2+} and Ca^{2+}).
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1. Introduction

The accumulation of environmentally significant metal ions from aqueous solution by a variety of microorganisms including algae, bacteria, fungi and yeast is well documented [1,2]. This phenomenon has initiated the use of natural materials for potential use in metal reclamation and waste remediation. The use of living organisms [3] and the use of non-living (non-viable) organisms have both been applied to this end [4,5]. Living cells have been reported to bind metal ions through surface adsorption and various types of intracellular accumulation or sequestering processes [6]. The death and subsequent microbial decay of the biomaterial after attaining a critical concentration of metal ions significantly hinders its application to the treatment of waste streams or contaminated waters [7]. Alternatively, metal ion binding by non-living cells has been proposed to occur exclusively through surface adsorption, independent of active metabolic processes [8]. Because the preservation of cell growth and the maintenance of metabolic processes under adverse conditions are not required, methods employing non-living biomaterials represent a more viable approach for remediation.

The diversity in applications that the development of a biosorption-based technology offers numerous potential advantages compared to more conventional remediation schemes. Biologically derived materials are potentially less expensive, more efficient, and highly selective compared to conventional materials [9,10]. Additionally, biosorbent materials, unlike commercial resins, often exhibit a lower affinity for relatively innocuous alkaline earth metals prevalent in hard waters. (i.e., calcium and magnesium) [1,8]. Consequently, competition for available sites between these benign metals and toxic metals is thought to be greatly reduced. This results in an overall increase in the effective binding capacity of these biogenic materials. This phenomenon adds to the utility of biomaterials compared to synthetically derived commercial resins.

Unfortunately, biomaterials in their native form frequently suffer from poor mechanical strength, low density, and small particle size [11]. Physical properties such as these can be problematic with regard to the design of process arrangements capable of performing large scale metal extractions using any type of flowing or column-based system. Strategies employed

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to overcome this limitation involve entrapment or "immobilization" of the biomaterial in any one of a number of inert polymer materials. Some advantages of immobilization include: (1) the usage of the biomaterial in fixed column, batch, or fluidized bed reactors; (2) realization of enhanced biomaterial chemical or physical stability; (3) improvement in the metal adsorption (and desorption) characteristics resulting from the creation of rigid pores through cross-linking of the polymers thus promoting better metal loading and elution [12].

A survey of the literature reveals the investigation and evaluation of several immobilization schemes including the use of silica-based [8,13,14], agarose-based [15], formaldehyde-based [16], porous polysulfone [17] and polyacrylamide-based polymers [8,17,18]. In each of these studies, the material exhibited superior properties in terms of mechanical and physical properties and enhanced metal binding capabilities after immobilization. The reported increases in metal binding were determined to be because of improvements in the porosity, chemical inertness, and structural integrity of the biosorbent rather than a result of metal binding to the polymeric material [8]. The objective of this study was to investigate the competitive metal binding properties of a specific immobilized biologically generated material, organic peat [13,14].

The physical and chemical properties of peat have been reported to be dependent in part upon the nature of the plants from which it originated, and the properties of the water in which the plants were growing [19]. There exists considerable speculation and disagreement regarding the mechanism(s) responsible for metal binding to humic materials. In developing models to describe proton and metal binding behavior to these substances, some have emphasized the heterogeneity of sites expected in humic molecules, while others feel the observed acidity is best described by consideration of only the most predominant acid moieties. Ephraim et al. [20], utilizing a physicochemical approach developed by Marinsky and Ephraim [21], described humic substances as a highly complex mixture of non-identical functional groups with pK_a values that span the entire possible range. Furthermore, humic materials were indicated to behave as "ideal" sorbents containing an infinite number of binding sites.

Brown et al. [22] demonstrated the effectiveness of biosolids in removing a variety of inorganic contaminants, including Zn, Cd, and Pb. Eger et al. [23] also utilized batch reactor tests as well as column experiments to determine the ability of sphagnum peat to remove trace metals (Cu, Ni, Co, and Zn) from mining stockpile drainages. The results from these studies concluded that peat could be an effective natural sorbent for various pollutants, but problems concerning low permeability, the leaching of organic matter into the solution being treated, and the dissolution of humic acids in alkali media needed to be addressed [24].

In the present study, materials derived from organic peat have been immobilized within polysilicate matrix to address the limitations of poor mechanical properties and leach rates. The competitive binding of a heavy metal ion (Cu^{2+}) in the presence of benign metal ions (Ca^{2+} and Mg^{2+}) and a group of heavy metal ions (Cu^{2+}, Hg^{2+}, and Pb^{2+}) with differing Lewis acidities was also investigated for this biogenic material.

2. Experimental

The immobilization procedure used throughout this work is based upon the method of Darnall et al. [25] and has been described in detail elsewhere [13,14]. Briefly, this method involves the *in situ* encapsulation of the biomaterial within a polysilicate matrix. The biomaterial used was a fraction of organic peat from a bog in Salida, Colorado (Paul Brinkerhoff, Salida, CO). Fractionation of the raw material was accomplished by drying the material, grinding and subsequent collection of the 100/200 mesh size component. The final immobilized material was gravimetrically determined to contain about 67% organic material (by mass). All materials were equilibrated to the solution conditions (pH, etc.) before each experiment.

The experimental configuration used for these studies has been described elsewhere [14]. Briefly, nitrogen gas purged solutions were drawn through 0.7 cm i.d., columns (bed volume of 5.0 mL) containing the biosorbent material. The pH of the effluent was then recorded and one bed volume of every 20 passing through the column was then collected for subsequent analysis using flame atomic absorption spectroscopy. All conditions were evaluated using three columns of the sorbent operated in parallel.

2.1. Metal selection

These studies were performed using columns containing the immobilized organic peat with influents containing equimolar concentrations of three different metal ions. The metal ions were each selected for their environmental significance, practical utility, and varying Lewis acidity. These studies involved two different three-metal influent solutions. The first solution was an equimolar mixture of Ca^{2+}, Mg^{2+}, and Cu^{2+} (0.157 mM) adjusted to pH 5.0. This particular matrix was chosen to evaluate those chemical functionalities demonstrating hard to intermediate Lewis acidities. The impact of alkaline earth metals on the overall copper(II) binding ability of this material was also investigated. Earlier studies [13,14] determined maximum binding occurred for this material under pH 5 conditions.

The second part of the study examined the competitive binding by this same material of a solution containing Cu^{2+}, Hg^{2+}, and Pb^{2+} (0.050 mM) also adjusted to an initial pH of 5.0. These metal ions were selected to further evaluate and compare the binding characteristics of the immobilized Colorado peat to additional environmentally significant metal ions.

The premise behind these experiments was that hard Lewis acid metal ions will bind to ligands which exhibit hard Lewis basicity (e.g., oxygen-containing functionalities). Similarly, it was assumed soft metal ions would demonstrate greater affinity for those functionalities exhibiting soft Lewis acidities (e.g., those containing nitrogen or sulfur). With the inclusion of the intermediate Cu^{2+} ion to both matrices, the binding exhibited by groups possessing intermediate Lewis acid values should be occupied by these ions. The primary rationale in performing investigations was to enable further evaluation of the binding behavior of the material from which selectivity information can be obtained. Relative binding affinities and capacities data can

Table 1
Experimental conditions (estimated uncertainties)

	Study 1	Study 2
Metals investigated	Ca, Mg, Cu	Cu, Hg, Pb
Influent concentration (mM)	0.157	0.050
Hydraulic flow		
Bed-volume per minute (bvm)	1/6	1/6
mL min^{-1}	0.83	0.83
Biosorbent volume (mL) ($\pm$0.2)	5.0	5.0
Biosorbent mass (g) ($\pm$0.04)	1.58	1.67
Influent pH	5.0	5.0
Total influent volume (L) ($\pm$0.015)	7.6	19.04

Fig. 1. Differential moles bound and released proton to bound metal ratio ($\bigcirc$) obtained from equimolar competitive binding to Ca^{2+} ($\triangle$), Mg^{2+} ($\square$), and Cu^{2+} ($\lozenge$) by immobilized Colorado organic peat. Influent was 0.157 mM of each metal and the pH 5.0. Hydraulic flow through the column was 1/6 bed volumes per minute (0.83 mL min^{-1}).

also be extracted. Combined with the pH behavior, this information can offer additional insight regarding the metal-biosorbent interactions. Table 1 is a summary of the experimental conditions employed for each of the three-metal studies.

Prior to performing the actual competitive binding studies, it was necessary to independently evaluate the binding of each of the respective metals separately by the immobilized Colorado organic peat substrate. Rather than present each of the generated elution profiles, Table 2 lists the experimental conditions and results obtained from those baseline experiments.

3. Results and discussion

Table 2 lists the effective and apparent binding capacities resulting from these independent metal binding experiments. Increased overall binding capacity with decreasing metal Lewis acidity provides insight regarding the chemical functionalities responsible for the observed metal binding prior to breakthrough (effective binding capacity). These data suggest common (or similar) sites to be the same for binding Cu^{2+}, Pb^{2+}, and Hg^{2+}. These data also indicate this material to exhibit some propensity towards binding alkaline earth metals, but evidently not to the same degree as for the transition and heavy metals. What is not clear from these experiments is the affinity of those chemical functionalities present on the peat for these representative
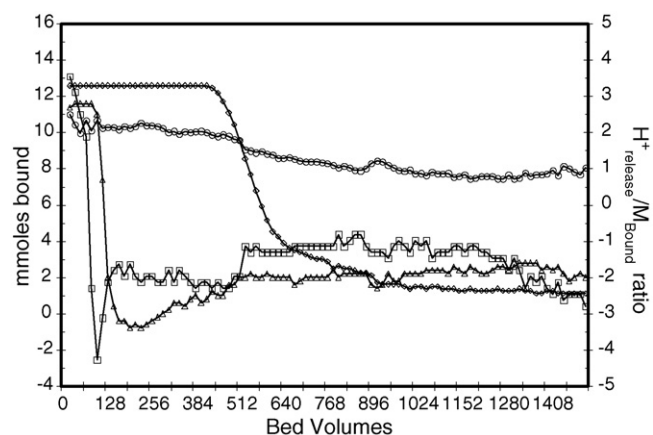
metal ions. Performance of these equimolar competitive binding experiments provides insight regarding the classification and characterization of the respective types of binding sites.

Figs. 1 and 2 show the number of moles of each metal ion bound relative to the influent content for each respective study as a function of bed volumes of influent passed through the material. Readily apparent are the efficiencies of extraction for each metal ion as the chemical functionalities present on the biomaterial become occupied. The ratio of total moles of hydrogen ions released from the immobilized peat to the moles of metal ions bound for each metal ion mixture are also shown.

A typical set of data generated by the first three-metal study is shown in Fig. 1. Each of the three replicates resulted in nearly identical plots. The data for a single column is shown to maximize the internal consistency of the data for their interpretation.

Readily apparent from these data is the presence of significant Cu^{2+} binding. Initial breakthrough of Cu^{2+} occurred after 464 bed volumes (2.320 L). Conversely, inspection of the Ca^{2+} and Mg^{2+} curves indicate only this initial binding by the peat. Break-

Table 2
Results of separate column experiments of metal binding under non-competitive conditions (estimated uncertainties)

|	Ca	Mg	Cu	Hg	Pb
Influent concentration (ppm)	10	10	10	10	10
Hydraulic flow					
bvm	1/6	1/6	1/6	1/6	1/6
mL min^{-1}	0.83	0.83	0.83	0.83	0.83
Biosorbent volume (mL) ($\pm$0.2)	5.0	5.0	5.0	5.0	5.0
Biosorbent mass (g) ($\pm$0.04)	1.33	1.33	1.54	1.87	1.59
Breakthrough volume					
bv ($\pm$5)	160	48	480	1856	1568
L ($\pm$0.015)	0.80	0.24	2.40	9.28	7.84
Breakthrough metal bound (mmol) ($\pm$0.003)	0.200	0.099	0.378	0.463	0.378
Total metal bound (mmol) ($\pm$0.003)	0.230	0.174	0.453	0.693	0.435
Effective binding capacity (mmol g^{-1}) ($\pm$0.01)	0.150	0.074	0.245	0.247	0.238
Apparent binding capacity (mmol g^{-1}) ($\pm$0.01)	0.173	0.131	0.294	0.371	0.274
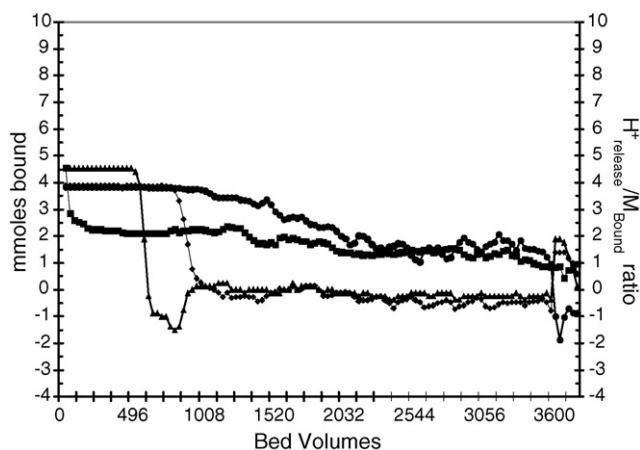
Fig. 2. Differential moles bound and released proton to bound metal ratio (■) obtained from equimolar competitive binding to Cu^{2+} (△), Hg^{2+} (●), and Pb^{2+} (♦) by immobilized Colorado organic peat. Influent was 0.050 mM of each metal and the pH 5.0. Hydraulic flow through the column was 1/6 bed volumes per minute (0.83 mL min^{-1}).

through occurred rapidly in both cases with a subsequent loss of some of those bound calcium and magnesium ions indicated by negative values of the moles bound of each of these metals by the biomass. These negative values are indicative of replacement by Cu^{2+} ions at sites previously bound to Ca^{2+} and Mg^{2+}. As the extraction of these three metals from the influent solution progresses, some binding of Ca^{2+} and Mg^{2+} by the immobilized peat has been observed. The mechanism responsible for this binding is apparently relatively inefficient (as evidenced by the low number of differential moles bound as compared to the influent concentration).

The most significant Ca^{2+} and Mg^{2+} binding is seen to occur after Cu^{2+} breakthrough where competition by these three metals for the lower affinity sites on the peat based biosorbent would be greatest. The released-proton to bound-metal ratio curve indicates an initial value of nearly two but decreases to a value of one proton released per metal ion bound. This suggests the presence of multiple mechanisms of metal ion binding by this biomaterial. An ion exchange type mechanism appears to be responsible for the initial high-affinity binding with the later binding dominated by a coordination-based mechanism.

Similarly, Fig. 2 shows the results of the second equimolar three-metal ion binding study. This study was directed toward investigation of the impact of metal ion Lewis acidity on their simultaneous binding by the immobilized organic peat. Initially, significant binding was observed for all three metal ions by the immobilized peat. The ions Cu^{2+} and Pb^{2+} exhibited breakthrough rather sharply after approximately 624 and 880 bed volumes (3.120 and 4.400 L), respectively, whereas breakthrough of Hg^{2+} occured after approximately 1136 bed-volumes (5.680 L) with a gradual decrease in observed Hg^{2+} binding. This behavior suggests a preponderance of binding sites on the peat with a greater affinity for softer in Lewis acid metal ions. Inspection of the copper binding profile indicates replacement of bound Cu^{2+} by the Pb^{2+} and Hg^{2+}. This is similar to the first equimolar study for the Ca^{2+} and Mg^{2+} metal ions (Fig. 1). Also, as in the first study, the released proton to bound metal ratio revealed an
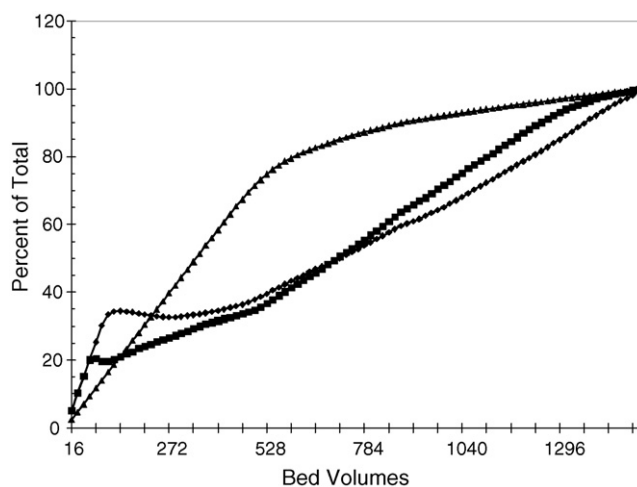
initial value of approximately 2. This then gradually decreased to a value of one at the end of the elution profile. Again, this suggests a dual mechanism of metal binding by this material: an ion exchange process responsible for the high affinity (pre-breakthrough) binding followed by complexation of the metal ions by lower affinity sites.

Figs. 3 and 4 show the respective cumulative binding (normalized to the total amount bound) of each of the metals by the immobilized peat as a function of treated influent volume for each study. Changes in the slope of the individual curves indicate changes in the binding behavior by the biosorbent. A positive slope represents uptake by the biosorbent for a particular metal species whereas a negative slope indicates a release of previously bound metal.

Fig. 3 shows the data displayed in this manner as it pertains to the first of the three-metal equimolar binding studies, where metals of hard to intermediate Lewis acidities. At the onset of
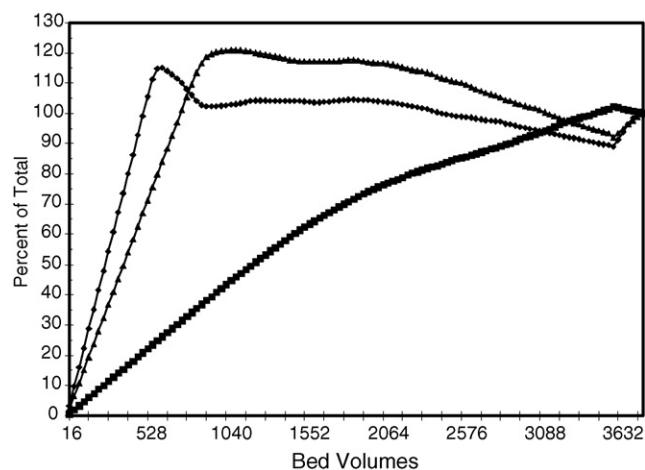

Fig. 3. Cumulative moles bound as percent of total obtained from competitive binding to Ca^{2+} (□), Mg^{2+} (?), and Cu^{2+} (○) by immobilized Colorado organic peat. Influent was 0.157 mM in each metal with the influent pH 5.0. Hydraulic flow through the column was 1/6 bvm (0.83 mL min^{-1}).

Fig. 4. Cumulative moles bound as percent of total obtained from competitive binding to Cu^{2+} (○), Hg^{2+} (●), and Pb^{2+} (■) by immobilized Colorado organic peat. Influent was 0.050 mM in each metal with the influent pH 5.0. Hydraulic flow through the column was 1/6 bvm (0.83 mL min^{-1}).

exposure of the biomaterial to an equimolar solution of Ca^{2+}, Mg^{2+}, and Cu^{2+}, all three cumulative binding curves exhibit a positive slope. This is indicative of the region of the differential binding curve (Fig. 1) where the number density of available binding sites on the peat is sufficient to accommodate each of the metals in the influent. This was independent of their respective Lewis acidities.

As the extraction process was continued, most of the high affinity sites were occupied. It is at this point where competition among the remaining sites would be predicted to intensify and result in changes in the slopes of the individual cumulative binding curves. It is evident from this figure that the initial calcium and magnesium binding occurs as a result of binding to these high affinity sites and is subsequently displaced by copper ions. After breakthrough of Cu^{2+}, an indication of the consumption of the higher affinity sites, all three ions compete for the remaining lower affinity sites. Both the calcium and magnesium curves in this plot exhibit multiple slopes and regions where the slopes are negative, indicating release of previously bound metal. Conversely, prior to copper breakthrough, its corresponding cumulative binding curve displays a non-varying slope. These observations lead to the conclusion that, for this system under study, the majority of available binding sites present on this biomaterial exhibit intermediate Lewis acidity.

Fig. 4 similarly illustrates the respective cumulative binding curves for the case of the equimolar competitive binding of copper, lead, and mercury ions. From the separate binding experiments, roughly the same number of moles of each metal was bound prior to breakthrough. A definite preponderance of those sites participating in the binding of Lewis metals. This is evidenced by negative values in the slopes for the Cu^{2+} and Pb^{2+} cumulative binding (Fig. 4).

Table 3 lists the numerical results obtained from mass balance calculations performed on the flow data obtained from each of the respective equimolar competitive binding experiments. This table lists total millimoles of each metal ion bound, occurring both at breakthrough and at the completion of the experiment (i.e., effective and apparent binding capacities, respectively). Both studies indicated similar trends for increased molar binding as the Lewis acid character was varied from hard to soft for the metals investigated. The only anomaly in this trend occurs for the case of overall calcium binding. A slight decrease was observed

relative to the magnesium binding. Study 1 (Table 3) indicated the possibility of interferences in toxic metal binding by the presence of less innocuous alkaline earth metals. These data suggests that an effective treatment of water containing these metals would only be minimally hindered. This observation is significant for potential use of this biomaterial for the selective removal of toxic metals from hard water.

A slight decrease in the apparent binding capacities for copper and lead compared to their respective effective binding capacities was observed in the second study group of metal ions (Table 3). This indicates a replacement of these ions by metals softer in Lewis acid character as the extraction process progresses. Competition for those soft Lewis acid sites appears to increase near the end of the experiment when competition among these metals for available binding sites is greatest.

Fig. 5 shows the observed molar binding as percent of total occurring at initial metal breakthrough, and at the completion of the experiment, for both equimolar competitive binding studies. Prior to breakthrough, approximately 24% of the total distribution of sites can be attributed to sites intermediate to hard in Lewis acid character. Likewise, for binding occurring in this same region of the binding curve, the data indicate 44% of the pre-breakthrough binding to be attributed to sites soft to intermediate in Lewis acidity.

A grouping of the functional sites responsible for the high affinity binding (that binding which occurs prior to breakthrough) into classifications based upon their Lewis acidity characteristics is thus possible. These groupings have been obtained through phenomenological-based observations and rely on data interpretation. However, these results begin to provide a chemical-based description of the metal binding process. From this understanding, the binding behavior of this biomaterial can be further explained. Fig. 5A illustrates the distribution of functional sites as a percentage of the total into groupings based upon their observed Lewis acidity behavior. These results indicate that >76% of the functional groups responsible for the pre-breakthrough binding by this material have Lewis acid characteristics soft to intermediate in nature. This is corroborated by the inefficient calcium and magnesium binding demonstrated by this material and also from the poor aluminum binding which was observed previously [11].

Table 3
Results of three-metal equimolar competitive metal binding studies (estimated uncertainties)

|	Study 1			Study 2		
	Ca	Mg	Cu	Cu	Hg	Pb
Influent concentration (mM)	0.157	0.157	0.157	0.050	0.050	0.050
Biosorbent mass (g) (± 0.04)	1.58	1.58	1.58	1.67	1.67	1.67
Breakthrough volume (bv) (± 5)	96	48	448	560	1088	816
Breakthrough volume L (± 0.015)	0.48	0.24	2.24	2.8	5.44	4.08
Breakthrough metal bound (mmol) (± 0.003)	0.75	0.38	0.352	0.140	0.272	0.204
Total metal bound (mmol) (± 0.003)	0.210	0.276	0.590	0.129	0.563	0.177
Effective binding capacity (mmol g^{-1}) (± 0.01)	0.048	0.024	0.223	0.084	0.163	0.122
Apparent binding capacity (mmol g^{-1}) (± 0.01)	0.133	0.175	0.373	0.077	0.337	0.106
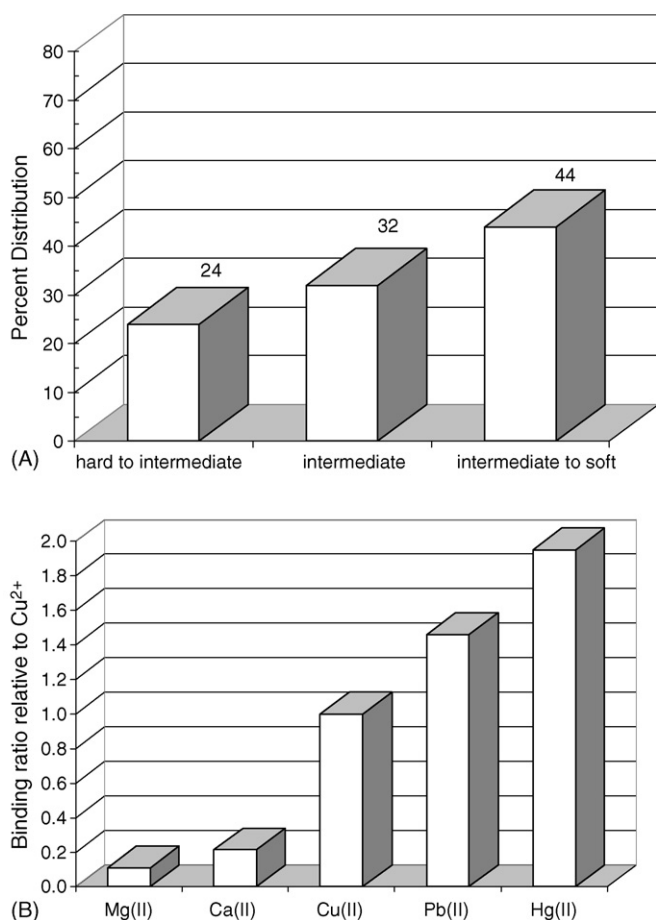
Fig. 5. (A) Estimated grouping based on Lewis acidity of high affinity functional sites found on immobilized Colorado organic peat. (B) Relative binding affinity normalized to Cu^{2+} binding of metals.

Fig. 5B shows graphically the relative binding affinity (normalized to the observed Cu^{2+} binding) by the immobilized Colorado peat to the metals included in these equimolar competitive binding studies. These results indicate binding affinity by the peat to increase according to the order:

$$Mg^{2+} < Ca^{2+} \ll Cu^{2+} < Pb^{2+} < Hg^{2+}$$
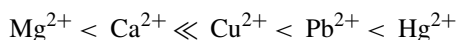
The experiments described have provided additional information pertinent to describing how immobilized Colorado organic peat binds metals from aqueous solutions. The multitude of chemical functionalities known to be contained in this material can be categorized into groups based upon their Lewis acidity behavior useful for predicting which types of metals might be amenable to extraction by this material. The released-proton to bound-metal ratio information has indicated primarily an ion-exchange mechanism to be responsible for the initial high-affinity binding. Also, due to the chemical make-up of the chemical functionalities responsible for the high affinity binding, little interference by waters containing appreciable amounts of calcium and magnesium should be anticipated. Overall these studies have indicated that divalent transition and heavy metals with soft to intermediate Lewis acidity characteristics are the best candidates for extraction from aqueous systems by this material.

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