

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

Electrophilic Aromatic Substitutions of Amine and Sulfonate onto Fine-Grained Activated Carbon for Aqueous-Phase Metal Ion Removal

Wassana Yantasee^a; Yuehe Lin^a; Kentin L. Alford^a; Brad J. Busche^a; Glen E. Fryxell^a; Mark H. Engelhard^a

^a Pacific Northwest National Laboratory, Richland, Washington, USA

Online publication date: 08 July 2010

To cite this Article Yantasee, Wassana , Lin, Yuehe , Alford, Kentin L. , Busche, Brad J. , Fryxell, Glen E. and Engelhard, Mark H.(2004) 'Electrophilic Aromatic Substitutions of Amine and Sulfonate onto Fine-Grained Activated Carbon for Aqueous-Phase Metal Ion Removal', Separation Science and Technology, 39: 14, 3263 — 3279

To link to this Article: DOI: 10.1081/SS-200033140

URL: <http://dx.doi.org/10.1081/SS-200033140>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Electrophilic Aromatic Substitutions of Amine and Sulfonate onto Fine-Grained Activated Carbon for Aqueous-Phase Metal Ion Removal

Wassana Yantasee, Yuehe Lin, Kentin L. Alford,
Brad J. Busche, Glen E. Fryxell,* and Mark H. Engelhard

Pacific Northwest National Laboratory, Richland, Washington, USA

ABSTRACT

Two new materials for adsorption of metal ions from aqueous media have been developed. The organic functional groups amine ($-\text{NH}_2$) and sulfonate ($-\text{SO}_3\text{H}$) were successfully attached to a commercially available fine-grained activated carbon (AC) *via* electrophilic aromatic substitutions. The surface properties of the materials were investigated using FTIR spectroscopy, XPS, BET surface area analysis, gravimetric methods, and elemental analysis. The $\text{NH}_2\text{-AC}$ and $\text{SO}_3\text{H-AC}$ each had a functional group density of 3 mmol/g. Batch metal ion adsorption experiments were conducted to determine metal binding properties of the adsorbent materials. Based on the distribution coefficients (K_d) of

*Correspondence: Glen E. Fryxell, Pacific Northwest National Laboratory, Richland, WA 99352, USA; Fax: 509-375-3856; E-mail: glen.fryxell@pnl.gov.

metal ions tested, the unmodified AC and sulfonated-AC both had an affinity for metal ions in decreasing order of $\text{Nd} > \text{Lu} \approx \text{La} > \text{Pb} > \text{Cu} > \text{Ni} \approx \text{Cd} > \text{Mn} \approx \text{Ca}$, while the amine-AC had an affinity for metal ions in the order of $\text{Cu} \gg \text{Nd} \approx \text{Lu} \approx \text{La} > \text{Pb} > \text{Ni} > \text{Cd} > \text{Mn} \approx \text{Ca}$. With maximum K_d values of 130,000 for amine-AC and 25,000 for sulfonated-AC, compared to a K_d of 2,000 for unmodified AC, the modified activated carbons have a strong potential for use in removing heavy metal ions and lanthanide ions from aqueous wastes.

Key Words: Metal separation; Nanoporous sorbent; Chemically modified carbon.

INTRODUCTION

Separation of metal ions from aqueous solutions represents a significant portion of waste treatment applications in various industrial operations. Using adsorbent materials is one of the most convenient and cost effective ways for large-scale removal of metal ions from aqueous wastes. Metal ion adsorbent materials can be categorized according to whether they are ion exchange resins or chelating resins, but chelating resins have been considered to be more useful for selective separation of metal ions in aqueous streams.^[1]

Immobilization of chelating agents on silica and polymers for selective removal of heavy metal ions from aqueous wastes has been performed for decades, but attaching functional groups to activated carbons has not been widely studied. Activated carbon has many advantages over conventional substrates: it can be engineered to have higher surface areas than silica materials of the same mass, it does not break down or dissolve in basic solution ($\text{pH} > 9$) as do silica materials, it does not shrink or swell with changes in solution pH as do polymers, and it is less expensive than most silica and polymers. Unmodified activated carbon has been studied extensively for removal of metal ions from aqueous wastes,^[2–8] capitalizing on the high surface area, fast adsorption kinetics, and nanoporous structure of activated carbon materials. Nevertheless, metal ion uptake from aqueous solutions is believed to primarily be a function of the quantity and nature of the functional groups on the carbon surface, rather than the surface area and the porosity of the activated carbon.^[9–11]

Activated carbon is obtained from pyrolysis/carbonization of carbonaceous precursors (e.g., coconut shells, bituminous coal, peat) followed by an activation step using air/steam/gases. The resulting material is composed of dehydrated sugars that are fused into a crosslinked, polymeric chain of oxygenated aromatic nuclei, such as phenols, coumarins, and benzofurans. Unmodified activated carbons may contain some functional groups (e.g., carboxyls,

phenols, esters, ketones, and alcohols), formed as a result of the oxidation or activation of the precursor materials under air or steam at high temperature. However, such native functional groups are not engineered for specific metal removal needs and are usually present at modest concentrations, which corresponds to a low metal ion adsorption capacity.

As an alternative to activation using steam/air/gases, the carbon char is often activated by addition of chemicals such as zinc chloride^[12] and phosphoric acid^[8,13] and processing the material at elevated temperatures (400–1000°C). Residual chemicals such as phosphate and zinc are commonly found on chemical activated carbons. Some oxidizing agents, such as nitric acid, hydrogen peroxide, and ammonium peroxydisulfate,^[14,15] have been used to introduce acidic surface oxides (e.g., carboxylic, phenolic, or lactonic groups) on activated carbon, with the reactions occurring at moderate temperatures (25–80°C). Using these oxidizing agents, especially nitric acid, may decrease the surface area and microporosity of the activated carbon.^[15] Some oxygen complexes may be fixed at the entrance of the micropores, resulting in resistance to metal ion diffusion within the micropores.

Metal ion adsorbents have been created by adsorptive immobilization of commercially-available ligands such as organophosphorus extractants,^[16] amine,^[16] thiol-based ligands,^[17] sodium dodecylsulphonate,^[18] sodium diethyldithiocarbamate,^[18,19] and tetrabutyl ammonium iodide^[19] onto activated carbon. Immobilization *via* adsorption has disadvantages because (1) the quantity of the functional group that can be immobilized is limited by the adsorption equilibrium, (2) because activated carbon is highly hydrophobic, the molecules used for the physical adsorption must contain large hydrophobic groups, (3) precipitates can occur on the surface of the activated carbon, thereby reducing the pore volume and effective surface area, and (4) the activated carbon adsorbents obtained by physical adsorption of molecules containing functional groups may degrade over time because the attachment is not done through a strong covalent bonding.

Researchers in the area of composite materials have acknowledged covalent bondings between nucleophiles in the epoxy matrix and the oxygen-containing functional groups on the carbon fibers^[20,21] or between the nucleophiles (i.e., amine) and the vinylic C=C bonds on the carbon fibers.^[22] Pretreatment of carbon surfaces with functional groups, such as azo and amino groups, has been done to improve the adsorption of polymers.^[22,23] A similar concept may be used in chemical modifications of activated carbon surfaces to enhance the adsorption of metal ions. Alves and coworkers^[24] has anchored organic molecules with amine groups and with chloride leaving groups onto activated carbons, but the process requires pre-treatment of the activated carbon to increase the quantity of specific surface carbon groups (e.g., hydroxyl carbon groups, acid chlorides) in order for the anchoring of organic molecules to succeed.

At the Pacific Northwest National Laboratory (PNNL), we have successfully attached various organic functional groups on activated carbon *via* electrophilic aromatic substitutions, using standard chemistry for sulfonation, nitration, amidation, chloromethylation, phosphorylation, sulfenylation, etc. Such synthesis methods allow the attachments of ligands onto activated carbon through very strong covalent bonding, are relatively easy, do not require significant pretreatment of the activated carbon, and do not involve high temperatures. This chemistry exploits what we learned through our studies of high efficiency silica-based sorbent materials self-assembled monolayers on mesoporous supports (SAMMS) to give high affinity and selectivity for lanthanides, actinides, heavy metal ions, and oxometallate anions.^[25–29] For SAMMS, functionalization of the silica surface requires the addition of an anchor or a tether, to which the functional moiety can attach. In electrophilic aromatic substitutions of activated carbons, the desired ligand is introduced directly to the carbon backbone, without the need for an anchor and tether, making this approach highly economic atomically. Electrophilic aromatic substitution may lack the dense coverage that SAMMS achieves through self-assembly, but does have advantages in terms of direct ligand incorporation and lack of an anchor/tether diluent. A typical functional group density of 2–4 mmol/g can be obtained on activated carbons, compared to 1–4 mmol/g on SAMMS.

This paper describes a new class of adsorbent materials resulting from electrophilic aromatic substitutions of amine and sulfonate functional groups on activated carbon. The surface functional groups of the materials are investigated using FTIR spectroscopy, XPS, BET surface area analysis, and gravimetric methods. The metal binding properties of the materials are measured as a function of pH. The relative K_d values of the metal ions are used to obtain the selectivity sequence of metal ions. The most successful ligands will be chosen for further study as potential metal ion adsorbent materials.

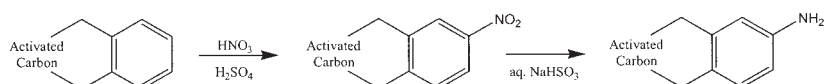
EXPERIMENTAL

Materials

The activated carbon used in this study was Darco[®] KB-B (Aldrich Co.) in a wet powder form. This activated carbon was manufactured by phosphoric activation, followed by steam oxidation of wood chips. It typically has a polydisperse pore structure in which a small amount of micropores (<20 Å) are found together with large amount of mesoporous pores (~40 Å), and essentially all pores are smaller than 200 Å.

Synthesis of Amine-Activated Carbon (NH₂-AC)

Synthesis of the amine-functionalized activated carbon was a two-step process as follows:

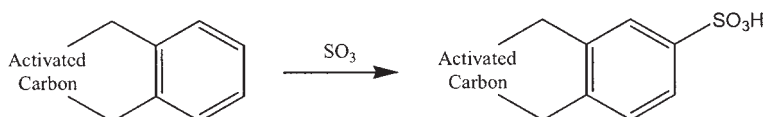


The first step involves an electrophilic substitution resulting in the nitration of activated carbon. At 0°C (ice-bath), 50 mL of concentrated (18 M) sulfuric acid (H₂SO₄) was added slowly to 50 mL of concentrated (15.7 M) nitric acid (HNO₃). Then, an 8.97 g quantity of as-received activated carbon was slowly added to the acid mixture and stirred for 50 minutes. The mixture was filtered and the filtered solids were washed with deionized (DI) water and subsequently isopropanol. The solids were then air-dried at room temperature. The resulting product from this first step was a nitroaromatic activated carbon.

The second step is the conversion of nitroarene to aniline in a procedure adapted from Redemann & Redemann.^[30] A 5.05 g quantity of treated activated carbon equivalent to 0.0476 mol of NO₂⁻, 50 mL of water (2.78 mol), 20 mL of 15 N ammonium hydroxide (0.30 mol), and a stir bar were placed in a 250 mL round bottom flask and stirred for 10 minutes. A 28 g (0.16 mol) quantity of sodium hydrosulfite (Na₂S₂O₄) was added to this solution slowly and allowed to stir overnight at room temperature. A reflux condenser was fitted on the flask and water-cooled to avoid solvent evaporation due to the increase in solution temperature. A 20 mL volume of 17.5 M glacial acetic acid (0.35 mol) was diluted in 100 mL of water and was then added to the solution and stirred for 5 hours at reflux (100°C). The solution was then cooled to room temperature, filtered, washed with copious amount of DI water, followed by an isopropanol wash, and finally air-dried at room temperature. The final product is amine-activated carbon (NH₂-AC).

Synthesis of Sulfonated-Activated Carbon (SO₃H-AC)

The sulfonation of dry activated carbon was performed using sulfur trioxide (SO₃) as follows:



Approximately 1 g of as-received activated carbon was dried in a vacuum oven at 85°C for 48 hours to remove water in the sample. The dried sample was placed in a Tupperware[®] container along with approximately 0.5 g of solid SO₃. The container was closed for 48 hours. The sample was then washed with DI water and dried under vacuum. The resulting product was sulfonated-activated carbon (SO₃H-AC).

Material Characterizations

X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, BET surface area analysis, and gravimetric methods were used to characterize the properties of the adsorbent material. XPS measurements were made with a Physical Electronics Quantum 2000 Scanning ESCA Microprobe (Physical Electronics, Inc., MN) which used a focused monochromatic Al K α X-ray (1486.7 eV) source for excitation and a spherical section analyzer. FTIR spectroscopy was used to qualitatively determine the functional groups on the unmodified and the functionalized activated carbons. The FTIR spectra were obtained by collecting 200 scans for a wavelength range of 4000–400 cm⁻¹ on a Nicolet Magna-IR 860 spectrometer (Thermo Nicolet, WI). Gravimetric measurements of the weight gain or weight loss after the synthesis of NH₂-AC and SO₃H-AC were correlated to functional group density (in mmol of functional groups per gram dry-weight) of material. An Autosorb-6B BET surface area analyzer (Quantachrome Corp., FL) was used to determine the surface area and pore size of solid materials by nitrogen adsorption at 77 K.

Metal Ion Binding Properties

The pH-dependant adsorption isotherms of metal ions on as-received activated carbon (AC) and NH₂-AC were measured in batch experiments. The experimental conditions are summarized in Table 1. A 0.05 g quantity of activated carbon and a 10 mL volume (a solution to solids ratio of 200) of a diluted multi-component metal ion solution were shaken in a polyethylene bottle at a speed of 200 rpm at room temperature for a total contact time of 2 hours. Each metal ion, including Cd²⁺, Cu²⁺, Mn²⁺, Pb²⁺, Ni²⁺, La³⁺, Lu³⁺, Nd³⁺, and Ca²⁺, had an equimolar (0.1 mmol/L) initial concentration. To maintain essentially constant ionic strength and pH, the multi-component metal ion solution was prepared by diluting the stock solutions (comprised of 10,000 mg/L of each metal ion in a 1–4% HNO₃ solution) with a diluent containing 0.05 M NaNO₃ (for pH 2) or 0.05 M sodium acetate (CH₃CO₂Na) for (pH 3–6).

Table 1. Typical experimental conditions for batch competitive adsorption isotherms.

Conditions	Values
Mass of AC, NH ₂ -AC, or SO ₃ H-AC m_s , (g)	0.05
Volume of metal ion solution V , (mL)	10.0
Initial conc. of each metal ion $C_{i,o}$, (mmol/L)	0.1
Solvent solution (pH = 2)	0.05 M NaNO ₃
Solvent solution (pH > 2)	0.05 M CH ₃ CO ₂ Na
pH (held constant in each batch)	1.8–5.7
Contact time (h)	2
Mixing speed (rpm)	200
Temperature (°C)	25

The solution pH was then adjusted to a nominal pH of 2, 3, 4, or 6 by adding 0.1 M HNO₃ solution and/or 0.1 M NaOH solution. The pH was controlled to less than 6 to prevent hydroxide precipitation of metal ions. The pH values of solution before and after each batch experiment were measured. After the batch experiments, the metal-loaded AC material was filtered through a 0.2 micron Nylon filter in a polypropylene housing. Both initial and final solutions (before and after the batch experiment) were analyzed by ICP-OES (Perkin Elmer, model Optima 3000 DV). The percent removal is given by the percent change of metal ion concentration in solution before and after adding the adsorbent. The adsorption capacity of each metal ion, Q_i , is the mmol of metal ion loaded per gram (dry-weight) of adsorbent and is calculated as follows:

$$Q_i = \frac{(C_{i,o} - C_{i,f})V}{m_s} \quad (1)$$

where $C_{i,o}$ and $C_{i,f}$ are the initial and final concentrations of each metal ion in solution (mg/L), V is the solution volume (mL), and m_s is the mass of AC (g).

RESULTS AND DISCUSSION

Material Properties

Table 2 shows the chemical and physical properties of the unmodified AC (Darco KB-B), the SO₃H-AC, the intermediate NO₂-AC, and the final product NH₂-AC.

Table 2. Physical and chemical properties of materials.

Parameters	AC	SO ₃ H-AC	NO ₂ -AC	NH ₂ -AC
Function groups	–COOH, –OH	–SO ₃ H	–NO ₂	–NH ₂
Mass increase/decrease (%)	—	+26%	+14%	–7.9%
Functional group content (mmol/g)	—	3.2	3.0	2.6
Moisture content	27.24%	10.51%	—	18.02%
Surface area (m ² /g)	1587	1185	881	820
Particle size (μm)	149	—	—	—
Primary pore diameter (nm)	3.8	3.8	3.8	3.8

Gravimetric Method and Elemental Analysis

The functional group content was determined from gravimetric methods. For the NH₂-AC, a 14% weight gain after –NO₂ substitution onto the activated carbon was correlated to 3.0 mmol –NO₂ per gram of AC. After the reduction of –NO₂ to –NH₂, a 7.9% weight loss was correlated to the conversion of about 3 mmol of –NO₂ to –NH₂ per gram of AC. Almost a hundred percent conversion from –NO₂ to –NH₂ was also confirmed by the elemental analyses of O in the NO₂-AC and H in the NH₂-AC by an independent company (Galbraith Laboratories, Inc., Knoxville, TN). After the functionalization with –SO₃H, a 26% weight gain on the material was correlated to 3.2 mmol –SO₃H per gram of AC.

BET Analysis

The BET analysis showed a decrease in surface area density from 1587 m²/g to 1185 m²/g and 820 m²/g after the functionalizations with –SO₃H and –NH₂, respectively. The decrease was partly due to the weight gain of the functionalized materials. The BET analysis also showed that the primary pore diameter before and after the functionalizations was unchanged, and the median pore size remained constant at 3.8 nm.

FTIR

The FTIR spectra (not shown) indicated that the Darco[®] KB-B activated carbon contained hydroxyls (3428 cm^{–1}),^[31] carboxylic acids (1700 cm^{–1}),^[31] C=C stretches of the aromatic rings (1600–1580 cm^{–1}),^[31] and the C–O stretches (1300–1000 cm^{–1}) of perhaps acids, alcohols, phenols, ethers, and

esters.^[31–33] The intensity of aromatic and aliphatic structure bands decreased significantly after the substitution of $-\text{SO}_3\text{H}$ and the $\text{S}=\text{O}$ stretch was seen at approximately 1200 cm^{-1} ^[31] on $\text{SO}_3\text{H-AC}$. After the reduction reaction of $\text{NO}_2\text{-AC}$, the FTIR showed the disappearance of N-O stretches at 1340 cm^{-1} and 1534 cm^{-1} ^[32] and the appearance of the N-H stretch at 3440 cm^{-1} .^[31]

XPS

Figure 1 shows XPS spectra of the unmodified Darco[®] KB-B (AC), the $\text{SO}_3\text{H-AC}$, and the $\text{NH}_2\text{-AC}$. The XPS spectrum of the AC shows the carbon peak C1s , (284.6 eV), the oxygen peak (O1s , 533.4 eV), as well as the impurity phosphorous peak (P2p , 133.6 eV). The XPS spectrum of $\text{NH}_2\text{-AC}$ clearly shows the nitrogen peak N1s , (399.5 eV), whereas that of $\text{SO}_3\text{H-AC}$ clearly shows the sulfur peaks (S2p , 168.4 eV). Standard atomic percents (assuming uniform distribution) are as follows: for AC, $\text{C1s} = 92.8$, $\text{O1s} = 7.1$, and $\text{P2p} = 0.2$; for $\text{NH}_2\text{-AC}$, $\text{C1s} = 78.8$, $\text{N1s} = 4.3$, $\text{O1s} = 15.9$, $\text{Na1s} = 0.4$, and $\text{S2p} = 0.6$; $\text{SO}_3\text{H-AC}$, $\text{C1s} = 85.2$, $\text{O1s} = 13.5$, and $\text{S2p} = 1.4$. Monoatomic overlayer calculations,^[34] suggest a 34 atomic percent overlayer coverage of nitrogen on the $\text{NH}_2\text{-AC}$ and an 11.6 atomic percent overlayer coverage of

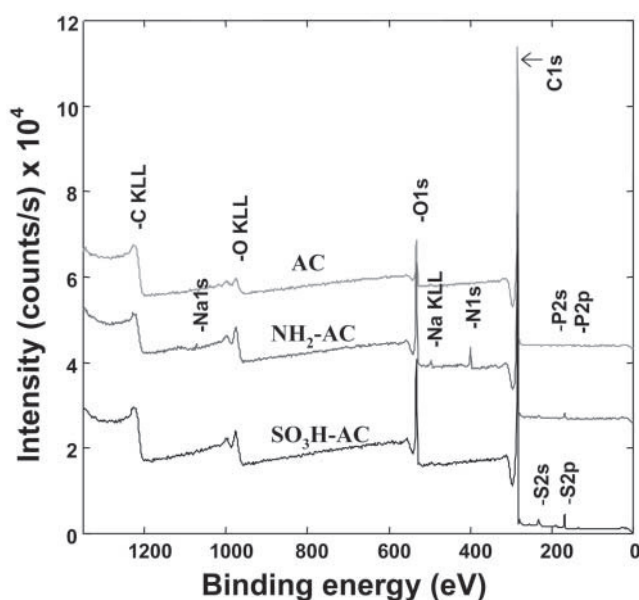


Figure 1. XPS spectra of unmodified Darco[®] KB-B AC, $\text{SO}_3\text{H-AC}$, and $\text{NH}_2\text{-AC}$.

sulfur on the SO₃H-AC. Since both of these numbers are significantly below full monolayer coverage, this supports the conclusion that the functionality is distributed throughout the carbon matrix and not clustered together (as would be expected since both the NO₂ and SO₃H groups are ring deactivators).

Metal Ion Binding Properties

The metal binding properties were measured as a function of pH using multi-component metal ions with equimolar concentrations.

pH Dependency of Metal Ion Binding

The pH of a solution is an important factor affecting a ligand's binding affinity to a given metal ion. The ability of a ligand to remove a metal ion depends not only on the pK_a of the ligands and the stability constant of the metal-ligand complex, but also on the pH of the solution.^[35] Figures 2a–2c

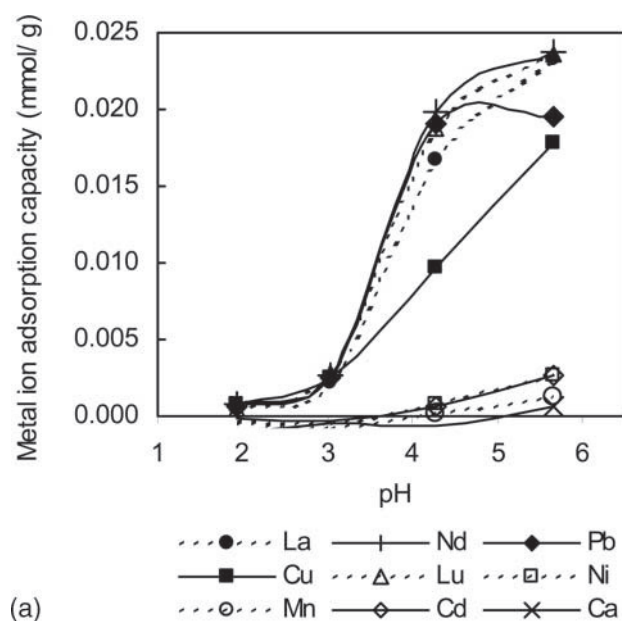
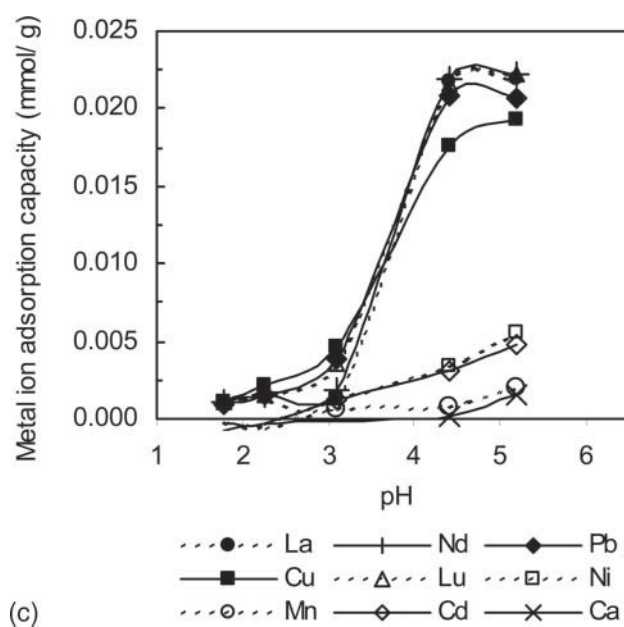
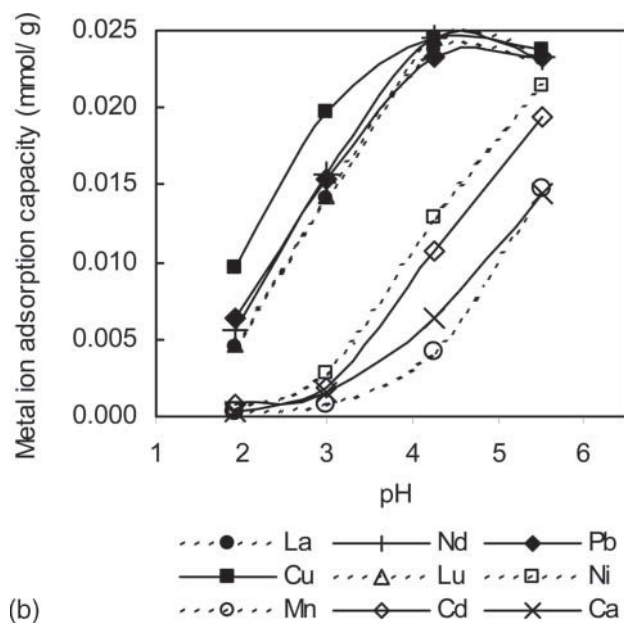


Figure 2. The metal ion adsorption capacity as a function of solution pH on (a) unmodified AC, (b) NH₂-AC, and (c) SO₃H-AC, C_{i,0} = 0.1 mmol/L.

(continued)

*Figure 2.* Continued.

show the metal ion adsorption capacities as a function of final solution pH on the unmodified AC, NH₂-AC, and SO₃H-AC, respectively. The adsorption of metal ions on these materials behaved in the same fashion: adsorption increased as the pH increased from 1.8 to 5.7 (for AC), 5.5 (for NH₂-AC) or 5.2 (for SO₃H-AC), which appeared to be the optimal pH for all metal ion removal. Each metal ion showed a different sensitivity to pH conditions. In general, the three materials preferably adsorbed Nd, Lu, La, Pb, and Cu more than they did Ca, Cd, Mn, and Ni. At pH below 3, only NH₂-AC was able to adsorb Ca, Cd, Mn, and Ni. Above pH 4.5, over 80% removal of Nd, Lu, La, Pb, and Cu was obtained on all materials. The % removals of metal ions on different adsorbents at the optimum pH are summarized in Table 3.

Comparative Performance of Unmodified AC, SO₃H-AC, and NH₂-AC

Figure 3 shows the logarithm of the distribution coefficients (K_d) of metal ions on the unmodified AC, SO₃H-AC, and NH₂-AC, plotted against metal ions with increasing atomic numbers. The distribution coefficient of each metal ion ($K_{d,i}$) is mass-weighted partition coefficient of the metal ion between the solid phase and solution phase and is given by:

$$K_{d,i} = \frac{(C_{i,o} - C_{i,f})}{C_{i,f}} \frac{V}{m_s} \quad (2)$$

In the experiment, metal ions were added in solution at equimolar concentrations, and the solution to solids ratio, ionic strength, and solution pH were

Table 3. Percent metal ion removals on different adsorbents at optimal pH conditions.

Metal ion	% Metal Ion Removal		
	AC (pH5.67)	NH ₂ -AC (PH 5.53)	SO ₃ -AC (pH 5.19)
Ca	2.10	61.03	7.15
Mn	4.45	61.01	8.92
Ni	9.92	90.03	24.52
Cu	65.50	99.82	86.01
Cd	9.88	81.63	21.17
Pb	71.72	98.11	91.71
La	86.55	99.32	98.43
Nd	87.89	99.32	99.07
Lu	86.59	99.38	98.14

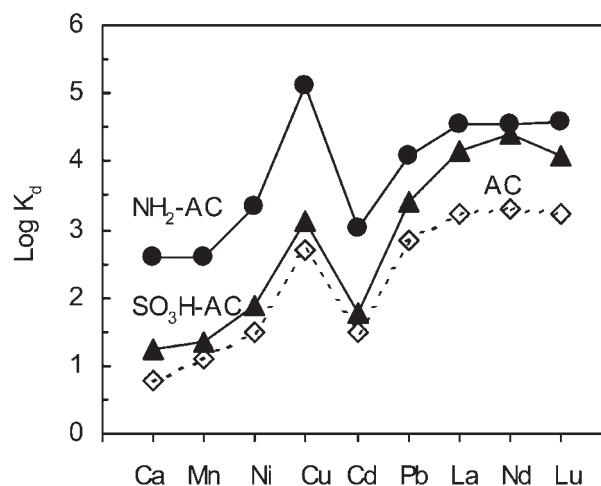


Figure 3. The logarithm of the distribution coefficients ($\log K_d$), plotted against metal ions with increasing atomic number, on AC (pH 5.67), NH₂-AC (pH 5.53), and SO₃H-AC pH (5.19), $C_{i,0} = 0.1$ mmol/L.

kept constant. Therefore, the K_d values reflect the stability of a metal-ligand complex at a particular pH. The higher the K_d value, the more stable the metal-ligand complex is, as well as the more effective of the adsorbent material is in sequestering the metal ion in dilute conditions.

Based on the K_d values at neutral pH (Figure 3), all metal ions studied exhibited a similar affinity toward the adsorbent materials in the decreasing order as follows:

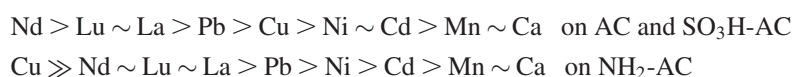


The residual functional groups of an activated carbon prepared by high temperature, aerobic, phosphoric acid activation of wood are likely to be carboxylic acids, phenolic acids, and phosphonic acids.^[36] On the unmodified AC, the K_d values were ranging from 6 for Ca to 1970 for Nd. Amines are known to be versatile ligands and when attached to the activated carbon increased the ligand strength of the surface, thereby increasing the affinity of the sorbent material for metal ions. On NH₂-AC, the K_d values were ranging from 380 for Ca to 134,500 for Cu. A ligand such as $-\text{SO}_3\text{H}$ may also function as an acid in combining with a metal atom by the replacement of hydrogen ions. The largest drop in solution pH was noticed after $-\text{SO}_3\text{H}$ combined with metal ions and released hydrogen ions into the solution. On SO₃-AC, the K_d values were ranging from 17 for Ca to 25,300 for Nd).

Selectivity Sequences of Metal Ions

The selectivity of a sorbent material toward different metal ions generally depends on many factors: the oxidation state of the metal ion, the geometry of the adsorption surface, the physicochemical properties of the functional groups incorporated on the surface, the stereochemistry of the ligand, size of the chelation cavity, and hardness/softness of the metal ion and ligand field.^[1] When summed together, these factors make prediction of metal ion selectivity of the final sorbent material questionable and of limited accuracy, emphasizing the need to determine these values experimentally. Selectivity information is important for designing effective separation processes for removal of metal ions from aqueous solutions.

Based on the K_d values showed in Figure 3, the selectivity sequences on different materials were as follows:



For all divalent metal ions in this study, with the exception of Cd, the stability of metal-ligand complexes (K_d) increased with increasing atomic number of the metal ions. There was little selectivity among trivalent lanthanide ions. The high K_d values also demonstrate that the $\text{NH}_2\text{-AC}$ and $\text{SO}_3\text{H-AC}$ were more selective to these metal ions than sodium ions, which were present in the solutions at five hundred times higher concentration than the metal ions. The difference in the selectivity sequences can be explained in part by Pearson's hard-soft acid-base theory.^[37] Sulfonate is a hard ligand and has a high binding affinity for hard Lewis acids like the lanthanide cations, whereas an aniline nitrogen atom is somewhat softer, preferring to undergo reaction with softer cations like Cu.

CONCLUSIONS

The amine- and sulfonated-activated carbons are superior over the unmodified activated carbon in sequestering metal ions from aqueous solutions in the pH range of 1.8 to 5.7. All adsorbent materials worked best at higher pH, but $\text{NH}_2\text{-AC}$ also worked satisfactory below pH 3. The amine-activated carbon has a potential use as an absorbent material for removing heavy metal ions, especially Pb, Cu, Ni, and Cd, from aqueous wastes with excess alkaline and alkaline earth metal ions. The sulfonated-activated carbon has a potential use for removal of lanthanide ions, but the presence of Pb^{2+} and Cu^{2+} at much higher concentrations than lanthanide ions must be considered. Better ligands for binding

lanthanide ions, such as carbamoylphosphine oxide (CMPO) analog ligands, which were proven successful on SAMMS^[27], are being investigated on activated carbon. The adsorption equilibrium and kinetics of cations on amine- and CMPO analog-activated carbon will be reported in due course.

ACKNOWLEDGMENTS

This work was supported by SERDP project CS-1267 and a laboratory directed research and development program at the Pacific Northwest National Laboratory (PNNL). PNNL is operated by Battelle Memorial Institute for the U.S. Department of Energy (DOE). The work was partially performed at the Environmental Molecular Sciences Laboratory, a national scientific user facility located at PNNL and sponsored by the U.S. DOE's Office of Biological and Environmental Research. The authors thank Christian D. Johnson for reviewing the manuscript and Todd R. Hart for the ICP instrumentation.

REFERENCES

1. Tavlarides, L.T.; Lee, J.S. *Ion Exchange and Solvent Extraction; A Series of Advances*; Marcel Dekker: New York, 2001; Vol. 14, 178.
2. Seco, A.; Marzal, P.; Gabaldon, C. Adsorption of heavy metals from aqueous solutions onto activated carbon in single Cu and Ni systems and in binary Cu-Ni, Cu-Cd and Cu-Zn systems. *J. Chem. Tech. Biotechnol.* **1997**, *68* (1), 23–30.
3. Ferro-Garcia, M.A.; Rivera-Utrilla, J.; Rodriguez-Gordillo, J.; Bautista-Toledo, I. Adsorption of zinc, cadmium, and copper on activated carbons obtained from agricultural by-products. *Carbon* **1988**, *26* (3), 363–373.
4. Corapcioglu, M.O.; Huang, C.P. The adsorption of heavy-metals onto hydrous activated carbon. *Water Res.* **1987**, *21* (9), 1031–1044.
5. Reed, B.E.; Arunachalam, S. Use of granular activated carbon columns for lead removal. *J. Environ. Eng-ASCE*. **1994**, *120* (2), 416–436.
6. Reed, B.E.; Matsumoto, M.R. Modeling cadmium adsorption by activated carbon using the Langmuir and Freundlich isotherm expressions. *Sep. Sci. Technol.* **1993**, *28* (13–14), 2179–2195.
7. McKay, G.; Bino, M.J. Adsorption of pollutants onto activated carbon in fixed-beds. *J. Chem. Technol. Biotechnol.* **1987**, *37* (2), 81–93.
8. Puziy, A.M.; Poddubnaya, O.I.; Martinez-Alonso, A.; Suárez-García, Tascón, J.M.D. Synthetic carbon activated with phosphoric acid, I. surface chemistry and ion binding properties. *Carbon* **2002**, *40*, 1493–1505.

9. Bansal, R.C.; Donnet, J.B.; Stoeckli, F. *Active Carbon*; Marcel Dekker: New York, 1988.
10. Solar, J.M.; Leon, Y.; Leon, C.A.; Osseo-Assare, K.; Radovic, L.R. On the importance of the electrokinetic properties of carbons for their use as catalyst supports. *Carbon* **1990**, *28* (2–3), 369–375.
11. Leon, Y.; Leon, C.A.; Radovic, L.R. *Chemistry and Physics of Carbon*; Thrower, P.A., Ed.; Marcel Dekker: New York, 1994; Vol. 24, 213.
12. Kailappan, R.; Gothandapani, L.; Viswanathan, R. Production of activated carbon from prosopis (*Prosopis juliflora*). *Biores. Technol.* **2000**, *75* (3), 241–243.
13. Toles, C.A.; Marshall, W.E. Copper ion removal by almond shell carbons and commercial carbons: Batch and column studies. *Sep. Sci. Technol.* **2002**, *37* (10), 2369–2383.
14. Pradhan, B.K.; Sandle, N.K. Effect of different oxidizing agent treatments on the surface properties of activated carbons. *Carbon* **1999**, *37* (8), 1323–1332.
15. Moreno-Castilla, C.; Ferro-Garcia, M.A.; Joly, J.P.; Bautista-Toledo, I.; Carrasco-Marin, F.; Rivera-Utrilla, J. Activated carbon surface modifications by nitric-acid, hydrogen-peroxide, and ammonium peroxydisulfate treatments. *Langmuir* **1995**, *11* (11), 4386–4392.
16. Kasaini, H.; Goto, M.; Furusaki, S. Adsorption performance of activated carbon pellets immobilized with organophosphorus extractants and an amine: A case study for the separation of Pt(IV), Pd(II), and Rh(III) ions in chloride media. *Sep. Sci. Technol.* **2001**, *36* (13), 2845–2861.
17. Miller, T.C.; Holcombe, J.A. Characterization of metal ion-exchange on modified surfaces of porous carbon. *Anal. Chim. Acta.* **2002**, *455*, 233–244.
18. Monser, L.; Amor, M.B.; Ksibi, M. Purification of wet phosphoric acid using modified activated carbon. *Chem. Eng. Proc.* **1999**, *38*, 267–271.
19. Monser, L.; Adhoum, N. Modified activated carbon for the removal of copper, zinc, chromium and cyanide from waste water, *Sep. Puri. Technol.* **2002**, *26*, 137–146.
20. Fitzer, E.; Geigl, K.H.; Huttner, W.; Weiss, R. Chemical interactions between the carbon-fiber surface and epoxy-resins. *Carbon* **1980**, *18* (6), 389–393.
21. Barbier, B.; Pinson, J.; Desarmot, G.; Sanchez, M. Electrochemical bonding of amines to carbon-fiber surfaces toward improved carbon-epoxy composites. *J. Electrochem. Soc.* **1990**, *137* (6), 1757–1764.
22. Buttry, D.A.; Peng, J.C.M.; Donnet, J.B.; Rebouillat, S. Immobilization of amines at carbon fiber surfaces. *Carbon* **1999**, *37* (12), 1929–1940.
23. Tsubokawa, N.; Koshiba, M. Grafting of polymers onto activated carbon surface: Graft polymerization of vinyl monomers initiated by azo groups that were introduced onto the surface. *J. Macromol. Sci. Pure.* **1997**, *A34* (12), 2509–2524.

24. Alves, J.A.C.; Freire, C.; Castro, B.; Figueiredo, J.L. Anchoring of organic molecules onto activated carbon. *Coll. Surface. A: Phy. Eng.* **2001**, *189*, 75.
25. Feng, X.D.; Fryxell, G.E.; Wang, L.Q.; Kim, A.Y.; Liu, J.; Kemner, K. Functionalized monolayers on mesoporous supports. *Science* **1997**, *276*, 923–926.
26. Lin, Y.; Fryxell, G.E.; Wu, H.; Engelhard, M. Selective sorption of cesium using self-assembled monolayers on mesoporous supports (SAMMS). *Env. Sci. Technol.* **2001**, *35* (19), 3962–3966.
27. Birnbaum, J.C.; Busche, B.; Lin, Y.; Shaw, W.; Fryxell, G.E. Synthesis of carbamoylphosphonate silanes for the selective sequestration of actinides. *Chem. Communications* **2002**, *13*, 1374–1375.
28. Liu, J.; Feng, X.D.; Fryxell, G.E.; Wang, L.Q.; Kim, A.Y. Hybrid mesoporous materials with functionalized monolayers. *Adv. Mater.* **1998**, *10* (2), 161–165.
29. Fryxell, G.E.; Liu, J.; Hauser, T.A.; Nie, Z.; Ferris, K.F.; Mattigod, S.V.; Feng, X.; Gong, M.; Hallen, R.T. Design and synthesis of selective mesoporous anion traps. *Chem. Mater.* **1999**, *11* (8), 2148–2154.
30. Redemann, C.T.; Redemann, C.E. *Organic Syntheses*; Wiley: New York, 1941; Collective Vol. 3, 69.
31. Silverstein, R.M.; Bassler, G.C.; Morrill, T.C. *Spectrometric Identification of Organic Compounds*, 5th Edition; Wiley: New York, 1991.
32. Zawadzki, J. *Chemistry and Physics of Carbon*; Thrower, P.A., Ed.; Marcel Dekker: New York, 1989; Vol. 21, 147.
33. Vinke, P.; van der Eijk, M.; Verbree, M.; Voskamp, A.F.; van Bekkum, H. Modification of the surfaces of a gas-activated carbon and a chemically activated carbon with nitric-acid, hypochlorite, and ammonia. *Carbon* **1994**, *32* (4), 675–686.
34. Briggs, D.; Seah, M.P. *Practical Surface Analysis*, 2nd Edition; Wiley publishing: West Sussex, England, 1990; Vol. 1, 244–248.
35. Mellor, D.P. Chemistry of Chelation and Chelating Agents. In *The Chelation of Heavy Metals*; Levine, W.G., Ed.; Pergamon Press: New York, 1979; 13.
36. Seron, A.; Benaddi, H.; Beguin, F.; Frackowiak, E.; Bretelle, J.L.; Thiry, M.C.; Bandosz, T.J.; Jagiello, J.; Schwarz, J.A. Sorption and desorption of lithium ions from activated carbon. *Carbon* **1996**, *34*, 481.
37. Pearson, R.G. Hard and soft acids and bases. *J. Am. Chem. Soc.* **1963**, *85*, 3533.

Received November 2003

Accepted July 2004