Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

REMOVAL OF MERCURY(II) NITRATE AND OTHER HEAVY METAL IONS FROM AQUEOUS SOLUTION BY A THIOMETHYLATED LIGNIN MATERIAL

H. Fred Koch[a]; D. Max Roundhill[a]
[a] Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas, U.S.A.

To cite this Article Koch, H. Fred and Roundhill, D. Max(2001) 'REMOVAL OF MERCURY(II) NITRATE AND OTHER HEAVY METAL IONS FROM AQUEOUS SOLUTION BY A THIOMETHYLATED LIGNIN MATERIAL', Separation Science and Technology, 36: 1, 137 — 143

To link to this Article: DOI: 10.1081/SS-100000857

URL: http://dx.doi.org/10.1081/SS-100000857

SEPARATION SCIENCE AND TECHNOLOGY, 36(1), 137–143 (2001)

REMOVAL OF MERCURY(II) NITRATE AND OTHER HEAVY METAL IONS FROM AQUEOUS SOLUTION BY A THIOMETHYLATED LIGNIN MATERIAL

H. Fred Koch* **and D. Max Roundhill**

Department of Chemistry and Biochemistry, Texas Tech
University, Lubbock, Texas 79409-1061

ABSTRACT

Lignin has been derivatized with methylthioether functional groups in order to reduce its solubility in water. This new chemically modified lignin material has been used as a solid adsorbent for mercury(II) nitrate from aqueous solution. This adsorbent strongly adsorbs nitrate salts of lead(II), cadmium(II), and copper(II) from their solutions in water. The nitrate salts of the trivalent metals chromium(III) and iron(III) are also strongly adsorbed. Sodium(I) nitrate is not adsorbed from aqueous solution and calcium(II) nitrate only moderately so. These metal extraction data are compared with those obtained with methylthioether functionalized calix[4]arenes, which show a similar preference for mercury(II), but a lower preference for lead(II), cadmium(II), and iron(III).

Key Words: Lignin; Mercury; Methylthioether.

---

*Address correspondence to H. Fred Koch.

INTRODUCTION

Recently we have prepared a series of *N*,*N*-dimethyldithiocarbamoyl and methylthioether substituted calix[4]arenes. These derivatized calix[4]arenes have been found to be selective phase transfer extractants for mercury(II) and other heavy and precious metals from aqueous solution into chloroform (1). Because calixarenes can be chemically attached onto polymers, such an approach offers a potentially convenient method for the preparation of metal selective solid resins (2).

An alternate approach is to employ a polymer that is structurally analogous to a calix[4]arene and that can be derivatized in an analogous similar manner. Such a strategy can also result in solid polymeric materials that are selective adsorbents for mercury(II) and other heavy metals. The *N*,*N*-dimethyldithiocarbamoyl and methylthioether derivatized calixarenes were obtained by introducing these sulfur-containing functionalities onto the narrow rim of the calix[4]arenes that contain the phenolic residues. Thus, in order to derivatize a polymer for it to exhibit analogous extraction properties to the functionalized calix[4]arenes, it also needs to have phenolic groups to which can be introduced sulfur-containing functionalities. Another necessary feature of such a polymer is that it be nontoxic and preferably available from a renewable resource. Finally, a very important factor is that such a polymer be available inexpensively in large quantities. An attractive candidate for such a polymer is lignin (3). Lignin is obtained as a by-product from the paper and pulp industry in the form of a powder. As a result, lignin is inexpensive, renewable, and available in abundant quantities (4). Furthermore, lignin has multiple phenolic groups that can be chemically modified to obtain metal selective materials (5–10). Figure 1 shows a plausible chemical structure for lignin. Although lignin itself adsorbs metal ions, there is a need to increase its selectivity toward heavy metals if it is to be used as an adsorbent for mercury(II). In addition, if lignin is to be useful as a solid phase adsorbent for heavy metal ions from aqueous solutions, it will be necessary to decrease its water solubility (11). The methylthio functionality meets both of these requirements. The introduction of the air-stable hydrophobic thioether group increases the heavy metal selectivity of the lignin in addition to decreasing its water solubility. An added advantage is that the neutral thioether group does not bind heavy metal cations so strongly that they cannot be subsequently removed (1,12).

In this paper we describe our results obtained from attaching methylthio substituents onto lignin. Derivatizing lignin in such a manner results in a material that is insoluble and that is a useful solid phase extractant for the removal of mercury(II) and other metal ions from aqueous solution.

EXPERIMENTAL SECTION

Lignine (90%) Alkaline (Catalog number L0082) was purchased from TCI Americas, Portland, OR. A lignin sample (6.0 g) was derivatized by first refluxing

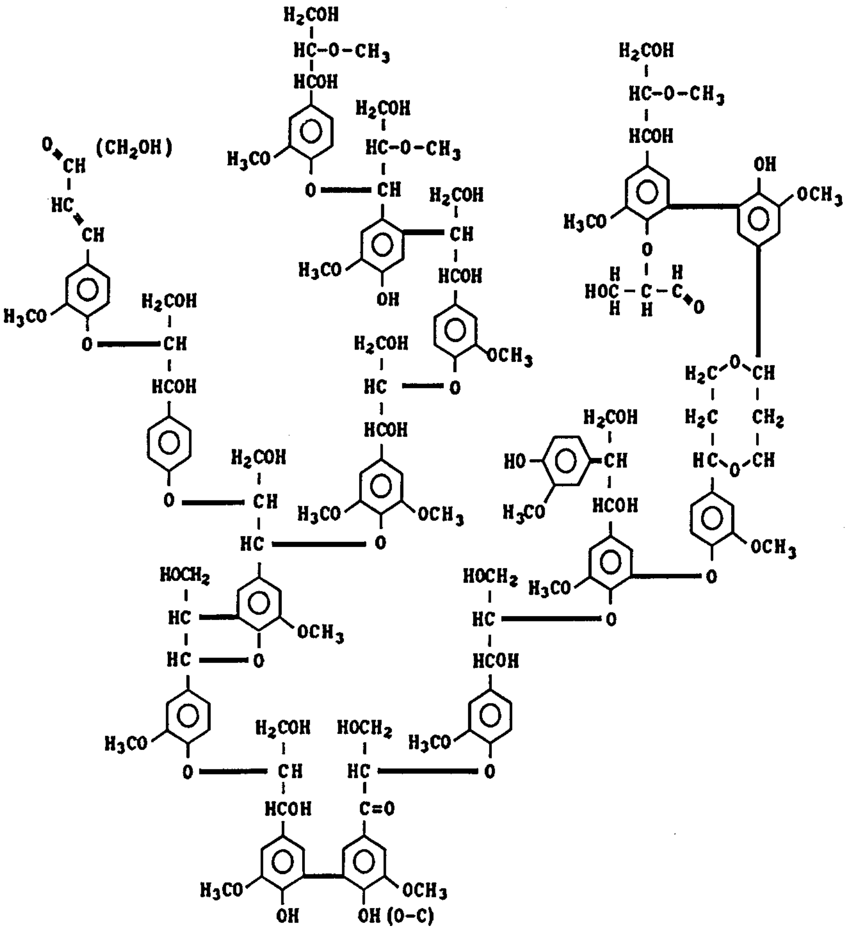

Figure 1. Structural representation of the chemical structure of lignin.

for 1 h in aqueous potassium carbonate (2.00 g). To the cooled stirred solution was slowly added 2-chloroethyl sulfide (4.40 g, 4.32 mL). A small quantity of dioxane was also added to increase the solubility of the reactants. The reaction with 2-chloroethyl sulfide is exothermic and leads to solidification of the reaction mixture. Additional dioxane was added to assist the mobility of the magnetic stirring bar. After the reaction was complete, the water and dioxane were removed by trap to trap distillation under vacuum to give the product as a solid residue. This derivatized lignin was then packed into a short column and used as the adsorbent for the metal ions.

The derivatized lignin was investigated by qualitatively testing whether it had higher solubility in organic solvents than its precursor. Because of the inhomogeneous nature of lignin, this was done by observing visually whether coloration developed in the solvent after leaving the derivatized lignin in contact with the solvent for 30 min. Because of the intense dark color of lignin, even slight solubility could be detected. The derivatized lignin was also investigated by ^1H nuclear magnetic resonance spectroscopy in both d^6-acetone and D_2O solvent, and the spectra was compared with a D_2O solution of the material prior to its being derivatized. Additional strong resonances are observed at δ 1.91 and 1.92, which are in the expected region for SMe functionalities. In the d^6-acetone solution these resonances are observed at δ 2.03 and 2.06.

Individual aqueous solutions containing the metal salts were analyzed both before and after passage through the adsorption column using the characteristic wavelength for each metal. The metal salts were introduced onto the column as $1 \times 10^{-3} M$ solutions. Details of the ICP-AES method used in our laboratories for metal analysis has been described elsewhere (13). From the ratios of these values the percentage of each metal ion extracted from solution was obtained.

RESULTS AND DISCUSSION

The thiomethylation reaction has been carried out both to introduce more heavy metal binding sites into the lignin and to increase its hydrophobicity. An indication that the latter has been achieved is the observation that the thiomethylated lignin does not bind to silica gel, whereas the unreacted sample does, as evidenced by its failure to be washed off the silica with water. Table 1 shows the qualitative solubilities for our lignin samples, both before and after the thiomethylation reaction has been carried out. The dark color of the lignin material allows for these solubilities to be visually estimated. From these observations, it is apparent that lignin thiomethylation leads to a material that has decreased solubility in water,

Table 1. Solubility Properties of the Thiomethylated Lignin

Solvent	Solubility
Water	Insoluble
Aqueous dioxane	Soluble
Chloroform	Very slightly soluble
Acetone	Very slightly soluble
Diethyl ether	Very slightly soluble
Acetonitrile	Insoluble
Benzene	Insoluble
Toluene	Insoluble

Table 2. Extraction of Metal Ions from Water by the Solid Thiomethylated Lignin

Salt	% Extraction	Salt	% Extraction
$Pb(NO_3)_2$	99	$Ca(NO_3)_2 \cdot 4H_2O$	43
$Hg(NO_3)_2 \cdot H_2O$	100	$Ni(NO_3)_2 \cdot 6H_2O$	56
$Cd(NO_3)_2 \cdot 4H_2O$	85	$Cu(NO_3)_2 \cdot 2 \cdot 5H_2O$	86
$Cr(NO_3)_3 \cdot 9H_2O$	100	$NaNO_3$	<1
$Fe(NO_3)_3 \cdot 9H_2O$	90	—	—

along with a slightly increased solubility in organic solvents. From the structure of lignin there are two principal types of hydroxylic groups present. These are phenol groups bound to aromatic carbons and alcohol groups bound to aliphatic carbons. Because the phenolic groups have the higher acidities, it is these functionalities that are more likely to be thiomethylated, thereby making this derivatized lignin analogous to the narrow rim thiomethylated calixarenes.

Table 2 shows the metal extraction properties of this thiomethylated material when it is used as an adsorbent for metal nitrates from aqueous solution. Aqueous solutions of the individual metal ions are passed through a short column of the thiomethylated lignin, and the eluted solution is analyzed for remaining metal ion by ICP-AES. The percent of metal extracted ranges from $<1\%$ for sodium(I) nitrate to 100% for mercury(II) nitrate and chromium(III) nitrate. Lead nitrate at 99% is also essentially quantitatively extracted. These extraction percentages show that the soft heavy metal ions lead(II), mercury(II), cadmium(II), and copper(II) that show a preference for soft donor sulfur ligand donors are strongly bound by the thiomethylated lignin adsorbent. In addition, the trivalent metals chromium(III) and iron(III) are also strongly adsorbed. The adsorption of these ions is likely due to ion exchange caused by their high positive charge, leading them to be strongly held to anion binding sites that have not been derivatized by 2-chloroethyl sulfide. The most weakly adsorbed metal nitrates are those of calcium(II) and sodium(I). This is an important selectivity characteristic for this adsorbent because these two metals are often present in high concentrations in both soils and waters.

By comparison, the calix[4]arene functionalized with methylthioether (Fig. 2) that groups on the narrow rim shows both similarities and differences with this derivatized lignin adsorbent, although a *direct* comparison cannot be made because the calix[4]arenes have been used as liquid–liquid phase extractants rather that solid phase extractants (1). However, a qualitative comparison concludes that the methylthioether functionalized calix[4]arenes are somewhat poorer extractants for mercury(II), but much poorer extractants for cadmium(II) and iron(III), than is this lignin-based adsorbent. This difference is likely due to the multiplicity of binding sites in the lignin adsorbent that are not available in the functionalized calix[4]arenes. As a result, this approach of functionalizing lignin may result in a

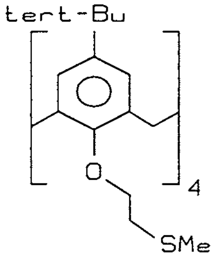

Figure 2. Structure of the methylthioether derivatized calix[4]arene.

lower selectivity than can be achieved by attaching a metal ion-selective complexant to a solid support, but it has the advantages of being inexpensive and of having a sufficiently wide range of functionalities that different binding groups can be attached, depending on the metals that are being targeted for absorption. Before such functionalized lignin materials are suitable for general application, however, a more environmentally benign route to introducing the thiomethyl moiety onto the lignin will need to be found.

ACKNOWLEDGMENTS

We thank the Army Research Office for support of this research. We also thank the Department of Energy, through the Pacific Northwest National Laboratory, for partial support of this research. We thank the National Science Foundation for funds to purchase the 500-MHz nuclear magnetic resonance spectrometer. We thank Dr. Stéphane Quideau for helpful discussions.

REFERENCES

1. Yordanov, A.T.; Whittlesey, B.R.; Roundhill, D.M. Inorg. Chem. **1998**, *37*, 3526.
2. Georgiev, E.M.; Troev, K.; Roundhill, D.M. Supramolec. Chem. **1993**, *2*, 61.
3. Glasser, W.G.; Sarkanen, S., Eds. *Lignin-Properties and Materials*; American Chemical Society: Washington, DC, 1989; ACS Symposium Series, Vol. 397.
4. Falkehag, S.I.; Braddon, D.V.; Dougherty, W.K. *Lignin Polymer Applications*; Westvaco Corp.: Charleston, SC, 1990.
5. Lalvani, S.B.; Wiltowski, T.S.; Murphy, D.; Lalvani, L.S. Environ. Tech. **1997**, *18*, 1163.
6. Masri, M.S.; Reuter, R.W.; Mendel, F. J. Appl. Polym. Sci. **1974**, *18*, 675.

7. U.S.E.P.A. Office of Emergency and Remedial Response. *Technology Alternatives for the Remediation of Soils Contaminated with As, Cd, Cr, Hg, and Pb*; Office of Research and Development: Cincinnati, OH, 1997.
8. Pahlman, J.E. *Use of Lignochemicals and Humic Acids to remove Heavy Metals from Process Waste Streams*; U.S. Department of the Interior, Bureau of Mines: Minneapolis, 1988.
9. Stevenson, F.J. *Humus Chemistry: Genesis, Composition, Reactions*, 2nd Edn.; Wiley: New York, 1994; Ch. 17.
10. Perdue, E.M. *Advances in Chemistry Series*; Suffet, I.H., MacCarthy, P., Eds.; American Chemical Society: Washington, DC, 1989; Ch. 19.
11. Srivastava, S.K.; Singh, A.K.; Sharma, A. Environ. Tech. **1994**, *15*, 353.
12. Yordanov, A.T.; Whittlesey, B.R.; Roundhill, D.M. Supramolec. Chem. **1998**, *9*, 13.
13. Koch, F.; Girard, L.A.; Roundhill, D.M.; Philip, C.V.; Anthony, R.G.; Pitt, W.W.; Beard, C. Atomic Spectrosc. **1999**, *20*, 30.

Received December 16, 1999
Revised May 2000

Downloaded At: 10:53 25 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at
http://www.dekker.com/servlet/product/DOI/101081SS100000857