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Use of a Novel Formulation of Kraft Lignin for Toxic Metal Removal from Process Waters

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ABSTRACT

Kraft lignin, a by-product in paper production, was converted to a material with high potential for applications in removing toxic metals from process waters. The acid form of kraft lignin in powder form was first converted to Ca-loaded material by treatment with various amounts of calcium hydroxide and then to a hard solid by combination with a resin in dimethylformamide (DMF) and heating. Strips of these lignin products (LP) were effective in removing Pb and Cd from solutions, with a Pb capacity of ca. 350 μmol/g. One mole of Ca was released to solution for each mole of Pb sorbed, thereby demonstrating that metal uptake was an ion exchange process and not simple adsorption.

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Advantages to these LP are that 1) they are reuseable with no loss in Pb uptake after eight cycles of uptake/regeneration, 2) their high structural stability is maintained even after immersion in water for 6 weeks, and 3) the DMF used in their preparation can be recovered and recycled.

Key Words: Kraft lignin; Process waters; Toxic metals; Ion exchange.

INTRODUCTION

Efforts to remove toxic metals from process waters have included use of various biosorbents such as peat moss,[1–3] chitosan,[4] bark,[5] fungi,[6] algae,[7] and lignin.[8,9] In a study of low-cost sorbents carried out by the US Army Corp of Engineers in 1997,[10] lignin was chosen along with 11 others as materials worth further study.

Lignin, a main structural component of wood, is converted to a by-product in paper production. Currently, this residue is generally used for fuel, although at least one company isolates kraft lignin from acidified black liquor for other purposes. The structure of kraft lignin is a complex polymer of coniferin, with propane units containing various acidic functions such as phenolic, carboxylic, and enolic groups.[11]

Most metal uptake studies assume a simple adsorption model, such as the Langmuir Isotherm [12] or the Biotic Ligand Model,[13] which can be modified so that it appears to account for metal competition for sites.[14] However, work in our laboratories with algae[2,15] and peat moss[2,3] has shown that the actual process is one of ion exchange in which metal uptake occurs with release of an existing sorbed metal [Eq. (1)] or protons [Eq. (2)]. We recently found that metal uptake with kraft lignin powder also occurs by these ion exchange equilibria.[16]

$$M^{2+} + (CaX_2) \rightleftharpoons (MX_2) + Ca^{2+} \quad K_{ex} = \frac{[Ca^{2+}](MX_2)}{[M^{2+}](CaX_2)} \tag{1}$$

$$M^{2+} + 2(HX) \rightleftharpoons (MX_2) + 2H^{+} \quad K_{ex}^{H} = \frac{[H^{+}]^2(MX_2)}{[M^{2+}](HX)^2} \tag{2}$$

We now report our results with a kraft lignin powder modified so as to be more useful in practical applications. Advantages to this lignin product (LP), or materials prepared in similar ways, are that it is reusable, stable in water, has a high capacity, and solvents can be recovered for recycling. We also have investigated the mechanism of uptake by this material.

EXPERIMENTAL

Kraft pine lignin (hereafter referred to as lignin) was kindly provided by MeadWestvaco, Charleston Heights, SC as Indulin AT. It is a powder with particle size 200–300 μm containing a small amount of Na and Ca. Other materials used in this study and analytical procedures were previously described.[16]

Preparation of LP Samples

Lignin was converted to the acid form HLg by slowly adding a dilute solution of nitric acid to a stirred suspension of 6.0 g of lignin in 40 mL of water to achieve a pH of 1.5. After additional stirring at that pH for 30 min, the HLg was centrifuged and the supernatant liquid removed. The product was washed twice by stirring, centrifugation, and decantation cycles. To a stirred suspension of this HLg, a desired amount of calcium hydroxide powder (20, 50, or 80 mg/g HLg) was added. After stirring for several hours, centrifugation gives CaLg, which was washed several times with water and air-dried overnight or dried at 70°C for 20 min to give powders referred to as CaLg-20, CaLg-50, and CaLg-80 corresponding to the mg of calcium hydroxide added per gram of HLg.

The calcium-loaded powder CaLg was converted to a plastic material by mixing 1.0 g of CaLg with 0.1 g of clipped glass wool and 0.6 mL of a dimethylformamide (DMF) solution of a resin (1.0 g resin per 10 mL DMF), which serves as a binding agent. In the experiment relating Pb solution decrease with sample uptake, a poly(methyl methacrylate), MW 30,000, resin was used, while in all other experiments a polysulfone resin $[-C_6H_4\,4\text{-}C(CH_3)_2-C_6H_4\text{-}4\text{-}O-C_6H_4\text{-}4\text{-}SO_2-C_6H_4\text{-}4\text{-}O-]_n$, MW 30,000 was used. Mixing and pressing repeatedly with a spatula gave a uniform, putty-like plastic material. As a standard procedure, a 0.20 g cylinder of this material was placed lengthwise along a 1.3 mm-thick microscope slide. Rolling a glass rod along the top of the slide flattened the cylinder to produce a strip 1.3 mm thick, 4 mm wide, and 10 mm long. Unless otherwise stated, all strips used were made in this way. The strips could easily be cut into chips of desired sizes.

Various types of heat treatment produced hard particles. Rapid heating to 160°C for 15 min formed blisters. A flat strip becomes tubular in the process. Presumably, DMF and residual water vapors are formed faster than they can diffuse through the hot, soft, relatively impervious plastic material at the elevated temperature. On cooling to room temperature (RT), the blisters became brittle and hard. Striking with a pestle gave small hard particles. Hard material can also be formed without blistering by slower rates of heating. For example, a sample heated at 120°C for 20 min and then at 160°C for 5 min gave an unblistered material on cooling to ambient temperature. Material heated to only 70°C was solubilized to a small extent, in some cases, in the presence of Pb. Unless otherwise stated, strips were therefore heated at 70°C for 20 min and then at 120°C for 10 min. For Cd uptakes, tapping the solid gently with a pestle decreased time for equilibration. Products obtained by this procedure are referred to as lignin products LP-20, LP-50, and LP-80 corresponding to 20, 50, and 80 mg of calcium hydroxide used per gram of HLg, respectively.

Structural Stability

To test structural stability in water, a $1.3 \times 4.0 \times 38\text{-mm}^3$ strip of LP-50, which had been heated at 120°C for 20 min, was clamped to a shelf so that 30 mm extended unsupported horizontally past the end of the shelf. A plastic strip 55 mm long, glued to the unsupported end, served as a "pointer" to provide more accurate measurements. A small weight (ca. 3.3 g) was hung at the junction to cause a bend in the LP, which was measured as the vertical deflection of the pointer end. The sample was then immersed in water in a test tube. After 1 week, the sample was dried at 70°C for 20 min and retested. The process was continued for five more weeks with essentially no difference in deflections from the initial value.

Uptake Procedures

In a typical uptake procedure, a strip was immersed at the side of a beaker containing a Pb or Cd nitrate solution stirred magnetically. In the case of chips, these were placed in one side of a beaker separated into two compartments by a stainless steel wire screen. At the desired time, or after 3 hr of equilibration depending on the experiment, the solution was removed by decantation and an aliquot analyzed for metals by atomic absorption (AA) as previously described.[16] Results are expressed as μmol sorbed per gram of sorbent.

To test whether LP was reuseable, a strip of LP-50 was prepared using 0.5 mL of DMF/resin and heated at 70°C for 20 min, then at 150°C for 10 min. After cooling, it was suspended in 10 mL of water. Lead nitrate was added to give a solution 0.10 mM in lead. The amount of Pb sorbed was given by the decrease in Pb concentration. After 1 hr, the solution was poured off and the sample washed several times with water. Sorbed Pb was removed by three extractions with 10 mL of a 0.01 M EDTA solution containing 0.01 M

Ca to regenerate the LP. The sample was then washed with water and reused by adding a fresh 0.1 mM lead solution.

In a preliminary column operation to remove Cd, 1.2 g of LP-50 strips were cut into chips ca. $1.3 \times 2 \times 2\,\mathrm{mm}^3$ and put in a 1.5 cm diameter column giving a height of 10 cm. A solution of 0.10 mM Cd was put through the column. For Pb, strips of LP-50 were scraped on a stainless steel screen (100 holes per in.^{2}) giving particles 1.5–2.2 mm in size. An 8-mm diameter column was packed with 2.0 g of this material giving a height of 9.0 cm. A 1.0 mM solution of Pb was passed through this column at 1 mL per 5 min. In both cases, metal concentrations of 10 mL eluent samples were measured.

RESULTS AND DISCUSSION

Analysis Method and Stoichiometry

The preparation of CaLg powder involved treating a suspension of the acid form of lignin with solid calcium hydroxide followed by several washings. It is important to know whether the Ca remained on the sample, and hence was available for ion exchange. Suspensions of CaLg-30, CaLg-50, and CaLg-80 powder were analyzed by AA and found to contain 405, 650, and 800 μmol Ca/g. Comparison of values calculated from weights of $Ca(OH)_2$ used, 405, 676, and 1080 μmol Ca/g, respectively, show that all Ca was retained by the two lower Ca-containing samples. Experiments were, therefore, done on samples prepared from CaLg-50 or powders of lesser Ca content, which were also easier to form into strips than CaLg-80.

Since heavy metal uptake is more easily determined by measuring the decrease in solution concentration, control experiments were done to compare these values with those from direct analysis of the solids. A 50-mg sample of LP-50 was stirred with 20 mL of 0.4 mM Pb for 3 hr. Metal uptake by decrease in solution concentration was 656 μmol/g. The Pb content of the solid, measured by successive extractions with 10 mL of 0.01 M EDTA, showed a comparable value of 608 μmol/g sorbed. An experiment with material heated at 70°C for 20 min, 120°C for 20 min, 140°C for 5 min, and then 160°C for 5 min showed similar results with 528 μmol/g sorbed by solution decrease and 468 μmol/g by analysis of the solid. Uptakes measured by solid analysis, while lower perhaps due to incomplete solid dissolution, are close enough (7% and 11%) to solution measurements to justify use of concentration decrease as a valid measure of uptake.

The stoichiometry of divalent Pb uptake by LP-50 strips was determined by stirring samples with solutions of Pb and measuring both Pb uptake by the sample (by decrease in solution concentration) and Ca release (by decrease in amount of Ca on the sample). The ratio of $Pb_{ON}:Ca_{OFF}$ was found to be 1.2 ± 0.1 for solutions initially 0.10, 0.30, and 1.0 mM in Pb. The ratio for LP-30 material was 1.1 ± 0.1. This stoichiometry result over a tenfold range of initial Pb concentration demonstrates that one Ca^{2+} is released for one Pb^{2+} sorbed. The Pb uptake process for divalent Pb on LP material is, therefore, one of ion exchange [Eq. (3)], not simple adsorption, as also found for lignin powder.[16]

$$Pb^{2+} + \text{Ca-LP} \rightleftharpoons Ca^{2+} + \text{Pb-LP} \tag{3}$$

The 1 : 1 ratio of $Pb_{ON}:Ca_{OFF}$ is also apparent in results plotted in Fig. 1 for a higher Pb range of 0.50–10 mM.

Capacity for Lead (Pb)

Since, Pb uptake occurs by an ion exchange equilibrium [Eq. (3)], the total capacity of a given LP sample cannot be obtained by a single batch experiment in which the reverse reaction limits the amount of Pb that can be sorbed. To measure Pb capacity for a given sample of LP, 0.70 g of LP-50 chips was stirred with 20 mL of 0.10 M Pb. After 1 hr, the released Ca from that equilibration was measured in a filtrate. The solid sample was then treated with a fresh 20 mL of 0.10 M Pb, and the process was repeated. After 11 extractions of Ca by Pb uptake, additional Ca released was negligible. The sample was then analyzed for total Pb sorbed by adding amounts of Pb extracted from

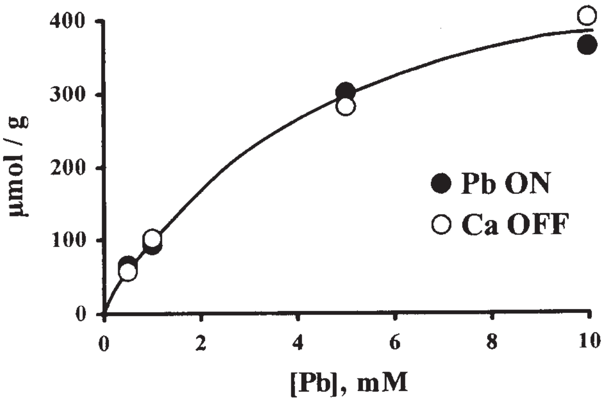

Figure 1. Pb uptake and Ca released after 8 hr from 0.20 g LP-50 strips immersed in 20 mL of various Pb solutions.

the sample by three treatments with 10 mL of 0.01 M EDTA and the small amount in the residual solid. The Pb capacity for this sample is on the order of 350 μmol/g as shown by data in Fig. 2, in which cumulative Ca released is plotted against the number of Pb treatments.

Further evidence for the ion exchange process for Pb is evident in the observation that the 334 μmol/g Pb content of the sample after these 11 treatments is essentially the same as the 340 μmol/g of cumulative Ca released (see points for final treatment in Fig. 2). Comparing these values with the theoretical amount of Ca present in 676 μmol/g shows that about half of the Ca in LP-50 is available for exchange by Pb.

Uptake of Cadmium (Cd)

An initial experiment with CaLg powder showed that Cadmium (Cd) could be sorbed by this material. A 20-mg sample of CaLg-50 powder was added to 25 mL of a 0.50 mM Cd solution. After stirring for 1 hr, 460 μmol/g Cd were removed from solution. Since that sample contained 676 μmol/g Ca initially, 68% of the Ca was available for displacement by Cd. The LP-50 samples prepared with heat treatments ranging from 70°C to 160°C also effectively removed Cd from solution. In all cases, final uptakes of ca. 65% and 50% were found for 0.20 mM and 0.50 mM solutions, respectively.

The stoichiometry of Cd uptake by LP-50 strips was determined as described above for Pb by stirring samples with solutions of Cd and measuring both Cd uptake by the sample and Ca release to the solution. The results simi-

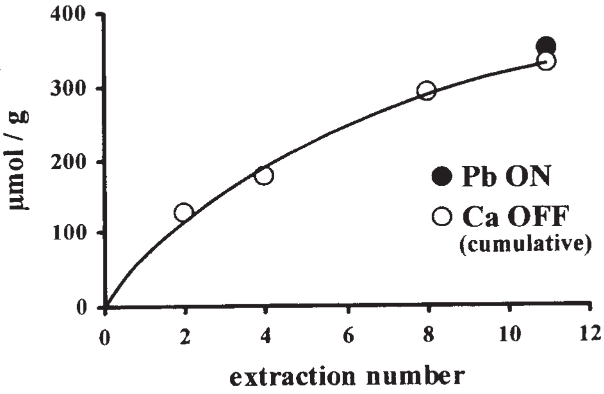

Figure 2. Cumulative Ca released from 0.70 g of LP-50 chips repeatedly extracted with 20 mL of 0.1 M Pb. After the final treatment, the amount of Pb on the sample was measured.

lar to those in Fig. 1 were obtained for solutions initially 2.0 mM and 4.0 mM in Cd, namely that the μmol of Ca released was the same within experimental error as the μmol of Pb taken up. Hence, the process for Cd is also ion exchange and not adsorption.

Batch Versus Column Operations

Reduction of toxic metal concentrations to EPA limits is not possible in a single batch experiment, since the metal concentration would be given by the equilibrium amounts determined by ion exchange equilibrium such as Eq. (3). However, in a column operation, successive metal uptakes are possible, as released Ca is removed by fresh solution passing down the column.

An example with Cd uptake illustrates this difference. In a batch experiment using a 0.2-g strip of LP-50 immersed in 25 mL of a 0.20 mM solution of Cd, 35% of the Cd remained in solution at equilibrium. However, essentially, all the Cd could be removed in a column, as shown by the following preliminary experiment. A 0.10 mM solution was passed through a column containing 1.2 g of LP-50 chips. No measurable concentration of Cd could be detected in the eluent after 300 mL. This was also the case for an additional 200 mL of a 0.20 mM solution of Cd, and for ca. 170 mL of a 0.40 mM solution. These amounts correspond to a negligible Cd concentration after treating ca. 1.4 L of a 0.10 mM solution.

Uptake of Pb by a column was likewise very efficient. A 1.0 mM solution of Pb was passed through a column containing 2.0 g of LP-50 as small chips. There was a negligible amount of Pb in the eluent until the breakthrough point at ca. 280 mL.

LP Formulations Are Reuseable

A considerable advantage to LP would be if strips or chips were reuseable. This possibility was tested with a 0.20 g LP strip heated at 70°C for 20 min and then at 150°C for 10 min. After cooling, it was suspended in 10 mL of a 0.10 mM solution of Pb. After 1 hr, the amount of Pb sorbed was given by the decrease in Pb solution concentration. To reuse the sample, the sorbed Pb was removed by stirring with 10 mL of 0.01 M EDTA, which also contained 0.01 M $CaCl_2$, to renew the exchangeable sites.

Results in Table 1 show that the Pb extraction by EDTA completely removed sorbed Pb, with a ratio for $Pb_{ON} : Pb_{OFF}$ of 0.96 ± 0.16 for eight cycles. Of more importance is the observation that the amount of Pb sorbed was essentially the same for each cycle of reuse, showing that the efficiency

Table 1. Reuse of an LP-50 sample.

Cycle	1	3	5	8
Pb sorbed (μmol)	0.54	0.62	0.73	0.50
Pb off by EDTA (μmol)	0.77	0.61	0.69	0.56
Ratio $Pb_{ON}:Pb_{OFF}$	1.42	1.00	0.92	1.12

Note: A 0.20 g strip of LP-50, 1.3 × 4 × 10 mm^3, was immersed in 10 mL of a stirred 0.10 mM solution of Pb. After 1 hr, the amount of Pb sorbed was given by the decrease in solution concentration. The sorbed Pb was then extracted from the sample by ETDA extraction. Fresh Pb solution was added and the process repeated for a total of eight cycles.

of Pb uptake is not diminished by repeated use. The EDTA, or other possible complexing agents, can be regenerated by stripping off Pb with acid. Precipitation of Pb from a concentrated solution can lead to its removal.

Recovery of DMF

To determine whether DMF could be recovered for recycling, a strip of LP-20 was heated at 160°C for 20 min (to constant weight), and the weight loss corresponded to the amount of DMF used in the preparation. In a second experiment, a strip was heated to 120°C and held at that temperature for 20 min. A stream of nitrogen passing over the sample in a glass tubing was cooled at dry ice temperature, and the weight of condensed gases was essentially the same as weight loss by the sample. These experiments show that DMF used in sample preparation can be removed from the solid LP and can be available for recycling. The rate of DMF loss was determined by weight loss from a strip at a given temperature for various times. From Fig. 3, it can be seen that most of the weight loss at 100°C occurs in the first 15 min.

CONCLUSIONS

The present work describes a novel formulation of kraft lignin which shows considerable potential in applications to remove toxic metals from polluted waters. A by-product in paper production, the commercial lignin can be converted to a Ca-loaded material and then formulated as strips or chips of high structural stability to water. Several advantageous properties of this material include 1) high capacity for toxic metal uptake, which occurs

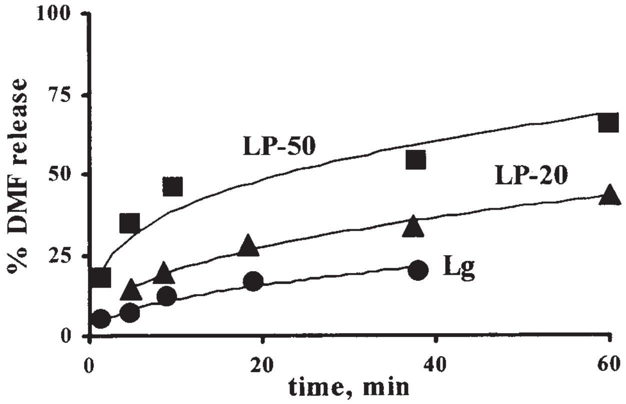

Figure 3. Rate of DMF release at 100°C as a percentage of the amount used in sample preparation. For a control (Lg), the same procedure for making LP materials was used on lignin (Indulin AT) with no Ca.

by an ion exchange process; 2) suitability for use in columns in order to decrease concentrations below that possible in batch operations; 3) ability to be reused; and 4) recovery of solvents used in preparing the material. Future work could involve scale-up methods of preparation and also investigations of less expensive chemicals for preparation of the material and chelating agents for its regeneration.

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