Removal of Heavy Metal Ions from Aqueous Solutions Using Lignocellulosic Fibers

Beom-Goo Lee
Roger M. Rowell

ABSTRACT. Spruce, coconut coir, sugarcane bagasse, kenaf bast, kenaf core, and cotton were tested for their ability to remove copper, nickel and zinc ions from aqueous solutions as a function of their lignin content. The fibers were analyzed for sugar and lignin content and extracted with diethyl ether, ethyl alcohol. hot water, or 1% sodium hydroxide.

The order of lignin content in un-extracted fibers is coconut coir > spruce > kenaf core > bagasse > kenaf bast > cotton. The fiber with the highest level of heavy metal removal was kenaf bast that had a very low level of lignin, showing that removal of heavy metals does not correlate with lignin content. Cotton, with about 1% lignin, was very low in metal ion sorption while all of the fibers containing lignin did remove heavy metal ions showing that lignin does play a role in metal ion sorption. Extraction with the various solvents removed different cell wall components and did change heavy metal sorption that indicates that cell wall chemistry and architecture may also be important factors in the sorption of heavy metals from aqueous solutions using lignocellulosic fibers. *[Article copies available for a fee from The Haworth Document Delivery Service: 1-800-HAWORTH. E-mail address: <docdelivery@haworthpress.com> Website: <http://www.HaworthPress.com>]*

Beom-Goo Lee and Roger M. Rowell are affiliated with the USDA, Forest Service, Forest Products Laboratory, Madison, WI 53726-2398 USA.

Journal of Natural Fibers, Vol. 1(1) 2004
http://www.haworthpress.com/web/JNF
Digital Object Identifier: 10.1300/J395v011101_07

KEYWORDS. Heavy metals, wood, coir, bagasse, kenaf, cotton, copper, nickel, zinc, chemical composition, extraction, lignin content, lignocellulosics

INTRODUCTION

About 80% of the fresh water in the United States originates on the 650 million acres of forestlands that cover about 1/3 of the nation's land area. The nearly 192 million acres of national forest and grasslands are the largest single source of fresh water in the United States. In many cases, the headwaters of large river basins originate in the national forests. In 1999, the EPA estimated that 3,400 public drinking-water systems were located in watersheds contained in national forests and about 60 million people lived in these 3,400 communities (Sedell et al. 2000).

In order to maintain healthy ecosystems in our national forests, it is necessary to remove small diameter trees, underbrush, and undesirable species. Other agricultural residues may also be available at low cost. Wood-based and agricultural-based fiber can be produced from these residues and used as filters to remove various types of contaminants from water. There are over 38,000 abandoned mine and hazardous material waste sites on national forest lands (Sedell et al. 2000). It may be possible to use lignocellulosic-based fiber filters to remove heavy metals from these acid mine sites.

Laszlo and Dintzis have shown that lignocellulosics have ion-exchange capacity and general sorptive characteristics, which are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin and protein. These are adsorbents for a wide range of solutes, particularly divalent metal cations (Laszlo and Dintzis 1994). Lignocellulosic resources all contain, as a common property, polyphenolic compounds, such as tannin and lignin, which are believed to be the active sites for attachment of heavy metal cations (Waiss et al. 1973, Masri et al. 1974, Randall et al. 1974, Bhattacharyya and Venkobachar 1984, Phalman and Khalafalla 1988, Verma et al. 1990, Shukla and Sakhardande 1991, Maranon ande Sastre 1992, Lalvani et al. 1997, Vaughan et al. 2001). Sawdust has been used to remove cadmium and nickel (Basso et al. 2002) and several types of barks have been used to remove cadmium, copper, lead, zinc, nickel, or cobalt (Randall et al. 1974, Kumar and Dara 1980, Pawan and Dara 1980, Tiwari et al. 1997) from aqueous solution. Cellulose can also sorb heavy metals from solution (Acemioglu and Alma 2001). Isolated kraft lignin has been used to remove copper and cadmium (Verma et al. 1990, Cang et al. 1998) and organosolv lignin has been used to remove copper (Acemioglu et al. unpublished data) from aqueous solutions.

Acemioglu et al. postulate that metal ions compete with hydrogen ions for the active sorption sites on the lignin molecule (Acemioglu et al. Unpublished data). They also conclude that metal sorption onto lignin is dependent on both sorption time and metal concentration.

Basso et al. studied the correlation between lignin content of several lignocellulosics and their ability to remove heavy metals from aqueous solutions (Basso et al. 2002). Brazil nut shell, sugarcane bagasse, *Prosopis ruscifolia* wood sawdust, and stems of *Arundo donax*, were used with lignin contents of 57%, 28%, 28%, and 23%, respectively. The efficiency of removing Cd(II) and Ni(II) from aqueous solutions was measured and they found a direct correlation between heavy metal sorption and lignin content. They also noted that the cell wall structures and compositions were different for the different lignocellulosics selected, which may have also influenced heavy metal sorption.

It is difficult to compare data from different literature sources since sorption of heavy metals is very dependent on temperature, heavy metal concentration and contact time and no two researchers use identical conditions. However, it is interesting to note that under similar experimental conditions, Vaughan et al. (2001) using corncobs with a lignin content of 9.1% and Acemioglu et al. (Unpublished data) using isolated organosolv lignin found about the same efficiency in removing Cu(II) from aqueous solutions.

Lignocellulosic materials are very porous and have a very high free surface volume that allows accessibility of aqueous solutions to the cell wall components. One cubic inch of a lignocellulosic material, for example, with a specific gravity of 0.4, has a surface area of 15 square feet. Even when the lignocellulosic material is ground, the adsorptive surface increases only slightly. Thus, the sorption of heavy metal ions by lignocellulosic materials does not depend on particle size.

Lignocellulosics are hygroscopic and have an affinity for water. Water is able to permeate the non-crystalline portion of cellulose and all of the hemicellulose and lignin. Thus, through absorption and adsorption, aqueous solution come into contact with a very large surface area of different cell wall components.

Extracting fibers with different solvents will change both the chemical and physical properties of the fibers. It is known, for example, that during the hot water and 1% sodium hydroxide extraction of fibers, the cell walls delaminate (Kubinsky 1971). At the same time, some of the amorphous matrix and part of the extractives, which have a bulking effect, are removed (Kubinsky and Ifju 1973), so that the individual microfibrils become more closely packed and shrunken (Kubinsky and Ifju 1974). Therefore, delamination and shrinkage may also change the amount of exposed lignin and other cell wall components that may affect the heavy metal ion sorption capacities of the fibers.

Each different extraction chemical will swell lignocellulosics to a different extent, thus removing different amounts and types of extractives as well as cell wall components. The relative swelling, for example, of diethyl ether, ethyl alcohol and water is 3, 83 and 100, respectively. Fats, unsaturated fatty acids, such as oleic acid and linoleic acid, saturated fatty acids, resins, resin acids, waxes, oils and sterols in lignocellulosics are soluble in diethyl ether. Ethyl alcohol can dissolve coloring matter, such as flavonoids and anthocyanins, tannins, phlobaphenes, some water solubles and stilbenes from lignocellulosics. Carbohydrates, such as parts of the hemicelluloses, starch and pectic material, proteins, alkaloids, inorganic materials, such as Ca, K, Mg, Na and Fe, some phenolic substances, oxalate, citrates, humic acid-like substances, mucilages, gums, and uronic acids are extractable by hot water. One percent sodium hydroxide can extract major amounts of the hemicelluloses and part of the lignin along with a major portion of the extractives (Browing 1967). Extracting lignocellulosic fibers with different solvents will also change the accessibility of heavy metal solutions to cell wall components.

The purpose of this research was to study the correlation between lignin content of several native and extracted lignocellulosic fibers and their ability to remove heavy metal ions from aqueous solutions. The selected fibers ranged in lignin content from 33.7% for coconut coir to 1% for cotton.

MATERIALS AND METHODS

Lignocellulosic Fibers

Spruce, kenaf bast, kenaf core, sugarcane bagasse, cotton, coconut coir and spruce were used as raw materials.

Kenaf was grown at the University of Wisconsin in Madison. Cotton was purchased from Absorbent Cotton Co. Sugarcane bagasse and coconut coir was donated from Danforth International Trade Associates, Inc., and spruce from Adams-Columbia Electric Power Co-Op, Sub-Station "R" Roslin, South Central Marqutte Co., Wisconsin.

Kenaf bast and kenaf core were hand separated while the samples were wet. All lignocellulosics were air dried and then ground in a Wiley mill to pass a 20 mesh screen.

Heavy Metal Ions

One thousand ppm of copper, nickel and zinc chloride in 1-2 wt. % HNO_3 were used in the experiments. In heavy metal ion sorption experiments, the selected heavy metals were made up as 10 ppm solutions.

Carbohydrate

Extractive free samples were prepared as described by Rowell and Han (1999). Three grams of samples were placed into pre-weighed fritted disc glass extraction thimbles, and then dried in a vacuum oven at 50°C for 48 hours. The samples were cooled in a desiccator and weighed. The thimbles were covered with aluminum foil with small holes to prevent any loss of specimen during the extraction. Toluene: ethanol mixture (one volume of ethanol and two volumes of toluene 250 ml) was put into a 500 ml round bottom flask along with several boiling chips to prevent bumping. The fibers were extracted in the solvent in a Soxhlet extractor for 12 hours, siphoning no less than four times per hour. After the extraction, the solvents were drained from the thimbles and dried in a vacuum oven for 48 hours at 40°C. The samples were cooled in a desiccator and then weighed to determine extractive content. Carbohydrate was analyzed by FPL HPLC procedure (Pettersen and Schwandt 1991).

Isolation of Klason Lignin

Klason lignin was isolated as described by TAPPI Standard T222 om-88. Each sample was dried at 50°C in a vacuum oven over night. Two hundred milligrams of each dried sample was placed into a 100 ml centrifuge tube. One milliliter of 72% (w/w) H_2SO_4 for each 100 mg of sample was added to the sample in a 10 ml centrifuge tube. The mixture was stirred and dispersed thoroughly using a glass rod. Then each tube was incubated in a water bath at 20°C for 60 minutes.

Fifty-six ml of distilled water (60 ml syringe used) was added to prepare a 4% solution for the secondary hydrolysis. One milliliter of fucose internal standard was added to aid quantitation of five sugars by HPLC as a part of the analysis. The samples were autoclaved at 121 °C, 15 psi, for 60 minutes. The samples were removed from the autoclave, and the lignin filtered, keeping the solution hot. The samples were filtered through glass fiber filters in crucibles using suction. The residue was thoroughly washed with hot water, and then dried in the vacuum oven at 50°C over night. The samples were cooled in the desiccator, weighed and Klason lignin contents were calculated.

Sorption Experiments of Heavy Metal Ions

Fifty milliliters of 10 ppm solutions of Cu(II), Ni(II) or Zn(II) ions were added to a 60 ml screw cap jar. A half gram of lignocellulosic fiber was placed into the solution and shaken for 24 hours. The initial and final concentrations of heavy metal ions were determined using an ICP Spectrometer. Three replications were made for each sample.

Diethyl Ether Extraction

The samples were extracted as described by Browing (1967). Ten gram samples were weighed in an extraction thimble and placed in the Soxhlet extractor. Two hundred and fifty ml of diethyl ether was added to the flask and the samples were extracted for 4 hours, siphoning the solvent at least six times per hour. The samples were dried in the vacuum oven at 50°C over night. The samples were cooled in the desicator and weighed to determine the weight loss.

Hot Water Extraction

The samples were extracted as described in TAPPI T207 om-93. Ten gram samples were weighed and then heated with 500 ml of distilled water in a flask immersed in a bath of boiling water for 3 hours. The samples were filtered on a tared filtering funnel of gritted glass and then washed with several small portions of hot water. The samples were dried at 105°C, cooled in the desicator and weighed to determine the weight loss.

One Percent Sodium Hydroxide Extraction

The samples were extracted as described in TAPPI Standard T212 om-93. Ten gram samples were treated with 1% sodium hydroxide solution (500 ml) in a 1000 ml tall form beaker. The beaker was covered with a watch glass and heated in a water bath, maintaining the temperature of the solution at 97-100°C and stirring at intervals. After heating for 1 hour the samples were filtered by suction on a tared fritted glass funnel. The samples were washed with hot water, then with 10% acetic acid (250 ml), and finally the samples were washed thoroughly with hot water. The samples were dried at 105°C, cooled in the desiccator and weighed to determine the weight loss.

RESULTS AND DISCUSSION

Table 1 shows weight loss data due to extraction. In the organic solvent extractions (diethyl ether and ethyl alcohol), the weight loss was quite low (less than 4%). Extraction with hot water removed a large amount of material from kenaf bast (19%) and bagasse (10%). One percent sodium hydroxide extracted major amounts of materials from bagasse (37%), kenaf core (32%), spruce (26%), and kenaf bast (24%).

Table 2 shows the total carbohydrate content and Table 3 shows the lignin content of fibers before and after extraction. Total carbohydrates did not decrease significantly in any of the extractions with the exceptions of kenaf core (13%) and spruce (14%) in 1% sodium hydroxide. The largest lignin loss occurred in bagasse (76%), kenaf core (24%) and spruce (20%) using 1% sodium hydroxide but the hydroxide had little effect on kenaf bast (1%) and coconut coir (7%).

Table 4 shows the Cu(II) ion sorption characteristics of the natural and extracted fibers. Kenaf bast shows the highest copper ion sorption followed by spruce, coconut coir, kenaf core, bagasse and finally, cotton. The order of sorption does not follow a pattern of lignin content. The highest level of copper removed is from kenaf bast that has the second lowest lignin level of the fibers tested. Copper sorption also in-

TABLE 1. Weight loss of extracted lignocellulosic fibers.

	Ether (%)	Ethanol (%)	Water (%)	NaOH (%)
Kenaf Bast	4	0	19	24
Kenaf Core	1	0	6	32
Bagasse	1	4	10	37
Cotton	1	0	4	9
Coconut Coir	1	1	5	5
Spruce	0	3	7	26

TABLE 2. Total carbohydrate of extracted lignocellulosic fibers.

	Control (%)	Ether (%)	Ethanol (%)	Water (%)	NaOH (%)
Kenaf Bast	57	54	58	55	56
Kenaf Core	60	59	61	58	52
Bagasse	69	67	68	64	64
Cotton	97	97	98	94	89
Coconut Coir	54	53	54	53	53

TABLE 3. Klason lignin of extracted lignocellulosic fibers.

	Control (%)	Ether (%)	Ethanol (%)	Water (%)	NaOH (%)
Kenaf Bast	9.7	9.1	9.5	9.1	9.6
Kenaf Core	21.4	20.5	19.9	20.2	16.3
Bagasse	18.9	18.4	17.7	17.2	4.6
Cotton	1.1	0.9	0.5	0.9	0.6
Coconut Coir	33.7	33.2	32.4	31.2	31.2
Spruce	27.2	26.5	24.8	24.9	21.8

TABLE 4. Cu(II) ion sorption capacity of extracted lignocellulosic fibers.

	Control (mg/g)	Ether (mg/g)	Ethanol (mg/g)	Water (mg/g)	NaOH (mg/g)
Kenaf Bast	0.61	0.58	0.60	0.75	0.59
Kenaf Core	0.38	0.38	0.38	0.58	0.10
Bagasse	0.11	0.11	0.11	0.07	0.05
Cotton	0.03	0.04	0.03	0.03	0.03
Coconut Coir	0.42	0.44	0.42	0.31	0.25
Spruce	0.51	0.44	0.47	0.56	0.35

creases in kenaf bast with extraction of hot water. In most cases, extraction of the fibers results in a lowering of the copper ion sorption. Kenaf bast lost very little carbohydrate or lignin during extraction. Coconut coir also did not lose very much carbohydrate or lignin during extraction but Cu(II) removal went down after extraction with hot water and 1% sodium hydroxide.

Table 5 shows the Ni(II) ion sorption and, again, kenaf bast fiber removed the highest amount of metal ion. There was a slight increase in Ni(II) sorption in kenaf bast fiber after extraction with 1% sodium hydroxide but was essentially unchanged after all of the other extraction procedures. Ni(II) sorption for coconut coir and spruce decreased after extraction with hot water. Ni(II) sorption also decreased in kenaf core, bagasse, coconut coir and spruce after extraction with 1% sodium hydroxide.

Table 6 shows the Zn(II) sorption and, as with Cu(II) and N(II), kenaf bast had the highest level of Zn(II) removal. Zn(II) sorption increased in kenaf bast and kenaf core but decreased in coconut coir and spruce after extraction with hot water. Extraction with 1% sodium hydroxide resulted in a decrease in Ni(II) sorption in kenaf core, bagasse, coconut coir, and spruce, but increased the sorption in kenaf bast.

TABLE 5. Ni(II) ion sorption capacity of extracted lignocellulosic fibers.

	Control (mg/g)	Ether (mg/g)	Ethanol (mg/g)	Water (mg/g)	NaOH (mg/g)
Kenaf Bast	0.39	0.35	0.34	0.37	0.43
Kenaf Core	0.23	0.21	0.22	0.22	0.06
Bagasse	0.10	0.11	0.10	0.06	0.04
Cotton	0.07	0.09	0.09	0.09	0.07
Coconut Coir	0.20	0.18	0.19	0.14	0.14
Spruce	0.27	0.19	0.23	0.12	0.05

TABLE 6. Zn(II) ion sorption capacity of extracted lignocellulosic fibers.

	Control (mg/g)	Ether (mg/g)	Ethanol (mg/g)	Water (mg/g)	NaOH (mg/g)
Kenaf Bast	0.53	0.51	0.49	0.63	0.67
Kenaf Core	0.49	0.48	0.47	0.57	0.15
Bagasse	0.20	0.21	0.20	0.17	0.09
Cotton	0.18	0.18	0.17	0.17	0.13
Coconut Coir	0.31	0.29	0.32	0.23	0.21
Spruce	0.49	0.44	0.45	0.20	0.20

CONCLUSIONS

All of the lignocellulosic fibers used in this study removed heavy metals from aqueous solutions. Using kenaf bast, kenaf core, cotton, coconut coir, and spruce as models with very different types and amounts of lignin, the heavy metal ion sorption capacities do not correlate with lignin contents. The order of decreasing lignin contents in un-extracted fibers is coconut coir > spruce > kenaf core > bagasse > kenaf bast > cotton. The decreasing order of Cu(II) removal is kenaf bast > spruce > coconut coir > kenaf core > bagasse > cotton. The decreasing order of Zn(II) removal is kenaf bast > kenaf core = spruce > coconut coir > bagasse > cotton. The decreasing order of Ni(II) removal is kenaf bast > spruce > kenaf core > coconut coir > bagasse > cotton. Of the fibers tested, all are more efficient in removing Cu(II) and Zn(II) as compared with Ni(II).

Extraction of the fibers with diethyl ether, ethyl alcohol, hot water and 1% sodium hydroxide removed different extractives and cell wall components. In most cases, however, heavy metal sorption did not increase to any great extent after extraction. When the cell wall constituents are removed, more lignin may be exposed but data from this study does not show any consistent pattern between lignin availability and heavy metal sorption. The extraction with 1% sodium hydroxide may have resulted in a cell structure with greatly reduced free surface area that may greatly decrease the accessibility of the cell wall components.

All of the fibers with lignin contents greater than about 10% readily sorb heavy metals while cotton, with a very low lignin content, is a very poor heavy metal sorbent. This shows that lignin does play some role in heavy metal ion sorption but is not the most important factor in the mechanism of ion removal. It may also be the type of lignin and the number of available free phenolic groups. Kraft lignin is highly condensed and many of the active sites may have been eliminated in cross-linking reactions. The hemicelluloses contain ionizable carboxylic acid groups in the uronic acids that are known to contribute to metal ion sorption (Reddad et al. 2002). A very preliminary look at the IR spectra, shows almost identical sorption for kenaf bast and core in the carbonyl region of approximately 1740 cm^{-1}, while this peak is missing from the cotton specimen. This would also indicate that there is more involved in the mechanism of heavy metal removal using lignocelluloiscs than simply carbonyl and lignin content.

Research is continuing to determine other factors, such as permeability, surface area, cell wall architecture and exposed chemical composition, pour size, and other chemical constituents in the fibers that may be important in the removal of heavy metals from aqueous solution using lignocellulosic fibers. The ultimate goal of this research is to be also to select the most effective lignocellulosic fiber to remove selected heavy metal ions based on know criteria.

REFERENCES

Acemioglu, B. and M.H. Alma (2001). Equilibrium studies on the adsorption of Cu(II) from aqueous solution onto cellulose. J. Colloid Interf. Sci., 243:81.

Acemioglu, B., A. Samil, M.H. Alma and R. Gundogan. Copper(II) removal from aqueous solution by organosolv lignin and its recovery. Unpublished data.

Basso, M.C., E.G. Cerrella and A.L. Cukierman (2002). Lignocellulosic materials as potential biosorbents of trace toxic metals from wastewater. Ind. Eng. Chem. Res. 3580-3585.

Bhattacharyya, A.K. and C. Venkobachar (1984). Removal of cadmium (II) by low cost adsorbents. J. Envir. Eng. Division (ASCE), 110:110.

Browning B.L. (1967). The extraneous components of wood in "Methods of Wood Chemistry," Chapter 5, pp. 75-90, John Wiley & Sons, Inc., New York, NY.

Kubinsky, E. (1971). Influence of steaming on the properties of *Quercus rubra* L. Wood. Holzforschung, 25(3):78-83.

Kubinsky, E. and G. Ifju (1973). Influence of steaming on the properties of red oak. Part I. Structural and chemical changes. Wood Science, 6(1):87-94.

Kubinsky, E. and G. Ifju (1974). Influence of steaming on the properties of red oak. Part I. Changes of structural and related properties. Wood Science, 7(2):103-110.

Kumar, P. and S.S. Dara (1980). Modified barks for scavenging toxic heavy metal ions. Indian J. Envir. Health, 22:196.

Lalvani, S.B., T.S. Wiltowski, D. Murphy, and L.S. Lalvani (1997). Metal removal from process water by lignin. Environ. Technol., 18(11):1163-1168.

Laszlo, J.A. and F.R. Dintzis (1994). Crop residues as ion-exchange materials. Treatment of soybean hull and sugar beet fiber (pulp) with epichlorohydrin to improve cation-exchange capacity and physical stability. J. Applied Polymer Sci., 52:521-528.

Maranon, E. and H. Sastre (1992). Behaviour of lignocellulosic apple residues in the sorption of trace metals in packed beds. Reactive Polymers, 18:172-176.

Masri, M.S., F.W. Reuter, and M. Friedman (1974). Binding of metal cations by natural substances. J. Applied Polymer Sci., 18:675-681.

Pawan, K. and S.S. Dara (1980). Modified barks for scavenging toxic heavy metal ions. Indian J. Envir. Health, 22:196.

Pettersen, R.C. and V.H. Schwandt (1991). Wood sugar analysis by anion chromatography. J. of Wood Chemistry and Technology, 11(4):495-501.

Phalman, J.E. and J.E. Khalafalla (1988). Use of ligochemicals and humic acids to remove heavy metals from process waste streams. U.S. Department of Interior, Bureau of Mines: RI 9200.

Randall, J.M., R.L. Bermann, V. Garrett, and A.C. Waiss (1974). Use of bark to remove heavy metal ions from waste solutions. Forest Product Journal, 24(9):80-84.

Reddad, Z., C. Gerente, Y. Andres, M-C. Ralet, J-F. Thibault, and P.L. Cloirec (2002). Ni(II) and Cu(II) binding properties of native and modified sugar beet pulp. Carbohydrate polymers, 49:23-31.

Rowell, R.M. and J.S. Han (1999). Changes in kenaf properties and chemistry as a function of growing time. In: Kenaf Properties, Processing and Products: Mississippi State University, Ag & Bio Engineering. pp. 33-41.

Sedell, J.S., D.D. Maitland, and M. Appl (2000). Copenhagen, and M. Furniss. Water and the Forest Service, USDA, Forest Service Washington Office, ES 660, Jan.

Shukla, S.R. and V.D. Sakhardande (1991). Metal ion removal by dyed cellulosic materials. J. Applied Polymer Sci., 42:825-829.

Sun, R-C., J.M. Lawther, and W.B. Banks (1998). Isolation and characterization of organosolv lignins from wheat straw. Wood and Fiber Sci., 30(1):56-63.

TAPPI Standard T 207 om-93, "Water solubility of wood and pulp," TAPPI, Atlanta, GA.

TAPPI Standard T212 om-93, "One percent sodium hydroxide solubility of wood and pulp," TAPPI, Atlanta, GA.

TAPPI Standard T 222 om-88, "Acid-insoluble lignin in wood and pulp," TAPPI, Atlanta, GA.

Tiwari, D.P., D.N. Saksena, and D.K. Singh (1997). Kinetics of adsorption of Pb(II) on used tea leaves and Cr(VI) on *Acacia Arabica* bark. Dev. Chem. Eng. Miner. Process. 5, 79.

Vaughan, T., C.W. Seo, and W.E. Marshall (2001). Removal of selected metal ions from aqueous solution using modified corncobs. Bioresource Tech., 78:133-139.

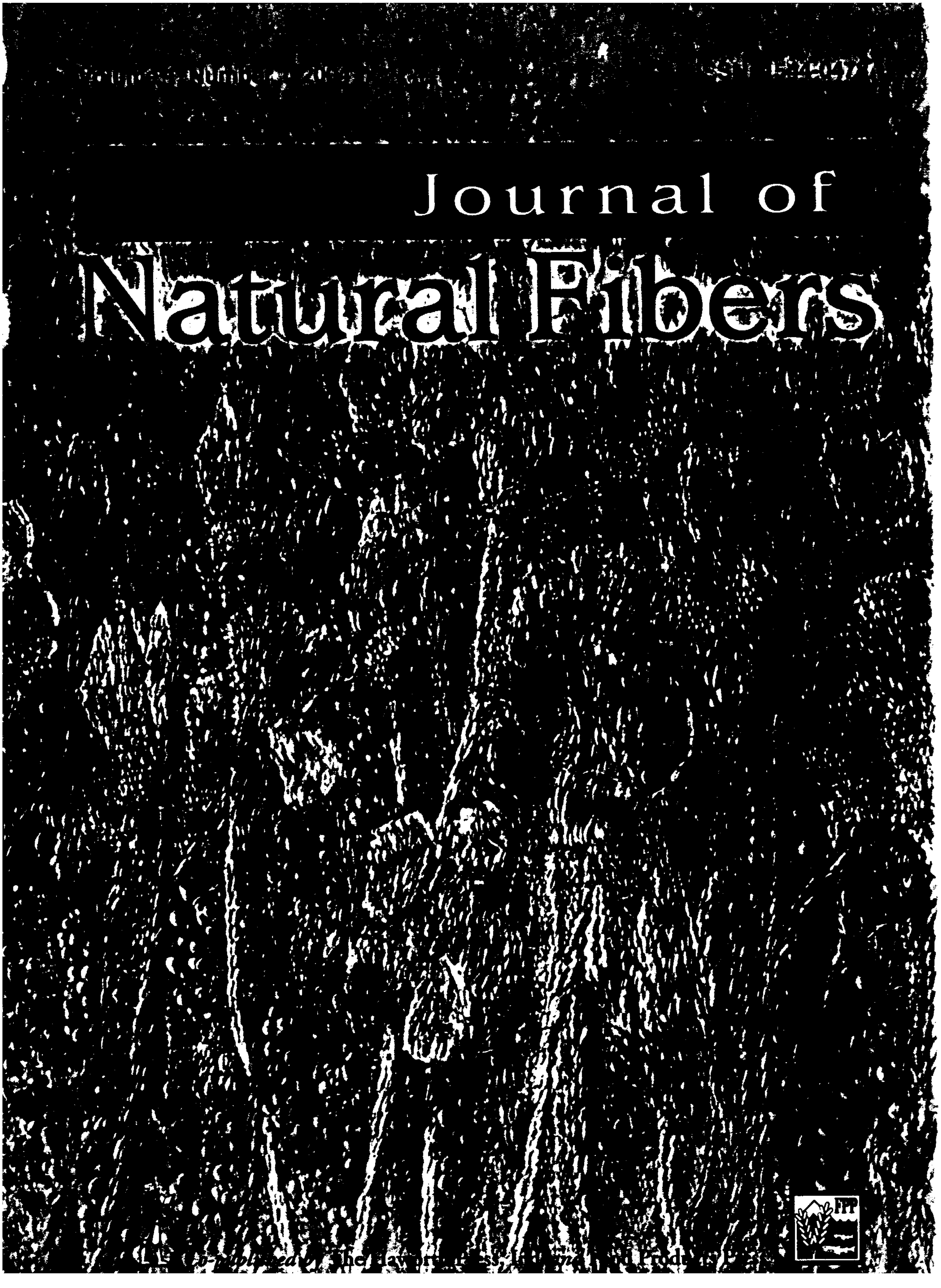
Verma, K.V.R., T. Swaminathan, and P.V.R. Subrahmnyam (1990). Heavy metal removal with lignin. Journal of Environmental Science and Health, A25(2): 242-265.

Waiss, A.C., M.E. Wiley, J.A. Kuhnle, A.L. Potter, and R.M. McCready (1973). Adsorption of mercuric cation by tannins in agricultural residues. J. Env. Quality, 2:369-371.

RECEIVED: February 20,2003
REVISED: May 16,2003
ACCEPTED: July 4,2003

[illegible]

Journal of
Natural Fibers



co-published by The Haworth Press, Inc. and Food Products Press