Adsorption of metal ions on lignin

Xueyan Guo, Shuzhen Zhang *, Xiao-quan Shan

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

Abstract

This study investigated the adsorption of the heavy metal ions Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) on a lignin isolated from black liquor, a waste product of the paper industry. Lignin has affinity with metal ions in the following order: Pb(II) > Cu(II) > Cd(II) > Zn(II) > Ni(II). The adsorption kinetic data can be described well with a pseudosecond-order model and the equilibrium data can be fitted well to the Langmuir isotherm. Metal ion adsorption was strongly dependent on pH and ionic strength. Surface complexation modelling was performed to elucidate the adsorption mechanism involved. This shows that lignin surfaces contain two main types of acid sites attributed to carboxylic- and phenolic-type surface groups and the phenolic sites have a higher affinity for metal ions than the carboxylic sites.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Lignin; Surface complexation model; Heavy metal ions; Adsorption

1. Introduction

Water pollution is a serious problem and heavy metals are common pollutants in water that threaten human health and environmental quality. Methods of minimizing heavy metal concentrations in surface waters and wastewaters are therefore crucial for environmental protection. The main techniques that have been used to remove heavy metals from water include chemical precipitation, membrane filtration, ion exchange, and adsorption on activated carbon [1–6]. However, these methods have limitations such as high operational costs in the case of adsorption by activated carbon and difficulties meeting strict regulatory requirements in the case of chemical precipitation. Intensive studies have therefore been carried out to develop more effective and inexpensive metal adsorbents. Candidate materials include industrial or agricultural waste products such as waste slurry [7,8], fly ash [9,10], lignite [11,12] pine bark [13], peat [14,15], and lignin [16–25]. Babel and Kurniawan [26] and Bailey et al. [27] have reviewed the application of low-cost adsorbents for heavy metal removal from contaminated waters.

Lignin is a natural polymer that is present in large quantities in the cell walls of terrestrial plants and is the main binding agent for fibrous plant components, typically comprising from 16 to 33% of plant biomass. More than 50×10^4 metric/tonnes/year of lignin are produced worldwide by pulping [28,29]. About 90–95% of the reactive lignin biopolymer is solubilized to oligomers that contribute to the pollution load. Lignin disposal is therefore subject to significant environmental constraints.

Lignin is a natural amorphous cross-linked resin that has an aromatic three-dimensional polymer structure containing a number of functional groups such as phenolic, hydroxyl, carboxyl, benzyl alcohol, methoxyl, and aldehyde groups [30], making it potentially useful as an adsorbent material for removal of heavy metals from water. Suhas et al. [31] have reviewed the literature on lignin as a biosorbent. Srivastava et al. [16] obtained remarkably high uptake of Pb(II) and Zn(II), up to 1587 and 73 mg/g for Pb(II) and Zn(II), respectively, by using lignin extracted from black liquor. Demirbas [24] reported a maximum adsorption capacity of 8.2–9.0 mg/g for Pb(II) and 6.7–7.5 mg/g for Cd(II) on lignin from beech and poplar wood modified by alkaline glycerol delignification. From the above data and the review by Suhas et al. [31] we find that there are significant differences in the metal sorption capacities of different types of lignin. Moreover, the related mechanisms of metal sorption by lignin are still subject to debate. Some studies have found that ion-exchange mechanisms may be responsible for the sorption of metal ions on lignin [17,21–23]. Srivastava et al. [16] and Mohan et al. [20] suggested that no single mechanism could explain the pro-

cess of metal removal by lignin. Several processes including ion exchange, surface adsorption, and complexation, have been suggested to explain the mechanisms involved. Detailed studies are therefore required to achieve a quantitative and mechanistic understanding of the sorption of metal ions by lignin.

The aim of the present study was to obtain a quantitative and mechanistic description of the adsorption of the metals ions Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) on lignin based on surface characterization and metal ion adsorption. The surface physico-chemical characteristics of lignin such as surface site densities, acidity constants, and metal binding constants, were investigated by potentiometric titrations and metal ion adsorption experiments. Surface complexation modelling was performed to elucidate the adsorption mechanisms involved.

2. Materials and methods

2.1. Adsorbent characteristics

Lignin was obtained from a paper mill in Yunnan Province, south China as follows. The black liquor, a recycled by-product of the pulping of wood, was acidified to pH 2–3 with sulfur dioxide. The liquid-sediment suspension was transferred to a lignin reactor in which solids and acid liquor were separated at 60–80 °C. The solids containing $80 \pm 2\%$ lignin were dried and termed lignin. Prior to the experiments the lignin was washed with deionized water (20 g/L) shaken on an end-over-end shaker for 12 h and filtered. This procedure was repeated three times, and the solid obtained was oven-dried at 45 °C for one day and ground to pass a 0.25-mm standard sieve. Lignin prepared in this way was then ready for use in the following experiments.

Total C, H, N, and S contents of the lignin were determined by dry combustion in an autoanalyzer (Vario EL, Elementar Analysensyteme, Hanau, Germany). The pH value of a lignin suspension was measured using a solid-to-water ratio of 1:1 (w/v). Cation exchange capacity (CEC) was determined by the method of Rhodes [32]. Specific surface area and pore diameter were measured using a Micromeritics Flowsorb II surface area analyzer (ASAP 2000, Micromeritics Company, Norcross, GA), and by applying the BET equation to the sorption of N_2 at a relative partial pressure of 0.3 at 77 K. The Fourier-transformed infrared spectra (FT-IR) were recorded with pellets obtained by pressing a mixture of 1 mg of sample and 100 mg of KBr under reduced pressure using a Perkin–Elmer GX2000 Fourier transform infrared spectrophotometer.

2.2. Adsorption kinetics

The kinetic experiments were performed in 500-ml batch reactors at 20 °C. One gram of lignin was firstly mixed thoroughly with 400 ml of a 0.01 M $NaNO_3$ electrolyte solution in a flask. Prior to the introduction of the metal ions, the suspension was magnetically and vigorously stirred for 2 h to hydrate the lignin. The initial concentration of the metal ions Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) was 0.8 mM. After the introduction of the metal ions individually the samples were magnetically stirred, collected at different time intervals, and filtered through a

0.45-μm cellulose acetate membrane. The metal concentrations in the filtrate were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 2000 DV, Perkin Elmer, Wellesley, MA). The quantity of metal adsorbed was deduced from the mass balance between the initial concentration and the concentration in solution at a given time.

2.3. Adsorption isotherms

The adsorption isotherms were determined by a batch technique in a background electrolyte of 0.01 M $NaNO_3$ at 20 °C. A 20-ml aliquot of 2.5 g/L lignin suspension was transferred to a 40 ml polyethylene centrifuge tube. The initial concentrations of each metal ranged from 0.2 to 2.5 mM. The pH of the system was maintained at 5.5. After the samples were shaken end-over-end for 24 h the suspensions were centrifuged at $7200 \times g$ for 15 min, filtered through a 0.45-μm cellulose nitrate membrane, acidified, and analyzed for metal ion concentrations.

2.4. Effect of pH on the adsorption

One gram of lignin was introduced into a reaction vessel with 400 ml background electrolyte inside and hydrated for 2 h. The suspension was then spiked with metal stock solution to achieve a starting concentration of 0.2 mM for each metal ion. The suspension was stirred and titrated to higher pH by stepwise addition of dilute HNO_3 or NaOH. After each pH increment was reached a 20-ml aliquot was transferred from the reaction vessel to a 40-ml centrifuge tube and shaken at 25 rpm on an end-over-end shaker for 24 h. Afterwards, the final pH was measured and the suspensions were centrifuged, filtered, acidified, and analyzed for metal ion concentrations. To examine the effect of ionic strength, adsorption of metal ions on lignin was performed in background electrolytes of 0.01 and 0.1 M $NaNO_3$.

2.5. Potentiometric titrations

An automatic titration system (Microprocessor 682, Metrohm) was employed at a constant temperature of 25.0 ± 0.2 °C. For each titration a given volume of the stock suspension in a reactor (100-ml conical flask) was diluted using 1.0 M $NaNO_3$ solution and deionized water to a particle concentration of 2 g/L. Three final ionic strengths in the sample suspensions supported by the background electrolyte ($NaNO_3$) were 0.005, 0.01, and 0.1 M, respectively. The reactor, equipped with a combined glass electrode, was agitated using a magnetic stirrer and purged with pure N_2 during the whole titration procedure. Nitrogen gas was prepurified by passing through wash bottles containing NaOH (0.1 M) and HCl (0.1 M), and then saturated with distilled water. A back-titration procedure was carried out by which the suspension was first acidified to an approximate pH 3 and then back-titrated with a standardized 0.0979 M NaOH solution at a rate of 0.01 ml/min until the pH exceeded 8.0. Stable pH values were recorded when the drift of the potential of the glass electrode cell was less than 10 μV/s. Blank titrations were also performed under the same experimental conditions.