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Heavy metal ions retention by bi-functionalized lignin: Synthesis, applications, and adsorption mechanisms

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ABSTRACT

Bi-functionalized lignin with amino and sulfonic groups (ASL) was synthesized via Mannich reaction and sulfomethylation. It was systematically characterized by FT-IR, element analysis, surface charge and XPS. Effects of initial pH, contact time and initial metal ion concentration on the adsorption of Cu(II) and Pb(II) onto ALS were studied. Results indicated that the biosorbent showed excellent performance for metals even from low pH solutions. The adsorption kinetics and isotherms could be described well with Pseudo-second-order and D–R model, respectively. Further investigation of the metal-loaded ASL by FT-IR and XPS elucidated the amino and sulfonic groups reacted with metals in different way.

1. Introduction

Contamination by toxic heavy metals has been a major environmental problem with the development of industry. The main sources of heavy metals such as mercury, lead, copper, cadmium, nickel, and zinc are mining, automobiles, and metal industries. The removal of heavy metal ions from wastewater because of their detrimental effects on living organisms is extremely important. Several technological methods have been developed for the decontamination of heavy metal ions from wastewater, including precipitation, ion-exchange, membrane separation, and adsorption, etc. [1–3]. However, high capital costs for the above process have led researchers to explore more cost-effective options including the use of sorption media developed from natural abundant materials (i.e. bio-sorbents) [4–6].

Lignin, one of the main constituents of lignocellulosic biomass, is the second abundant biopolymer on the earth [7]. More than 50×10^4 tons/year of lignin is produced worldwide by pulping, but only approximately 2% of the total lignin is used as dispersants or binding agents and the remainder burned as low value fuels [8]. Due to the merits of natural abundant, low-cost, environmentally friendly and most importantly containing various functional groups including phenolic hydroxyl, aliphatic hydroxyl, carbonyl, and methoxyl, etc. [9], lignin has great potential in the cleanup of wastewater [10]. However, the as-obtained lignin from hardwood, softwood and so on has been reported quite low adsorption capacity for heavy metal ions, which is commonly less than 10 mg/g [10–12]. In order to improve the adsorption capacity, some lignin-based bioadsorbents were prepared by incorporating oxygen- [13], nitrogen- [14,15] or sulfur-containing [16] functional groups. Peternele et al. [13] prepared a carboxymethylated lignin which reached a much higher maximum adsorption capacity of 80.3 mg/g for Pb(II) and 37.9 mg/g for Cd(II), respectively. Lu et al. [15] prepared amino functionalized lignin which showed a high adsorption of ~60 mg/g for Cu(II). But these lignin-based biosorbents were generally anchored only sole main functional group that still suffered from the disadvantages of limitation of pH values.

To our knowledge, sulfonic groups can be introduced into lignin for improving its water-solubility and applications [17,18]. Considering the strong ionization of sulfonic groups in aqueous environment, which could result in well dispersion of lignin and provide a strong electrostatic attractive potential to cations, and also the strong chelating ability of N and S element, the lignin-based biomaterial bi-functionalized with amino and sulfonic groups are expected to display an excellent adsorption performance toward metal ions. To this end, we newly synthesized the bi-functionalized lignin biomaterial with amino and sulfonic groups (ASL) by Mannich reaction and sulfomethylation. This study illustrated the possibility of using ASL to adsorb Pb(II) and

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Cu(II) from water, which are known to be common toxic metals. In addition, the adsorption behavior including influence of pH, adsorption kinetics, adsorption isotherms and adsorption mechanisms were also investigated.

2. Experimental

2.1. Materials

Aqueous solutions of $CuSO_4{\cdot}5H_2O$ and $Pb(NO_3)_2$ with different concentrations were prepared by dilution of 1000 mg/L stock solutions by distilled water. All chemicals used were of analytical reagent grade. Alkaline lignin was obtained by precipitation from the black liquor (Nanpu Pulp Mill, China) with H_2SO_4 [19].

2.2. Synthesis of ASL

ASL was prepared by a three-step method including pre-oxidation, Mannich reaction and sulfomethylation (Fig. 1). (i) 20.0 g alkaline lignin and 100 mL distilled water were poured into a flask bottle equipped with an electric heating device, a motor stirrer, a thermometer, a dropping funnel, and a reflux condenser. The temperature was elevated to 50 °C and the pH was adjusted to 10 by 0.1 M NaOH. Pre-calculated H_2O_2 was added dropwisely to oxidize lignin with $FeSO_4$ as a catalyst for 30 minutes, (ii) formaldehyde (0.05 g/g lignin) and diethylenetriamine (0.6 g/g lignin) was added carefully, and the temperature was elevated to 90 °C for Mannich reaction for 5 h, (iii) another part formaldehyde (0.06 g/g lignin) and Na_2SO_3 (0.49 g/g lignin) was added for sulfomethylation for 2 h. The mixture was ultrafiltrated by a hollow fiber membrane (Da = 1000) to remove the inorganic residues and low molecular organics. After dried under vacuum (65 °C) overnight, a brown powder, i.e. ASL was obtained.

2.3. Characterizations

Fourier transform infrared (FT-IR) spectroscopy was recorded on a FT-IR spectrophotometer (Thermo Nicolet 510, United States) using a KBr disk method. Element analysis (EA) was performed on a PE 2400 II (Perkin–Elmer, USA). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 XPS spectrometer (Thermo-VG Scientific Co., USA). A monochromatic Al Kα X-ray source (1486.6 eV of photons) was used, with a spot area of 200 μm in diameter. The base pressure in the working chamber was 10^{-9} Torr. All binding energies were referenced to the neutral C_{1s} peak at 284.6 eV.

2.4. Batch adsorption

The batch adsorption test for adsorption of the single metal ion was conducted as follows: using one set of sealed flasks, 0.25 g ASL was added to 50 mL solution with different concentration. The mixtures in the flasks were stirred to guarantee a good dispersion of the materials and placed in a water bath at 25 ± 0.5 °C for a suitable time to allow complete equilibration and then were filtered through 0.22 μm membranes. The concentrations of the initial and residual ions were determined by an inductively coupled plasma optical emission spectrometry (ICP-OES, optima 5300DV, Perkin–Elmer). The removal efficiency (R) and adsorption capacity (Q_e, mmol/g) were calculated by the following equations:

$$R = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

$$Q_e = \frac{V(C_o - C_e)}{m} \quad (2)$$

where C_o and C_e (mmol/L) are the initial and final concentrations of metal ions, respectively; V (L) is the volume of the solution, and m (g) is the mass of ASL.

The initial pH values of the solutions were adjusted from 3.0 to 8.0 with 0.1 M HNO_3 and 0.1 M NaOH to investigate the influence of pH on the adsorption with or without ASL. Kinetic Adsorption was conducted at 25 ± 0.5 °C (500 mL ion solution with 50 mg/L, 1.0 g of ASL, pH = 6.0) in a conical flask. At predetermined time intervals, 5 mL volumes of supernatant solutions were pipetted from the conical flask. The concentrations were determined by ICP-OES.

2.5. Mathematical modeling

The Lagergren-first-order and Pseudo-second-order models were used to evaluate the experimental data, which were given by Eqs. (3) [20] and (4) [21], respectively:

$$\log(Q_e - Q_t) = \log Q_e - \left(\frac{k_1 t}{2.303}\right) \quad (3)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (4)$$

where Q_e and Q_t are the amounts of the metal ions adsorbed (mmol/g) at equilibrium and at contact time t (min), respectively, k_1 (1 min^{-1}) and k_2 (g/mmol min) are the rate constant.

The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models, which are well-known and widely used models, were chosen to analyze the bioadsorption equilibrium data. Linearized form of the Langmuir equation was given by Eq. (5) [22]:

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{bQ_m C_e} \quad (5)$$

where Q_e is the amount of metal ion adsorbed on the adsorbent (mmol/g), C_e is the equilibrium metal ion concentration (mmol/L), Q_m represents a saturated adsorption capacity when the surface of

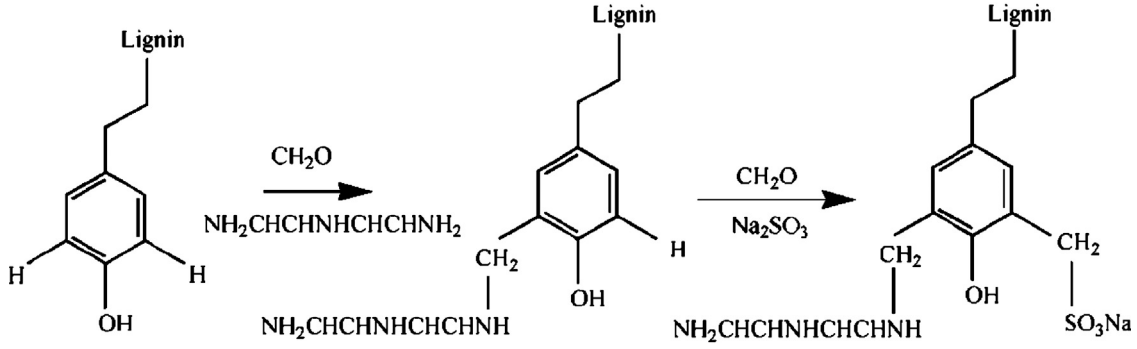

Fig. 1. Synthesis of amino and sulfonic bi-functionalized lignin (ASL).