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Microwave-assisted functionalized lignin with dithiocarbamate for enhancing adsorption of Pb(II)

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ABSTRACT

This study firstly reported a microwave-assisted functionalized lignin with dithiocarbamate (LD) for enhancing adsorption of Pb(II) in water. It was found that LD particles were about 1 μm in diameter with plenty of dithiocarbamate functional groups. LD showed a fast adsorption to Pb(II) with an equilibration time of 45 min. The saturated adsorption capacity to Pb(II) was 106 mg/g, which was 7.5 times of the original lignin and also higher than other lignin-based adsorbents. The prepared material can not only effectively adsorb Pb(II) in water, but also be easily prepared. These findings demonstrate that LD has great potential applications in adsorption and separation.

1. Introduction

Lignin, the second most abundant natural polymer next to cellulose, offers the advantages of CO_2 neutral, eco-friendly, abundant, and low-in cost [1]. Recently, due to the rising environmental awareness and depletion of fossil resources, lignin has emerged as a potential component for various applications, such as stabilizing agents, surfactants, adhesives, and adsorbents [2,3]. Water pollution by heavy metals has become a serious environmental issue due to their high toxicity and carcinogenicity, such as lead, cadmium, and mercury etc. [4]. The removal of heavy metals from contaminated water is an urgent need for our society. Although there are some reports about lignin in adsorbing heavy metals, unfortunately, the adsorption capacity is quite low, for example, only 9.0 and 7.5 mg/g for Pb(II) and Cd(II), respectively [5]; 5.1 and 3.2 mg/g for Cu(II) and Cd(II), respectively [6]. This seriously limits the practical usage of lignin-based adsorbents in wastewater treatment. Chemical functionalization of materials is critical for enhancing their properties [7,8]. However, much effort so far was involved in conventional heating methods, which was slow in reaction rate due to the low convection currents and thermal conductivity of materials [8,9]. In contrast, microwave radiation can produce fast and efficient internal heating by coupling of microwave energy with solvent/reagents in reaction mixture, and accordingly provides the advantages of rapid reaction, efficiency, simplicity, and eco-friendliness [10,11].

In this work, we demonstrated a microwave-assisted synthesis of lignin/dithiocarbamate (LD) by a two-step method. The first step involves Mannich reaction of lignin with amine and formaldehyde (Scheme 1(a)). The second step involves esterification with carbon disulfide (Scheme 1(b)). The adsorption performance of LD was evaluated by adsorbing Pb(II), a typical hazardous pollutant in water.

2. Experimental

2.1. Synthesis

Lignin (provided by Nanpu Pulp Mill, China) and diethylenetriamine (1:2, g/g) were dissolved in water. After adding formaldehyde, the flask-containing mixture was fitted in a microwave oven (XH-MC-1, with a condenser) and subjected to microwave treatment of 20 min. Then, it was cooled to 40 °C, and carbon disulfide was added drop wisely for esterification. After that it was filtered and washed with deionized water, dried under vacuum at 50 °C for 24 h.

2.2. Characterizations

The morphologies of samples were taken in a Hitachi SU8020

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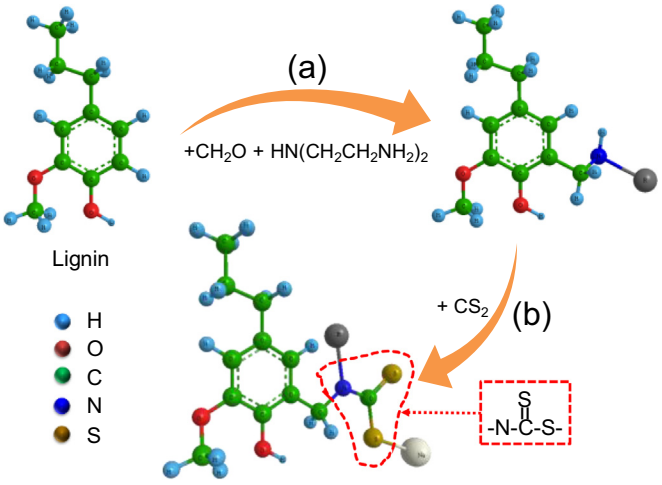

Scheme 1. Synthetic diagram of lignin/dithiocarbamate (LD).

microscope by immobilizing the sample with conductive glue. FT-IR spectra were recorded by a Nexus 470 spectrometer. Pb(II) concentration was determined by an inductively coupled plasma optical emission spectrometry (ICP-OES, optima 5300DV, Perkin-Elmer).

3. Results and discussion

3.1. Characterizations

SEM images of lignin (Fig. 1(A)) and LD (Fig. 1(B)) demonstrated the morphological changes occurred after reactions. Lignin was irregular, heterogeneous and grainy with large particle size ($>4\,\mu m$), while the LD particles became homogeneously and much smaller ($\sim 1\,\mu m$).

FT-IR spectra were shown in Fig. 1(C). The peaks at 1112 and 960 cm^{-1} could be assigned to the stretching vibrations of the C=S and C–S bonds in LD [12], respectively. The peaks at 1492 and 1434 cm^{-1} indicated the stretching vibration of C–N in LD [12]. That confirmed the introduction of dithiocarbamate groups in LD. The peak at 1609 cm^{-1} indicating the "aromatic core" structure of lignin [13] shifted to 1639 cm^{-1} in LD. Such a wavenumber shift was caused by the substitution of hydrogen with dithiocarbamate groups on the aromatic ring [14]. While the band at 1384 cm^{-1} indicating C–O stretching of ether groups shifted to 1323 cm^{-1}. That was due to the conjugation between the aromatic ring and double bonds in dithiocarbamate groups [15]. The broad peaks at 3430 cm^{-1} were attributed to O–H stretching. The peaks at 2920 and 2848 cm^{-1} were due to the CH_2 asymmetric and symmetric stretching [16].

3.2. Adsorption studies

Effect of contact time on adsorption was investigated by contacting 0.01 g LD with 50 mL Pb(II) solution (20 mg/L) in stoppered conical flasks at 25 °C. The samples were analyzed at certain time intervals. As shown in Fig. 2(A), the adsorption increased sharply at short contact time and slowed gradually as equilibrium was approached. This was due to the availability of initial large number of vacant surface active sites on LD and thus rapidly increased the amount of Pb(II) accumulated on LD surface within 45 min. Afterward the filling of vacant sites became difficult due to repulsive forces between Pb(II) on LD surface and solution [9].

The adsorption mechanism of Pb(II) on LD was further analyzed by fitting with pseudo-first-order (Eq. (1)) and pseudo-second-order (Eq. (2)) models [17]:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \tag{2}$$

where q_t (mg/g) is the amount adsorbed at time t (min), q_e (mg/g) denotes the amount adsorbed at equilibrium, k_1 (min^{-1}) and k_2 (g/mg min) are the adsorption rate constants. The results were tabulated in Table 1. As exhibited, the experimental data fitted well with pseudo-second-order model, indicated by the higher correlation coefficient (R^2=0.9710). According to the assumption of pseudo-second-order model, the adsorption Pb(II) on LD was controlled by chemisorption mechanism [12].

To obtain the saturated adsorption capacity of LD for Pb(II), effect of initial concentration was determined by contacting 0.01 g LD with 50 mL Pb(II) solution within 10–120 mg/L at 25 °C. The results were presented in Fig. 2(B). As seen, the adsorption amount increased with increasing initial Pb(II) concentration. The saturated adsorption capacity was 106 mg/g, 7.5-time of the original lignin (14 mg/g) [18], which was also much higher than other reported lignin-based adsorbents, such as, poplar lignin (9 mg/g) [5], kraft lignin (15 mg/g) [19], lignosulfonate (27 mg/g) [3], lignin-xanthate (63 mg/g) [20], even silica-gel (83 mg/g) [21] and activated carbon (27 mg/g) [17]. The high adsorption capacity was due to the smaller particle size of LD for diffusion and the soft basic dithiocarbamate functional groups for binding soft acidic Pb(II) [22].

Langmuir and Freundlich models were further applied to fit the experimental data, which are given by [23,24]:

$$q_e = \frac{q_m b c_e}{1 + b c_e} \tag{3}$$

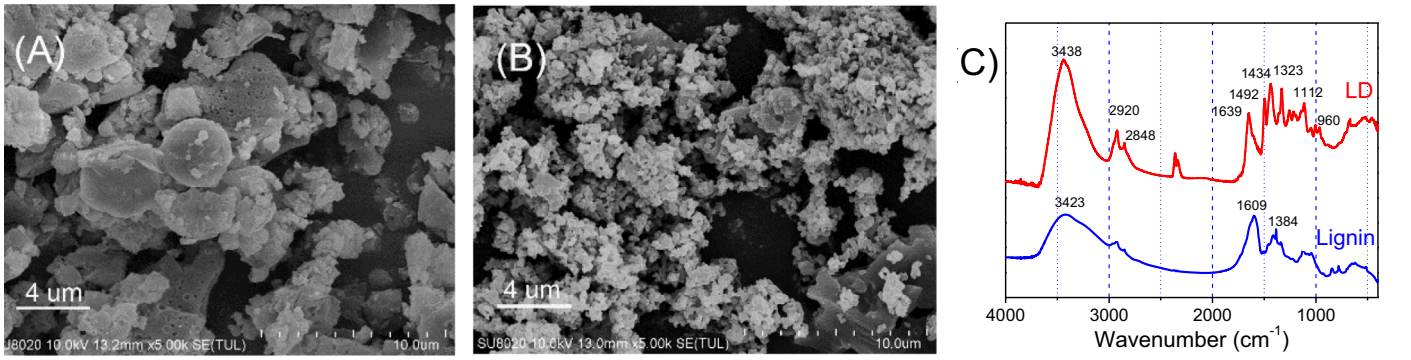

Fig. 1. SEM micrographs of (A) lignin, (B) LD; (C) FT-IR spectra.