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Microwave-assisted synthesis of high carboxyl content of lignin for enhancing adsorption of lead

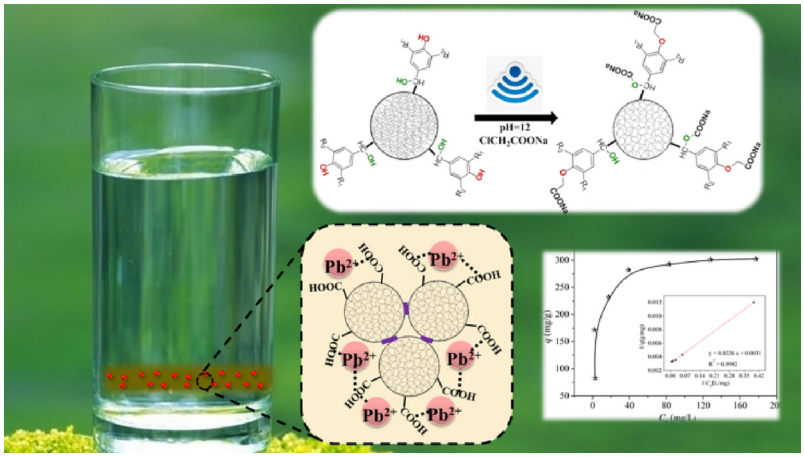
Yuan Li[a,b,c], Rubin Zhao[a,c], Yuxia Pang[a,c,*], Xueqing Qiu[a,c], Dongjie Yang[a,c]

[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, China
[b] Guangdong Research Institute of Petrochemical and Fine Chemical Engineering, Guangzhou, China
[c] Guangdong Engineering Research Center for Green Fine Chemicals, Guangzhou, China

GRAPHICAL ABSTRACT

Synopsis

Crosslinking microwave-assisted carboxymethyl lignin adsorbent exhibited superior adsorption performance for Pb^{2+}, which was attributed to high carboxyl group content.



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ABSTRACT

An efficient lignin adsorbent for Pb^{2+} in water was synthesized by crosslinking microwave-assisted carboxymethyl lignin (C-MCML) and the saturated adsorption capacity for Pb^{2+} was 302.3 mg/g. Microwave irradiation showed a greater assisted ability in the carboxymethylation than that of traditional heating, and the carboxyl content of microwave-assisted carboxymethyl lignin could be raised to 3.61 mmol/g. The adsorption behavior of C-MCML also was studied by varying different parameters like pH, initial concentration of metal ions and shaking time. The adsorption isotherm was fitted well by Langmuir model, and the fitting saturated adsorption capacity was 323.6 mg/g. Meanwhile, the results of FTIR and XPS shown that main Pb^{2+} adsorption mechanimis was ion exchange by carboxyl. The adsorption capacity of C-MCML was still maintained at 90% after recycled for 10 times.

* Corresponding author at: School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, China.
E-mail address: ceyxpang@scut.edu.cn (Y. Pang).

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1. Introduction

Heavy metal ions, including Pb, Cu, Cd, Ni, Cr, and Co, are not biodegradable and have been classified as major pollutants, causing numerous diseases and disorders at even very low levels [1]. Therefore, how to remove heavy metal ions effectively has been a crucial issue [2]. Among various treatment technologies, such as ion exchange, membrane separation and adsorption et al., adsorption has been of attracting great interest due to its advantages of low cost, easy operation and cyclic utilization. Until now, activated carbon, zeolites, carbon nanotubes and polymeric materials have been widely commercialized. However, the cost, adsorption capacity and regeneration performance are often unsatisfactory [3,4].

Lignin is one of the most abundant components in plants. Annually, more than 70 million tons of industrial lignin is obtained from the biorefinery in the pulp mill and more and more efforts are devoting to the high-value utilization of lignin. Intense researches have been focus on lignin-based heavy metal adsorbent because of its abundance, environmental friendly nature, thermal and biological stability, and easy accessibility [5–8]. Nevertheless, progress on lignin-based adsorbent is slow and the adsorption capacity is quite low, and for example, only 147.1 mg/g for Pb^{2+} [9]; 84.0 mg/g for Cu^{2+} [10]; 70.1 mg/g for Cd^{2+} [11]; 7.7 and 5.3 mg/g for Co^{2+} and Hg^{2+}, respectively [12].

It is generally known that carboxyl has a good adsorption capability for heavy metal ions [13,14]. Thus, the adsorption capacity could be greatly enhanced by grafting carboxylic functional groups. In our previous work [15], carboxymethylation had been found to be an effective method to improve carboxylic groups of lignin. Carboxymethyl lignin was obtained from the reaction between sodium monochloroacetate and alkali lignin under alkaline and conventional heating condition, and the main reaction site of lignin turned out to be phenolic hydroxyl [16]. The alcohol hydroxyl of lignin, which quantities is large, could not be substituted by sodium monochloroacetate under conventional heating methods. The improvement of carboxyl content of lignin was limited by low content of phenolic hydroxy and low reaction efficiency under traditional synthesis methods yet [15]. It needs to develop a new synthetic method for improving the carboxyl content.

Compared to the conventional heating method, microwave irradiation has been becoming a new type of efficient heating mode [17]. The main advantages of microwave-assisted reaction are high reaction selectivity and fast reaction speed due to its rapid heating and energy homogeneous penetration [18]. Many simple, fast, and energy-efficient microwave-assisted routes have been developed and applied in the synthetic reaction [19]. To date, several reactions, such as syntheses of Poly(3,3′-Bisazidomethyl Oxetane) [20], g-C_3N_4 [21] and Kenaf Cellulose Carbamate [22], were reported for high reaction efficiency under microwave irradiation. Meanwhile, it was reported that etherification reaction could be occurred between alcohol hydroxyl and halogenated alkane under microwave irradiation [23]. As for alkali lignin, not only phenolic hydroxyl but also alcoholic hydroxyl can react with sodium monochloroacetate under microwave irradiation. Therefore, microwave irradiation might open up a new way to prepare carboxymethyl lignin with high functional groups contents.

Herein, in order to increase the carboxyl content of lignin for heavy metal adsorption, we investigated the application of microwave irradiation in the synthesis of carboxymethyl lignin. Because the water solubility of carboxymethyl lignin significantly increased after the carboxymethylation, the solid phase adsorbent was obtained by extra formaldehyde crosslinking (Fig. 1). The molecular weights, carboxyl content and chemical structure of the products were studied and the adsorption performance of carboxymethyl lignin was evaluated by adsorbing Pb^{2+}. The results showed that the product have higher carboxyl content and amount of adsorption for Pb^{2+} than the traditional composite sample other literature reported. Therefore, carboxymethyl lignin under microwave irradiation is an effective adsorbent for removal of metal ions.

2. Experimental

2.1. Materials

Alkali lignin (AL) was provided by Xiangjiang Pulp Mill, Hunan, China. Sodium monochloroacetate was obtained from Sinopharm Chemical Reagent Co., Ltd., China. The other reagents were purchased commercially as analytical or chromatographic grade products and used directly without further purification.

2.2. Synthesis

2.2.1. Synthesis of microwave-assisted carboxymethyl lignin (MCML)

AL powder (1.75 g), sodium monochloroacetate (1.17 g) and sodium hydroxide (0.40 g) were completely dissolved in water (25 ml) under stirring. Then, the mixtures were fitted in the microwave reaction kettle ((ETHOS ONE)) and subjected to microwave treatment with 20 min at 110 °C. When the solution had cooled to room temperature, the pH value of the solution was adjusted to 7 using dilute nitric acid. The precursor (MCML) was obtained by filtration.

2.2.2. Synthesis of crosslinked microwave-assisted carboxymethyl lignin (C-MCML)

Then, MCML was further crosslinked by formaldehyde to avoid the dissolution of MCML in adsorption process. The typical procedure is as follows. MCML (1.80 g), sodium hydroxide (0.75 g) and 10 ml of 30 wt % formaldehyde solution were added into a 50 ml stand-up flask and stirred for 60 min at 95 C. At the end of reaction, the solution pH was adjusted to 2.0 ± 0.1 by dilute nitric acid and centrifuged at 10,000 rpm for 10 min. The mixture was filtered and washed by distilled water for 3 times. Finally, the C-MCML was obtained after dried at 50 °C in vacuum for 2 days.

2.2.3. Synthesis of crosslinked carboxymethyl and alkali lignin (C-TCML and C-AL)

The carboxymethylated lignin (TCML) was prepared according to the literature [15] under traditional heating condition, and the reaction time was 90 min. Crosslinked carboxymethyl and alkali lignin were synthesized following the crosslinking conditions above, respectively.

2.3. Methods

The nonaqueous potentiometric titration method was used to measure the carboxyl group content of samples with an automatic potentiometric titrator (809 Titrando, Metrohm Co., Switzerland [15].

The FTIR spectra of samples were recorded using Fourier transform infrared spectrometry of Auto system XL = I-series = Spectrum 2000 spectrometry (Thermo Nicolet Co., Madison, WI, USA). The samples were dried under vacuum and mixed with KBr in the concentration of about 1–100 mg in a mortar box. Then, the mixtures were tableted for FTIR analysis. The spectra were recorded between 4000 and 500 cm^{-1}.

The water solubility of samples was measured by a UV spectrophotometer (type UV- 2450, Shimadzu Corp., Japan) in 280 nm ultraviolet wavelength, and deionized water was used as reference sample in the reference cell. 20 mg of samples were added into the 10 mL of water with pH values at 4, 5.5, 7 and 9, respectively, under stirring for 1 h. Then the concentrations of supernatant were measured by a UV spectrophotometer.

The molecular weight (*Mw*) of samples was determined by an Agilent 1100 series gel permeation chromatography system (Agilent Technologies Corp., Santa Clara, USA) with PLgel 5 μm 1000 Å and PLgel 5 μm 500 Å columns. The mobile phase was THF with a flow rate of 1 mL/min and polystyrene was employed as the standard.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Thermo Fisher Scientific K-Alpha$^+$ system. An Al Ka X-ray source at 1486.6 eV was used in the XPS analysis. Binding energy