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Surface sodium lignosulphonate-immobilized sawdust particle as an efficient adsorbent for capturing Hg^{2+} from aqueous solution

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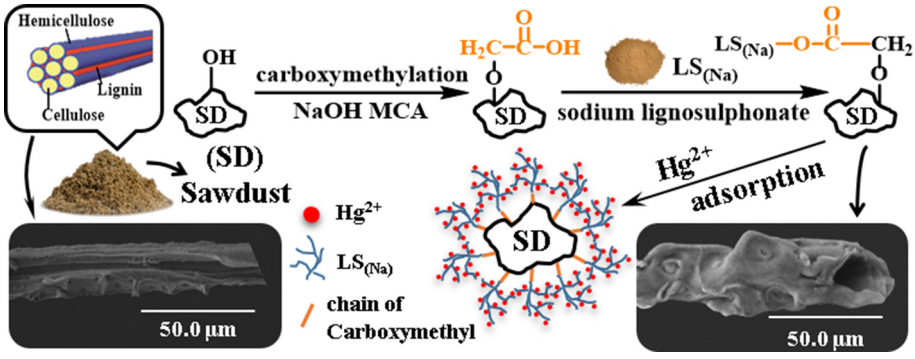
GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the soluble sodium lignosulphonate (LS_{Na}) molecules were successfully grafted onto the surface of pine sawdust (PSD) particles to obtain an efficient adsorbent (PSD-LS) for removing Hg^{2+} from wastewater. In advance, the surface of sawdust particles were carboxymethylated by chloroacetic acid, the LS_{Na} would be anchored on the surface by a heterogeneous esterification reaction occurred between the hydroxyl of LS_{Na} and carboxyl on PSD surface. The resultant product (PSD-LS) exhibited a good adsorption performance for Hg^{2+} with adsorption capacity up to 164.77 mg/g and it was characterized by scanning electron microscope (SEM), energy dispersive X-ray diffraction (EDX), Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). The effects of pH, contact time, adsorption temperature and initial concentration on the adsorption of Hg^{2+} were investigated. Results showed that the pseudo–second–order kinetics and Langmuir isotherm model could describe the adsorption process better. In addition, the composite adsorbent has outstanding reusability with high and stable desorption rates under several continuous cycle. These findings suggested that PSD-LS was a potential adsorbent to remove hazardous metal ions from wastewater.

1. Introduction

Heavy metal pollution has been attracting more and more attention all over the world. Among them, mercury is the only one which can be completely cycled with strong biological toxicity in ecosystem [1,2]. Divalent mercury ions are easily converted to organic mercury with highly toxic by organic matter and microorganisms, which would release to the atmosphere or damage people's health through biomagnification such as minamata disease [3–6]. It is worth noting that there are large quantities of mercury pollution wastewater continuously discharged to environment

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around the world. As a big industrial country, China's mercury emissions usually occupy a high proportion of the global total in the past few years [7–10]. More and more countries have taken measures to reduce mercury emissions, but there still existed a large amount of mercury in water released from the deposited mercury [11]. Therefore, the removal of mercury from water has become significantly important.

Adsorption method is widely used in the removal of heavy metal ions due to its high efficiency, low investment, simplicity of operator and non-toxic [12–15], but almost all of the adsorbents used for sewage treatment are expensive or hard to use, thus, the development of a cheap, easy-to-use and efficient adsorbent becomes extremely urgent [16,17]. As a waste from wood processing, sawdust has sustainable sources and huge production. Previous studies have reported that this material rich in cellulose, lignin and hemicellulose to be used for adsorbing heavy metal ions from wastewater [18,19]. Surface modification is usually regarded as an effective way to further enhance the adsorption performance, the abundant hydroxyl groups distributed on the surface of sawdust from cellulose and phenolic hydroxyl from lignin indicate that it is an ideal substrate for modification [20,21], which has attracted lots attention of researchers [22]. Usually, the surface decoration on substrate with polymers could be achieved via two approaches, including "grafting to" and "grafting from" [23]. But both of them suffer from some overcomes, the former is difficult to achieve higher adsorption capacity when grafting molecules with small amounts of adsorbed groups on sawdust surface and the latter often faced a tough situation: a lot of self-polymer will generate in the process of grafting.

In this work, a natural functional macromolecule of sodium lignosulphonate (LS_{Na}) was grafted on to the pinewood sawdust (PSD) surface via the way of "grafting to". Sodium lignosulphonate, as a modification molecule, is a by-product generated in the paper industry. It has a large number of hydroxyl, sulfonic acid group, methoxy group and a small amount of carbonyl in its molecule as well as shows a high hydrophilicity. All of these characteristics of LS_{Na} are conducive to capture metal ions. In order to increase the number and accessibility of surface hydroxyl, the sawdust particles was treated by sodium hydroxide solution to destroy hydrogen bonds between cellulose molecules in its structure [24]. Those primary hydroxyls from cellulose molecules can be carboxymethylated in alkaline condition, by this way, carboxyl groups were introduced onto sawdust surface of particles. The sodium lignosulfonate was anchored onto the sawdust surface by a heterogeneous esterification reaction between hydroxyls of sodium lignosulfonate and carboxyl groups on sawdust surface, which can be carried out efficiently at room temperature in the presence of catalyst. And the modified sawdust particles were easy to be separated from aqueous solution. Therefore, both the adsorption property of high adsorption capacity and fast rate were obtained due to the rich groups on sawdust from sodium lignosulfonate and the loose and porous structure of sawdust.

2. Method

2.1. Materials and reagents

Pine sawdust (PSD) was collected from the plant processing factory in Zengcheng, Guangdong province, China. The main reagents monochloroacetate (MCA), sodium hydrate (NaOH), isopropyl alcohol (IPA), aluminum chloride ($AlCl_3$), sodium lignosulphonate (LS_{Na}), mercury bichloride ($HgCl_2$) and hybrochloric acid (HCl) were purchased from Geao Chemical Products Company (Wuhan, Hubei, China). And all chemicals are of reagent grade and used as received without further purification.

2.2. Adsorbent preparation

Fig. 1 illustrated the preparation process of PSD-LS. Pinewood sawdust was sieved to 80 mesh after washing and drying. Then decrystallization treatment was taken for these natural pinewood sawdust (PSD(N)) microfiber by immersing them into 7 wt% NaOH solution at room temperature soaking for 12 h. After that, they were washed with distilled water to neutralize and dried to obtain the decrystallized PSD (PSD(D)). For surface modification, 4.0 g of PSD(D) was added to a 250 mL conical flask, 30.0 g of sodium hydroxide was slowly added to a beaker which containing 110 mL of deionized water, 30.0 g of chloroacetic acid was added to 30 mL of isopropanol and the solution was slowly dropped into the conical flask. The conical flask was placed in a table concentrator at 60 °C and shaken for 1 h. Next the temperature was raised to 75 °C and the reaction was continued for 30–45 min. The product was soaked in a weakly acidic condition for 3 h, washed with deionized water until neutral and then dried at 45 °C to obtain carboxymethylation of pinewood sawdust (PSD(C)). Subsequently, 0.25 g of carboxymethylated pinewood sawdust was taken in a 100 mL conical flask, added 40 mL of 8% sodium lignosulphonate (LS_{Na}) solution, 0.25 g of imidazole and 1 mL of pyridine, and then the conical flask with mixture was placed in a water bath at 80 °C and magnetically stirred for 4 to 6 h. The product was washed with deionized water and dried in an oven at 45 °C to obtain the final product (PSD-LS).

2.3. Adsorption experiments

A stock solution of Hg^{2+} (500 mg/L) was prepared by dissolving 0.3384 g $HgCl_2$ in 500 mL deionized water. Hg^{2+} concentrations ranging from 50 to 300 mg/L were prepared by appropriate dilution of the stock solution. The pH of the working solutions was adjusted from 2 to 8 by the addition of 0.1 M HCl or 0.1 M NaOH solutions. The effects of adsorption time and initial Hg^{2+} concentration on Hg^{2+} adsorption were investigated by shaking conical flasks containing 0.02 g adsorbent and 20 mL solution of different concentrations (50, 100, 150, 200 and 250 mg/L) of mercury ion at pH 6 for 180 min and at 30 °C. Also, kinetic experiments were done at the temperature range 30–60 °C with 200 mg/L Hg^{2+} solution. Isotherm experiments were conducted at 30 °C with initial concentrations ranging from 50 to 300 mg/L. In all these batch processes, the solution was separated from the adsorbent by centrifugation after adsorption equilibrium and the concentration of mercury

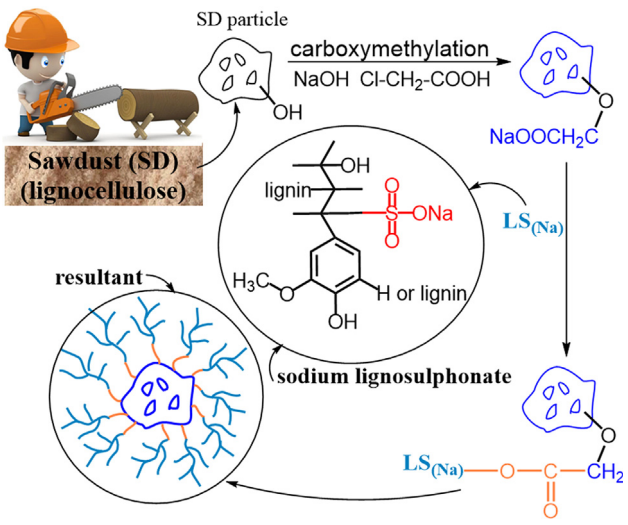

Fig. 1. The preparation process diagram of PSD-LS.