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Poly (ethylene imine) anchored lignin composite for heavy metals capturing in water

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ABSTRACT

An eco-friendly composite was facilely synthesized by grafting poly (ethylene imine) onto the natural polymer-based lignin matrix with dithiocarbamate groups (PLCD). The PLCD was characterized using scanning electron microscopy (SEM), Fourier transform infrared spectrum (FTIR), gel permeation chromatography (GPC) and thermo gravimetric analysis (TGA) techniques. The effects of pH, sorbent dosage, contact time and metal concentration on the adsorption of Cu(II), Zn(II) and Ni(II) by the PLCD were systemically investigated. The PLCD was found to be an efficient adsorbent for capturing heavy metal ion in water. For example, 98.5% Cu (II) was removed to a final concentration of 0.3 mg/l, which is below the limitation value of Environmental Quality Standard for Surface Water (GB 3838-2002). The PLCD showed a highest adsorption capacity of 98 mg/g to Cu(II), followed by 78 mg/g to Zn(II) and 67 mg/g to Ni(II). Besides, the PLCD had good reusability performance with an insignificant adsorption efficiency loss after 5 cycles. The kinetic and isotherm analysis indicated that the adsorption mechanism was well-explained by the pseudo-second-order model and Langmuir model. These results suggested that the PLCD has great potency in the cleanup of heavy metal containing waste water.

1. Introduction

Heavy metals are non-biodegradable and can be accumulated in the environment and living tissues, causing various diseases and disorders of living organisms. Excessive intake of heavy metals can lead to severe mucosal irritation and corrosion, hepatic and renal damage [1]. The wastewater containing heavy metal is a serious threat to plants, animals and human beings. Therefore, effective removal of heavy metals from water by appropriate technologies has been a crucial issue. The technologies for the cleanup of heavy metals from water include electrochemical process, ion exchange, adsorption and membrane separation [2]. Among these technologies, adsorption is attractive due to its advantages of high efficiency, easy handling and availability of various adsorbents [3,4]. The widely used adsorbents include activated carbon, zeolites, carbon nanotubes, polymeric materials and so on [5,6]. However, most of the sorbents showed low adsorption capacities, slow adsorption rate and difficulty of regeneration. Therefore, the design and fabrication of promising adsorbents with good adsorption capacity, fast adsorption rate and reliable reusability are urgently important [5].

Organic amine-based materials have received considerable attention in the removal of heavy metals due to their plenty of nitrogen-containing basic groups and easily obtainable sources [7,8]. However, the solubility and low stability are the main disadvantages for the application of organic amines. Hence, numerous methods have been devoted to improve the solubility and stability of organic amines. For example, by combining the soluble amines onto a stable matrix like mesoporous silica [9], alumosilicate [10] and metal-organic frameworks (MOF) [11]. These studies show that the organic amines composite can be used for waste water treatment. However, the preparation processes still have the disadvantages of using expensive sacrificial templates (surfactants and block copolymers), secondary pollution, and accordingly are not eco-friendly.

Lignin is one of the most abundant natural polymer on the Earth, which has received considerable attention due to its excellent biocompatibility, abundance and eco-friendliness [12]. Lignin contains aromatic structures that make it stable to resist most thermal and biological attack. Some studies have been carried out to explore the application of lignin in various polymer composites, *e.g.*, stabilizing agents, lubricants, coatings, plasticizer, surfactants and adsorbents [12–16]. It has been reported that lignin is a promising adsorbents for Cr(VI), Cd(II), Cu(II), Zn(II) in water [17]. Our previous work also reported a kind of lignin microspheres with a maximum adsorption capacity of 33.9 mg/g to Pb(II) ion with reliable recyclability [18].

In this paper, lignin is selected as the supporting material for organic amine anchoring due to its biocompatibility, abundance,

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eco-friendliness and high stability. The fabrication of amine-anchored lignin matrix with functionality appears indeed desirable for heavy metal capturing from water. Herein, we propose a new adsorbent by combining poly (ethylene imine) together with lignin matrix through the facile Mannich reaction [19]. Since there are abundant amine groups in poly (ethylene imine), it is adaptable to be modified with new functionalities. For example, the amine groups can be converted to dithiocarbamate groups, which have been studied extensively for effective adsorbing heavy metals [20–22], by esterification with carbon disulfide. Thus, it is highly anticipated to develop a cost-effective, eco-friendly composite, strong functionality as well as reliable recyclability, thereby extensively applied in the cleanup of heavy metal containing waste water. We choose Cu (II), Zn (II) and Ni (II), the most common toxic heavy metals, as models to evaluate the adsorption performance of the newly prepared poly (ethylene imine) anchored lignin composite dithiocarbamate (PLCD). The effects of experimental parameters including pH value, sorbent dosage, contact time, and metal ion concentration on the adsorption efficiency/amount of heavy metals by the PLCD have been studied. The adsorption kinetics, isotherms as well as adsorption mechanisms are carefully discussed. The reusability of the adsorbent has been also evaluated by the proposed regeneration method.

2. Experimental section

2.1. Materials

Lignin was obtained from Nanpu Pulp Mill, Nanning, China. Poly (ethylene imine) was purchased from Aladdin Co. Ltd., Beijing, China. Carbon disulfide and formaldehyde were purchased from Shantou Xilong Chemicals Ltd., Shantou, China. Cu $(NO_3)_2{\cdot}3H_2O$, $NiCl_2{\cdot}6H_2O$, and Zn $(NO_3)_2{\cdot}6H_2O$ were purchased as analytical purity and used to prepare the simulated wastewater.

2.2. Synthesis of poly (ethylene imine) anchored lignin composite (PLCD)

The synthesis of PLCD was based on our previous work [19], with some modifications as follows, 0.8 g lignin was dissolved in water under alkaline condition (pH = 11), the solution was transferred into a three-neck flask with 1.6 g of poly (ethylene imine). Then the temperature was elevated to 90 °C, and 4 ml of formaldehyde was added drop-wise for Mannich reaction for 5 h under stirring at 120 rpm. After the reaction completed, it was cooled down to 40 °C, then CS_2 was added carefully for esterification under stirring 2 h. In order to minimize the vaporization during the reactions, an ice-cooled condenser was equipped on the three-neck flask. Finally, the mixture was filtered and washed with ethanol and distilled water. The PLCD was obtained after drying under vacuum at 50 °C for 24 h Scheme 1.

2.3. Characterizations

The surface morphology of the samples was characterized by scanning electron microscopy (SEM) with a Hitachi SU8020 microscope. The surface elemental composition was determined by the energy-dispersive spectrometry (EDS). The specific surface areas (S, m^2/g) of the samples were determined by the Brunauer–Emmett–Teller (BET) method from the nitrogen adsorption isotherms recorded with a Micromeritics Gemini VII 2390 Instrument. Fourier transform infrared (FTIR) spectra were recorded with a Nexus 470 spectrometer using a KBr pellets method. Gel permeation chromatography (GPC) was used to determine the molecular weight of the samples by a Waters 1515GPC. Thermo gravimetric analysis (TGA) was performed with a thermal analyze (Netzsch, STA449C, Germany) at a heating rate of 10 °C/ min in nitrogen flow. The zeta potential of PLCD was measured by the Zetasizer (Nano ZS, Malvern Instruments Ltd., Malvern, UK) to determine the point of zero charge (pH_{PZC}). The particle sizes distribution was obtained by using a Mastersizer 3000. The concentration of metal ion aqueous solution was determined by an inductively coupled plasma optical emission spectrometry (ICP-OES, optima 5300DV, Perkin-Elmer).

2.4. Adsorption experiment

The batch adsorption experiment was performed in conical flasks containing 50 ml heavy metal solution with different concentrations (0~120 mg/l) and 0.02 g PLCD at 25 °C. The suspensions were stirred at 100 rpm for 180 min to achieve adsorption equilibrium. Kinetic adsorption was conducted in one set of conical flasks containing 0.02 g PLCD/50 ml heavy metal solution with an initial concentration of 20 mg/l at 25 °C. At certain time intervals the sample (5 ml) was taken out and filtered for ICP-OES analysis. The pH of solution was adjusted by 0.1 mol/l HCl or NaOH. The removal/adsorption efficiency (E) and adsorption amount (Q_e) were calculated by the following equations.

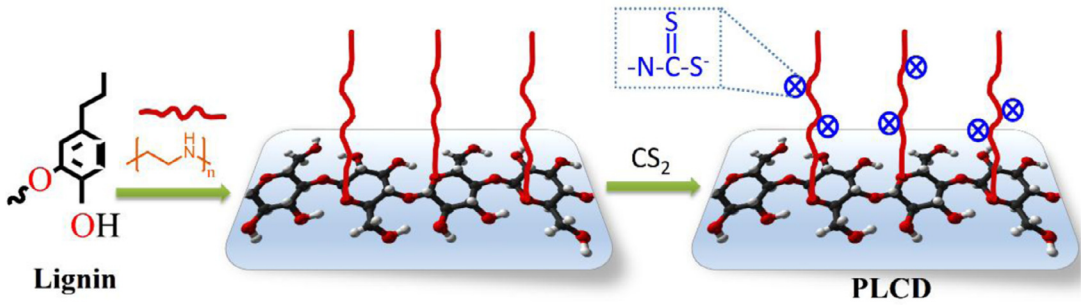
$$E\ (\%) = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

$$Q_e\ (\mathrm{mg/g}) = \frac{C_o - C_e}{w} \times V \quad (2)$$

where V is the volume of solution (L); C_o and C_e are the initial and final concentrations of heavy metal in water (mg/l), respectively; w is the mass of PLCD (g).

2.5. Regeneration of the PLCD

The reusability of the PLCD sorbent was assessed by repeating sorption-desorption cycling test 5 times with Cu(II) as a representative. The Cu(II)-sorbed PLCD was regenerated by using 100 ml of



Scheme 1. Schematic representation of the route for synthesis of PLCD.

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