Synthesis of Lignin-Poly(N-methylaniline)-Reduced Graphene Oxide Hydrogel for Organic Dye and Lead Ions Removal

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A B S T R A C T

Lignin is one of the major contents of lignocellulose and can be used as feedstock for adsorbent materials for wastewater treatment. Here, a lignin-poly(N-methylaniline)-graphene oxide (lignin-PNMA-rGO) hydrogel has been prepared by a two-step method, microspheres of lignin-PNMA was synthesis by the polymerization of NMA monomer in the presence of lignin in aqueous solution, and then they were encapsulated by the as-prepared reduced graphene oxide (GO) hydrogel via a reduction induced self-assembly of the GO nanosheets. The scanning electron microscopy (SEM), Fourier transform infrared (FT-IR), X-ray diffraction (XRD), and UV-Vis studies have been carried out and revealed that the formation of the 3D porous nanocomposite hydrogel with multilevel structures and sufficient active sites. The lignin-PNMA-rGO adsorbent exhibited high adsorption capacity for both organic dye methylene blue (MB, 201.7 mg/g) and Pb2+ ion (753.5 mg/g). The new lignin-based adsorbent is a low-cost, environmentally benign, which is an attractive adsorbent for wastewater treatment.

1. Introduction

Dye and heavy-metal containing wastewater are tough environmental problems, and plenty of effort had been carried out to remove efficiently and economically. Traditional disposal methods include membrane filtration, ion exchange, adsorption, and chemical precipitation or degradation (He et al., 2012). Adsorption is considered to be an efficient method for its lower operating cost and convenience of design, such as activated carbon has been widely applied as adsorbent (Yan et al., 2009; Yang et al., 2014). However, the effective lifetime of such adsorbent is short while the cost is still high. Low-cost adsorbents based on waste biomass have attracted much attention recently for they are abundant natural materials at low cost (Godwin et al., 2019). Waste wheat straw and modified straw powder, cellulose, and its derivatives had been studied as cheap adsorbents for wastewater treatment (Chen et al., 2018; Godwin et al., 2019). However, the methods to prepare efficient adsorbents from biomass feedstock still needed to be developed.

Lignin, one of the three major biomacromolecules in lignocellulose biomass (Yan et al., 2007; Su et al., 2019), possesses plenty oxygen-containing functional groups such as phenolic hydroxyl groups and a three-dimensional structure, and is a candidate for adsorbents synthesis. Lignin and lignin-based adsorbents had been widely applied to removing heavy metal ions such as copper, lead, gold, and silver (Jiang et al., 2019; Ma et al., 2019). Organic dyes can also be removed by lignin-based adsorbents (Gao et al., 2015; Chen et al., 2018; Ge and Li, 2018). However, new kinds of lignin-based materials for both dyes and metal ions removal should be studied.

Aromatic amine polymers have been also used as adsorbents for metal ions for its various nitrogen-containing functional groups and aromatic structure. Recently, amino-N-substituted aniline (N-methylaniline, NMA) has been utilized to the synthesis poly(N-methylaniline) (PNMA) microsphere as novel adsorbents for metal ions while the PNMA can also be applied as...
electrocatalytic electrodes, corrosion protection, and microwave shielding materials (Lü et al., 2013; Lü et al., 2014; Jiang et al., 2018).

Graphene is a famous material recently for its theorized huge specific surface area, also has potential applications in the environmental field as efficient adsorbents for molecular adsorption. Graphene oxide (GO) nanosheets, a derivative of graphene, own plenty of oxygen-containing groups (hydroxyl, epoxide, carboxyl, and carbonyl groups) on both sides of the nanosheets, can be easily assembled into 3D porous frameworks with pores in size of nanometers to micrometers, and is an idea encapsulated material for composites to increase the removal ability of adsorbents (Yang et al., 2014; Li et al., 2016; Musielak et al., 2019).

In this study, a new lignin-poly(N-methylaniline)-graphene oxide (lignin-PNMA-rGO) hydrogel nanocomposite adsorbent has been prepared, with a porous and multilevel structure. It shows high removal ability for both organic dye and metal ions.

2. Materials and Methods

2.1. Materials

Graphite powder, natural briquette grade, ~100 mesh, 99.9995% (metal basis) was purchased from Alfa Aesar. Analytical grade KMnO₄, 98% H₂SO₄, 30% H₂O₂, N-methylaniline, ammonium persulfate, aqueous ammonia, Pb(NO₃)₂, Cr(NO₃)₃, and methylene blue were purchased from Shanghai Chemical Reagen Company. Industrial lignin was purchased from a local paper mill, prior to use, washed with deionized water for three times. Deionized water used with a resistivity of 18 MΩ·cm was produced by a Milli-Q (Millipore, USA).

2.2. Synthesis of lignin-PNMA microsphere

The 0.24 g lignin powder (<80 mesh) was added into 10 mL of 0.1 mol/L aqueous ammonia, and then 2.18 mL of N-methylaniline was added under strong stirring. The aqueous ammonia containing ammonium persulfate was added and the system was heated at 25 °C for 24 h for polymerization.

2.3. Preparation of lignin-PNMA-rGO hydrogel

Typically, GO was prepared from graphite powder via a modified Hummers’ method as described previously (Wang et al., 2018; Wang et al., 2019a; Wang et al., 2019b). Then the GO solution was dialyzed to remove residual metal ions, and after 1 h ultrasound treatment, the as-prepared lignin-PNMA powder was added into the solution under the assistant of mild ultrasound, then the hydrothermal method was employed to prepare the hydrogel while the system was heated under seal at 180 °C for 8 h.

2.4. Characterization of composites

The Fourier transform infrared (FT-IR) spectra were recorded by an EQUINOX55 spectrometer (Bruker Germany) by using KBr pellets. A Shimadzu scanning electron microscopy (SEM) (Superscan SSX-550, Japan) equipped with a low vacuum system was used for the space-resolved analysis of the hydrogel without gold coating. The backscattered electron images were recorded at a low vacuum. The X-ray diffraction (XRD) patterns were studied on a Bruker D8 Advance diffractometer at 40 kV and 40 mA equipped with Cu Kα radiation (λ = 0.15406).

2.5. Dye and metal adsorption

Adsorption tests of dye (MB) and lead ions (Pb²⁺) on the lignin-PNMA-rGO nanocomposite at varying adsorption time was carried out by a batch method. In brief, the dye solution was prepared by dissolving the MB in ultrapure water to the required concentrations. In the experiment of equilibrium adsorption isotherm, the mixture of dried hydrogel powder (0.01 g) and dye solution (50 mL) and buffer solution of the desired pH was shaken for 4 d in a water-bath at a controlled temperature. The initial dye concentration is 0.04 g/L. The dye concentrations were measured by adjusting the solution pH to 7.8 and analyzed by an SP-721E UV-VIS spectrophotometer (Shanghai spectrum instruments Co. Ltd., China) at 484 nm. Desorption of the MB from the adsorbents was performed by using ethanol for regeneration and reuse. For the adsorption tests of Pb²⁺ and Cr³⁺ ions, a test solution (250 mL) containing metal ions (5 mg/L) and dry nanocomposite (40 mg) were loaded in a 100-mL conical flask. The adsorption solution was stirred for 5 min, and then the adsorption proceeded under static conditions at 30 °C for 4 d to reach equilibrium. Next, the nanocomposite was filtered from the solution, and then the concentration of metal ions in the filtrate after adsorption was measured by Inductive Coupled Plasma Emission Spectrometer (ICP). The pseudo-first-order models have been used to describe the kinetics of the MB and metal ions adsorption.
3. Results and Discussion

Figure 1 shows the typical synthesis route of the lignin-PNMA-rGO hydrogel. At first, in the presence of lignin, NMA monomer was polymerized by using ammonium persulfate as the initiator, and a complex of lignin-PNMA was prepared, where the lignin network interacted with PNMA chains by the $\pi-\pi$ stacking and hydrophobic interaction of the alkyl groups. Next, GO nanosheets were added, and a new composite was formed via the new $\pi-\pi$ stacking and hydrogen bonding system. After the reduction induced self-assembly, the nanosheets of reduced GO constructed a new 3D hydrogel framework, where the lignin-PNMA nanoparticles were encapsulated inside the new network. Figure 2 shows the photoimage of the as-prepared lignin-PNMA-rGO hydrogel after freeze-drying. Clearly, it looks black with some elastic.

The SEM was used to measure the microstructure of the as-prepared materials, as shown in Figs. 3a–3c, plenty microspheres were obtained when NMA monomer was polymerized in the presence of lignin, and the size of them is in a range of about 200 nm to 1 $\mu$m and the surface of the microsphere is smooth. During the formation of the hydrogel of reduced GO nanosheets, the lignin-PNMA microspheres were encapsulated into the network, as shown in Fig. 3d (the arrows indicates the wall of the network with porour structure), a network of rGO hydrogel wit pore structure in size of micrometers was formed and the microspheres of lignin-PNMA were distributed homogeneously inside the network. The multilevel structure will be helpful for the solvent diffusion and interaction of dye molecules or metal ions with the microspheres and makes it a potential material for wastewater treatment.

Figure 4 shows the FT-IR spectra of lignin, lignin-PNMA, and lignin-PNMA-rGO. The broad band located at 3250 cm$^{-1}$ was assigned to the N—H stretching vibration of the aromatic amine, and the adsorption peaks at around 1580 cm$^{-1}$ and 1645 cm$^{-1}$ were assigned to the stretching of the benenoid rings. The peak at 1310 cm$^{-1}$ was contributed from the C—N stretching vibration of the quinoid rings (Lü et al., 2014). The peaks of 1058 cm$^{-1}$ and 1635 cm$^{-1}$ and the broad peak at around 3000 cm$^{-1}$ could be assigned to the oxygen-containing groups of GO (Li et al., 2016). These results reveal that the formation of the lignin-PNMA-rGO nanocomposite.
The UV-visible spectra of lignin, PNMA, and lignin-PNMA are shown in Fig. 5. For the lignin, the two characteristic peaks were found at 205 nm and 280 nm while for the PNMA, the three major peaks were found at 220 nm, 320 nm, and 600 nm, and the peak at around 320 nm was assigned to the $\pi-\pi^*$ transitions of the benzenoid while the peak at around 600 nm was contributed to the n-$\pi^*$ transitions of the quinoid structure (Lü et al., 2013). Interestingly, for lignin-PNMA microspheres, the peak had a redshift to 750 nm, which might be come from the formation of new conjugation. In addition, for the lignin-PNMA microspheres, both the characteristic peaks could be found in the spectra, indicating the formation of the composite.

Figure 6 shows the XRD patterns of lignin, lignin-PNMA and lignin-PNMA-rGO composite respectively. All of the samples exhibit less crystalline nature, and the wide peaks reveal weak aggregates of the major components in the composites. It also suggests that the presence of nano-structural polymeric aggregates in a range of 20–30 nm calculated by the Scherrer’s formula (Mary and Sheem Mers, 2019). For the lignin-PNMA-rGO composite, a new peak appears which can be assigned to the stacking of rGO nanosheets.

Methylene blue (MB) is a typical cationic organic dye and has been widely applied in various industrials such as cottons or wools dyeing, temporarily coloring hair, paper coloring, and coating for paper stock. The MB often serves as a model compound.
for removing dyes and organic contaminants from aqueous solutions. The adsorption capacities of dye MB on the lignin-PNMA-rGO hydrogel prepared by hydrothermal method were studied. As shown in Fig. 7, the highest adsorption capacity is 210.7 mg/g, while the adsorption capacities of pure rGO hydrogel and lignin are 120.64 mg/g and 160.6 mg/g, respectively, which indicates that the nanocomposite with multilevel structure exhibits an enhanced adsorption capacity contributing to the existence of a synergistic effect among the various groups in the composite. The aromatic structure in lignin can form a strong π-π bond interaction with the benzene ring structure in the dye molecule whereas the presence of hydrophilic oxygen-containing functional groups and negative charge in GO nanosheets makes it easy to form a strong interaction with dye molecules. In addition, the state of the composite is also a key factor in the performance of the MB adsorption. The hydrogel is in the wet state while aerogel is in solid-state after the adsorbed water was removed by freeze-drying, and the hydrophilicity of the aerogel will decrease and the pore volume will also decrease. For lignin-PNMA-rGO aerogel, the highest adsorption capacities of rGO, lignin-GO, and lignin-PNMA-rGO hydrogels are 60.53 mg/g, 102.31 mg/g, and 123.45 mg/g, respectively, nearly half of that of the hydrogel. Therefore, it is better to utilize the hydrogel directly in the wet state.

![Fig. 6](image)
**Fig. 6** The XRD patterns of lignin, PNAM, and lignin-PNMA-rGO

![Fig. 7](image)
**Fig. 7** Effect of sorption time on dye removal performance of lignin-PNMA-rGO hydrogel

The loading amount of lignin-PNMA microspheres in the hydrogel composite is another key factor in the performance. Different lignin-PNMA-rGO hydrogels with various lignin-PNMA loading amounts had been prepared with the weight ratio of GO to lignin-PNMA changed from 10:1 to 70:1, and Fig. 8 shows their performance on the adsorption balance of MB aqueous solution. The more the lignin-PNMA loaded, the more MB can be adsorbed, and the values are 210.7 mg/g (10:1), 161.3 mg (30:1), 140.9 mg/g (50:1), and 117.2 mg/g (70:1), respectively. The performance of the new adsorbent is superior to other reported biomass-based adsorbents, such as the balance adsorption ability of the MB is 81.3 mg/g for the mixture of eucalyptus biomass and kaolin clay (Tan and Sen, 2020), and 203.6 mg/g for beta-glucosidase immobilized organosolv lignin/Fe$_3$O$_4$ nanoparticles (de Araújo Padilha et al., 2020).

![Fig. 8](image)
**Fig. 8** Photoimages of methylene blue (MB) solution after treated by different lignin-PNMA-rGO hydrogels with various lignin-PNMA loading amount (from left to right: MB aqueous solution, adding rGO hydrogel, adding lignin-PNMA-rGO hydrogels with ratio of GO to lignin-PNMA of 10:1, 30:1, 50:1, and 70:1)
The regeneration and reuse of the adsorbent were also studied by using ethanol as the desorption solvent. As shown in Fig. 9, five MB adsorption-desorption regeneration experiments were performed on the as-prepared adsorbent. As the number of cycles increased, the adsorption capacity decreased slowly. After repeated three adsorption-desorption cycles, the results indicated that the adsorbent had good regeneration performance.

The as-prepared lignin-PNMA-rGO hydrogels also showed excellent metal ions adsorption ability. Here, Pb$^{2+}$ was used to study the performance of rGO, lignin-rGO and lignin-PNMA-rGO hydrogels, and the highest adsorption capacities of Pb$^{2+}$ were 180.5 mg/g, 660.2 mg/g and 753.5 mg/g, respectively. The mechanism of the high adsorption capacity is own to the interaction of Pb$^{2+}$ ion with oxygen containing groups such as phenolic and carboxylic groups on the surface of the hydrogel (Li et al., 2016).

4. Conclusion

In this study, a simple two-step method was employed to prepare a new adsorbent lignin-PNMA-rGO nanocomposite hydrogel, where lignin worked as the template for N-methylaniline polymerization to form microspheres in size of hundreds of nanometers, and then the microspheres were encapsulated by the as-prepared reduced graphene oxide hydrogel to form a new nanocomposite with porous structure and multi-active sites. The nanocomposite hydrogel is an ideal adsorbent for both organic dye and metal ions, which makes it a potential cheap adsorbent for wastewater treatment.

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References


