

Magnetization of aminated lignin and characterization

XUEQING QIU, YINGZHI MA, AND DAFENG ZHENG

ABSTRACT: A magnetic lignin-based nanomaterial (MLN) was prepared from alkaline lignin through an amination and precipitation strategy and characterized with Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TG), Brunauer-Emmett-Teller (BET) method, scanning electron microscope (SEM), dynamic light scattering (DLS), and vibrating sample magnetometer (VSM). The results illustrated that MLN was thermostable and had an extensive degree of aminated lignin coating. The specific surface area of MLN was 65.43 m²/g, with the total pore volume of 0.311 cm³/g. The zeta potential of MLN was positive when pH was less than 2.9, and the saturation magnetization was 50.8 emu/g. The characterization data discovered that the physico-chemical properties of MLN were helpful for the adsorption application.

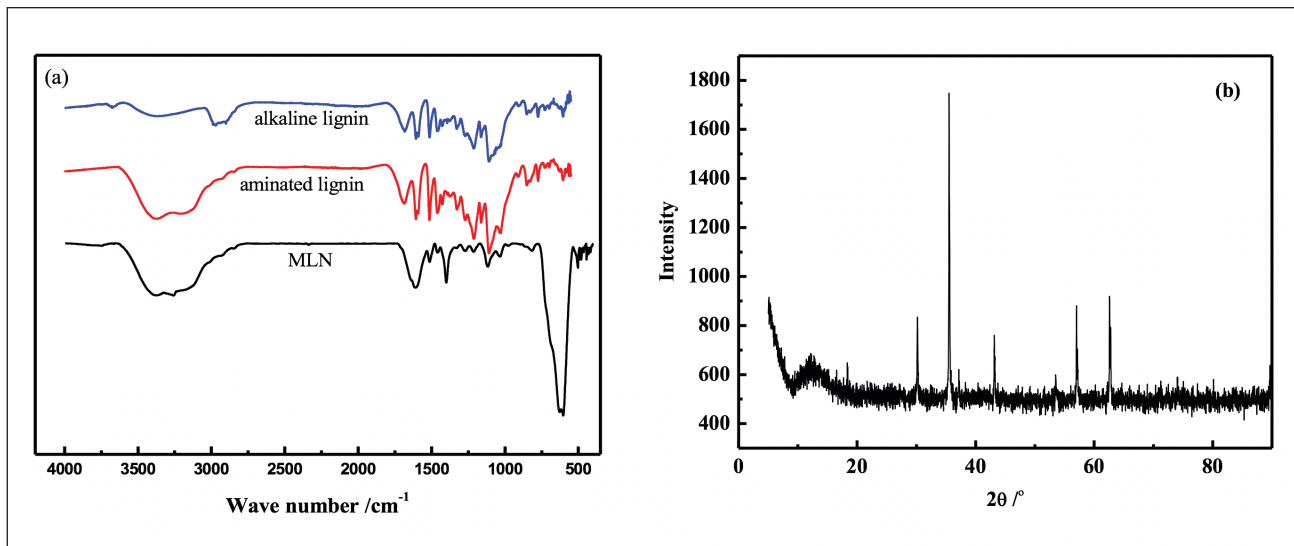
Application: This study provides insight into the preparation of a novel lignin-based magnetic material for adsorbents that mills can prepare with co-precipitation strategy, increasing the value of lignin.

In recent years, magnetic materials have been used in a wide variety of applications such as adsorption [1] and trace detection [2] due to their easy separation from other materials in an external magnetic field. Functionalization of magnetic materials by various polymers is an important way to increase their range of applications [3,4]. Morneta et al. [5] first formulated a DNA-bound Fe²⁺ and Fe³⁺ salt complex and then produced DNA-modified Fe₃O₄ composite nanoparticles by adding aqueous ammonia. Xu et al. [6] used dopamine as a chelator to introduce amino groups onto the surface of magnetic iron oxides, then grafted proteins to these particles via peptide bonds. The polymer-functionalized magnetic materials exhibited efficient adsorption performance to many pollutants. Zhou et al. [7] prepared Fe₃O₄@polydopamine core-shell nanoparticles (NPs) by coating a layer of polydopamine (PDA) onto the surface of magnetic Fe₃O₄ NPs, and then carbonized Fe₃O₄@PDA to obtain Fe₃O₄@C nanoparticles. The removal efficiency of Fe₃O₄@C for methylene blue and methyl orange was about 50% and 70%, respectively. The Fe₃O₄@APF@Au nanoparticles synthesized by Gong et al. possessed excellent catalytic activity as well as efficient reusability for the reduction of organic dyes [8]. The activated carbons with the surface decorated with Fe₃C/Fe₃O₄ nanosheets were prepared by Yao et al. [9], and the dye adsorption capacity of this activated carbon was enhanced by five times. Li et al. [10] synthesized the aminated hollow magnetic nanospheres with oxidized mesoporous carbon to gain a good adsorption capacity for methylene blue at mild conditions. The adsorption was found to obey the Freundlich model and the pseudo-second-order model.

Lignin, an integral part of the cell wall of plants, is the second most abundant and renewable resource on the earth after

cellulose [11]. As a type of renewable resource, lignin is rich in sources and cheap in price. Lignin is primarily used as an energy source via combustion; only a small percentage is modified as commercial dispersants to disperse concrete, pesticides, coal water slurry, etc [12,13]. Due to the hydroxyl and carboxyl groups in the molecule, lignin has recently attracted intensive attention for use as a biosorbent. Demirbas et al. [14] reported an alkaline lignin for the adsorption of Pb(II) and Cd(II), and the saturated adsorption amount was 9.0 and 7.5 mg/g, respectively. Wu et al. [15] extracted an alkaline lignin from black liquor and the maximum adsorption amount for Cr(III) was 1797 mg/g. Acemioglu et al. [16] reported the adsorption capacity of an organosolv lignin for Cu(II) was 1.68 mg/g at 20°C. These published articles show that the adsorption capacity of as-obtained lignin is usually low due to the low quantity functional groups such as sulfo, carboxyl, amino groups, as well as weak reactivity. Therefore, to enhance the adsorption performance, O, N, S-containing functional groups are introduced onto lignin. Li et al. [17] reported that an aminated and sulfomethylated lignin could have the maximum adsorption amounts of 45.4 mg/g for Cu(II) and 53.8 mg/g for Pb(II) at pH 6.0 and 25°C. Ge et al. [18] prepared a lignin dithiocarbamate (LDTC), which presented a maximum adsorption amount of 103.4 mg/g for Pb(II) at 25°C. However, there are few reports on the preparation of magnetic adsorbents by using lignin as a precursor.

In order to increase the extra value of lignin and extend its application, the current work enhanced the amino content of lignin first through the Mannich reaction [19], and then the aminated lignin was coated onto the surface of iron oxide powder to prepare a magnetic composite nanomaterial (MLN) through a precipitation strategy. The structure and physico-chemical properties of MLN were characterized with various



1. The (a) Fourier transform infrared (FTIR) spectrum and (b) X-ray diffraction (XRD) pattern of the magnetic lignin-based nanomaterial (MLN).

analysis methods to explore its potential application in pollution control. This study can provide a new insight into the preparation of a novel magnetic adsorbent; it can also increase the value of lignin.

MATERIALS AND EXPERIMENTS

Materials

Alkaline lignin, obtained through the soda pulping process of pinewood, was purchased from Xiangjiang Paper Co. Ltd. (Hunan province, China). It was first purified by acid precipitation before usage.

Ferric chloride hexahydrate, ferrous sulfate heptahydrate, 25 wt% ammonia, formaldehyde (37 wt%), hydrochloric acid, sodium hydroxide, and ethanol were all purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Ethanediamine was purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. (Shanghai, China). All chemicals were of analytical grade and used as received. Deionized water was used for the preparation of all solutions.

Preparation of aminated lignin

In brief, 10 g of alkaline lignin was dissolved in DI water to make a 30 wt% aqueous solution, and then placed in a four-necked flask with 4 g of ethanediamine, keeping pH = 12. The solution was heated to 85°C while stirring, and then 16 g of formaldehyde was added drop-wise. The mixture was then incubated for 1.5 h. After cooling down, the product was dried under a vacuum at 60°C to obtain aminated lignin.

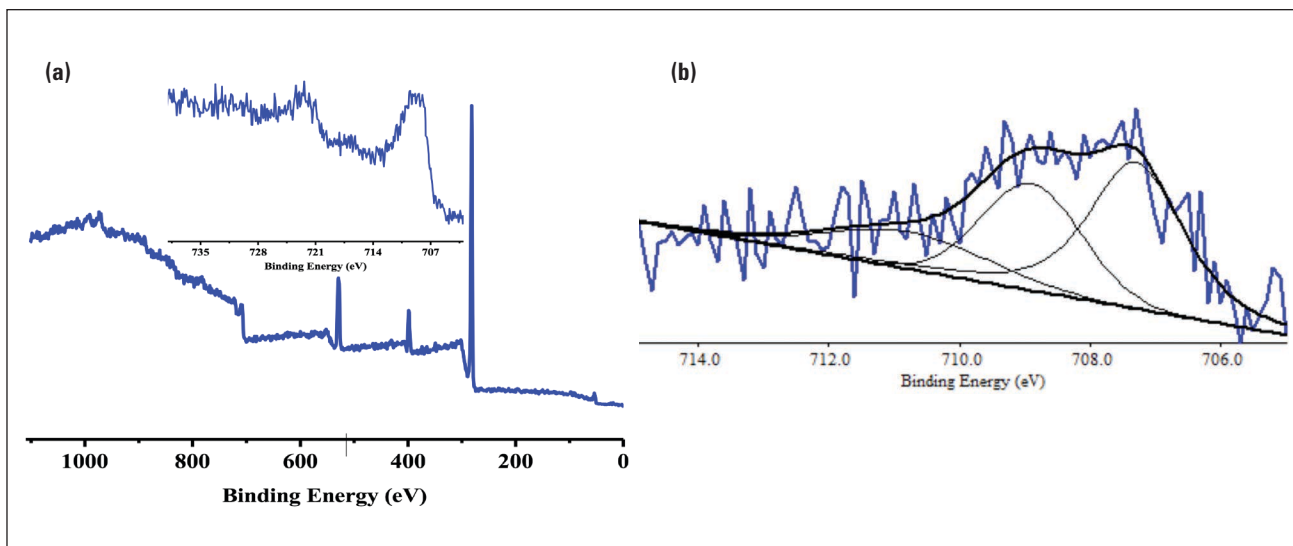
Synthesis of magnetic lignin-based nanoparticles

The magnetic lignin-based nanoparticles (MLN) were synthesized by using a precipitation process. Briefly, 5.4 g of ferric chloride hexahydrate and 4.0 g of ferrous sulfate heptahydrate were put in a four-necked flask and dissolved in deionized

water. Then, 30 mL of 10 wt% ammonia was slowly added drop-wise to the solution as the temperature was increased to 90°C (pH = 10 during the reaction). The product was then aged at 90°C for 1.5 h, after which 25 mL of 20 wt% aminated lignin solution was added drop-wise into the reaction system, followed by 20 mL absolute ethanol. The mixture was then incubated with stirring at 90°C for 3.0 h. After cooling down, the magnetic composite particles were separated from the system with a permanent magnet, washed several times with 50 mL absolute ethanol, and then dried in a vacuum at 60°C.

Characterization of MLN

MLN was characterized using different techniques in order to illustrate its physical properties. Fourier transform infrared (FTIR) spectra were recorded using a Thermo Nicolet Nexus spectrometer (Thermo Fisher Scientific; Waltham, MA, USA). The dried samples were embedded in potassium bromide (KBr) pellets to a concentration of approximately 1 mg/100 mg. A scanning region of 400~4000 cm⁻¹ was recorded, with a resolution of 4 cm⁻¹ and a scans number of 32. X-ray diffraction (XRD) analysis using Cu Kα radiation ($\lambda = 1.5418 \text{ \AA}$) was carried out on an X-ray diffractometer (XD-3A; Shimadzu, Japan) with Bragg-Brentano geometry for 2θ values in a range of 5°~90°. The measurement conditions were as follows: step size 0.15 s/step, scan spin at a revolution time of 4 s, and nickel filter as incident beam. The composition of aminated lignin in MLN was measured using a thermogravimetric analyzer (TGA 7, PerkinElmer; Waltham, MA, USA). The temperature range was 25°C~600°C, and the heating rate was 10°C/min. The surface area and pore size of samples were measured in a surface area and pore size analyzer (ASAP2020, Micromeritics Instrument Corp.; Norcross, GA, USA) at constant temperature (-196°C). The dry samples were pretreated for 2 h at 200°C under N₂ atmosphere to remove any surface water or gas. Morphological analysis was done with a Hitachi (Tokyo,



2. The (a) XPS spectrum of MLN and (b) X-ray photoelectron spectroscopy (XPS) plot (iron [Fe] spectrum) of MLN.

Japan) S-4800 scanning electron microscope (SEM). The particle size and the zeta potential were performed on a Zetasizer Nano S (Malvern Panalytical; Malvern, UK). XPS spectrum of MLN was performed by X-ray photoelectron spectroscopy (XPS) (Axis Ultra DLD; Kratos, UK) with the monochromatic Al K α X-ray radiation (1486.7 eV) and a spot area of 200 μ m in diameter. The magnetic property of MLN was determined using a vibrating sample magnetometer (VSM) (7410 series, Lake Shore Cryotronics; Westerville, OH, USA) at room temperature.

RESULTS AND DISCUSSION

FTIR

The FTIR spectra of alkaline lignin, aminated lignin, and MLN are shown in **Fig. 1(a)**. In alkaline lignin, the bands near 3400–3500 cm^{-1} are due to O-H stretching vibration and the bands near 2800–2950 cm^{-1} are due to asymmetrical C-H stretching vibration. The peaks at 1505 and 1608 cm^{-1} are due to the skeletal vibration of the aromatic ring, and those at 1130 and 1236 cm^{-1} are due to the stretching vibration of aromatic groups. After amination, the peaks between 2800–2900 cm^{-1} are weakened, while those near 3300 cm^{-1} and 3500 cm^{-1} (the characteristic adsorption for $-\text{NH}_2$) become much stronger, indicating large amounts of amine groups were grafted to the lignin molecule and C-H bonds were broken during amination. In MLN, the acute peak near to 590 cm^{-1} is the characteristic adsorption peak for Fe_3O_4 , and those at 1130 and 1236 cm^{-1} are significantly decreased, indicating the formation of Fe_3O_4 and reduction of lignin content. The spectra demonstrate the formation of aminated lignin/ Fe_3O_4 composite nanoparticles.

XRD

The XRD pattern of MLN is shown in **Fig. 1(b)**. The diffraction at 30.1°, 35.0°, 43.3°, 57.3°, and 62.9° is assigned to the (220), (311), (400), (511) and (440) Bragg reflection, respectively,

showing that the sample contains the cubic spinel structure of Fe_3O_4 [20]. The peak at $2\theta = 12.5^\circ$ can be assigned to organic carbon. The XRD pattern further demonstrates that the sample contains Fe_3O_4 ultra-fine crystallite.

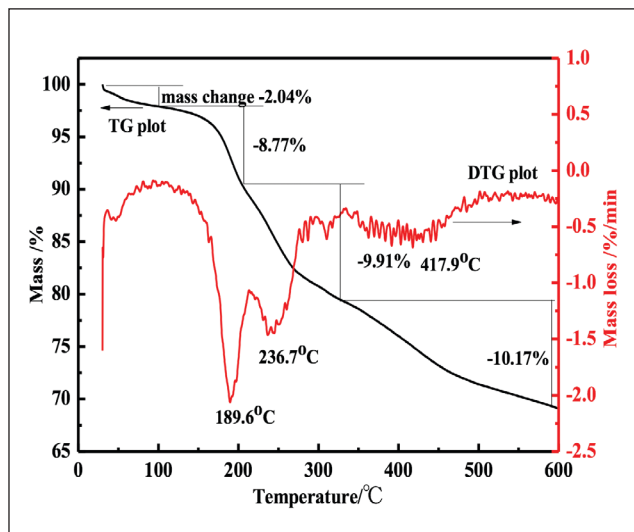
XPS

An XPS test was performed to further explore the composition of MLN. The results are shown in **Fig. 2**. From the full spectrum shown in **Fig. 2(a)**, the sharp photoelectron peaks of carbon (C), nitrogen (N), oxygen (O), and iron (Fe), at 282.2 eV (C 1s), 398.2 eV (N 1s), 529.9 eV (O 1s), and 708.0 eV (Fe 2p), respectively, can be seen. The embedded graph clearly illustrates the photoelectron peak of Fe.

Figure 2 (b) is the enlarged Fe spectrum. The Fe 2p peak is subjected to a peak separation process, from which it can be seen that there are three peaks in the range of 707–712 eV. By examining the standard table of the elements characteristic peaks, the three peaks correspond to the binding states of FeO, Fe_2O_3 , and Fe_3O_4 .

TG analysis

Fig. 3 is the thermal analysis curve of MLN. MLN exhibits weight loss in several stages as the temperature rises from room temperature to 600°C. In the initial stage (room temperature to 100°C), the weight loss percentage of MLN is about 2.04%, mainly due to the evaporation of water adsorbed on the surface. The second stage with a temperature range of 100°–340°C is due to the high-temperature decomposition of lignin, and results in a weight loss of 18.68%. During this second stage, dehydration and decomposition of lignin occurs, resulting in generation of coke, phenolic substances, and gas [21]. In the final stage with a temperature range of 340°–600°C, the residue continues to decompose and oxidation of the carbon occurs. In this stage, the weight loss is 10.17%. The results further illustrate that MLN is thermostable and has extensive degree of aminated lignin coating, which will be beneficial to



3. Thermogravimetric (TG) analysis of MLN.

the adsorption performance for amounts of functional groups in the lignin molecule.

BET analysis

The Brunauer-Emmett-Teller (BET) method was applied for evaluation of the surface area of MLN. The N_2 adsorption/desorption isotherms of MLN at 77 K are shown in **Fig. 4(a)**. The N_2 adsorption curve is similar to a Type II adsorption isotherm, exhibiting the characteristics of the inverse S-shaped curve. The adsorption curve can be roughly divided into three sections. In the initial section, the interaction between the surface of the adsorbent and the adsorbate is strong. This stage belongs to the monolayer adsorption, slowly shifting to the multi-molecular layer adsorption. The transition section is relatively gentle, characterized as a multi-molecular layer adsorption phase. In the final section, large pore volume filling occurs due to capillary condensation. At the specific pressure zone of $P/P_0 = 0.6$ -1.0, there is a signif-

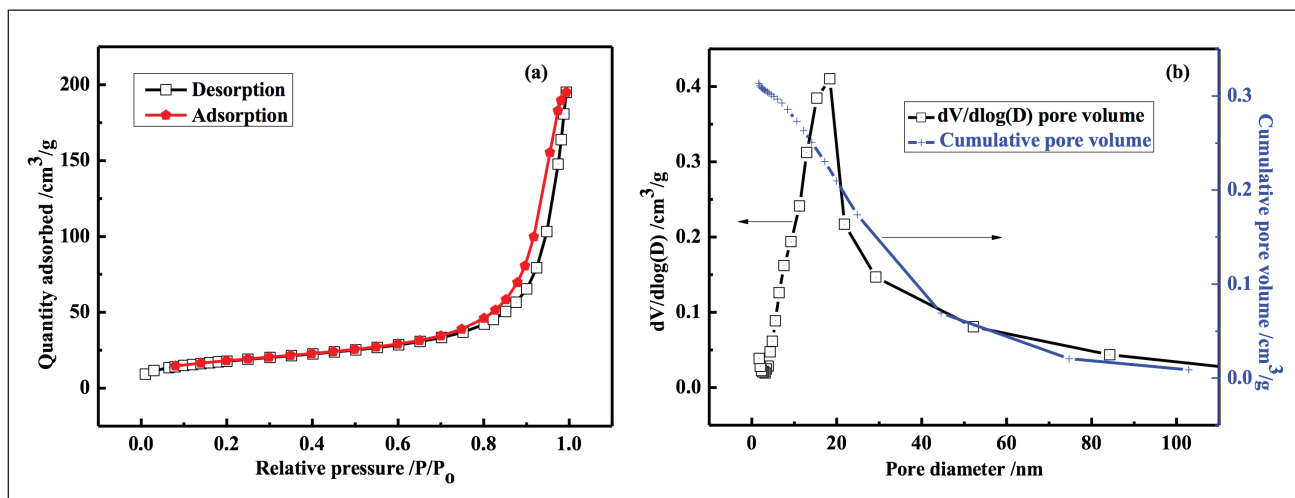
icant hysteresis loop, which shows the characteristics of the Type H3 loop based on IUPAC. The result indicates that the MLN sample has distinct mesoporous structure, with mainly amorphous, slit-shaped and wedge-shaped pores [4,5]. The specific surface area of MLN is $65.43 \text{ m}^2/\text{g}$ according to the BET equation. The pore size distribution was determined by the Barrett-Joyner-Halendra (BJH) model, as shown in **Fig. 4(b)**. The total pore volume was found to be $0.311 \text{ cm}^3/\text{g}$, with an average pore diameter of 16.3 nm. MLN has plenty of pores.

Morphology analysis

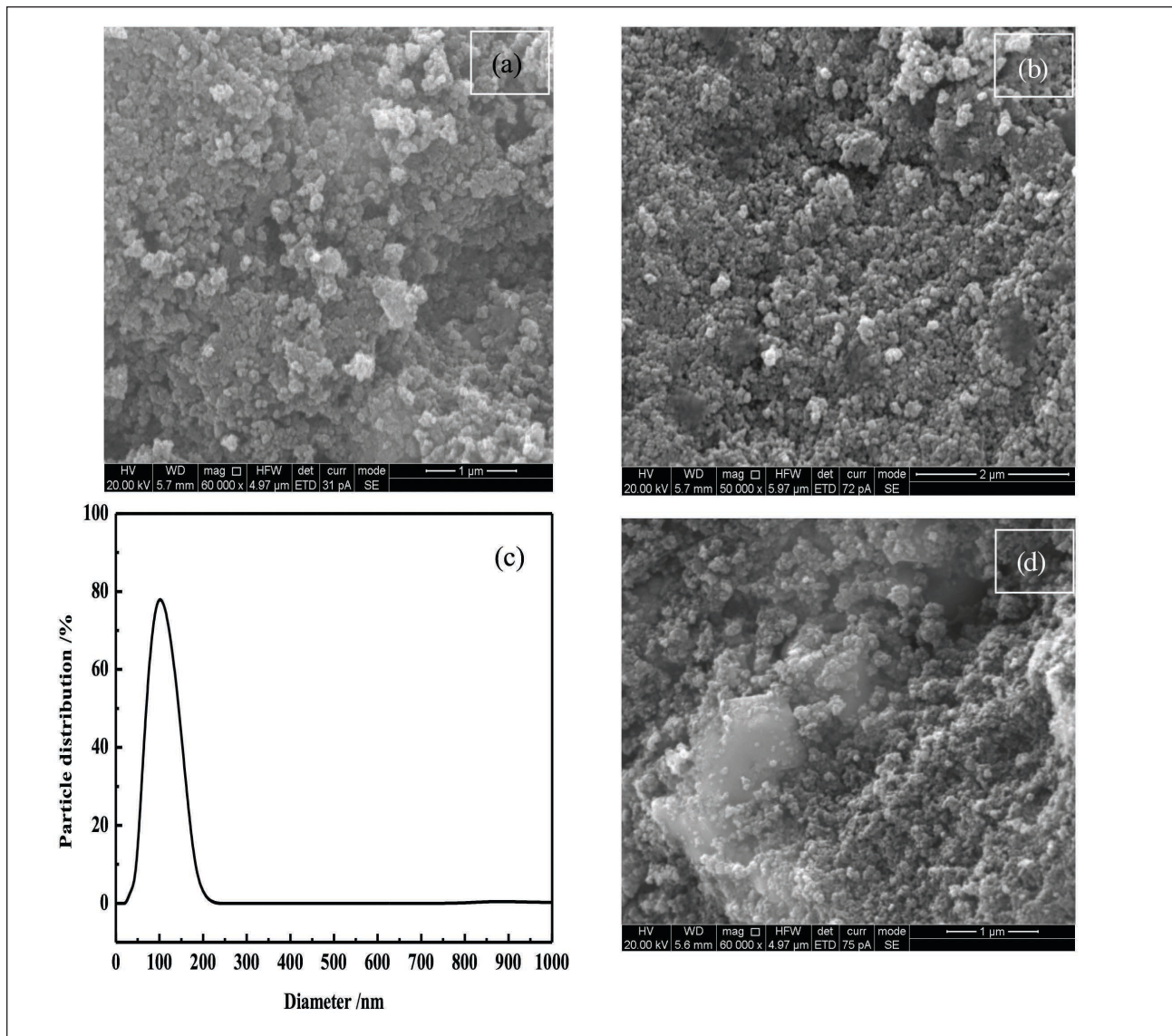
Figure 5(d) shows the morphology of Fe_3O_4 particles prepared through the precipitation of Fe^{2+} and Fe^{3+} . It can be seen the Fe_3O_4 particles are basically spherical. After the encapsulation of aminated lignin, the MLN particles become bigger, and the surface turns rough and porous, as shown in **Figs. 5(a)** and **5(b)**. The rough, porous surface is helpful to the adsorption capacity. From the dynamic light scattering (DLS) results in **Fig. 5(c)**, it can also be seen that MLN has an average diameter of 113 nm and a relatively narrow size distribution.

Zeta potential

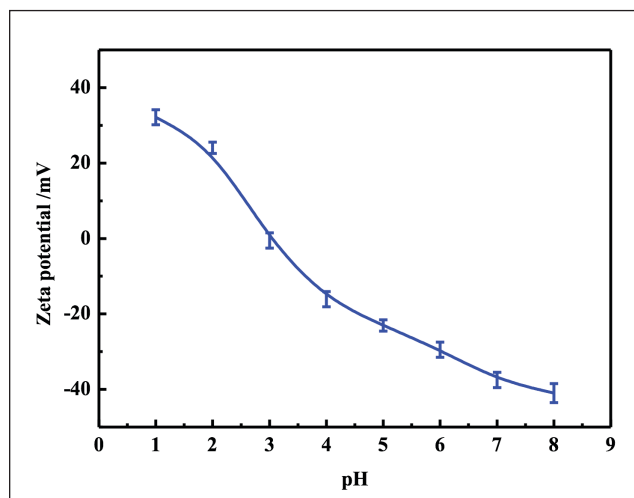
The zeta potential of MLN is shown in **Fig. 6**. The surface charge of MLN is negative in neutral aqueous solutions. As the pH decreases, the zeta potential rapidly increases, especially in the range of pH 2.0~4.0. When pH is decreased to 1.0, the zeta potential increases to 32.2 mV, which is due to the protonation of phenolic hydroxyl groups and amine groups. It can also be seen that the isoelectric point of MLN is 2.9, which is also an indicator of amino groups introduced into the lignin structure [22]. As the pH increases, the zeta potential decreases and the value is -41.0 mV at pH 8.0 due to ionization of phenolic hydroxyl groups and deprotonation of amine groups. Since Cu(II) and Cd(II) both carry positive charge, the adsorption for these ions is more favorable in pH 3.0~7.0. Basic conditions will result in precipitation of the ions.



4. The (a) N_2 adsorption/desorption isotherms of MLN and (b) pore size distribution of MLN (77 K).



5. (a),(b) Scanning electron microscopy (SEM) of MLN, (c) dynamic light scattering (DLS) of MLN, and (d) SEM of Fe₃O₄.



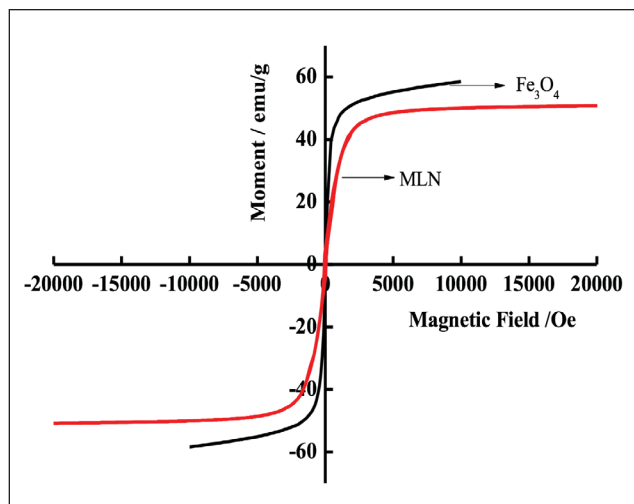
6. Zeta potential of MLN.

VSM

Figure 7 is the standard hysteresis loop of MLN (300 K). The saturation magnetization of Fe₃O₄ is 58.4 emu/g, and that of MLN is 50.8 emu/g, 87% of the pure Fe₃O₄, indicating MLN has favorable magnetism. Additionally, the hysteresis loop of MLN is symmetrical with respect to the origin, indicating that MLN is superparamagnetic, with the particle size smaller than the critical size [23].

CONCLUSIONS

MLN was effectively prepared following an amination and precipitation strategy. The structure, morphology, and magnetism of the material were studied by FTIR, XRD, XPS, BET, TG, SEM, DLS, and VSM. The XRD illustrated that MLN contained Fe₃O₄ ultra-fine crystallite. FTIR and XPS spectrum showed that nitrogen was introduced in the structure of MLN. TG spectrum showed that MLN was thermostable and had an



7. Hysteresis loop of MLN (300 K).

extensive degree of aminated lignin coating. According to the BET result, the specific surface area of MLN was 65.43 m²/g, with the total pore volume of 0.311 cm³/g. The zeta potential of MLN was positive when pH was less than 2.9, and the saturation magnetization was 50.8 emu/g. The results illustrated that the physico-chemical properties of MLN were favorable as a magnetic adsorbent. **TJ**

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ABOUT THE AUTHORS

Magnetic materials have been used in a wide variety of applications, but lignin is seldom used to fabricate the magnetic particles. This study can provide new insights into the preparation of a novel magnetic adsorbent.

The most difficult aspect of this study was controlling the morphology of the material. It was controlled by adjusting the preparation process. The most interesting finding of this study was that magnetic particles, after fabricated with lignin, still retain strong magnetism, so it is well responsive in a magnetic field.

This study shows that mills can prepare a lignin-based magnetic material through simple co-precipitation. Our next step is to fabricate magnetic materials with different kinds of lignin.



Qiu



Ma



Zheng

Qiu is professor and Zheng is associate professor at Guangdong Engineering Research Center for Green Fine Chemicals, South China University of Technology, Guangzhou, China. Ma is an undergraduate student in the School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, China. Email Zheng at zhengdafeng0501@163.com.

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