Fabrication of mesoporous lignin-based biosorbent from rice straw and its application for heavy-metal-ion removal

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Abstract:

Lignocellulosic biomass offers the most abundant renewable resource in replacing traditional fossil resources. However, it is still a major challenge to directly convert the lignin component into value-added materials. The availability of plentiful hydroxyl groups in lignin macromolecules and its unique three-dimensional structure make it an ideal precursor for mesoporous biosorbents. In this work, we reported an environmentally friendly and economically feasible method for the fabrication of mesoporous lignin-based biosorbent (MLBB) from lignocellulosic biomass through a SO₃ micro-thermal-explosion process, as a byproduct of microcrystalline cellulose. BET analysis reveal the average pore-size distribution of 5.50 nm, the average pore value of 0.35 cm³/g, and the specific surface area of 186 m²/g. The physicochemical properties of MLBB were studied by FT-IR, ATR-FTIR, XPS, and element analysis. These results showed that there are large amounts of sulfonic functional groups exist on the surface of this biosorbent. Pb(II) was used as a model heavy-metal-ion to demonstrate the technical feasibility for heavy-metal-ion removal. Considering that lignocellulosic biomass is a naturally abundant and renewable resource and SO₃ micro-thermal-explosion is a proven technique, this biosorbent can be easily produced at large scale and become a sustainable and reliable resource for wastewater

treatment.

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Introduction

Heavy metal pollution has been drawing world-wide concerns, because heavy-metal-ions even in trace amount are hazardous to human health and ecosystem (Babel et al., 2003; Sud et al., 2008; Hlihor and Gavrilescu, 2009). Heavy metal pollution resulting from the indiscriminate disposal of wastewater from many industries, such as mining, refining ores, tanneries, batteries, and paper industries, has becoming a global environment threat. Unlike organic pollutants, heavy-metal-ions are recalcitrant and accumulative in the environment and living tissues, causing diseases and disorders of living organisms even at low concentrations (Dabrowski et al., 2004; Hadi et al., 2013). Therefore, it is necessary to eliminate the toxic heavy-metal-ions from wastewater prior to their release into the environment.

Many techniques have been employed for the treatment of heavy-metal-ion contaminated wastewater, including chemical precipitation (Sun et al., 2003), ion exchange (Dabrowski et al., 2004; Metwally et al., 2013), chemical oxidation/reduction (Ortega et al., 2008), and membrane filtration (Jawor and Hoek, 2010). Among which, sorption technique is the most widely-used solution due to its simplicity and efficiency (Ngah and Hanafiah, 2008; O'Connell et al., 2008, Klapiszewski et al., 2015). Various sorbents, such as clay minerals (Dias and do Carmo, 2006), oxides (Zhao et al., 2011), and carbon materials (Cao et al., 2012; Stafiej and Pyrzynska, 2007), have been used in heavy-metal-ions removal. However, these materials often suffer from the shortcoming of high-costs. Therefore, developing more efficient, low-cost, and environment-friendly adsorbents is always being pursued.

Lignocellulosic biomass, as the most abundant renewable resource (Wyman et al., 1994; Lucas et al., 2008; Alonso et al., 2008; Lucas et al., 2010; Chen et al., 2014), which is predominantly composed of cellulose, hemicellulose, and lignin. Recently, numerous processing techniques have been developed on the lignin removal of lignocellulosic biomass and made great successes in recycling cellulose (Lynd et al., 1991; Huber et al., 2006; Taherzadeh et al., 2007). However, it is still a major challenge to directly convert the lignin component into value-added materials mainly

because lignin has evolved complex structural and chemical mechanisms for resisting chemical and biological assault (Ahvazi et al., 2011; Zhang et al., 2011). On the other hand, as a complex polymer of aromatic alcohols containing abundant functional groups, lignin shows potential capacities for the sorption of heavy-metal-ions (Celik and Demirbas, 2005; Conrad, 2008; Wu et al., 2008; Liu et al., 2013).

Up to now, various lignin-based biosorbents have been fabricated and successfully used to remove heavy-metal-ions from aqueous solutions (Wu et al., 2008; Liu et al., 2013; Li et al., 2015; Ge et al., 2016). It is envisioned that we can develop a conceptually new method for the synthesis of value-added mesoporous materials using the lignin component. The unique structure of the lignin may provide large surface area and large pore volume, and possess better diffusion, dispersion, and mass transfer behavior in the field of heavy-metal-ions removal (Zhang et al., 2008). Unfortunately, the intrinsic structure of lignin often has been wrecked during conventional pre-treatment processes of lignocellulosic biomass. Thus, it is still highly-desired to develop new effective strategy which can maintain the three-dimensional-structure of the lignin component in the recycle of cellulose component.

With regard to our continuing efforts toward environmentally friendly biomass disposal and resource recovery (Yao et al., 2011; Xu et al., 2011; Li et al., 2012; Li et al., 2012), we proposed a facile and sustainable approach to fabricate mesoporous lignin-based biosorbent (MLBB) from lignocellulosic biomass as a byproduct in the recycle of cellulose, through a sulfur trioxide (SO_3) micro-thermal-explosion process. This approach can maintain the three-dimensional-structure of the lignin component in the recycle of cellulose component. Rice straw (RS), the largest agricultural byproduct around the world, was used as a model of lignocellulosic biomass. In-situ generated SO_3 gas diffused into the internal structure and reacted with the water contained in RS, initiating a internal physical explosion, then, dilute alkali solution was used to dissolve the lignin component. The physicochemical properties of MLBB were studied by FTIR, ATR-FTIR, SEM, XPS, BET and element analysis. Lead ion (Pb(II)), a typical heavy-metal-ion (Zhu et al., 2007; Peng et al., 2012; Guo et al.,

2013; Li et al., 2015), was selected as a target heavy-metal-ion to evaluate the adsorption properties of this mesoporous adsorbent in heavy-metal-ion removal.

1 Materials and methods

1.1 Materials

RS, harvested in early October 2013, was collected from a suburb of Hefei, Anhui province, China. The RS was naturally air-dried to get rid of the surface water until the constant moisture was reached, with the moisture content of around 13 wt.%. The elemental compositions of the RS are shown in **Table 1**. Oleum (H_2SO_4), ammonium hydroxide ($\text{NH}_3\cdot\text{H}_2\text{O}$), sodium hydroxide (NaOH), and analytical grade $\text{Pb}(\text{NO}_3)_2$ were purchased from Sinopharm Chemical Reagent Co., Ltd. China and used without further purification. Ultrapure (Millipore Inc., USA) water (resistivity of $18.2\text{ M}\Omega\cdot\text{cm}$) was used in the experiments.

1.2 Preparation of MLBB

MLBB was prepared from RS via a physical-chemical process of SO_3 micro-thermal explosion (**Fig. 1a**), which was described in detail elsewhere (Yao et al., 2011; Li et al., 2012; Li et al., 2012). SO_3 plays a dual role of physical detachment between lignin and cellulose, and chemical modification of the lignin component. This in-situ physical detachment between lignin and cellulose can maintain the three-dimensional-structure of the lignin component. Chemical modification provides abundant sulfonic groups on the surface of lignin, which is propitious to the removal of heavy-metal-ion. A portion of RS sample at a weight of 1.0 kg was firstly treated with SO_3 gas (about 1.0 g, originated from the decomposition of oleum) for 2.5 hr in a home-made reactor (**Fig. 1b**). The pretreated RS sample was washed with ammonia solution (10 L, 0.3% $\text{NH}_3\cdot\text{H}_2\text{O}$). The solid residues were further washed with NaOH solution (10 L, 2% NaOH). High-value microcrystalline cellulose was further refined from the solid residue, and MLBB was separated from the liquid residue (~10 L, the black solution) through a pH-dependent flocculation process. The pH of the black solution was adjusted to around 7.0 with HCl solution (1.0 mol/L). Then, the solution was centrifuged at 5000 g for 1.0 min. The as-prepared MLBB sample was oven dried

at 45°C for 24 hr and then stored for the following adsorption experiments.

1.3 Characterization of MLBB

The morphologies of the MLBB samples were observed by field emission scanning electron microscopy (FESEM, SU8020, Hitachi, Japan) with an accelerating voltage of 5.0 kV. The fine structures were characterized using transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) operating at 80 kV accelerated voltage. Prior to TEM imaging, the pH values of the lignin solution (pH = 12.10) were adjusted to 9.60, 7.00, and 2.00 with dilute HCl and NaOH solutions, respectively. Several drops of each sample were added onto copper grids. SEM instrument operated at 5.0 kV accelerated voltage was used to examine the morphology and size of the MLBB powder.

FTIR spectra were recorded on a VERTEX 70 FT-IR spectrometer (Bruker Inc., Germany) operated at a setting of 32 scans at a spectral resolution of 4 cm⁻¹. Well-blended material-KBr (1:100) mix was ground, then desorbed at ambient temperature (20°C) and pressed to obtain IR-transparent pellets. Triplicate spectra were collected for each sample. All spectra were recorded from 4000 to 400 cm⁻¹ and processed with the OPUS software (Bruker Inc., Germany). A daily spectrum of the clean KBr window was used as background. All FTIR spectra were normalized after acquisition for comparison purposes. ATR-FTIR spectra of the samples were recorded on a ZnGe attenuated total reflection (ATR) attachment of Bruker Vertex 70 spectrometer equipped with a DTGS detector. The bands between 4000 and 600 cm⁻¹ were recorded, and 32 scans were averaged with a spectral resolution of 4 cm⁻¹.

X-ray photoelectron data were acquired with an X-ray photoelectron spectrometer system (ESCALAB250, Thermo-VG Scientific Inc., UK) with a monochromatic Al K α source (excitation energy, $h\nu = 1486.6$ eV) at a voltage of 10 kV and a current of 15 mA. Low resolution spectrum for the whole range was acquired at 70 eV pass energy, whereas the high resolution narrow range spectra for elements of interest were acquired at 20 eV pass energy. Spectra were corrected using C(1s) at 284.6 eV binding energy as reference. Elemental composition analysis of the MLBB and RS sample was also performed using an elemental analyzer (Vario EL III,

Varian, Germany) was used to determine the carbon, hydrogen, nitrogen, and sulfur (CHNS) contents (**Table 1**).

Specific surface areas of MLBB and RS samples were analyzed using a accelerated surface area and porosimetry analyzer system (Tristar II 3020M, Micromeritics, Georgia, USA). Prior to analysis, the target sample was subjected to the degas vacuum system under ultra high vacuum (10^{-9} bar) at a temperature of 120°C overnight. Sorption analysis was carried out at liquid nitrogen temperature (-196°C). Helium was used for the free space determination before sorption analysis, both at ambient temperature (20°C) and at -196°C. Adsorption/desorption isotherms, performed under a constant nitrogen flow rate to an adsorption cutoff $p/p_0 = 0.98$, typically required 8-12 hr to complete. Specific surface area (SSA) and total micropore volumes were estimated by application of the BET equation and the t-plot method, respectively. Mesopore volumes were calculated by subtracting the micropore volume (obtained from the application of t-plot method) from the total pore volume of nitrogen adsorbed at $p/p_0 = 0.98$.

1.4 Adsorption experiments

The absorption activities of MLBB sample were evaluated with Pb(II) as a model pollutant. Analytical grade $\text{Pb}(\text{NO}_3)_2$ was used as Pb(II) source. Batch experiments were carried out using 250-mL glass flasks. The aqueous adsorption efficiencies of MLBB were carried out by mixing 100 mg biosorbent with 100 mL of the Pb(II) solutions (1000 mg/L). All experiments were run in quintuplicate and data were presented as mean $\pm$ standard deviation.

Effect of adsorption time on the adsorption efficiency was investigated. All adsorption tests were carried out at 20°C in a temperature-controlled shaker. The mixtures were shaken and the sampling was performed at specified times (0, 0.25, 0.5, 0.75, 1, 2, 3, 4, 5, 6, 7, and 8 hr) followed by filtration. In order to study the effects of pH, the initial pH values of stock solutions were adjusted from 2 to 7 with dilute HCl solution (1.0 mol/L) or NaOH solution (1.0 mol/L). The dosage of biosorbent was set at 100 mg and the adsorption time was set at 5 hr. Effect of the temperature on the adsorption efficiency was also investigated under similar conditions (biosorbent

dosage of 100 mg, adsorption time of 5 hr, and initial pH value of 7.0). The tested temperature ranged from 20 to 80°C.

A total amount of 100 mg MLBB sample was added to 100 mL of Pb(II) solution (50-2000 mg/L) to test the effect of the initial metal ion concentrations on adsorption capacity. The suspension was centrifuged and filtered, and the amount of metal ions adsorbed on the MLBB was calculated according to **Eq. 1**,

$$q_e = (C_0 - C_e)V/W \quad (1)$$

where, C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium concentrations of metal ion, V (L) is the volume of the metal ion solution used in the adsorption experiment, and W (g) is the weight of the MLBB sample, respectively. Data are representative of at least five experiments, and standard deviations are less than 10.0%.

Initial and final concentrations of Pb(II) were measured using a ICP-AES system (710-ES, Varian, USA). The plasma conditions used were an RF power of 1.10 kW applied to the plasma and flow rates of 15.0 L/min for the plasma gas and 1.5 L/min for the auxiliary gas with the nebulizer gas pressure of 200 kPa. The wavelength for Pb analysis was 220.353 nm. The sample uptake was 1.5 mL/min for each of three replicate scans. Data are representative of at least three experiments, and standard deviations are less than 10.0%.

2 Results and discussion

2.1 TEM and TEM observations

Fig. 2a shows the pH-dependent flocculation of MLBB solution. The MLBB solution was homogeneous at pH above 9.60. An obvious turbidity was observed at pH 9.6-2.0. As pH was decreased to lower than 9.60, the solution became heterogeneous and more globule-like. The MLBB-macromolecules changed to congregated particles at acidic condition (pH 2.0). TEM imaging also illustrates that MLBB was colloidal-sized macromolecule with variable structures at different pHs. As shown in Figure 2B, an obvious porous structure can be observed from the TEM imaging. SEM imaging (**Fig. 2c**) illustrates that MLBB samples were small granules in size range from 100 to 1000 nm.

2.2 FTIR and ATR-FTIR measurements

In order to determine the structure of the raw material (RS) and the product (MLBB), analytical characterization of the materials by FTIR spectroscopy was used to monitor the changes in the course of chemical modification. Typical normalized FTIR spectra of MLBB sample and RS sample are shown in **Fig. 3a**. The functional groups identified from FTIR spectrum of MLBB are listed in **Table 2**. FTIR analysis of RS was carried out under similar condition. Two new characteristic peaks appeared at 1100 cm^{-1} and 800 cm^{-1} , which are ascribed to the entity of sulfonic groups ($-\text{SO}_2\text{OH}$) (Peng et al., 2004; Xu et al., 2007; Manoilova et al., 2007; Zhao et al., 2011). The absorbance band at 1100 cm^{-1} was assigned to symmetric and asymmetric stretching vibration of $\text{S}=\text{O}$ of $-\text{SO}_2\text{OH}$, whereas the absorbance band at 800 cm^{-1} was attributed to asymmetric stretching vibration of $\text{S}-\text{O}$ of $-\text{SO}_2\text{OH}$. It is envisaged that the sulfur trioxide micro-thermal explosion process results in a surface modification of lignin causing the availability of surface sulfonic functional groups.

ATR-FTIR spectroscopy was used to investigate the surface functional groups of solid particles. **Fig. 3b** shows the normalized ATR-FTIR spectra for the samples of MLBB and RS. In addition, the absorbance intensity of the peaks of $3360, 2902\text{ cm}^{-1}$ decreased significantly in the ATR-FTIR spectrum of MLBB sample. The characteristic peak at around 3360 cm^{-1} implies the stretching $\text{O}-\text{H}$ bond whose intensity is considerably decreased in the spectrum of lignin compared to the spectrum of RS sample. This is due to the dehydration and the removal of cellulose after the treatment process. The most significant change was three characteristic peaks of sulfonic group at $1080, 970$ and 800 cm^{-1} in the spectrum of MLBB sample. These peaks indicate that large amounts of sulfonic functional groups existed on the surface of MLBB. The results of ATR-FTIR analysis give clear information about the successful surface modification of MLBB.

2.3 XPS Studies

The surface chemistry of the MLBB and RS was further analyzed by XPS. As shown in **Fig. 4**, the most intense photoelectron peaks are found in $168.1, 284.6$ and 532.2 eV , which are attributed to $\text{S} (2p), \text{C} (1s)$ and $\text{O} (1s)$. The intensities of sulfur and carbon

peaks have considerably increased on the surface of the material after the activation process, whereas an obvious decrease of the intensity of oxygen peak has been detected on the surface of lignin compared to RS sample. This is in good agreement with the elemental analysis data (**Table 1**) and ATR-FTIR data (**Table 2**) showing the same trend for the sulfur increase after the SO₃-modification process.

2.4 Structural properties

The porous structure of the absorbent is one of the essential properties in determining its ability in heavy-metal-ion removal from the waste effluents. Therefore, the specific surface areas (S_{BET}), and micropore volumes of lignin were calculated by applying the Brunauer-Emmett-Teller (BET) equation and t-plot method, respectively. It was determined from the results that S_{BET} of the material increases from the trivial amount of 1.6 m²/g for the rice straw to 186 m²/g after the treatment making it more likely to function as a highly efficient adsorbent (**Fig. 5a**). Barrett-Joyner-Halenda (BJH) calculations for the pore-size distribution, derived from desorption data, reveal an average distribution at 5.50 nm (**Fig. 5b**). The average pore value was 0.35 cm³/g.

2.5 Absorption Performance

Fig. 6a shows Pb(II) sorption on MLBB as a function of time in neutral solution at 20°C. The amounts of metal ion adsorbed after 8 hr were not significantly different from the amounts adsorbed that after 5 hr. Therefore, 5 hr was considered sufficient to reach heavy-metal-ion adsorption equilibrium. To examine the controlling mechanism of the adsorption process, pseudo-first-order and pseudo-second-order models were used to fit the experimental data and evaluate the adsorption kinetic process (Najafi et al., 2012, Wang et al., 2012). The linear pseudo-first-order (**Eq. (2)**) and pseudo-second-order (equation 3) are illustrated as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (3)$$

where, q_t (mg/g) is the adsorption capacity at time t (hr), q_e (mg/g) is the adsorption capacity at adsorption equilibrium, and k_1 (hr⁻¹) and k_2 (g/(mg·hr)) are the kinetics rate constants for the pseudo-first-order and pseudo-second-order models, respectively. The values of correlation coefficients indicated a better fit of the pseudo-second-order

model ($R^2 = 0.998$, $k_2 = 0.133$ g/(mg·hr)) with the experimental data than of the pseudo-first-order model ($R^2 = 0.719$, $k_1 = 0.417$ hr⁻¹). Therefore, the adsorption kinetics follows the pseudo second-order model, suggesting the following chemisorption process.

Effect of temperature on the Pb(II) absorption efficiency was also evaluated. Batch experiments of Pb(II) absorption under different temperatures (20 to 80°C) is illustrated in Figure 6B, the Pb(II) absorption efficiency decreased at higher temperature. In addition, the results of Pb(II) removal at different pHs indicate that lignin-initiated absorption was enhanced at a higher pH (**Fig. 6c**). Pb(II) will be precipitated as Pb(OH)₂ under alkaline conditions. Therefore, the adsorption experiments to evaluate the effects of pH were performed under acidic or neutral conditions. The lowest Pb(II) removal efficiency was obtained at acidic condition (pH 2.0), whereas the highest removal efficiency was achieved at pH 7.0. The sorption of Pb(II) increases slowly at pH < 4, quickly at pH 4-7 and then maintains at a high level at pH = 7. At low pH value (pH < 4), the surface charge of MLBB is positive because of the protonation reaction (Reaction 1, where **R** represents lignin). The positive metal ions are difficult to adsorb on the positively charged surface because of electrostatic repulsion. Under neutral condition, the surface charge become negative because of the deprotonation process (Reaction 2, where **R** represents lignin). The pH value of solution significantly affected the degree of deprotonation and the speciation of the surface functional groups. With increasing pH, the surface charge is more negative and the electrostatic interactions between the metal ions and lignin become stronger, which favors the metal ion sorption.

The adsorption isotherms at different initial Pb(II) concentrations are shown in **Fig. 6d**. The $q_{e,\max}$ value of Pb(II) sorption reached up to 952 ± 31 mg/g. At low initial concentrations (less than 1000 mg/L), adsorption capacities of metal ions increased

almost proportionally with the increment in the initial concentrations of metal ions, suggesting that the adsorption process is highly concentration dependent. At higher initial concentrations (more than 1000 mg/L), the increase in uptake is relatively slow.

The adsorption isotherm is important for determining the adsorption behavior of an biosorbent. Two widely-used isotherm equations (Langmuir isotherm equation and Freundlich isotherm equation) were employed to fit the experimental data (Ma et al., 2009, Zhou et al., 2012). The Langmuir isotherm assumes monolayer coverage of adsorbate over a homogenous adsorbent surface. The Langmuir equation is expressed as **Eq. (4)**, where q_e (mg/g) is the amount of Pb(II) adsorbed per unit mass of adsorbent under equilibrium, Q_0 (mg/g) is the maximum adsorption capacity, K_l (L/mg) represents the Langmuir adsorption constant, C_e (mg/L) stands for the equilibrium concentration of Pb(II). The linearized form of the Langmuir equation is given as **Eq.(5)**.

The Freundlich isotherm is an empirical equation which is based on based on a heterogeneous surface, and it has been used for the adsorption process of multilayer adsorption. The Freundlich equation is represented as equation 6, where q_e (mg/g) is the amount of Pb(II) adsorbed per unit mass of adsorbent under equilibrium, C_e (mg/L) is the equilibrium concentration of Pb(II), K_F and n are Freundlich constants, which represent the adsorption capacity and adsorption intensity of the adsorbent. The value of $1/n$ below one indicates a normal Langmuir isotherm, otherwise, it indicates a cooperative adsorption. The linearized form of the Freundlich equation is given as **Eq. 7**.

$$q_e = (Q_0 K_l C_e) / (1 + K_l C_e) \quad (4)$$

$$C_e/q_e = 1 / Q_0 K_l + C_e / Q_0 \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (6)$$

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (7)$$

As shown in **Fig. 5e**, the Langmuir model effectively described the adsorption data with $R^2 > 0.99$, suggesting a better fit of the Langmuir isotherm with the experimental data compared to those with the Freundlich isotherm (**Fig. 5f**), which demonstrates the adsorption process occurs on a homogeneous surface of the

adsorbent and each binding site can be occupied only once. With the analysis above, the number of available functional groups on the surface of adsorbent actually became the limiting factor that controlled the amount of sorption.

3 Conclusions

In summary, we have developed a facile and sustainable method for the fabrication of MLBB from RS, as a byproduct of microcrystalline cellulose, through a SO₃ micro-thermal explosion process. The MLBB showed excellent performance for Pb(II) capture with a maximum capacity of 952 ± 31 mg/g, which were mainly attributed to their special structure (i.e., mesoporous structure with large surface area and abundant sulfonic functional groups on the surface). Considering that biomass is a naturally abundant and renewable resource and SO₃ micro-thermal explosion is a proven and easy-to-operated technique, the MLBB can be easily produced at large scale and become a sustainable and reliable resource for wastewater treatment. This work would open up a new pathway for all-round utilization of waste biomass as well as resolve the water pollution of heavy-metal-ion.

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List of Figures

- Fig. 1 (a) Schematic illustration of preparation of mesoporous lignin-based biosorbent (MLBB) from rice straw via a SO_3 micro-thermal-explosion process, and (b) Home-made sulfur trioxide (SO_3) micro-thermal-explosion instrument.
- Fig. 2 (a) Flocculation behaviors of mesoporous lignin-based biosorbent (MLBB) solution (0.6 g/L) at different pHs (clear solution in $\text{pH} > 9.6$ region, flocs in $\text{pH} < 9.6$ Region), (b) SEM image of MLBB (Amplification scale of 20000), and (c) TEM image of MLBB (Scale bar=100 nm).
- Fig. 3 FTIR spectra (a) and ATR-FTIR spectra (b) of mesoporous lignin-based biosorbent (MLBB) granules and rice straw (RS).
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- Fig. 6 (a) Adsorption kinetics of $\text{Pb}(\text{II})$ onto mesoporous lignin-based biosorbent (MLBB), (b) Effect of pH on the metal ion adsorption of MLBB absorbent, (c) Effect of temperature on the metal ion adsorption of MLBB absorbent, (d) Adsorption isotherms at different initial $\text{Pb}(\text{II})$ concentrations, (e) Langmuir adsorption isotherm of $\text{Pb}(\text{II})$ onto the MLBB absorbent, and (f) Freundlich adsorption isotherm of $\text{Pb}(\text{II})$ onto the MLBB absorbent.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Table

Table 1. Elemental compositions of mesoporous lignin-based biosorbent (MLBB) and rice straw (RS) (wt.%).		
Element	MLBB	RS
Carbon (C)	75.22±0.07	32.62±0.07
Hydrogen (H)	16.99±0.09	10.62±0.08
Oxygen (O)	5.23±0.10	55.90±0.12
Nitrogen (N)	0.05±0.02	0.65±0.04
Sulfur (S)	2.51±0.01	0.21±0.01

Table 2 - Evaluation of FT-IR spectrum of mesoporous lignin-based biosorbent (MLBB).

Absorbance frequency (cm ⁻¹)	Assignment
3630, 3268 (broad absorbance)	O-H stretching vibration of the hydroxyl groups N-H stretching vibration of the amino groups Broad absorbance: hydrogen-bond effect in the present of water.
2920	Symmetric and asymmetric stretching vibration of the aliphatic CH ₂ group Symmetric and asymmetric stretching vibration shoulder of the aliphatic CH ₃ group
1645	C=C stretching vibration of Carbon-carbon double bonds C=O stretching vibration of carbonyl groups
1100	Bending vibrations of the CH ₂ and CH ₃ aliphatic groups Symmetric and asymmetric stretching vibration of S=O of -SO ₂ OH group
1050	Stretching vibration of C-O bonds
800 (broad absorbance)	Overlapping of the CH ₂ rocking vibration and the out-of-plane vibration of aromatic group Asymmetric stretching vibration of S-O of -SO ₂ OH group

Graphic Abstract