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

Fang Xu1,⁎, Ting-Ting Zhu1,2, Qing-Quan Rao3, Sheng-Wen Shui1, Wen-Wei Li2, Hong-Bo He1, Ri-Sheng Yao1,⁎

1. School of Medical Engineering, Hefei University of Technology, Hefei 230009, China
2. CAS Key Laboratory of Urban Pollutant Conversion, Department of Chemistry, University of Science & Technology of China, Hefei 230026, China
3. Environmental Monitoring Center of Taizhou, Taizhou 31800, China

ARTICLE INFO

Article history:
Received 2 December 2015
Revised 11 March 2016
Accepted 25 March 2016
Available online 6 June 2016

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 fourier transform infrared spectroscopy (FTIR), attenuated-total-reflection fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), and element analysis. These results showed that there are large amounts of sulfonic functional groups existing 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.

© 2016 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Keywords:
Lignocellulosic biomass
Mesoporous biosorbent
Rice straw
Lignin
Sulfur trioxide
Micro-thermal-explosion

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 and Kurniawan, 2003; Sud et al., 2008; Hilhor 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.

* Corresponding authors. E-mail: Fangxu@hfut.edu.cn (Fang Xu), yaors@hfut.edu.cn (Ri-Sheng Yao).

http://dx.doi.org/10.1016/j.jes.2016.03.026
1001-0742/© 2016 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.
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., 2011a, 2011b), and carbon materials (Cao et al., 2012; Stafiej and Pyrzynska, 2007), have been used in heavy-metal-ion 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, 1994; 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 and Karimi, 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., 2015a, 2015b; 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. 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., 2012a, 2012b), 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 (SO3) 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 SO3 gas diffused into the internal structure and reacted with the water contained in RS, initiating an internal physical explosion, then, dilute alkali solution was used to dissolve the lignin component. The physicochemical properties of MLBB were studied by fourier transform infrared spectroscopy (FTIR), attenuated-total-reflection fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscope (SEM), X-ray photoelectron spectrometry (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., 2015a, 2015b), 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 (H2SO4), ammonium hydroxide (NH3·H2O), sodium hydroxide (NaOH), and analytical grade Pb(NO3)2 were purchased from Sinopharm Chemical Reagent Co., Ltd., China and used without further purification. Ultrapure (Millipore Inc., USA) water (resistivity of 18.2 MΩ·cm) was used in the experiments.

1.2. Preparation of MLBB

MLBB was prepared from RS via a physical–chemical process of SO3 micro-thermal explosion (Fig. 1a), which was described in detail elsewhere (Yao et al., 2011; Li et al., 2012a, 2012b). SO3 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 SO3 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% NH3·H2O). 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.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Elemental compositions of mesoporous lignin-based biosorbent (MLBB) and rice straw (RS) (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>MLBB</td>
</tr>
<tr>
<td>Carbon (C)</td>
<td>75.22 ± 0.07</td>
</tr>
<tr>
<td>Hydrogen (H)</td>
<td>16.99 ± 0.09</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>5.23 ± 0.10</td>
</tr>
<tr>
<td>Nitrogen (N)</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>2.51 ± 0.01</td>
</tr>
</tbody>
</table>
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 FTIR 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\(_\alpha\) 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 an 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 Pb(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 ± 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),

\[ q_e = \frac{(C_0 - C_e)V}{W} \]

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 an 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 Fig. 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. Typically 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 (–SO\(_2\)OH) (Peng et al., 2004; Xu et al., 2007; Manoilova et al., 2007; Zhao et al., 2011a, 2011b). The absorbance band at 1100 cm\(^{-1}\) was assigned to symmetric and asymmetric stretching vibration of S==O of –SO\(_2\)OH, whereas the absorbance band at 800 cm\(^{-1}\) was attributed to asymmetric stretching vibration of S–O of –SO\(_2\)OH. It is envisaged that the sulfur trioxide microthermal 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 cm\(^{-1}\) decreased significantly in the ATR-FTIR spectrum of MLBB sample. The characteristic peak at around 3360 cm\(^{-1}\) implies the stretching O–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 the 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 S (2p), C (1s) and 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 SO$_3$-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 m$^2$/g for the rice straw to 186 m$^2$/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 cm$^3$/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 (Eq. (3)) are illustrated as follows:

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

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

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) 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). Therefore, the adsorption kinetics follows the pseudo-second-order model, suggesting the following chemisorption process.

$\text{R-S-OH} + \text{H}^+ \rightarrow \text{R-S-OH}_2^+$ \hspace{1cm} (Reaction1)

$\text{R-S-OH} \rightarrow \text{R-S-O}^- + \text{H}^+$ \hspace{1cm} (Reaction2)

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 Fig. 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 becomes 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 $q_{\text{e,max}}$ 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.

Fig. 4 – XPS survey spectrum (a) for the mesoporous lignin-based biosorbent (MLBB) and high-resolution XPS spectrum (b) for the sulfur on the surface of the MLBB. XPS: X-ray photoelectron spectroscopy.

Fig. 5 – (a) Nitrogen adsorption–desorption isotherms of mesoporous lignin-based biosorbent (MLBB) sample, and (b) Barrett-Joyner-Halenda (BJH) calculations for the pore-size distribution on the surface of MLBB.
The adsorption isotherm is important for determining the adsorption behavior of a 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 a heterogeneous surface, and it has been used for the adsorption process of multilayer adsorption. The Freundlich equation is represented as Eq. (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).

$$q_e = \frac{Q_0 K_l C_e}{1 + K_l C_e}$$  \hspace{1cm} (4)

$$C_e/q_e = 1/Q_0 K_l + C_e/Q_0$$  \hspace{1cm} (5)

$$q_e = K_F C_e^n$$  \hspace{1cm} (6)
described the adsorption data with the amount of sorption. 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 (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 SO$_3$ micro-thermal explosion process. The MLBB showed excellent performance for Pb(II) capture with a maximum capacity of $952 \pm 31$ 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 SO$_3$ 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.

Acknowledgments

The authors wish to thank the National Science Foundation of China (No. 21207031) and the National High Technology Research of China (863) (No. 2014AA021902) for the partial support of this study.

REFERENCES


