Iran. J. Environ. Health. Sci. Eng., 2011, Vol. 8, No. 3, pp.

THIOGLYCOLIC ACID ESTERIFIED INTO RICE STRAW FOR REMOVING LEAD FROM AQUEOUS SOLUTION

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Received 8 May 2010; revised 16 January 2011; accepted 18 June 2011

ABSTRACT

Thiol rice straw (TRS) was prepared by esterifying thioglycolic acid onto rice straw in the medium of acetic anhydride and acetic acid with sulfuric acid as catalyst. The sorption of lead (Pb) on TRS from aqueous solution was subsequently investigated. The batch experiments showed that Pb removal was dependent on initial pH, sorbent dose, Pb concentration, contact time, and temperature. The maximum value of Pb removal appeared at pH 5. For 100 mg/L of Pb solution, a removal ratio of greater than 98% could be achieved with 2.0 g/L or more of TRS. The isothermal data of Pb sorption conformed well to the Langmuir model, and the maximum sorption capacity (Q_m) of TRS for Pb was 104.17 mg/g. The equilibrium of Pb removal was reached within 120 min. The Pb removal process could be described by the pseudo-first-order kinetic model. The thermodynamic study indicated that the Pb removal process was spontaneous and endothermic.

Key words: Thioglycolic acid; Esterification; Rice straw; Lead removal

INTRODUCTION

Heavy metals are continuously released into the aquatic environment by industrial and domestic activities. The water bodies are polluted when excess heavy metals are introduced into them. Public concern over heavy metal pollution has grown constant since the outbreak of Minamata disease caused by methylmercury and itai-itai disease caused by cadmium in Japan (Matsuo, 2003). People's awareness of the hazards of heavy metals now covers a wide range of heavy metals such as lead, mercury, cadmium, chromium, copper, zinc, nickel and arsenic.

Due to their high toxicity and bioaccumulation tendency, heavy metals must be removed from municipal and industrial wastewaters before discharge. A number of techniques such as chemical precipitation (Esalah *et al.,* 2000), solvent extraction (Mellah and Benachour, 2006), flotation (Polat and Erdogan, 2007), electrodialysis (Mohammadi *et al.,* 2005), membrane separation (Mohammad *et al.,* 2004), reverse osmosis (Ozaki *et al.,* 2002), ion exchange (Fernández *et al.,* 2005), and sorption (Shokoohi *et al.,* 2009) have been employed to remove heavy metals from wastewater. But based on techno-economic considerations to conventional disposal methods, people still have been searching for new materials and techniques for heavy metal wastewater treatment.

In recent years, many agricultural wastes, including sago waste (Quek *et al.,* 1998), hazelnut shell (Cimino *et al.,* 2000), olive pomace

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(Pagnanelli *et al.,* 2003), wheat shell (Basci *et al.,* 2004), grape stalk waste (Villaescusa *et al.,* 2004), papaya wood (Saeed *et al.,* 2005a), black gram husk (Saeed *et al.,* 2005b), carrot residue (Nasernejad *et al.,* 2005), mustard oil cake (Ajmal *et al.,* 2005), ulmus leaves (Gholami *et al.,* 2006), platanus leaves (Mahvi *et al.,* 2007), tree fern (Ho and Wang, 2008), rice husk (Krishnani *et al.,* 2008), coffee husk (Oliveira *et al.,* 2008), and wheat bran (Nameni *et al.,* 2008), had been used to sorb heavy metals from aqueous solution. Generally, the heavy metal sorption capacities of these agricultural wastes are low. For improving their physicochemical property or enhancing their sorption capacity, some agricultural wastes had been subjected to various chemical modifications (Lee *et al.,* 1999; Wong *et al.,*2003; Shukla *et al.,*2006; Anirudhan *et al.,*2007; Namasivayam and Sureshkumar, 2009).

In the present work, thiol rice straw (TRS) was prepared by esterification of thioglycolic acid for enhancing heavy metal sorption capacity of rice straw. The resulting material was subsequently investigated for its potential as sorbent for removing lead from aqueous solution in a batch system.

MATERIALS AND METHODS

Chemicals and instruments

Thioglycolic acid was purchased from Sigma Chemical Co., St. Louis, MO, USA. All other chemicals were obtained commercially with the highest purity available and used without further purification. Doubly distilled water was used throughout this study.

A Perkin-Elmer Model 5100PC flame atomic absorption spectrophotometer (USA) was used for determination of lead under the manufacturer's recommended conditions.

Preparation of TRS

The TRS was prepared according to the following method: In a wide mouth bottle, the following reagents were added in order: 100 mL of thioglycolic acid, 60 mL of acetic anhydride, 40 mL of 36% (v/v) acetic acid, and 0.3 mL of concentrated sulfuric acid. The mixture was thoroughly stirred and cooled to room temperature, followed by adding 30 g ground rice straw (420-850 µm), which subsequently was thoroughly impregnated in solution. After being cooled, the bottle was covered with the lid and kept at 40°C in a water bath for 3 days. The final reaction product was recovered by suction filtration and washed extensively with doubly distilled water. After being dried at 40°C for 24 h, the TRS was kept at 4°C in a sealed dark bottle protected from sunlight.

The reaction scheme of preparing TRS was presented in Fig. 1. Firstly, the oxygen of carbonyl group in thioglycolic acid took a proton from the concentrated sulphuric acid and produced a carbocation. Secondly, the carbocation was attacked by the oxygen of hydroxyl group in cellulose. Lastly, water molecule and proton were lost and esterification was achieved.

Preparation of Pb solution

The lead stock solution corresponding to 500 mg/L of Pb was prepared by dissolving 0.7993 g of lead (II) nitrate in doubly distilled water and diluting to 1000 mL in a standard volumetric flask. All working solutions were obtained by diluting the Pb stock solution in accurate proportions to different initial concentrations.

Removal experiments

Removal experiments were carried out on a rotary shaker at 150 rpm and desired temperature (10-50 °C) using 250 mL shaking flasks containing 100 mL of Pb working solutions with known initial concentration (50-400 mg/L) and desired initial pH values. Because the precipitation of insoluble lead compound occurred at pH value greater than 5, the experiment of Pb removal was only conducted from pH=2.5 to 5. The initial pH values of the solutions were previously adjusted with diluted HNO_3 using a pH meter. Different doses of TRS (0.25-4.0 g/L) were added to each flask, and then the flasks were sealed to prevent a change in volume of the solution during the experiments. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and filtered through a membrane filter (0.45 µm). The concentration of residual Pb in the filtrate was determined with flame atomic absorption spectrometry. The amount of Pb sorbed on TRS was calculated by the following mass balance equation:

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

where q_e is the amount of Pb sorbed at equilibrium (mg/g), C_0 and C_e are the initial and equilibrium concentration of Pb solution, respectively (mg/L), V is the volume of Pb solution (L) and W is the mass of sorbent (g).

Following the removal experiments, Pb-laden TRS was separated by filtration and suspended into 20 mL of the eluting solution. Desorption of Pb from TRS was carried out on a rotary shaker at 150rpm for 120 min. Then the TRS was separated by filtration and the concentration of the Pb released into the eluent solution was determined. Desorption efficiency was calculated as a percentage of the amount of the released Pb ions relating to the total amount of Pb ions which were previously sorbed on TRS. All experiments were conducted in triplicate and mean values were used in the analysis of data.

RESULTS

Data of TRS

The thiol groups in TRS determined by iodimetry were 0.51 m mol/g. The BET surface area of TRS measured was 196 m^2/g. The micropore and mesopore volumes were 0.42 and 0.19 cm^3/g, respectively. The pH$_{zpc}$ of TRS was found to be 5.2 by titration method.

Effect of initial pH

As elucidated in Fig. 2, the amount of Pb removal increased as the initial pH value of Pb solution was increased from 2.5 to 5. For this reason, the pH=5 was selected for the further experiments.

Influence of sorbent dose

The influence of sorbent dose on the removal ratio of Pb was investigated over a range from 0.25 to 4.0 g/L of TRS. For the Pb solution at 100 mg/L initial concentration, the percentages of Pb removed increased from 25.92 to 98.14% with increasing the TRS dose from 0.25 to 2.0 g/L. Above 2.0 g/L of sorbent dose, the maximum sorption was reached and the removal ratio of Pb had only little change. So, the TRS dose of 2.0 g/L was chosen for subsequent experiments.

Effect of initial Pb concentration and sorption isotherm

The effect of Pb concentration on its removal percentage was shown in Fig. 3. When the Pb concentration was in the range of 50-150 mg/L, more than 98% of Pb in the solution could be removed by 2.0 g/L of TRS. With further increase of Pb concentration up to 400 mg/L, the percentage of Pb removed by 2.0 g/L of TRS decreased to 50.37%.

With the data in Fig. 3, Langmuir equation was employed to study the sorption isotherm of Pb. The linear Langmuir equation was shown as follows:

$$C_e/q_e = C_e/Q_m + (1/aQ_m) \qquad (2)$$

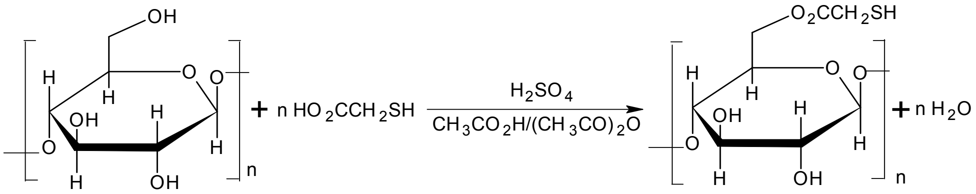

Fig. 1: The preparation scheme of TRS

where C_e (mg/L) is the concentration of the Pb solution at equilibrium, q_e (mg/g) is the amount of Pb sorbed at equilibrium, Q_m is the maximum sorption capacity and represents a practical limiting sorption capacity when the sorbent surface is fully covered with monolayer sorbate molecules and a is Langmuir constant. The Q_m and a values were obtained from the slope ($1/Q_m$) and intercept ($1/aQ_m$) of the linear plot of C_e/q_e versus C_e.

The Langmuir sorption isotherm of Pb sorbed on TRS was shown in Fig. 4. The maximum sorption capacity (Q_m) obtained from the slope ($1/Q_m$) of linear Langmuir equation was 104.17 mg/g.

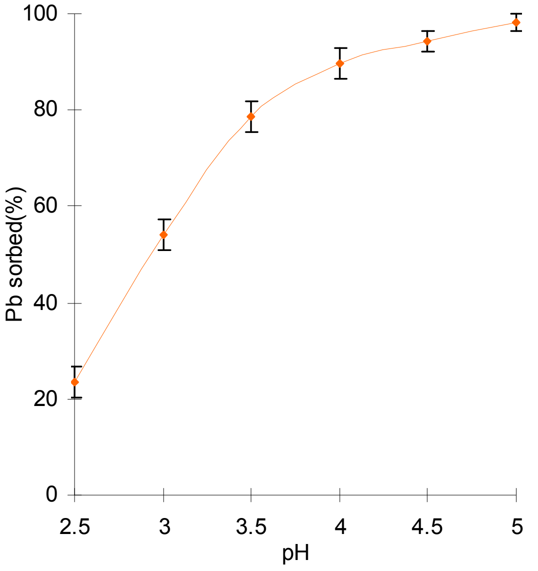

Fig. 2: Effect of initial solution pH on Pb removal by TRS (Pb concentration=100 mg/L; TRS dose=2.0 g/L; contact time=120 min)

Influence of contact time and sorption kinetics

The sorption kinetics was investigated by examining the influence of contact time on Pb sorption. The rate of Pb removal was very rapid at the initial stage of sorption. It was only 10 minutes that the percentage of Pb removed had reached 75.62%. After that, the Pb removal rate declined gradually and reached the equilibrium value at about 120 min.

To examine the kinetic model of Pb removed by TRS, The data of contact time influence were treated with the following Lagergren's pseudo-first-order rate equation:

$$\ln (q_e - q_t) = \ln q_e - k_{ad}\, t \qquad (3)$$

where q_e and q_t (mg/g) refer to the amount of Pb removed at equilibrium and time t (min), respectively, and k_{ad} is the rate constant. The rate constants k_{ad} could be calculated from the slope of the linear plot of $\ln (q_e - q_t)$ versus t. The above kinetic data were also treated with the following intraparticle diffusion rate equation:

$$q_t = k_{id} t^{1/2} + C \qquad (4)$$

where q_t (mg/g) is the amount of Pb removal at time t (min), k_{id} is the intraparticle diffusion rate constant, and C is the intercept. The k_{id} and C values were obtained from the slope and intercept of the linear plot of q_t versus $t^{1/2}$. When the line passed through the origin (C=0), the intraparticle diffusion will be the sole rate control step. If the plot does not pass through the origin, it implies that intraparticle diffusion is not the only rate control step and other processes may control the rate of sorption (Ramesh *et al.,* 2008).

Table 1: The pseudo-first-order rate and intraparticle diffusion rate equations, values of constants and correlation coefficient for Pb removal by TRS

Sorbate	pseudo-first-order rate			intraparticle diffusion rate		
	$\ln(q_e-q_t) = -0.0508t + 1.6018$			$q_t = 7.018t^{1/2} + 14.441$		
	q_e(mg/g)	k_{ad}(1/min)	R^2	k_{id}(mg/g·min$^{1/2}$)	C(mg/g)	R^2
Pb	4.962	0.0508	0.9903	7.018	14.441	0.9749

The pseudo-first-order rate and intraparticle diffusion rate equations, values of constants and correlation coefficients for Pb removal by TRS were shown in Table 1.

Sorption thermodynamics

The thermodynamic experiment was carried out at 283.15, 293.15, 303.15, 313.15, and 323.15 K using 2.0 g/L of TRS dose for 100 mg/L of Pb solution. The thermodynamic parameters, ΔH° and ΔS°, were obtained from the following van't Hoff equation:

$$\ln (q_e/C_e) = \Delta S^\circ/R - \Delta H^\circ/RT \qquad (5)$$

where q_e/C_e is the equilibrium constant (mL/g), ΔS° is standard entropy (J/mol·K), ΔH° is standard enthalpy (J/mol), T is the absolute temperature (K), and R is the gas constant (8.314 J/mol·K). From Fig. 5, the ΔH° and ΔS° values could be calculated from the slope ($-\Delta H^\circ/R$) and intercept ($\Delta S^\circ/R$) of the linear plot of $\ln (q_e/C_e)$ versus 1/T. The thermodynamic parameter, ΔG°, was calculated from the following Gibbs-Helmholtz equation:

$$\Delta G^\circ = \Delta H^\circ \Delta T \Delta S^\circ \qquad (6)$$

where ΔG° is the standard free energy (kJ/mol). The ΔG° values under different temperatures as well as ΔH° and ΔS° values were presented in Table 2.

Table 2: The values of thermodynamic parameters for Pb removal by TRS

Sorbate	ΔH° (kJ/mol)	ΔS° (J/mol·K)	ΔG° (kJ/mol)				
			283.15 K	293.15 K	303.15 K	313.15 K	323.15 K
Pb	69.42	302.85	-16.33	-19.36	-22.39	-25.42	-28.45

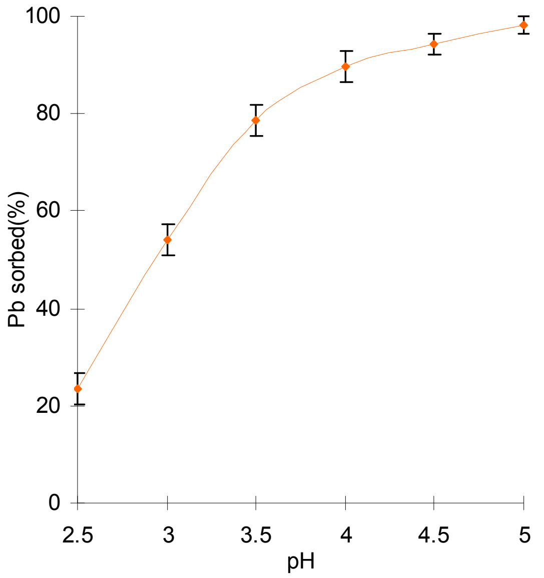

Fig. 3: Effect of initial Pb concentration on its removal by TRS (TRS dose=2.0 g/L; contact time=120 min; pH=5)

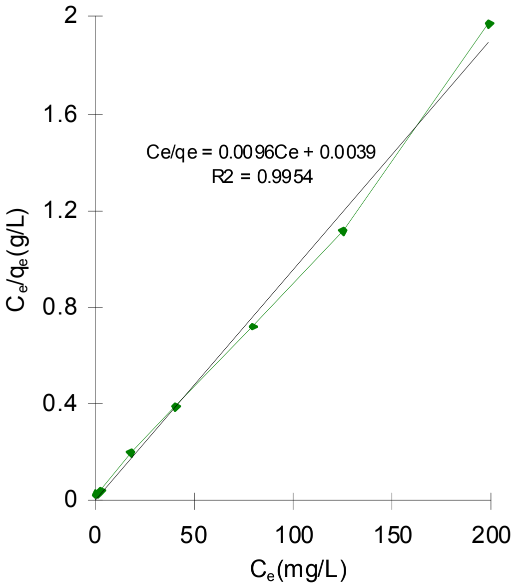

Fig. 4: The Langmuir plot of Pb removal by TRS

Desorption of Pb

The efficiency of Pb desorption was investigated with different concentration of HCl or EDTA as eluent. The result indicated that more than 90% of Pb sorbed could be desorbed from TRS by 0.1 M of HCl or EDTA.

FTIR spectra and SEM photographs

The FTIR spectra of crude rice straw and TRS were shown in Fig. 6. The SEM photographs of TRS before and after Pb sorption were shown in Fig. 7.

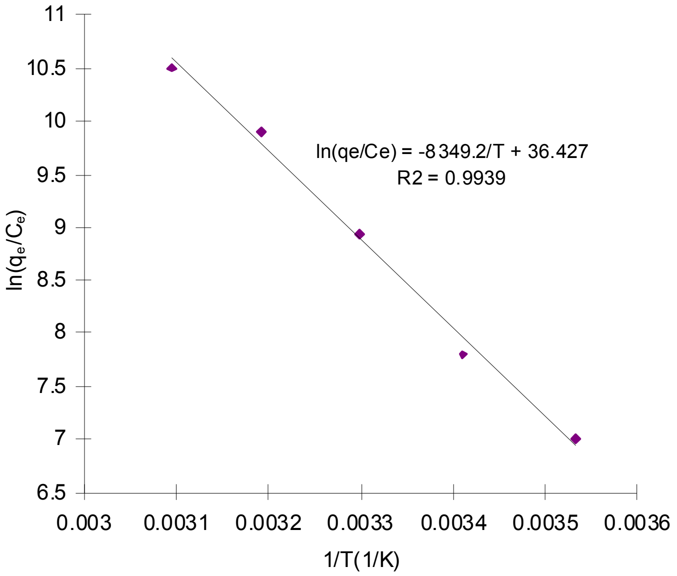

Fig. 5: The plot of ln q_e/C_e vs. $1/T$ for Pb removal by TRS (Pb concentration, 100 mg/L; TRS dose, 2.0 g/L; contact time, 120 min)

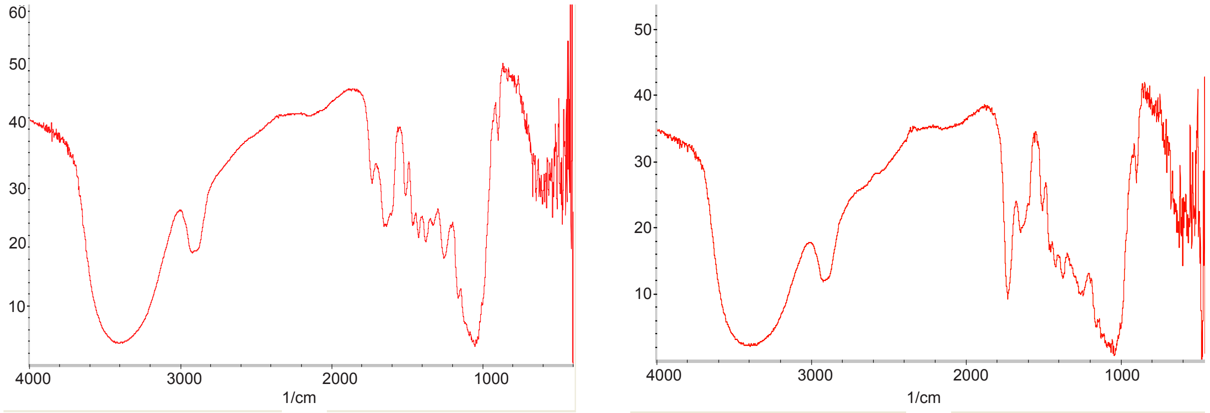

Fig. 6: The FTIR spectra of crude rice straw (left) and TRS (right) (X-axis and Y- axis represent wavenumber and transmittance, respectively)

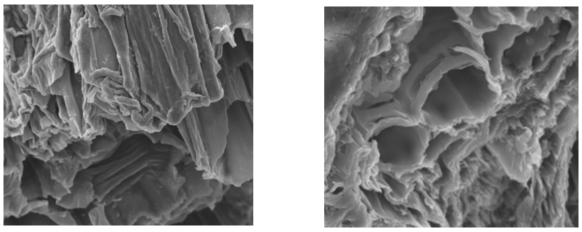

Fig. 7: The SEM photographs of TRS at 4000 × magnification (left: before Pb sorption; right: after Pb sorption)

DISCUSSION

Effect of initial pH

Effect of initial pH shown in Fig. 2 could be interpreted by the following explanation. At acidic pH, thiol or carboxyl groups on TRS were protonated into the nonionic even cationic form; the nonionic or cationic form of thiol or carboxyl groups did not favor the sorption of Pb cations. As the initial pH was increased to pH 5, the number of negatively charged thiol or carboxyl groups on TRS increased. It favored the sorption of Pb cations due to the electrostatic attraction. This was in accordance to the result reported by Muhammad *et al.* (2009).

Influence of sorbent dose

The influence of sorbent dose could be explained as follows: For a fixed initial solution concentration, that increase of sorbent dose provides a greater surface area (or sorption sites). So, before reaching the maximum sorption, the percentage of sorbate removed increased along with increase of sorbent dose; after reaching the maximum sorption, the removal ratio of sorbate kept constant. But the amount of Pb sorption per unit mass of TRS obviously decreased along with increase of sorbent dosage (Benguella and Benaissa, 2002).

Effect of initial Pb concentration and sorption isotherm

The decrease of Pb removal with increase of Pb concentration (shown in Fig. 3) could be attributed to the lack of available active sorption sites required for the high initial Pb concentration.

The excellent linear correlation coefficient in Fig. 4 indicated that the sorption isotherm of Pb on TRS followed the Langmuir model.

Sorption kinetics

The excellent linear correlation coefficient shown in Table 1 indicated that the Pb removal process could be described by the pseudo-first-order kinetic model. The intraparticle diffusion step was also involved in the removal process, although it was not the only rate control step ($C\neq0$).

Sorption thermodynamics

The negative values of ΣG° and the positive values of ΣH°shown in Table 2 indicated that the Pb removal was spontaneous and endothermic. High temperatures were favorable for the removal process. Because the process of metal ions diffusing into sorbent surface is energy-consuming, most of heavy metal sorptions are generally endothermic in nature (Panayotova, 2001; Ho and Ofomaja, 2005; Li *et al.,* 2005; Huang *et al.,* 2007).

Desorption of Pb and sorption mechanism

The main functional groups in TRS involved in Pb sorption were thiol, hydroxyl and carboxyl groups. In strong inorganic acid medium, thiol, hydroxyl and carboxyl groups on TRS were protonated into the cationic form. The cationic form of thiol, hydroxyl and carboxyl groups resulted in desorption of Pb ions. Because EDTA formed the stable chelate compounds with many metal ions, it could effectively elute Pb from TRS. The fact, the Pb sorbed could be effectively desorbed by strong inorganic acid and chelant indicated that maybe ion exchange and complexation were the sorption mechanism of Pb on TRS.

FTIR spectra and SEM photographs

Comparing with the IR spectrum of crude rice straw, it could be seen that in IR spectrum of TRS, the characteristic stretching vibration absorption band of carboxyl groups at 1750 cm^{-1} increased obviously but the broad mixed stretching vibration absorption band of amino and hydroxyl groups at 3400 cm^{-1} decreased. This result confirmed the occurrence of thioglycolic acid esterifying reaction. The SEM photograph before Pb sorption revealed the rough surface texture of TRS. After Pb sorption, the SEM image of TRS presented the uniform accumulation of Pb ions on its surface. The SEM photograph also indicated that the edges of TRS seemed to become fluffy after Pb sorption.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to the Key Project of Natural Science Foundation of Anhui Education Bureau, the Key Laboratory of Bioresource Protection and Utilization of Anhui Province, and the Key Laboratory of Biotic Environment and Ecological Safety of Anhui Province for the financial supports to this work.

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