Bioresource Technology 167 (2014) 569–573

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Short Communication

Sorption and cosorption of lead (II) and methylene blue on chemically modified biomass

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HIGHLIGHTS

- Modified biomass effectively removed lead and methylene blue.
- Lead preferentially adsorbed on the biosorbents.
- Competitive adsorption of the two contaminants on the biosorbents.

ARTICLE INFO

Article history:
Received 22 April 2014
Received in revised form 11 June 2014
Accepted 12 June 2014
Available online 19 June 2014

Keywords:
Agricultural by-products
Co-adsorption
Cationic dyes
Heavy metals
Chemical modification

ABSTRACT

Sorption and cosorption of lead (Pb(II)) and methylene blue (MB) in aqueous solutions on low-cost biosorbents made from chemically modified agricultural by-products was investigated. Modified cotton exhibited the highest adsorption capacity for Pb(II), while modified cotton and peanut hull had higher equilibrium adsorption capacity of MB than the other biosorbents. Different chemical modification methods of hickory resulted in no great variation on the equilibrium adsorption capacity of Pb(II) and MB except for the one treated with alkali. Simultaneous sorption of Pb(II) and MB on the biosorbents showed Pb(II) to be preferentially adsorbed at higher Pb(II)-to-MB molar ratios in solution except for modified peanut hull. The equilibrium Pb adsorption contents decreased with the increasing pre-loading of MB and vice versa, suggesting the competitive rather than synergistic adsorption of the two contaminants on the biosorbents.

1. Introduction

Both dyes and heavy metals are commonly discharged by textile, printing, and tanning industries and are major concerns in natural water and wastewater systems. It is well known that some ionic dyes and heavy metals are toxic to aquatic organism and are potential threats to human health. Adsorption is considered one of the best methods to remove dyes and heavy metals from contaminated waters due to its ease of operation and insensitivity to toxic substances (Kyzas et al., 2013). Activated carbon has been widely used as a versatile adsorbent for the adsorption of various pollutants from aqueous solutions (Bhatnagar et al., 2013). Production and regeneration of commercial activated carbons are still expensive. Emerging carbon sorbents, such as functionalized carbon nanomaterials and carbon-based nanocomposites are currently active research areas (Inyang et al., 2014; Zhang et al., 2013, 2012). However, due to their high-cost and the unclear ecotoxicological risks, further studies must be carried before they can be widely used in the field wastewater treatment. Therefore, low-cost adsorbents, such as those derived from agricultural wastes, are a promising alternative to contaminant removal while reducing both preparation and run costs (Ahmad et al., 2014; Mohana et al., 2014; Nguyen et al., 2013). The application of raw agricultural by-products, however, suffers from some drawbacks, such as low exchange or sorption capacity or poor physical stability (i.e., partial solubility) (Kumar, 2006). Therefore, chemical modification using base solutions (e.g., sodium hydroxide), acid solutions (nitric acid, sulfuric acid, citric acid, etc.) or oxidizing agent (hydrogen peroxide) has been investigated and shown to increase dyes and metal ions adsorption (Kumar et al., 2012; Nguyen et al., 2013). However, most of these studies have been conducted with test solutions containing either metal ions or ionic dyes (Gupta and Suhas, 2009; Nguyen et al., 2013) and do not often directly

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http://dx.doi.org/10.1016/j.biortech.2014.06.043
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compare the performance of a range of biomass types a modification method. Both metal ions and ionic dyes commonly occur in wastewater at different concentrations and likely influence the adsorption performance of these materials. Thus, this study examines the co-adsorption of metal ions and ionic dyes on a range of chemically-modified biosorbents. Specifically, sorption of aqueous lead (Pb(II)) and methylene blue (MB) onto hickory, cotton and peanut hulls chemically modified using sodium hydroxide solution and as well as hickory modified using nitric and citric acid was investigated.

2. Methods

2.1. Materials

Reagents of analytical grade included NaOH, HNO_3, $Pb(NO_3)_2$, H_2O_2, citric acid ($C_6H_8O_7$) and MB ($C_{16}H_{18}ClN_3S$) were purchased from Fisher Scientific. Stock solutions of MB (2000 mg/L) and Pb(II) (2000 mg/L) were prepared and diluted to the required concentrations using deionized water (Milli–Q Advantage A10 System, Millipore China Ltd.). Hickory chips, cotton stalks and peanut hulls were collected from local farmers in Gainesville FL and were washed in running tap water, and then dried at 65 °C, then milled by a universal high-speed smashing machine and sieved using an 80-mesh sieve. Sodium hydroxide has been widely used to break down the internal structure of lignocelluloses components and α-cellulose can be extracted with 17.5% aqueous sodium hydroxide (Júnior et al., 2009). At this concentration, polyoses are solubilized and lignin is degraded by hydrolysis of the ether bonds (Júnior et al., 2009). Therefore, the raw powders of hickory, cotton and peanut hulls were treated with 17.5% NaOH for 72 h to remove soluble compounds and to reduce hemicellulose and lignin and then rinsed several times with distilled water and dried. The adsorption capacity of agricultural by-products can be improved by the treatment of citric acid (0.6 mol/L) and nitric acid (1 mol/L) (Cerino-Córdova et al., 2013). As a comparison, subsamples of hickory were pretreated with 1 mol/L nitric acid or 0.6 mol/L citric acid. The obtained biosorbents are notated as hickory-nit, hickory-alk, hickory-cit, cotton-alk and peanut-alk. Because sodium hydroxide is a good reagent for saponification or conversion of ester groups of biomass to carboxyl groups, it is anticipated that the alkali treatment would increase the carboxyl groups on the modified biomass surface (Júnior et al., 2009). The alkali treatment would also remove lignin and hemicellulose, decrease crystallinity and increase amorphous region to exposure interior hydroxyl groups of the modified biomass (Júnior et al., 2009). Similarly, the oxidation of biosorbents by nitric acid and citric acid would increase oxygen-containing functional groups on biomass surfaces (Cerino-Córdova et al., 2013).

2.2. Characterization of biosorbents

The contents of C, H and N in the biosorbents were determined using an elemental analyzer (EA) (Vario MICRO, Elementar) via high-temperature catalyzed combustion. Major inorganic elements were determined by using inductively-coupled plasma emission spectroscopy (ICP-OES, Optima 2300, PerkinElmer, USA) after ashing at the temperature of 550 °C and acid dissolution. Specific surface areas of the samples were measured with a Quantachrome Autosorb-1 surface area analyzer using the N_2 (BET) adsorption methods. Cation exchange capacity for biosorbents was analyzed by using SW-846 method 9081 (US EPA) with minor modification. The TG and DSC curves for biosorbents were carried out using a Mettler TGA/DSC thermogravimetric analyzer (TGA/DSC 1, STAR^e System, METTLER TOLEDO, USA) at a heating rate of 10 °C/min from 50 °C to 900 °C in O_2 atmosphere. Surface functional groups of the biosorbents were examined using a Fourier-transform Infrared Spectrometer (FT-IR, NEXUS870, NICOLET Co., USA) in the range 4000–500 cm^{-1} with a resolution of 0.2 cm^{-1}, using pressed discs of finely ground sample 1% (by weight) with KBr.

2.3. Batch sorption experiments

Batch isotherm sorption experiments were carried out at a room temperature (20 ± 2 °C) by adding 0.1 g adsorbent to 100-mL polyethylene centrifuge tubes containing 50 mL Pb(II) and/or MB solution of between 2 and 250 mg L^{-1} for MB and 1 and 250 mg L^{-1} for Pb(II). Solution pH was adjusted to the desired pH value using 0.01 mol L^{-1} NaOH or HCl. After reaching equilibration by shaking for 24 h, the mixture was centrifuged at 4000 rpm for 10 min. The MB concentration in the supernatant solution before and after adsorption was determined using a UV–Vis spectrophotometer Evolution-60 (Thermo Fisher Scientific, USA) at 664 nm. The calibration curve was prepared from MB solutions with different concentrations that yielded absorbance ranging from 0.1 to 1.2. Pb(II) in the supernatant was determined using ICP–OES (Optima 2300, Perkin–Elmer SCIEX, USA) after digestion using HNO_3 and H_2O_2 to remove MB.

After the sorption experiments, the residual fractions were washed with deionized water repeatedly until solutions were colorless. Then, 50 mL of 50 mg L^{-1} of Pb(II) or MB solution were added to sorbent-laden residual fractions to investigate the sequential sorption of Pb(II) or MB. In simultaneous batch adsorption experiments, the biosorbents were added to tubes containing 50 mL Pb(II) and MB solution with the molar ratios (R) of 0.2, 1.0 and 5.0. In all cases, sorbed Pb(II) or MB was calculated as the difference between amount of each sorbate in the initial and final solutions.

3. Results and discussion

3.1. Physicochemical properties of the biosorbents

The surface areas of the tested biosorbents were small. Peanut-alk had the largest surface area of 1.1 m^2/g, while surface areas of all the other biosorbents were smaller than 0.2 m^2/g. The elemental composition varied greatly among the NaOH-treated biosorbents (Table 1). For example, K content of NaOH-treated peanut hull was about 16 and 200 times greater than that of NaOH-treated cotton and hickory, respectively. The elemental contents for hickory modified with sodium hydroxide, nitric acid and citric acid also differed greatly, suggesting that the different chemical modification altered more than just the surface functional groups of the biosorbents. The comparison of hickory modified with sodium hydroxide, nitric acid and citric acid found that NaOH-treatment improved O and N contents while decreased C contents. The range in inter-element ratios such as C/O and C/N and cation exchange capacity suggest the potential for differing sorption abilities.

TG and DSC showed the majority of thermal decomposition to occur in the temperature range of about 250–500 °C (Fig. S1, Supplementary Material). The percentages of the final mass to the initial mass were 5.27% for cotton-alk, 2.66% for peanut-alk, 1.62% for hickory-alk, 1.75% for hickory-nit and 1.35% for hickory-cit, respectively. The biomass burning point is generally about 250–350 °C. The combustible components in the biomass reacted with oxygen to product CO_2 and H_2O and emit heat. The DTG curves of the combustion process represent the variations of the burning rate with the increasing temperature. The DTG curve in Fig. S1 shows that there were two peaks for all biosorbents. The first peak values were about 0.52%/min for peanut-alk, 0.63%/min for hickory-nit,

Table 1
Elemental composition (%) and cation-exchange capacity (mmol 100 g^{-1}) of biosorbents studied.

	Al	Ca	Fe	K	Mg	C	H	N	O	C/O	C/N	CEC
Hickory-nit	<0.01	0.085	<0.01	<0.01	0.027	46.5	5.80	0.48	47.1	0.99	96.9	27.0
Hickory-alk	<0.01	0.051	<0.01	<0.01	<0.01	48.9	6.68	0.09	44.3	1.10	543	30.0
Hickory-cit	<0.01	0.21	<0.01	<0.01	0.033	49.3	5.15	0.09	45.2	1.09	548	62.2
Cotton-alk	0.013	0.25	0.013	0.021	0.054	48.5	6.86	0.12	44.2	1.10	404	36.6
Peanut-alk	<0.01	0.073	<0.01	0.33	0.031	51.4	6.52	0.27	41.4	1.24	190	28.8

Contents of O were obtain by subtraction method.

0.32%/min for hickory-cit, 0.66%/min for hickory-alk and 0.39%/min for cotton-alk, respectively and the corresponding temperature to the first peak were about 294.2 °C for peanut-alk, 316.3 °C for hickory-nit, 315.8 °C for hickory-cit, 322.8 °C for hickory-alk and 326.8 °C for cotton-alk, respectively. The second peaks were less than the first for all biosorbents. Those suggested the different inflammability of those biosorbents.

3.2. Sorption of Pb(II) and MB

The equilibrium adsorption capacities of all the tested biosorbents increased with increasing Pb(II) or MB concentration in the 0 to 50 mg L^{-1} range and reached maximum sorption capacities above that range (Fig. 1). Cotton-alk and peanut-alk had the highest equilibrium adsorption capacities of MB (Fig. 1a) though both citric and nitric acid treatment showed greater MB sorption capacity than NaOH-treated hickory. Cotton-alk exhibited an adsorption capacity for Pb(II) and was much greater than that of all the other biosorbents, whose sorption capacities were not significantly different (Fig. 1b). The adsorption capacity of activated carbon, emerging carbon nanomaterials, and other nanocomposites for aqueous Pb and MB was summarized in Table S1 (Supplementary Material), which showed that the tested biosorbents in this work have similar performances. In addition, contaminant adsorption capacity ranged from 9.8 to 914.6 g kg^{-1} for agricultural solid wastes and from 0.8 to 486.0 g kg^{-1} for activated carbons derived from agricultural and industrial wastes (Rafatullah et al., 2010). Given both cost and performance, the tested biosorbents are promising alternative adsorbents for contaminant removal. While the sorption isotherm data were well-fitted by using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models (all correlation coefficients of $R^2 > 0.60$), the isotherm data were best fitted by the Langmuir for MB ($R^2 > 0.94$) and Freundlich for Pb ($R^2 > 0.93$) (Table S2, Supplementary Material), suggesting the different adsorption mechanism. The Langmuir adsorption model assumes monolayer coverage by the sorbate over a homogeneous sorbent surface composed of a finite number of adsorption sites with equal adsorption energies (Langmuir, 1916; Ozcan et al., 2005). Therefore, the model results suggest monolayer coverage of Pb(II) and MB onto those biosorbents with maximum adsorption capacities ranging from 18.4.1 to 69.5 mg g^{-1} and from 28.9 to 49.6 mg g^{-1}, respectively (Table S2). The dimensionless parameter of the equilibrium or adsorption intensity (RL) defined by Weber and Chakravorti (Weber and Chakravorti, 1974) can be calculated by using the adsorption constant b and the initial concentration and the adsorption in the system is unfavorable (RL > 1), linear (RL = 1), favorable (0 < RL < 1) or irreversible (RL = 0) (Bhatnagar et al., 2013). All RL values were in the range of 0 and 1 in the studied initial concentration of Pb(II) and MB, suggesting favorable adsorption. The Freundlich isotherm was employed to describe heterogeneous systems and reversible adsorption, which does not restrict to the monolayer formations. Generally, the greater the adsorption capacity K_f value in the Freundlich isotherm, the greater adsorption capacity will be. K_f value in Table S2 was an index for the prediction of the adsorption capacity of MB and Pb(II) for those sorbents. The empirical parameter related to the adsorption intensity (n) indicates an unfavorable adsorption and a chemical process ($n > 1$) or a favorable adsorption and a physical process ($n < 1$) (McKay et al., 1982; Ozcan et al., 2005). The value of n in Table S2 lies between 0.1 and 0.5 for all biosorbents, which represents a favorable adsorption and a physical process. The Temkin isotherm model is used to explore the energy distribution (Wang and Qin, 2005). The equilibrium binding constant K_T varied greatly while the Temkin constant B ranged from 1.79 to 6.33 for both MB and Pb(II), suggesting a physical adsorption process (Table S2). The mean free-energy $E < 8$ kJ mol^{-1} in the Dubinin–Radushkevich isotherm indicates a physical adsorption process while $E > 8$ kJ mol^{-1} means chemical adsorption process (Onyango et al., 2004). E values ranged from 0.36 to 2.35 (Table S2), suggesting physical adsorption process for MB and Pb(II). Therefore, results from those models indicate the favorable adsorption and the physical process for both MB and Pb(II) adsorbed onto biosorbents. The comparison of the R^2 values indicates that the Langmuir model yielded the best fit with the highest R^2 value ($R^2 > 0.94$) for MB while Freundlich model for Pb(II) ($R^2 > 0.93$) (Table S2), suggesting a homogeneous nature and

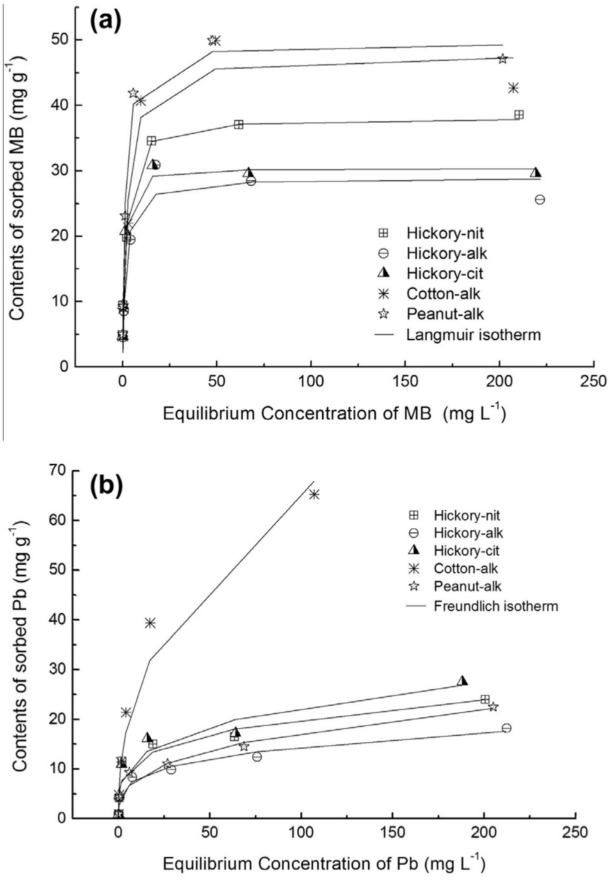

Fig. 1. Adsorption isotherms of MB (a) and Pb(II) (b) onto the biosorbents.

monolayer surface adsorption for MB while a heterogeneous nature and possible multilayer adsorption for Pb(II) onto those biosorbents.

3.3. Cosorption of Pb(II) and MB

The Pb(II) and MB adsorbed onto the biosorbents at approximately the same ratio as these sorbates were present in solution when at molar ratios of $R = 0.2$ and $R = 1.0$ at the simultaneous sorption of Pb(II) and MB on the biosorbents (Fig. 2a). However, when the Pb(II)-to-MB molar ratios was greater ($R = 5$), the ratio of sorbed Pb(II)-to-MB ranged from 4.65 to 7.58. In particular, Hickory-alk preferentially sorbed Pb(II) from solution compared to the other sorbents (Fig. 2a). The sorbed Pb(II) increased while the sorbed MB decreased for all the studied biosorbents (Fig. 2b). When at the higher Pb(II)-to-MB ratio in solution ($R = 5.0$) the sorbed Pb(II) increased greatly. The total molar contents of sorbed MB and Pb increased with the increasing Pb(II)-to-MB ratio in solution. Those may imply the independent adsorption between MB and Pb(II) on the biosorbents when at low molar ratios ($R = 0.2$ and $R = 1.0$) in solution (Fig. 2a) while competitive adsorption occurs at low molar ratios ($R = 5.0$) in solution. This may also result from the homogeneous and monolayer surface adsorption for MB (Langmuir isotherm adsorption) while a heterogeneous and possible multilayer adsorption for Pb(II) (Freundlich isotherm adsorption).

Biosorbents were laden with Pb(II) (or MB) and then were used to adsorb MB (or Pb(II)), respectively. In general, the equilibrium Pb adsorption contents decreased with the increasing pre-loading of MB (Fig. 3a) and vice versa (Fig. 3b). This indicates that Pb(II) and MB may have similar adsorption sites on the surface of biosorbents. When the adsorption sites were occupied by MB, the sorbed Pb on the biosorbents decreased and vice versa (Fig. 3). Those suggest that no synergistic or independent effect was found on the adsorption of Pb and MB while competitive adsorption for Pb and MB existed for all the present biosorbents pre-loaded with MB or Pb(II).

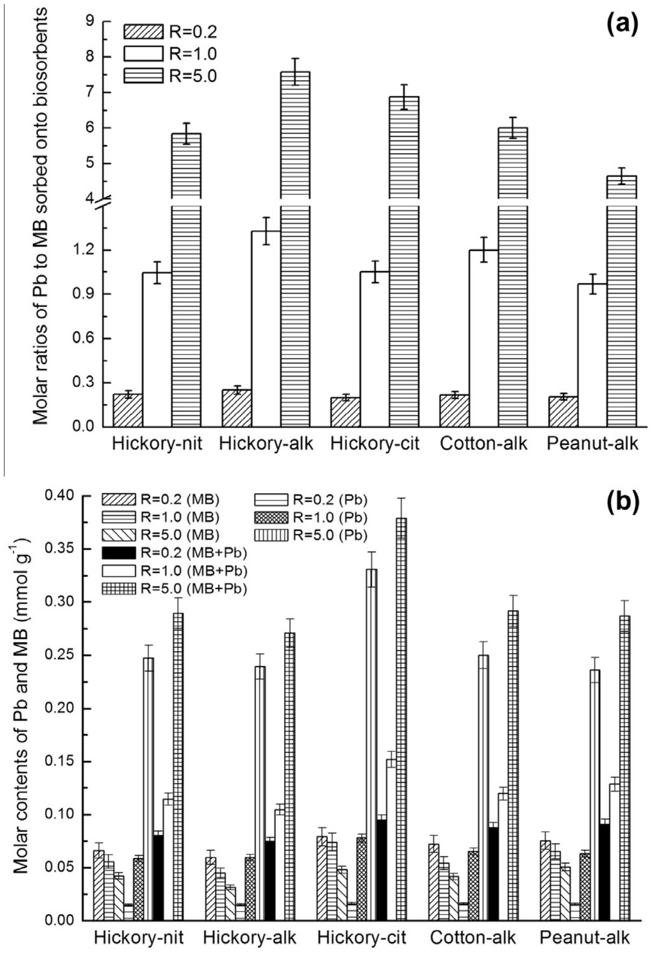

Fig. 2. Molar ratios of adsorbed Pb(II) to MB (a) and their molar contents (b) on the biosorbents during simultaneous batch adsorption experiments with different molar ratios of Pb(II) to MB (i.e., $R = 0.2$, 1.0, and 5.0) in solution.

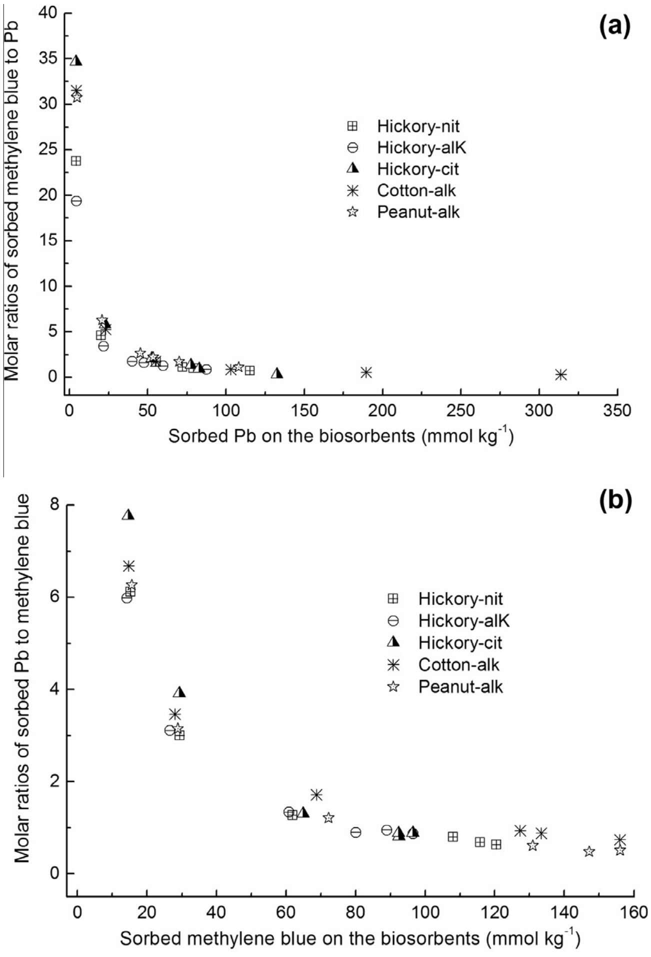

Fig. 3. Effects of sorbed Pb(II) on MB adsorption (a) and of sorbed MB on Pb(II) adsorption (b) by the biosorbents.

4. Conclusions

Experimental results showed that chemically modified biosorbents effectively removed both Pb(II) and MB from aqueous solutions. Pb(II) was found to be preferentially adsorbed onto the biosorbents at higher Pb(II)-to-MB molar ratios in solution except for modified peanut hull. The presence of pre-loaded Pb(II) reduced the adsorption of MB and vice versa, suggesting competitive rather than synergistic adsorption of the two contaminants on the biosorbents. Findings from this work indicated that chemically modified biomass can be used as a low-cost sorbent to remove both heavy metals and organic dyes from wastewater.

Acknowledgements

This work was partially supported by the National Natural Science Fund of China (21007026) and the NSF (CBET-1054405). Z. Ding acknowledges the support of the Jiangsu Overseas Research & Training Program.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.biortech.2014.06.043.

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