

Enhanced Adsorption of Mercury(II) and Cadmium(II) from Aqueous Solution onto Rice Bran Modified with Chelating Ligands

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To enhance the removal of mercury (Hg(II)) and cadmium (Cd(II)) from aqueous solutions, rice bran (RB) was reacted with epichlorohydrin and then modified with ethylenediamine and sodium chloroacetate to bear iminodiacetate functional groups. The modified rice bran (MRB) was characterized by Fourier transform-infrared spectroscopy (FT-IR), thermogravimetric analysis (TG), energy dispersive spectroscopy (EDS), back titration, and X-ray photoelectron spectroscopy (XPS). The adsorption properties of MRB for Hg(II)/Cd(II) ions were also evaluated in batch experiments. The sorption kinetic experimental data were best described by the pseudo-second-order model. The maximum adsorption capacity (163.9 mg/g for Hg(II) at pH 5.0 and 106.4 mg/g for Cd(II) at pH 6.0) was observed at 298 K, and the isotherm adsorption equilibrium of MRB was followed by Langmuir isotherm equation. The major adsorption mechanisms should be predominantly controlled by the formation of complexes between the functional groups of MRB and Hg(II)/Cd(II) ions as well as ion-exchange. The regeneration experiments showed that the MRB could be successfully reused for six cycles when 0.1 M HCl eluent was used.

Keywords: Adsorption; Modified rice bran; Mechanisms; Mercury; Cadmium

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INTRODUCTION

Heavy metals, such as mercury (Hg) and cadmium (Cd), are widely used in industrial production processes, and when heavy metals are converted into cationic form, there is a high probability of their discharge into the environment. Due to their toxicity and mobility in surface and ground water, these heavy metal ions are non-biodegradable and tend to accumulate in biological species, causing great harm to human health and ecosystems through the food chain (Li *et al.* 2015). Therefore, it is necessary for public health and ecological safety to remove mercury and cadmium from wastewater. Numerous techniques have been applied for the removal of hazardous heavy metal ions from aqueous solutions, such as chemical precipitation (Blue *et al.* 2010), ion exchange (Noh and Komarneni 2011), membrane separation (Cui *et al.* 2014), reduction (Ketir *et al.* 2008), electrochemical treatment (Pikna *et al.* 2015), and adsorption. Adsorption is one of the most studied methods due to its high efficiency, easy handling, low cost of the materials, and reversibility. Various materials have been developed for the adsorption of Hg(II) and Cd(II), including activated carbon (Gonzalez and Pliego-Cuervo 2014), clay minerals (Li

et al. 2012; Tran *et al.* 2015), zeolites (Fardmousavi and Faghihian 2014; Nguyen *et al.* 2015), and biomaterials (Kushwaha *et al.* 2015; Yu *et al.* 2015). Moreover, bio-sorbents like chitosan (Kandile *et al.* 2015; Karthik and Meenakshi 2015), algae (Carro *et al.* 2013), bacteria (Huang and Liu 2013), and agricultural by-products (Liu *et al.* 2010; Anagnostopoulos *et al.* 2012; Huang and Lin 2015) have excellent adsorption capacity for these toxic ions.

Rice bran (RB) is an agricultural by-product resulting from rice processing and represents approximately 10% of the entire rice grain weight. A large amount of this by-product is used as animal feed or discarded as waste. RB contains vitamins, carbohydrates, nitrogen, and phosphorus compounds, which have carboxyl groups, hydroxyl groups, and imino groups (Montanher *et al.* 2005). Due to its granular structure, chemical stability, insolubility in water, and local availability, RB is a potential adsorbent for removing toxic metals from wastewater. RB can remove Cd(II), Cu(II), Pb(II), Zn(II), Cr(III), Cr(VI), and Ni(II) from water (Wang *et al.* 2008; Chen *et al.* 2012). However, the adsorption capability of RB for these heavy metal ions is relatively poor due to its low content of active functional groups. Improving the adsorption properties of RB *via* carbonization (Zhang *et al.* 2014) or chemical modification (Fatima *et al.* 2013) is thus important.

It has been reported that the presence of $-COOH$ or $-NH_2$ groups can greatly improve the adsorption capacity of a sorbent on Hg(II)/ Cd(II) (Cui *et al.* 2015). The purpose of this study was to enhance the Hg(II) and Cd(II) adsorption capacities of RB by chemical modification using bearing iminodiacetate function on RB as chelating ligands. The characteristics of the resulting adsorbent were analyzed. The adsorption properties for Hg(II) and Cd(II) on the modified rice bran (MRB) from aqueous solution were evaluated at different pHs, contact times, temperatures, heavy metal ion concentrations, and ionic strength. The regeneration of the MRB was also investigated in its application.

EXPERIMENTAL

Materials

Rice bran was obtained from a local farmer's market (Mianyang, China), thoroughly washed with distilled water, dried, crushed, and screened by a 100-mesh sieve. 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) (98%) and sodium chloroacetate were procured from Aladdin Chemical Ltd. (Shanghai, China). Mercury (II) chloride, cadmium nitrate, epichlorohydrin, ethylenediamine, sodium hydroxide, and other chemicals were all analytical grade and purchased from Kelong Chemicals Company (Chengdu, China).

Preparation of MRB

Preparation of the MRB adsorption material included the epoxidation of RB, ammoniation of the epoxidized RB, and carboxymethylation of aminated RB. For the epoxidation reaction, 5 g of RB was dispersed into 100 mL of sodium hydroxide (4%) with vigorous stirring. The reaction vessel was immersed into a water bath at 70 °C, and 30 mL of epichlorohydrin was added. After 3 h at 70 °C, the mixture was cooled to 25 °C and adjusted to pH 6 with HCl. The product was precipitated with acetone, filtered thoroughly, washed with ethanol (95%), and dried overnight at 90 °C. For the ammoniation reaction, 5 g of epoxidized RB, 25 mL of ethylenediamine, and 0.1 g of sodium carbonate were added to a round-bottomed flask and refluxed with magnetic stirring in a water bath at 60 °C for

2 h. The product was thoroughly washed with distilled water and dried. Next, 4 g of this product was mixed with 100 mL of sodium chloroacetate (25%) and 50 mL of sodium hydroxide (30%) at 60 °C for 2 h and then heated continuously in a boiling water bath for 4 h. The mixture was filtered and washed with distilled water until the filtrate was colorless and the pH of the filtrate was near neutral range. The modified rice bran (MRB) sorbent was dried in a convection oven at 105 °C for 6 h. The preparation of MRB is illustrated in Fig. 1.

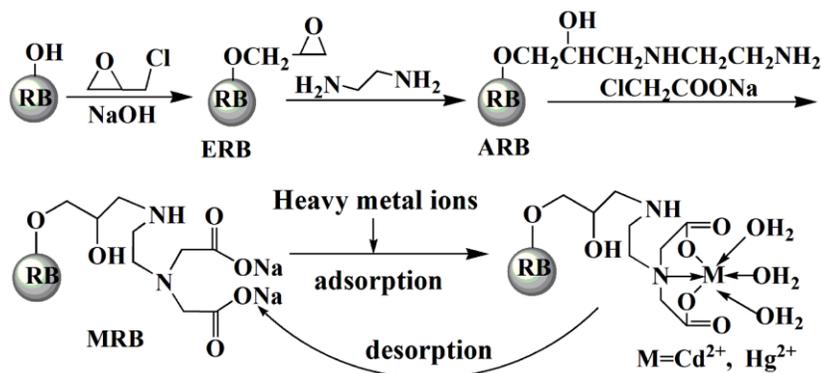


Fig. 1. Synthetic scheme of MRB and the adsorption mechanism of heavy metal ion on MRB

Characterization

The concentration of carboxyl groups in MRB was determined by back titration method (Huang *et al.* 2012). One gram of MRB was mixed with 100 mL of deionized water. To transform the $-\text{COONa}$ groups of the MRB into $-\text{COOH}$ groups (Liu *et al.* 2011), the pH of the suspension was adjusted to 2.0 with hydrochloric acid. After stirring for 2 h, the suspension was separated by filtration, and the obtained solid was dried at 353 K until constant weight was attained; 0.1 g of dried solid was dispersed in 100 mL of aqueous solution of NaHCO_3 (0.01 mol/L) and stirred for 2 h under argon atmosphere. Then the mixture was filtered, the obtained filtrate was divided into three aliquots (25.0 mL) and titrated with aqueous HCl (0.01 mol/L) using a pH meter (PHS-3C, Jiangfen Instruments, Jiangsu, China), and the results were given by average. The described procedure was run on the MB in the same manner. The concentration of carboxylic groups in the sample was calculated by the following equation,

$$C_{\text{COOH}} = \frac{C_{\text{NaHCO}_3} \times V_{\text{NaHCO}_3} - C_{\text{HCl}} \times V_{\text{HCl}}}{W} \quad (1)$$

where C_{NaHCO_3} and C_{HCl} (mol/L) are the concentration of NaHCO_3 solution and HCl solution, respectively; V_{NaHCO_3} and V_{HCl} (L) are the volume of NaHCO_3 solution and HCl solution, respectively; and W (g) is the weight of the RB or MRB.

Specific surface areas of samples were determined with N_2 adsorption at a liquid nitrogen temperature (77 K) on a surface analyzer (SSA-4200, Beijing Builder Electronic Technology Co.). Fourier transform-infrared (FT-IR) spectra of RB and MRB in KBr discs were recorded using a Nicolet 5700 FT-IR spectrometer (ThermoScientific, Waltham, USA). Thermogravimetric (TG) analyses were performed with a TGA Q500 instrument system (TA Instruments, New Castle, USA) at prescribed heating rates of 10 °C/min up to 800 °C under a steady flow of N_2 . The elemental contents of MRB before and after adsorption of Hg(II) and Cd(II) were determined in randomly selected areas on the Au-

coated solid surfaces. These areas were analyzed by energy dispersive spectroscopy (EDS) in conjunction with scanning electron microscopy (X-MaxN20; Oxford Instruments, UK). X-ray photoelectron spectroscopy (XPS) was performed on a spectrometer (XSAM-800, KRATOS Co, Japan) with an Al K X-ray source (1486.6 eV).

Sorption Experiments

Batch experiments were carried out by placing 0.1 g of MRB in 100 mL of aqueous solutions containing Hg(II) or Cd(II) ions at a predetermined concentration, desired pH, and ionic strength. The suspensions were shaken at 120 rpm in an electrically thermostatic reciprocating shaker (SHZ-B, Hede Instruments, Shanghai, China) for a predetermined period of time at the appropriate temperature. The solid and liquid phases were separated by centrifugation. The final concentrations of Hg(II) or Cd(II) in the supernatant were measured spectrophotometrically using 5-Br-PADAP chromogenic reagent at the wavelengths of 563 nm and 570 nm, respectively (Zhou *et al.* 2013, 2014). The initial pH of the metal ion solutions was adjusted by micro-additions of HCl or NaOH, using a pH meter; the ionic strength of the solution was adjusted with NaCl or KNO₃. All experiments were performed in triplicate, and the mean values of the results were used for data analysis. The standard deviations were less than 5%. Adsorption was quantified by the adsorption capacity q (mg/g),

$$q = \frac{(C_0 - C_f)V}{w} \quad (2)$$

where C_0 (mg/L) and C_f (mg/L) were the initial and final concentration of the metal ion in the solution, respectively. V was the volume (L) of the solution, and w was the weight (g) of the adsorbent.

Regeneration of MRB

The reusability of MRB was studied by static experiments. After adsorption of metal ions by MRB, 0.6 g of the loaded MRB was re-suspended in 250 mL of 0.1 mol/L HCl and stirred magnetically for 2 h at room temperature. Prior to the next adsorption-desorption cycle, the adsorbent was treated with 0.1 mol/L NaOH and thoroughly washed with distilled water until the filtrate was neutralized. The neutralized sorbent was dried at 105 °C for 6 h. The regenerated MRB was then used in the next adsorption process. The adsorption-desorption process was repeated 6 times.

RESULTS AND DISCUSSION

Characterization

The efficiency of introducing iminodiacetate function into the RB was estimated by comparing the carboxyl groups before and after chemical modification, and the results are shown in Table 1. Compared to the RB, the carboxyl concentration of the MRB increased from 0.032 mmol/g to 0.896 mmol/g in the test sample as the result of surface functionalization. There were no other carboxyls except that sodium chloroacetate was brought in during the whole synthesis process, and then it indicated that the iminodiacetate function was well introduced into the RB. The specific surface areas (BET surface) of RB and MRB are given in Table 1. The increment in carboxyl content in the MRB produces a

slight increase (from 5.18 m²/g to 5.43 m²/g) in the specific surface area which improves the loading capacity of the MRB.

Table 1. Carboxyl Group Contents and Surface Area of RB and MRB

| Sample | C-COOH (mmol/g) ^a | S _{BET} (m ² /g) ^b |
|--------|------------------------------|---|
| RB | 0.032 | 5.18 |
| MRB | 0.896 | 5.43 |

^a Obtained by back titration. ^b Obtained by surface area.

The FT-IR spectra for RB and MRB are shown in Fig. 2. The appearance of a new strong absorption peak at 1608 cm⁻¹ on MRB (which is in the range of stretching vibrations from -COO⁻ groups), the moving of -NH/-OH stretching vibration from 3380 cm⁻¹ to 3425 cm⁻¹, and the decreasing in the absorption peak strength of the broad overlapping peaks confirmed the carboxymethylation reaction on RB (Zhang *et al.* 2011). Additionally, this result confirmed the formation of iminodiacetic acid groups.

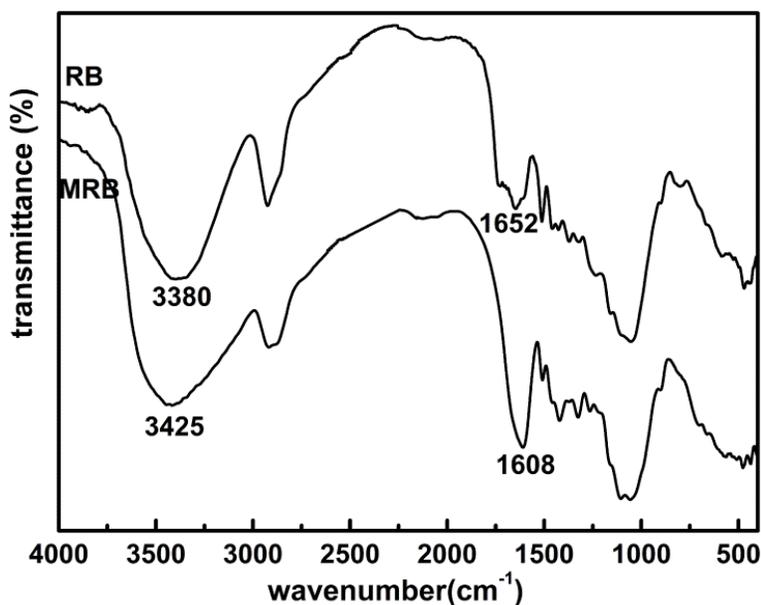


Fig. 2. FT-IR spectra of RB and MRB

The thermogravimetric decomposition curves for virgin RB and MRB were evaluated, and results are shown in Fig. 3.

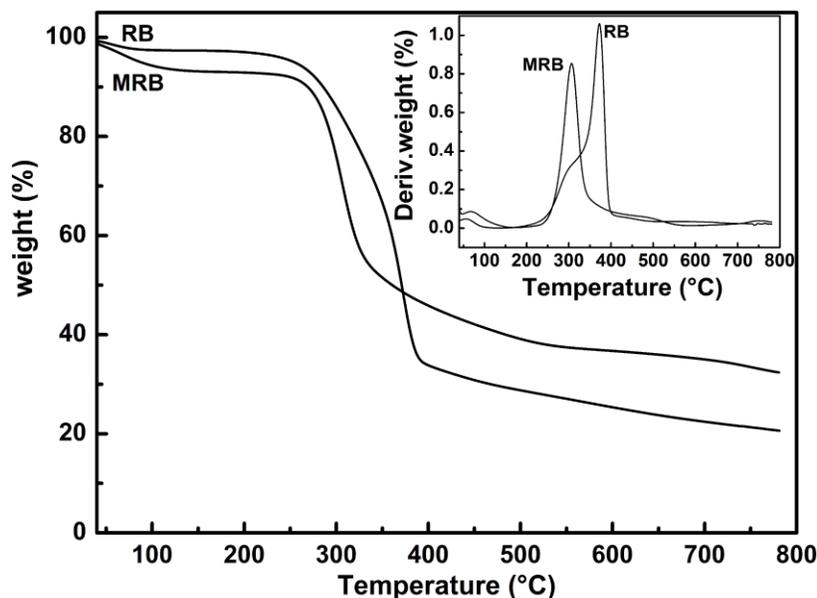


Fig. 3. TG and DTG curves of RB and MRB

For RB and MRB, the peaks from 50 to 150 °C were attributed to moisture elimination, and the relatively larger weight loss of MRB than RB (6.9% and 2.7%, respectively) implied that the introduction of iminodiacetic acid groups made MRB more hydrophilic. The mass loss from 220 through 450 °C corresponded to the loss of organic materials (Kyzas *et al.* 2014; Niticharoenwong *et al.* 2013). At 800 °C, the residual mass percentage was 20.6% for RB and 32.4% for MRB, which may be due to sodium oxide. The disappearance of the shoulder between 250 °C and 340 °C for the RB after modification and the change of maximum temperature of weight loss from 371 °C for RB to 307 °C for MRB suggested that the reactions shown in Fig. 1 were carried out as expected. Although the thermal stability of MRB was relatively low compared with RB, it was judged to be adequate for most needs in wastewater treatment.

The EDS spectra of MRB, Hg-sorbed MRB, and Cd-sorbed MRB are depicted in Fig. 4. The MRB spectrum indicated the presence of C, O, and Na but did not show the characteristic signals of Cd(II)/Hg(II) ions. Clear Cd(II) ions signals were observed at 2.77, 2.96, 3.13, 3.32, and 3.95 KeV on the surface of Cd-sorbed MRB, which was quite similar to Cd(II) ions observed on another Cd-loaded sorbent (Wang *et al.* 2010). The Hg(II) ions signals at 1.71, 2.2, 2.49, 8.72, 8.9, 11.82, and 11.92 KeV were clearly present on the surface of Hg-sorbed MRB. None of the samples show the presence of N, as the dispersive energy of N elements is 0.40 (Areco *et al.* 2013). These findings confirmed the adsorption of Hg(II) and Cd(II) ions on the surface of MRB. The total disappearance of the Na peak in Cd-sorbed MRB and Hg-sorbed MRB suggested that surface chelation and ion exchange were the main processes involved in adsorption.

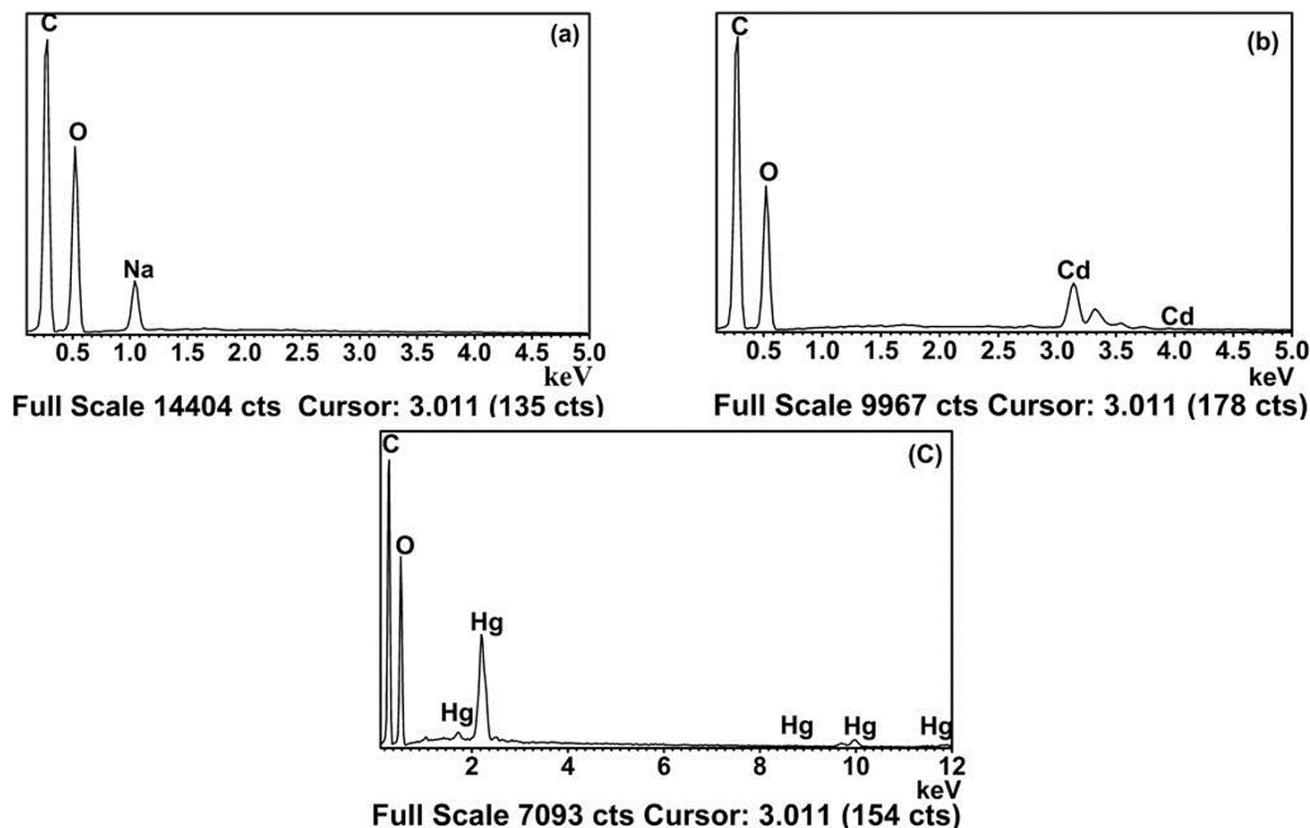


Fig. 4. EDS analysis of (a) MRB, (b) Cd-sorbed MRB, and (c) Hg-sorbed MRB

Figure 5 shows the XPS spectra for the RB and MRB surfaces before and after adsorption. The elemental surface composition of RB and MRB were calculated based on the peak area of each element. The concentrations of C, O, and N for RB were 47.9%, 48.1%, and 1.2%, respectively; the relative concentration of C, O, and N for MRB was 38.1%, 52.4%, and 3.2%, respectively. Compared with the XPS spectra of original RB and MRB, a new Na peak was observed. In MRB, the N and O contents increased while the content of C decreased, which indicated that iminodiacetic acid groups were successfully introduced to the RB surface. The presence of Hg 4f and Cd 3d in Hg-sorbed MRB and Cd-sorbed MRB spectra, respectively, confirmed the successful adsorption of Hg(II) and Cd(II) on MRB. The O 1s peak shifted to higher binding energies (531.76 eV for MRB, 531.80 eV for Cd-sorbed MRB, and 531.83 eV for Hg-sorbed MRB). The N 1s peak showed a similar tendency before and after adsorption, suggesting the strong combination between Hg(II)/Cd(II) and the surface functional groups of MRB. Nevertheless, the disappearance of Na 1s in Hg-sorbed MRB and Cd-sorbed MRB illustrated that both chelation and ion exchange occurred between heavy metal ions and MRB. These results are consistent with the EDS data, and they also are complementary to the reported results of Hg(II)/Cd(II) bound to nitrogen containing groups or carboxyl groups by complexation or coordination (Guo *et al.* 2014).

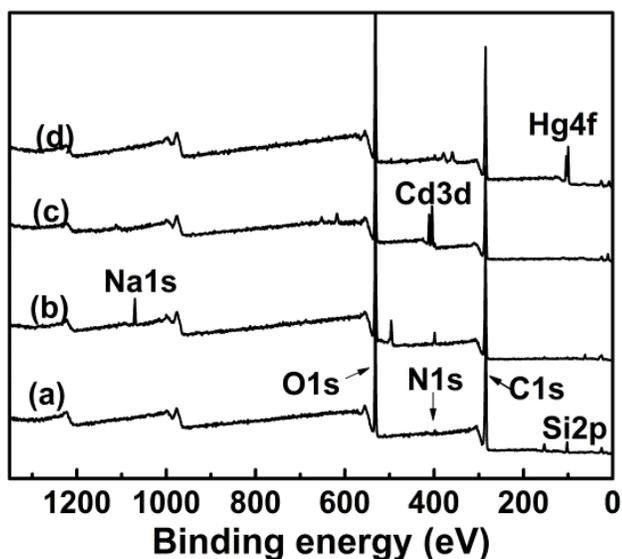


Fig. 5. XPS spectra of (a) RB, (b) MRB, (c) Cd(II)-loaded MRB, and (d) Hg(II)-loaded MRB

Adsorption of Hg(II) and Cd(II) on MRB

Effect of pH and adsorption mechanism

The effect of pH on the adsorption of Hg(II) and Cd(II) onto MRB was investigated from pH 2 to 6 at an initial metal ion concentration of 300 mg/L and 25 °C (Fig. 6). The initial solution was set to a pH below 6 to avoid precipitation. The adsorption capacities increased with the pH in the experimental conditions used, and the maximum adsorption capacity was achieved at pH values around 6 for Cd(II) and pH of 5 for Hg(II). Because the main functional groups of MRB are carboxyl and nitrogen-containing groups, there is no doubt that the protonation and deprotonation of these groups on the surface of MRB (which are attributed to the complexation and electrostatic interaction for adsorption mechanism) were affected by pH changes. With decreasing pH, more nitrogen-containing groups are protonated, and the surface matrix of MRB becomes more positively charged ($-\text{COO}^-$ protonated into $-\text{COOH}$ which restrain the formation of coordination compounds). Thus, the repulsive electrostatic interaction between surface sites of MRB and metal ions increases. Furthermore, the greater number of hydrogen ions compete with the metal ions for the sorption sites in the sorbent, resulting in the reduced adsorption of Hg(II) and Cd(II). At higher pH, the number of negatively charged $-\text{COO}^-$ groups on the adsorbent matrix probably increases; the greater number of negatively charged groups on MRB favors electrostatic attraction between cationic species. Figure 1 illustrates the possible mechanism for Hg(II)/Cd(II) adsorption on MRB. The lone pair electrons of oxygen and nitrogen atoms of functional groups (N- and O-containing) on MRB could be supplied to the empty atomic orbital of Hg(II)/Cd(II), which forms O, N–Hg(II)/Cd(II) complexes in the active sites of the biosorbent. The lower complexing capacity in a strongly acidic medium may be attributed to the partial protonation of the active groups on the surface of MRB. These mechanisms were partially confirmed by the EDS and XPS analyses of MRB and Hg(II)/Cd(II)-loaded MRB. Therefore, in further adsorption experiments, the optimum pH for Hg(II) and Cd(II) were selected as 5.0 and 6.0, respectively.

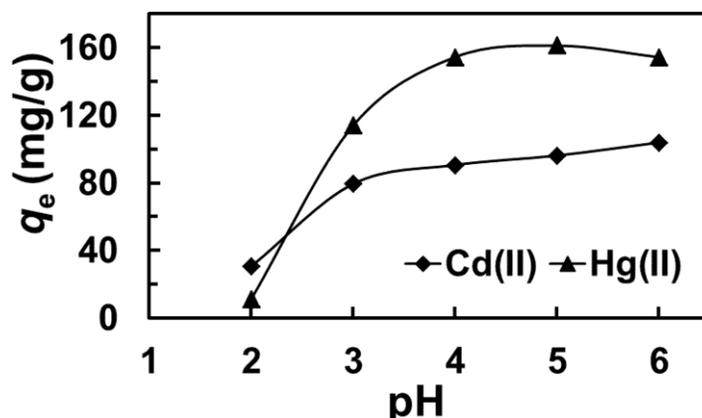


Fig. 6. Effect of pH on adsorption of Hg(II)/Cd(II)

Effect of contact time and adsorption kinetics

The effects of contact time on the extent of Hg(II) and Cd(II) adsorption on MRB were investigated at an initial metal ion concentration of 300 mg/L at 25 °C (pH 6.0 for Cd(II) and pH 5.0 for Hg(II)). As shown in Fig. 7, the adsorption capacities of the two metal ions increased rapidly with the contact time during the first 30 min. The variation reflects the vacant surface sites available for adsorption and the relatively high solute concentration during the initial stages. Thereafter, the adsorption rates declined and then slowed until the adsorbed metal ions reached the equilibrium value because of the decrease in metal ion concentration and the repulsive forces between metal ions adsorbed on MRB and the solution phases. To ensure that adsorption equilibrium was achieved, the contact time for Hg(II) and Cd(II) adsorption were maintained at 5 h for the following experiments.

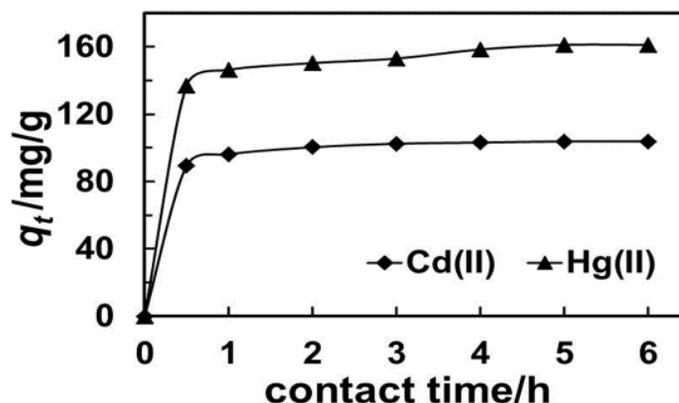


Fig. 7. Effect of contact time on adsorption of Hg(II)/Cd(II) on MRB

Adsorption kinetics are important in designing a sorption system. Thus, the mechanisms of Hg(II) and Cd(II) biosorption on MRB, including the chemical reactions involved and their potential rate-limiting steps, were investigated. In this work, pseudo-first-order (Eq. 3), pseudo-second-order model (Eq. 4), and intraparticle diffusion (Eq. 5) were used to test the experimental data.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

$$q_t = k_i \cdot t^{1/2} + C \quad (5)$$

In these equations, t is the contact time (h), q_t and q_e are the amounts of metal ions adsorbed at time t and at equilibrium (mg/g), respectively, and k_1 (h^{-1}), k_2 ($\text{g}/\text{mg}\cdot\text{h}$), and k_i ($\text{mg}/\text{h}^{1/2} \text{ g}$) are the rate constants of pseudo-first-order, pseudo-second-order, and intraparticle diffusion models, respectively. C (mg/g) is the constant that provides information about the thickness of the boundary layer. For example, when C is 0, intraparticle diffusion is the rate-controlling step, and when C is not equal to 0, intraparticle diffusion is not the only rate-controlling step.

Table 2. Kinetic Parameters for the Adsorption of Cd(II) and Hg(II) on CRB

| Ion | $q_e^{(\text{exp})}$ (mg/g) | Kinetic Model | | | | | | | | |
|--------|--------------------------------|--------------------|--------------------------------|--------|---------------------|--------------------------------|--------|--|---------------|--------|
| | | pseudo-first-order | | | pseudo-second-order | | | intraparticle diffusion | | |
| | | k_1 (1/h) | $q_e^{(\text{cal})}$ (mg/g) | R^2 | k_2 (g/mg h) | $q_e^{(\text{cal})}$ (mg/g) | R^2 | k_i ($\text{mg}\cdot\text{h}^{1/2}/\text{g}$) | C (mg/g) | R^2 |
| Cd(II) | 103.9 | 0.105 | 27.0 | 0.7854 | 0.100 | 105.3 | 1.000 | 7.78 | 87.1 | 0.8426 |
| Hg(II) | 161.2 | 0.376 | 31.0 | 0.9645 | 0.041 | 163.9 | 0.9997 | 13.49 | 130.2 | 0.9510 |

The kinetic rate constants k_1 , k_2 , and $q_{e(\text{cal})}$ were obtained by plotting $\ln(q_e - q_t)$ and t/q_t against t . k_i and C were computed from the slope and intercept of the plots of q_t versus $t^{1/2}$. The estimated parameters are presented in Table 2. The calculated equilibrium adsorption capacities ($q_{e(\text{cal})}$) of Hg(II) and Cd(II) on MRB were much closer to the experimental values ($q_{e(\text{exp})}$) for the pseudo-second-order adsorption model than the pseudo-first-order model. The R^2 correlation coefficients of pseudo-second-order kinetic models were relatively high (> 0.999). Therefore, the adsorption systems of Hg(II) and Cd(II) on MRB all obeyed pseudo-second-order kinetics. The plots of Hg(II) and Cd(II) adsorbed (q_t) versus the square root of time ($t^{1/2}$) presented two straight lines, but these lines did not pass through the origin. These results implied that adsorption involved intraparticle diffusion, but it was not the only rate-controlling step. The positive values of C in this work suggested that a chemisorption mechanism might have played a significant role in biosorption (Anagnostopoulos *et al.* 2012).

Effect of concentration and isotherm model

Solutions of different initial Hg(II)/Cd(II) concentrations (50 to 300 mg/L) were used to investigate the adsorption isotherms after 5 h with 1 g/L MRB at 25 °C and pH 5.0 for Hg(II) or pH 6.0 for Cd(II). As shown in Fig. 8, the equilibrium adsorption capacities of MRB increased with increasing the equilibrium concentration of Hg(II)/Cd(II) and reached almost a constant value in the higher equilibrium concentration range. The increase in the adsorption capacity of MRB with regard to Hg(II)/Cd(II) concentration is probably due to the higher driving force to overcome the mass transfer resistance of metal ions between the solid and aqueous phases. The greater number of metal ions adsorbed on MRB, the larger repulsive electrostatic interactions involved between the absorbed metal ions and

the metal ions in solution. Therefore, the increase of adsorption capacities is reduced in the higher equilibrium concentration range, and the saturation adsorption will be obtained until equilibrium is attained.

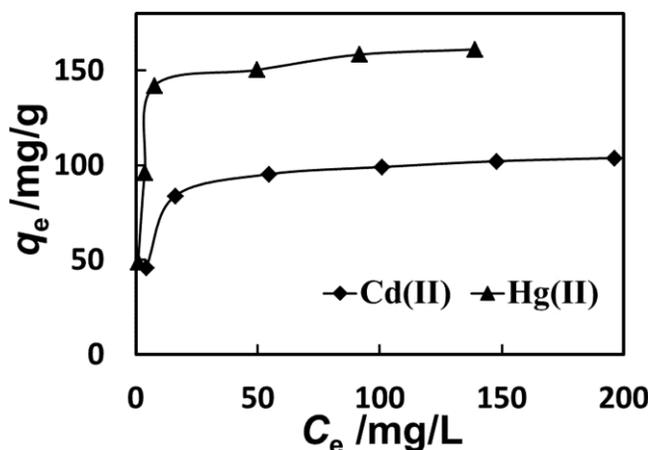


Fig. 8. Adsorption isotherms of MRB

To analyze the interactive behaviors between MRB and metal ions, two well-known and widely used adsorption isotherm models—Langmuir (Eq.(6)) and Freundlich (Eq.(7))—were adopted to describe the nature of adsorption using the equilibrium data.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max} b} \quad (6)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where C_e (mg/L) is the metal ion concentration in solution at equilibrium and q_e is the adsorption capacity (mg/g) at equilibrium. The constants q_{\max} and b are the theoretical maximum monolayer adsorption capacity of the adsorbent (mg/g) and Langmuir constant relating the free energy of adsorption (L/mg), respectively. K_F and n are Freundlich constants representing the multilayer adsorption capacity ((mg/g)(mg·L)^{1/n}) and empirical parameter related to the intensity of adsorption, respectively. The constant values q_{\max} and b were determined from the slopes and intercepts of the linear plots of C_e/q_e versus C_e ; n and K_F were determined from the plot of $\log q_e$ versus $\log C_e$. The fitted constants and regression coefficients (R^2) are represented in Table 3.

Table 3. Isotherm Parameters for the Adsorption of Cd(II) and Hg(II) on MRB

| | Langmuir isotherm | | | Freundlich isotherm | | |
|--------|-------------------|-------------------|--------|---------------------|-------------------------------------|--------|
| | b (L/mg) | q_{\max} (mg/g) | R^2 | n | K_F (mg/g (mg·L) ^{1/n}) | R^2 |
| Cd(II) | 0.177 | 106.4 | 0.9998 | 5.11 | 40.2 | 0.8484 |
| Hg(II) | 0.415 | 163.9 | 0.9997 | 4.80 | 65.7 | 0.7861 |

Based on the coefficient of determination values (R^2), the equilibrium data of Cd(II) and Hg(II) onto MRB were best described by the Langmuir isotherm equation rather than the Freundlich model. In the Langmuir isotherm, the calculated maximum adsorption

capacities ($q_{\max(\text{cal})}$) (106.4 mg/g and 163.9 mg/g for Cd(II) for Hg(II) ions, respectively) were very close to the experimental values. These results indicated that the adsorption of Cd(II) and Hg(II) onto MRB are typical monolayer adsorptions of the Langmuir type. In the Langmuir equation, a dimensionless constant known as the separation factor (R_L) is used to evaluate the favorability of adsorption, as defined by Eq. 8,

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

where b is the Langmuir constant (L/mg) and C_0 is the initial metal ion concentration in the solution (mg/L). An R_L value greater than 1 indicates unfavorable adsorption; R_L equal to 1 reflects linear adsorption. An R_L between 0 and 1 specifies favorable adsorption, and R_L less than 0 indicates irreversible adsorption (Gonzalez and Pliego-Cuervo 2014). In the current study, the calculated R_L values for the adsorption of Cd(II) and Hg(II) at 25 °C ranged from 0.101 to 0.018 and 0.046 to 0.008, respectively, for the initial metal ion concentration of 50 to 300 mg/g. These findings indicate that Cd(II) and Hg(II) adsorption on MRB were favorable. Similarly, the Freundlich constant values of n were 5.1 and 4.8 for Cd(II) and Hg(II), respectively, and the K_F values were 40.1 and 65.7, respectively. This data indicated that adsorption was favorable.

Effect of temperature

The variation of Cd(II) and Hg(II) sorption was investigated from 25 °C to 65 °C under the optimized conditions (Fig. 9). The adsorption capacity of MRB increased for both Cd(II) and Hg(II) with increasing temperature. However, the increments were not noticeable (only about 20 mg/g) for the temperature range investigated. These results indicated that Cd(II) and Hg(II) adsorption on MRB is endothermic but not sensitive to temperature. This data could greatly increase the convenience in practical application. Similar behavior has been reported previously (Doskočil and Pekař 2012; Khoramzadeh *et al.* 2013). Because temperature had a negligible effect on adsorption, subsequent experiments were performed at ambient temperature (25 °C).

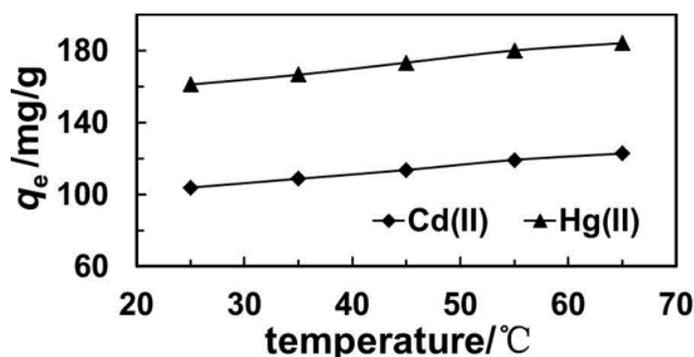


Fig. 9. Effect of temperature on Hg(II)/Cd(II) adsorption (initial metal ion concentration: 300 mg/L, contact time: 5 h, pH: 6.0 for Cd(II) and 5.0 for Hg(II), respectively)

Effect of ionic strength on adsorption

Industrial wastewater contains not only heavy metal pollutants but also various salts in a wide range of concentrations depending on the source. These coexisting ions often inhibit the removal of heavy metals because they compete for binding on adsorbents and decrease in the activity of heavy metal ions (Tran *et al.* 2015). The effects of the common

salts, NaCl and KNO₃ on the decontamination of Hg(II) and Cd(II) by MRB were examined (Fig. 10). Increasing the ionic strength from 0 to 1 mol/L reduced the adsorption capacities of Hg(II) and Cd(II) on MRB. The negative effects of NaCl were much more obvious than those of KNO₃, especially the concentration was greater than 0.1 M. The decrease in adsorption with increasing electrolyte concentration reflects the increasing competition between mercury/cadmium species and K⁺/Na⁺ ions. Secondly, the activity of heavy metal ions was reduced by enhanced electrostatic repulsion and a greater tendency to form metal-anion complexes such as CdOH⁺, CdCl⁺, CdNO₃⁺, HgCl₃⁻, and HgCl₄²⁻. As reported previously (Kim and Lee 2014; Hu *et al.* 2014), the coordinating ligands of Cl are much greater than NO₃⁻ with Hg(II) and Cd(II), which may explain the more negative effect of NaCl.

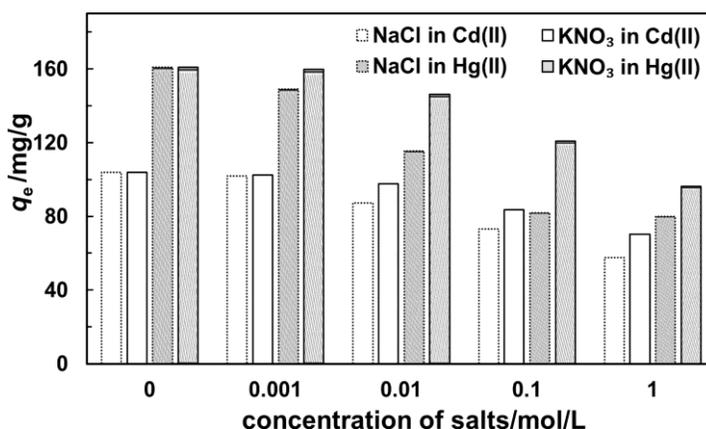


Fig. 10. Effect of ionic strength on Hg(II)/Cd(II) adsorption of MRB (initial metal ion concentration: 300 mg/L, contact time: 5 h, pH: 6.0 for Cd(II) and 5.0 for Hg(II), temperature: 25 °C, respectively)

Desorption and regeneration studies

In industrial wastewater treatment, the adsorption and desorption of metal ions coupled with the regeneration and recovery of spent adsorbents are crucially important to make the process more attractive and economical. As the adsorption behavior of Cd(II) and Hg(II) onto MRB are highly dependent on pH, the Cd(II)/Hg(II)-adsorbed MRB was eluted by adjusting the solution pH with 0.1 M HCl.

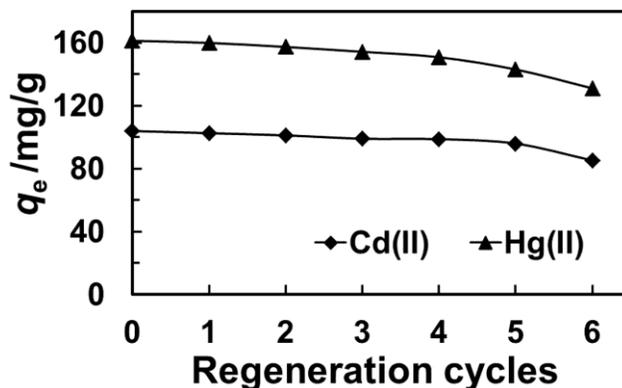


Fig. 11. Cd(II) and Hg(II) absorbed by regenerated MRB for six adsorption-desorption cycles (initial metal ion concentration: 300 mg/L, contact time: 5 h, pH: 6.0 for Cd(II) and 5.0 for Hg(II), temperature: 25 °C, respectively)

The regenerated adsorbent was recovered by neutralizing the carboxyl groups and the ammonium salt on the surface of MRB using 0.1 M NaOH. As shown in Fig. 11, the adsorption capacities decreased gradually with increasing cycle number, but MRB still retained considerable adsorption capacity even after six consecutive adsorption-desorption cycles. The adsorption of Cd(II) and Hg(II) on recovered MRB was decreased by only 18.0% and 18.7%, respectively. These results suggested that MRB is an economical and efficient adsorbent for practical applications in wastewater containing Cd(II) and Hg(II) ions.

CONCLUSIONS

1. Rice bran (RB) modified with iminodiacetate chelating ligands was an excellent adsorbent for Hg(II) and Cd(II). The maximum adsorption of Hg(II) and Cd(II) on modified rice bran (MRB) reached 163.9 and 106.4 mg/g at 298 K, respectively.
2. Ionic strength, but not temperature, had a significant effect on Hg(II)/Cd(II) uptake. The experimental data fit both the pseudo-second-order kinetic model and the Langmuir isothermal model. EDS and XPS studies showed that the adsorption mechanisms were chelation and ion exchange between Hg(II)/Cd(II) and MRB.
3. The adsorption capacity of regenerated MRB remained relatively high even after six cycles of regeneration.

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REFERENCES CITED

- Anagnostopoulos, V. A., Manariotis, I. D., Karapanagioti, H. K., and Chrysikopoulos, C. V. (2012). "Removal of mercury from aqueous solutions by malt spent rootlets," *Chem. Eng. J.* 213, 135-141. DOI: 10.1016/j.cej.2012.09.074
- Areco, M. M., Saleh-Medina, L., Trinelli, M., Marco-Brown, J. L., and Afonso, M. D. S. (2013). "Adsorption of Cu(II), Zn(II), Cd(II) and Pb(II) by dead *Avena fatua* biomass and the effect of these metals on their growth," *Colloid. Surface. B* 110, 305-312. DOI: 10.1016/j.colsurfb.2013.04.035
- Blue, L. Y., Jana, P., and Atwood, D. A. (2010). "Aqueous mercury precipitation with the synthetic dithiolate, BDTH₂," *Fuel* 89(6), 1326-1330. DOI: 10.1016/j.fuel.2009.10.031
- Carro, L., Barriada, J. L., Herrero, R., and de Vicente, M. E. S. (2013). "Surface modifications of *Sargassum muticum* algal biomass for mercury removal: A physicochemical study in batch and continuous flow conditions," *Chem. Eng. J.* 229, 378-387. DOI: 10.1016/j.cej.2013.06.014

- Chen, Y. N., Ding, L. C., and Nie, J. X. (2012). "Isotherm and thermodynamic studies of the biosorption of lead, cadmium and copper from aqueous solutions by rice bran," *Desalin. Water Treat.* 44(1-3), 168-173. DOI: 10.5004/dwt.2012.2999
- Cui, L. M., Wang, Y. G., Gao, L., Hu, L. H., Yan, L. G., Wei, Q., and Du, B. (2015). "EDTA functionalized magnetic graphene oxide for removal of Pb(II), Hg(II) and Cu(II) in water treatment: Adsorption mechanism and separation property," *Chem. Eng. J.* 281, 1–10. DOI: 10.1016/j.cej. 2015.06.043
- Cui, Y., Ge, Q. C., Liu, X. Y., and Chung, T. S. (2014). "Novel forward osmosis process to effectively remove heavy metal ions," *J. Membrane Sci.* 467, 188-194. DOI: 10.1016/j.memsci.2014.05.034
- Doskočil, L. and Pekař, M. (2012). "Removal of metal ions from multi-component mixture using natural lignite," *Fuel Process. Technol.* 101, 29-34. DOI: 10.1016/j.fuproc.2012.02.010
- Fardmousavi, O. and Faghihian, H. (2014). "Thiol-functionalized hierarchical zeolite nanocomposite for adsorption of Hg²⁺ from aqueous solutions," *Comptes Rendus Chimie* 17(12), 1203-1211. DOI: 10.1016/j.crci.2014.05.001
- Fatima, T., Nadeem, R., Masood, A., Saeed, R., and Ashraf, M. (2013). "Sorption of lead by chemically modified rice bran," *Int. J. Environ. Sci. Te.* 10, 1255-1264. DOI 10.1007/s13762-013-0228-x
- Gonzalez, P. G., and Pliego-Cuervo, Y. B. (2014). "Adsorption of Cd(II), Hg(II) and Zn(II) from aqueous solution using mesoporous activated carbon produced from *Bambusa vulgaris striata*," *Chem. Eng. Res. Des.* 92(11), 2715-2724. DOI: 10.1016/j.cherd.2014.02.013
- Guo, X. Y., Du, B., Wei, Q., Yang, J., Hu, L. H., Yan, L. G., and Xu, W. Y., (2014). "Synthesis of amino functionalized magnetic graphenes composite material and its application to remove Cr(VI), Pb(II), Hg(II), Cd(II) and Ni(II) from contaminated water," *J. Hazard. Mater.* 278, 211-220. DOI: 10.1016/j.jhazmat.2014.05.075
- Hu, X. J., Liu, Y. G., Zeng, G. M., You, S. H., Wang, H., Hu, X., Guo, Y. M., Tan, X. F., and Guo, F. Y. (2014). "Effects of background electrolytes and ionic strength on enrichment of Cd(II) ions with magnetic graphene oxide-supported sulfanilic acid," *J. Colloid Interf. Sci.* 435, 138-144. DOI: 10.1016/j.jcis.2014.05.028
- Huang, J., Ye M., Qu, Y. Q., Chu, L. F., Chen R., He Q. Z., and Xu D. F. (2012). "Pb(II) removal from aqueous media by EDTA-modified mesoporous silica SBA-15," *J. Colloid Interf. Sci.* 385, 137-146. DOI: 10.1016/j.jcis.2012.06.054
- Huang, S. M. and Lin, G. (2015). "Biosorption of Hg(II) and Cu(II) by biomass of dried *Sargassum fusiforme* in aquatic solution," *J. Environ. Health Sci.* 13, 21. DOI: 10.1186/s40201-015-0180-4
- Huang, W. and Liu, Z. M. (2013). "Biosorption of Cd(II)/Pb(II) from aqueous solution by biosurfactant-producing bacteria: Isotherm kinetic characteristic and mechanism studies," *Colloid. Surface. B* 105, 113-119. DOI:10.1016/j.colsurfb.2012.12.040
- Kandile, N. G., Mohamed, H. M., and Mohamed, M. I. (2015). "New heterocycle modified chitosan adsorbent for metal ions (II) removal from aqueous systems," *Int. J. Biol. Macromol.* 72, 110-116. DOI: 10.1016/j.ijbiomac.2014.07.042
- Karthik, R. and Meenakshi, S. (2015). "Removal of Pb(II) and Cd(II) ions from aqueous solution using polyaniline grafted chitosan," *Chem. Eng. J.* 263, 168-177. DOI: 10.1016/j.cej.2014.11.015

- Ketir, W., Bouguelia, A., and Trari, M. (2008). "Photocatalytic removal of M^{2+} ($=Ni^{2+}$, Cu^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} and Ag^{+}) over new catalyst $CuCrO_2$," *J. Hazard. Mater.* 158(2-3), 257-263. DOI: 10.1016/j.jhazmat.2008.01.074
- Khoramzadeh, E., Nasernejad, B., and Halladj, R. (2013). "Mercury biosorption from aqueous solutions by *Sugarcane Bagasse*," *J. Taiwan Inst. Chem. E.* 44(2), 266-269. DOI: 10.1016/j.jtice.2012.09.004
- Kim, Y. J., and Lee, Y. J. (2014). "Characterization of mercury sorption on hydroxylapatite: Batch studies and microscopic evidence for adsorption," *J. Colloid Interf. Sci.* 430, 193-199. DOI: 10.1016/j.jcis.2014.05.028
- Kushwaha, S., Sreedhar, B., Bhatt, R., and Sudhakar, P. P. (2015). "Spectroscopic characterization for remediation of copper, cadmium and mercury using modified palm shell powder," *J. Taiwan Inst. Chem. E.* 46, 191-199. DOI: 10.1016/j.jtice.2014.09.018
- Kyzas, G. Z., Travlou, N. A., and Deliyanni, E. A. (2014). "The role of chitosan as nanofiller of graphite oxide for the removal of toxic mercury ions," *Colloid. Surface. B* 113, 467-476. DOI: 10.1016/j.colsurfb.2013.07.055
- Li, Y., Wang, J. D., Wang, X. J., and Wang, J. F. (2012). "Adsorption-desorption of Cd(II) and Pb(II) on Ca-montmorillonite," *Ind. Eng. Chem. Res.* 51(18), 6520-6528. DOI: 10.1021/ie203063s
- Li, Z., Xiao, D., Kong, Y., and Ge, Y. (2015). "Enhancing lead adsorption capacity by controlling the chain length of alkyl amine grafted lignin," *BioResources* 10(2), 2425-2432. DOI: 10.15376/biores.10.2.2425-2432
- Liu, W. J., Zeng, F. X., Jiang, H., and Zhang, X. S. (2011). "Adsorption of lead (Pb) from aqueous solution with *Typha angustifolia* biomass modified by $SOCl_2$ activated EDTA," *Chem. Eng. J.* 170, 21-28. DOI: 10.1016/j.cej.2011.03.020
- Liu, Y., Sun, X. M., and Li, B. H. (2010). "Adsorption of Hg^{2+} and Cd^{2+} by ethylenediamine modified peanut shells," *Carbohydr. Polym.* 81(2), 335-339. DOI: 10.1016/j.carbpol.2010.02.020
- Montanher, S. F., Oliveira, E. A., and Rollemberg, M. C. (2005). "Removal of metal ions from aqueous solutions by sorption onto rice bran," *J. Hazard. Mater.* 117(2-3), 207-211. DOI: 10.1016/j.jhazmat.2004.09.015
- Nguyen, C., Loganathan, P., Nguyen, T. V., Vigneswaran, S., Kandasamy, J., and Naidu, R. (2015). "Simultaneous adsorption of Cd, Cr, Cu, Pb, and Zn by an iron-coated Australian zeolite in batch and fixed-bed column studies," *Chem. Eng. J.* 270, 393-404. DOI: 10.1016/j.cej.2015.02.047
- Niticharoenwong, B., Shotipruk, A., Mekasuwandumrong, O., Panpranot, J., and Jongsomjit, B. (2013). "Characteristics of activated carbons derived from deoiled rice bran residues," *Chem. Eng. Commun.* 200(10), 1309-1321. DOI: 10.1080/00986445.2012.744751
- Noh, Y. D. and Komarneni, S. (2011). "Mercury(II) exchange by highly charged swelling micas, sodium Engelhard titanosilicate-4, and sodium titanosilicate," *Environ. Sci. Technol.* 45(16), 6954-6960. DOI: 10.1021/es200712r
- Pikna, L., Hezelova, M., and Kovacova, Z. (2015). "Optimization of simultaneous electrochemical determination of Cd(II), Pb(II), Cu(II) and Hg(II) at carbon nanotube-modified graphite electrodes," *J. Environ. Sci. Heal. A* 50(8), 874-881. DOI: 10.1080/10934529.2015.1019810

- Tran, L., Wu, P., Zhu, Y., Yang, L., and Zhu, N. (2015). "Comparative study of Hg(II) adsorption by thiol- and hydroxyl-containing bifunctional montmorillonite and vermiculite," *Appl. Surf. Sci.* 356, 91-101. DOI: 10.1016/j.apsusc.2015.08.038
- Wang, F. Y., Wang, H., and Ma, J. W. (2010). "Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent-bamboo charcoal," *J. Hazard. Mater.* 177(1-3), 300-306. DOI: 10.1016/j.jhazmat.2009.12.032
- Wang, X. S., Li, Z. Z., and Sun, C. (2008). "Removal of Cr(VI) from aqueous solutions by low-cost biosorbents: Marine macroalgae and agricultural by-products," *J. Hazard. Mater.* 153(3), 1176-1184. DOI: 10.1016/j.jhazmat.2007.09.079
- Yu, J. X., Feng, L. Y., Cai, X. L., Wang, L. Y., and Chi, R. A. (2015). "Adsorption of Cu^{2+} , Cd^{2+} and Zn^{2+} in a modified leaf fixed-bed column: competition and kinetics," *Environ. Earth Sci.* 73(4), 1789-1798. DOI: 10.1007/s12665-014-3529-6
- Zhang, J., Wang, R. M., Cao, X. Y., Li, Y., and Lan, Y. Q. (2014). "Preparation and characterization of activated carbons from peanut shell and rice bran and a comparative study for Cr(VI) removal from aqueous solution," *Water Air Soil Poll.* 225(7), 2032. DOI: 10.1007/s11270-014-2032-8
- Zhang, Y. S., Zhu, J. Y., Zhang, L., Zhang, Z. M., Xu, M., and Zhao, M. J. (2011). "Synthesis of EDTAD-modified magnetic baker's yeast biomass for Pb^{2+} and Cd^{2+} adsorption," *Desalination* 278(1-3), 42-49. DOI: 10.1016/j.desal.2011.05.003
- Zhou, Y., Wang, Z. Q., Sun, L., and Luo, T. (2013). "Adsorption of Cu(II), Cd(II) in aqueous solutions using aminated lignin," *Chinese J. Environ. Eng.* 7(10) 3953-3957.
- Zhou, Y., Zhang, J. P., Luo, X. G., and Lin, X. Y. (2014). "Adsorption of Hg(II) in aqueous solutions using mercapto-functionalized alkali lignin," *J. Appl. Polym. Sci.* 131(18), 40749. DOI: 10.1002/app.40749

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