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Using pretreated chestnut endothelium to adsorb lead and cadmium ions from water



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ABSTRACT

The nature chestnut endothelium, as waste source from chestnut (*Castaneamollissima*) has pigment effecting the process of adsorbing heavy metal ions, and the decolorized endothelium has low adsorption capacity. In order to raise the adsorption capacity of heavy metal ions, the discolor endothelium was pretreated by acidic formaldehyde, cis-butenedioic acid and irradiation. Thermodynamic and kinetics model was fitted to the adsorption of Pb(II) and Cd(II) ions onto modified chestnut endothelium by cis-butenedioic acid. Three independent variables including pH, adsorption time and contact temperature were selected as affecting factors to Response Surface. The modified experiment results showed adsorption rate of Pb(II) and Cd(II) ions on the chestnut endothelium modified by 0.5 mol/L cis-butenedioic acid was higher than other modified methods. Thermodynamic and kinetics model was fitted with Langmuir and Pseudo-second-order kinetic model, respectively. 59.23 °C of the adsorption temperature, the 5.72 h of adsorption time and the 6.16 of pH are the optimized conditions of the adsorption rate of Pb^{2+} on modified chestnut endothelium. 55.93 °C of the adsorption temperature, the 4.43 h of adsorption time and the 6.06 of pH are the optimized adsorption conditions of Cd^{2+} . Under the optimized condition, the experiment value of the adsorption of Pb^{2+} and Cd^{2+} was 99.76% and 98.90%, respectively, which are close to the predicted value. The FTIR indicated that C–O, O–H and C–H involved in the adsorption process of Pb^{2+} and Cd^{2+} .

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1. Introduction

Along with the industrial activity and economic development, the heavy metal ions which was not biodegradable toxic chemicals pollutant, pose directly threat to human health and environment (Liu et al., 2008; Nema et al., 2017), because of toxicity, increased accumulation on the food chain and ecosystem (Lu et al., 2015a, b; Xiao et al., 2015).

Association of cadmium ions with enzymes can reduce their activities, influence fat and protein metabolism or digestion, easily induce heart cerebrovascular disease and high blood pressure. Cad-

mium ion also can exchange the calcium in calcium phosphate in human bone, and lead to bone osteoporosis due to the lack of calcium in the bone. Moreover, Cadmium is accumulated in the kidneys, liver and bone marrow, replace zinc ion in specific enzymes, and make the body prone to renal artery, sex atrophy, diabetes and other diseases (Du et al., 2015). Lead ion is also toxic to the human body. The human bone will store about 95% of lead, in the form of phosphate salts, and a small amount of lead will exist in the liver, kidney, spleen, lung, heart, brain, bones and muscles. Hence the toxicity of Pb ions causes damage to liver, kidney, mental retardation and infertility and abnormalities in pregnant women (Singh et al., 2008; Singh et al., 2007; Ismail and Harons, 2017).

Among the techniques applied to the removal of heavy metal from wastewater are chemical precipitation, chemical oxidation or reduction, electrochemical, and membrane separation (Huang et al., 2007; Amuda et al., 2007). However, these methods require high capital investment and cost of the equipment maintenance fee (Li et al., 2013), as well as creating sludge disposal problem, which contains a lot of by-products (Aziz et al., 2008; Wong,

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2017). Therefore, most of the recent researches to treatment of heavy metals in aqueous solutions was interested in much more effective low-cost adsorbents made from nature materials (Caner et al., 2015; Şenet et al., 2015; Gao, et al., 2017), such as biosorption, for removing heavy metals from wastewaters (Rojas et al., 2015; Hasan and Hanafiah, 2017). This, method use biomass which are the byproducts of agriculture, forestry and forestry waste to adsorb metal ions. There are many researches in which different waste bio-adsorbents in the world are used as adsorbent. For example, Lu (Lu et al., 2015a,b) used rice straw modified by fermentation and simple chemical treatment to remove chromium (III) from industrial wastewater. Yurtsever investigated the effect of pH of solution, contact temperature and initial concentration of Pb^{2+} on Pb (II) biosorption onto modified quebracho tannin resin (Yurtsever and Şengil, 2009). Humelnicu studied the sorption performances of two kinds of by-products (soy bran and mustard husk) resulted from the agriculture (Humelnicu et al., 2015). Dahiya used pre-treated crab and arca shell as adsorbent of lead and copper from aqueous solutions (Dahiya et al., 2008). Zhang studied on the kinetics and thermodynamics of Pb^{2+} , Cu^{2+} , Cr^{6+} and Cd^{2+} adsorption onto peanut hull (Zhang et al., 2010).

Chinese chestnut (*Castanea mollissima*) is a member of the family Fagaceae, and a species of chestnut native to Taiwan, Korea and China. It grows widely in Hebei, Liaoning, Shandong, Hunan, Hubei, Jiangxi, Fujian, Anhui, etc. The total annual production of 825,000 tons, accounted for over 75% of the total world Chinese chestnut. Traditional products of chestnut are sugar Fried chestnut, beverage, canned, frozen, and wine (Yang et al., 2007). In the process of those products, the endothelium after taking the production of chestnut has become the agriculture and forestry waste. The main component in the Chestnut endothelium is the lignin and cellulose, which account for about 80% of total weight. The remaining 20% consists of pentose, tannins, flavonoids, organic acids, phenols, phytosterol, glycosides and lactones. Chinese chestnut endothelium as a biological adsorbent was applied to the adsorption of heavy metals in water environment has been studied by some researches (Qi et al., 2009; Wang, 2009; Wu and Huang, 2010; Ding et al., 2010; Samad et al., 2017).

However, when chestnut endothelium was used as the adsorbent of the heavy metal ions, the pigment in the endothelium are easily dissolved in water, causing the change of the colors and limiting the reuse of aqueous solution after the removal of heavy metals. Moreover, the pigment can react with heavy metal ions and cause the precipitation of heavy metal ions. Therefore, removed the pigment material, which could be a nature pigment added into the food, are required before the chestnut endothelium is used as biological adsorbent. However, the real adsorption rate of Pb and Cd ions onto decolorized endothelium did not reach 80% and was relatively low (Zhang et al., 2016).

Vázquez (Vázquez et al., 2009) uses acid formaldehyde pre-treated chestnut endothelium as adsorbent to optimize the removal of Pb(II), Cu(II) and Zn(II) from aqueous solutions. The maximum adsorption capacity of pre-treated chestnut shell was obtained for Pb (II) ions, $8.5 \text{ mg}\cdot\text{g}^{-1}$, and the order of cation affinity was $Pb^{2+} > Cu^{2+} > Zn^{2+}$. Vázquez (Vázquez et al., 2012) also studied that chestnut endothelium was pretreated by an alkaline solution to increase its adsorption capacity, and the influence of the concentration of NaOH and contact time on Cd (II) ion adsorption. The highest adsorption capacity of Cd(II) ion was $9.9 \text{ mg}\cdot\text{g}^{-1}$.

The objective of this research was to modify the decolorized chestnut endothelium to improve the adsorption rate and sorption capacity of Pb(II) and Cd (II) ions from aqueous solution. The effects of the different experimental conditions on the chestnut endothe-

lium efficiency for removing of Pb(II) and Cd (II) ions were also investigated. The isotherms and dynamics were studied in the sorption process. This work increased the sorption capacity of Pb(II) and Cd (II) ions, which reached 52.91 mg/g and 51.28 mg/g respectively. It is important for us to reuse the waste of chestnut shell and apply the modified endothelium to remove the heavy metal pollution from the environment.

2. Materials and methods

2.1. Materials

The chestnut (from the market of Baoding, China) was peeled manually, and the endothelium was washed thoroughly with distilled water. It was dried in the air at the room temperature. Then it was grounded and sieved through with 40 mesh size. Finally, the natural chestnut endothelium was obtained and named as NO. 1 material.

The discolor process was performed in a 1 L glass Pyrex glass reactor with mechanical stirring. 5 g of endothelium powder was immersed in 400 mL sodium Hydroxide solution (0.1 M) at 70°C for 5 h, and then the suspension was filtered by filter paper. The solid residue was discolored twice more, and then was rinsed by distilled water until the pH of wash liquor was the same as that of the distilled water. Finally, the chestnut endothelium was dried in the vacuum dryer and the Decolorized chestnut endothelium (named as NO. 2) was obtained (Zhao et al., 2015).

2.2. Instrument and equipment

The SZ-93 automatic double distill Baporizer for the purification of water was made by Shanghai Yarong Biochemical Instrument Plant, China. Electronic analytical balance AR423CN and pH meter (Ohaus Instrument Co. Ltd, Shanghai, China). Super-heated water bath HH-601 (Hengfeng Instrument Co. Ltd, Jintan, Jiangsu, China). TAS-990-supper atomic adsorption spectrophotometer (Beijing Purkinje General Instrument Corporation, China). ^{60}Co - γ radiat Point (Heliyuan LID. CO. of Baoding, Hebei, China). FTS3000 FTIR Spectrometer (BIORAD Corporation).

2.3. Reagents

Sodium hydroxide, hydrogen nitrate, sulfuric acid, perchloric acid, formaldehyde, cis-butenedioic acid, lead nitrate and cadmium nitrate were all of analytic grade from Tianjin Chemical Co, China. $1000 \text{ mg}\cdot\text{L}^{-1}$ Lead standard solution and cadmium standard solution were obtained from Nation Institute Metrology, China. All the water was double distilled one made from the double distillation of the ion-free water.

2.4. Modification chestnut endothelium

2.4.1. Modified by Cis-butenedioic acid and formaldehyde acid

The discolored chestnut endothelium was put into flasks, and 0.5 mol/L cis-butenedioic acid or formaldehyde acid (0.1 M sulfuric acid:37% formaldehyde = 4:1) were also added individually into the flask with solid-liquid ratio of 1:20 and 2:5 (g:mL), respectively. The solutions in the flask were placed into the water bath at 50°C for 2 h and then were filtered. The solid fractions were collected washed with distilled water to pH > 4 and was dried in vacuum drier for 6 h, at 60°C , 0.08 MPa. The endothelium modified by cis-butenedioic acid and formaldehyde acid were named as NO. 3 and NO. 4, respectively.

2.4.2. Irradiation by γ -⁶⁰Co

The discolored Chestnut endothelium was placed in the test tubes. The distilled water, cis-butenedioic acid and Formaldehyde acid were added into the tubes individually. Then the solutions in the test tubes were placed under γ -ray at 2 kGy · 4 kGy and 6 kGy of adsorb dose, respectively, and were filtered. The solid fractions as washed with distilled water to pH > 4. The modified Chestnut endothelium was placed into Vacuum oven for 6 h, at 60°C, 0.08 MPa. To discuss further, the numbers of different modified endothelium by irradiation were named and showed in Table 1.

2.5. Preparation of simulative heavy metal solution

Stock solution of Pb²⁺ or Cd²⁺ were prepared at 500 mg·L⁻¹ in hydrogen nitrate solution (pH = 5). Aliquots of stock solutions were diluted in hydrogen nitrate solution to prepare working standards of Pb²⁺ and Cd²⁺ at 30 mg·L⁻¹.

2.6. Batch adsorption experiment

The pretreated chestnut endothelium (1–8 mg in per liter of solution) and concentration of heavy metals solution (100–600 mg/L) at certain pH (pH 1.0–7.0) were taken into conical flask, which was heated at certain time (0.5–7 h) with certain temperature (30–70 °C) and was shaken once per hour. Then the solution was filtered by using air pump water filtration. The concentrations of Pb²⁺ and Cd²⁺ in the solutions and adsorption on the chestnut endothelium are determined by atomic adsorption spectrophotometer. All the experiment was performed in triplicate.

2.7. The adsorption rate and adsorption capacity

The calculated Formula as follow:

$$R = \frac{C_0 - C_E}{C_0} * 100\% \quad (1)$$

$$q = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C₀(mg/L) is the initial concentration of the simulative heavy metal solutions which contained Pb²⁺ and Cd²⁺; C_e(mg/L) is the ion concentration of Pb²⁺ and Cd²⁺ in the simulation solution at equilibrium; m(g) is the amount of adsorbent used in the experiment; V (L) is the volume of adsorbed solution.

2.8. FTIR spectra of adsorbent

The decolorized, pre-treated and cation loaded pretreated chestnut endothelium were dried in vacuum drier and finely ground using a ball mill. A concentration of 1% (g of sample/100 g of pellet) were used to make KBr pellet and a FTS3000 FTIR Spectrometer (BIORAD Corporation) was used to run IR spectrum.

Table 1

The number of different modified endothelium by irradiation.

NO.	Solvent	Adsorb dose (kGy)
5	Distilled water	2
6	Distilled water	4
7	Distilled water	6
8	0.5 mol/lcis-butenedioic acid	2
9	0.5 mol/lcis-butenedioic acid	4
10	0.5 mol/lcis-butenedioic acid	6
11	Acid formaldehyde	2
12	Acid formaldehyde	4
13	Acid formaldehyde	6

Isothermal adsorption curve is an important theory method to describe the adsorption between the liquid phase and the solid phase at equilibrium. There are some adsorption models, for example, Langmuir model, Freundlich model, BET adsorption model, and Dubinin-Radushkevich (D-R) model. Langmuir model is also known as single-molecule adsorption theory, which was described by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_e} + \frac{1}{q_e k_L} \quad (3)$$

where C_e is the concentration of ion in solution at equilibrium; q_e is the adsorption quantity of the adsorbent at equilibrium; k_L is Langmuir constant, which characterizes the adsorbing ability of the surface of adsorbent.

Freundlich isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface. The model formula was given as:

$$\log q_e = \frac{1}{n} \log C_e + \log k_F \quad (4)$$

where k_F is Freundlich constant; n is constant, which gives an indication of how favorable the adsorption processes.

2.9. Kinetic model simulation

Adsorption kinetics model could be used to describe the relationship between adsorption rate and adsorption time. With respect to analyze the adsorption kinetics of Pb (II) and Cd (II) onto the chestnut endothelium, the Pseudo-first-order kinetic equation and Pseudo-second-order kinetic equation where test.

Where assumed adsorption driving force is the difference between adsorption capacity of adsorbent (q_e) at equilibrium and amount of metal adsorbed q_t at any time t. Adsorption rate is in direct proportion with driving force and the square of driving force.

Pseudo-first-order kinetic equation is given:

$$\ln \frac{q_e - q_t}{q_e} = -K_1 t \quad (5)$$

where q_e is adsorption capacity of chestnut endothelium at equilibrium; q_t is the amount of metal ion adsorbed onto the chestnut endothelium; q_t at any time t K₁ is pseudo-first-order kinetic constant, which could be determined from the slope of the plot of the log (q_e - q_t) versus t.

Pseudo-second-order kinetic equation is following:

$$\frac{t}{q_t} = \frac{q}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where k₂ is pseudo-second-order kinetic constant, which could be determined from the intercept of linearized plot of t/q_t versus t.

2.10. Response surface methods and designs

The basic theory of Response Surface Methods explores the relationships between several explanatory variables and one or more response variables. To get the maximum adsorption rate of Pb²⁺ and Cd²⁺ onto modified chestnut endothelium, the Response Surface Methods was used to optimize the experimental conditions. pH, adsorption temperature and adsorption time was chosen as factors. Software Design Expert 8.0.5 was adopted to design experiment and the experimental designs were showed in Tables 2 and 3.

Table 2
Experimental design levels and coding for Pb²⁺ Box-Behnken Design.

Factor	Level		
	–1 (low level)	0 (central point)	1 (high level)
pH of solution A	3	5	7
Temperature (°C) B	30	50	70
Reaction time (h) C	3	5	7

Table 3
Experimental design levels and coding for Cd²⁺ Box-Behnken Design.

Factor	Level		
	–1 (low level)	0 (central point)	1 (high level)
pH of solution A	3	5	7
Temperature (°C) B	30	50	70
Reaction time (h) C	4	5	6

3. The result and discussion

3.1. Effects of different modification methods on adsorption

The adsorption rate of Pb²⁺ and Cd²⁺ onto natural chestnut endothelium, discolored chestnut endothelium and different modified chestnut endothelium were performed at 50 °C and 5.0 of pH. 2 g of adsorbent was left in contact with 50 mL of each solution (40 mg/L for Pb²⁺ and 30 mg/L for Cd²⁺) for 5 h.

NO. 1. Natural endothelium; No. 2. Discolor endothelium; NO. 3 Discolor endothelium modified by cis-butene dioic acid; NO. 3 Discolor endothelium modified by formaldehydeacid; NO. 5–13. refer to Table 1.

NO. 1. Natural endothelium; No. 2. Discolor endothelium; NO. 3 Discolor endothelium modified by cis-butene dioic acid; NO. 3 Discolor endothelium modified by formaldehydeacid; NO. 5–13. refer to Table 1.

As the Figs. 1 and 2 showed, the adsorption rate of Pb²⁺ and Cd²⁺ onto natural chestnut endothelium (NO. 1) is 97% and 97.07%, respectively, but that onto decolorized endothelium (NO. 2) is 84.38% and 74.28%, respectively. According to the experiments in

our lab, the real adsorption rate of natural chestnut endothelium is the same with that of decolorized endothelium, because the soluble substance in the natural chestnut endothelium reacted with the heavy metal ion and cause the precipitation of aliquot of heave metal ion which cannot be determined directly by atomic adsorption spectrophotometer.

The adsorption rates of lead ion onto NO.3 to NO.13 are all greater than NO.2. Compared with the unreal adsorption rate on natural chestnut endothelium, the adsorption on NO.3 and NO.4 is greater by 0.72% and 0.12%, respectively. NO. 5 to NO.13 were the modified endothelium under different adsorb doses of irradiation. The adsorption rates of Pb²⁺ onto NO.5 to NO.7 which were exposure to gamma ray in distilled water are better than those onto NO.8 to NO.13 which were irradiated in organic acid.

Due to the greatest adsorption rate among the modified endothelium, 0.5 mol/L cis-butene dioic acid as modifying reagent was chosen in the following experiments.

3.2. FTIR spectra of adsorbent

The FTIR spectra of discolored and pre-treated chestnut endothelium (Fig. 3) showed that both materials contain cellulose, flavonoids, pentose, organic acid, phenols and tannin, that contain functional groups which could interact with heavy metal ions. The spectra also show the difference between the discolored and pre-treated chestnut endothelium. The bands at 1250 cm⁻¹ (deformation vibration of C–O and stretching formation of O–H of carboxylic acids and phenols) and 3100 cm⁻¹ (stretching vibration of C–H, O–H and N–H group group) increased in intensity. Whereas, the bands at 3450 cm⁻¹ (stretching vibration of C–N groups) decreased in intensity after pre-treated. Hence, spectra comparison demonstrated that some functional groups were changed in discolored chestnut endothelium pretreated by formaldehyde acid.

Additionally, to analyze the functional groups which could interact with heavy metal ions, the FTIR spectra of cation-loaded pre-treated chestnut endothelium were showed in Fig. 4. There were shifted bands after loading of cation at 3450 cm⁻¹ (stretching vibration of C–N groups) (Guibal et al., 1995), 3100 cm⁻¹ (stretching vibration of C–H, O–H and N–H group group) (Doshi et al.,

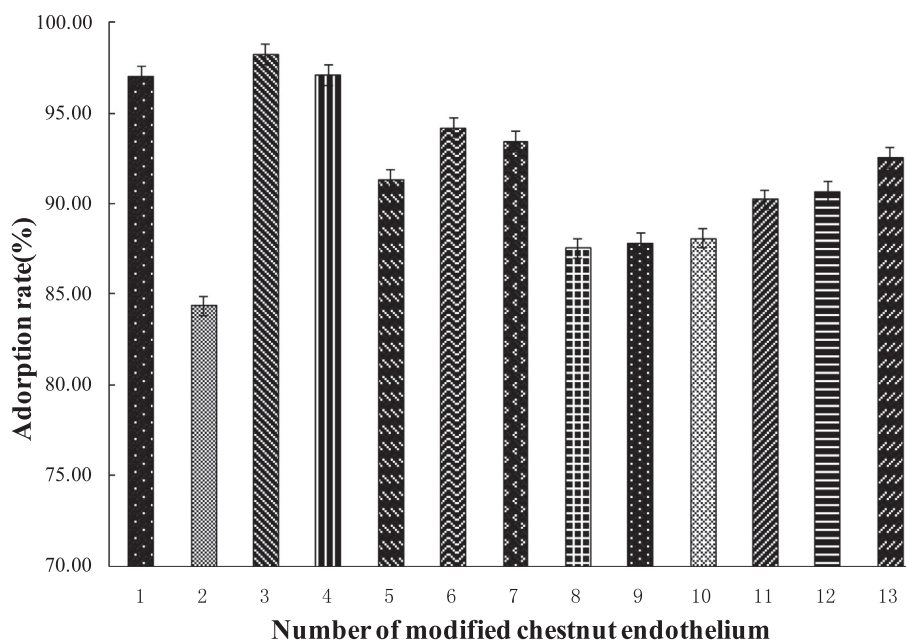


Fig. 1. The adsorption rate of Pb²⁺ onto different modification chestnut endothelium.

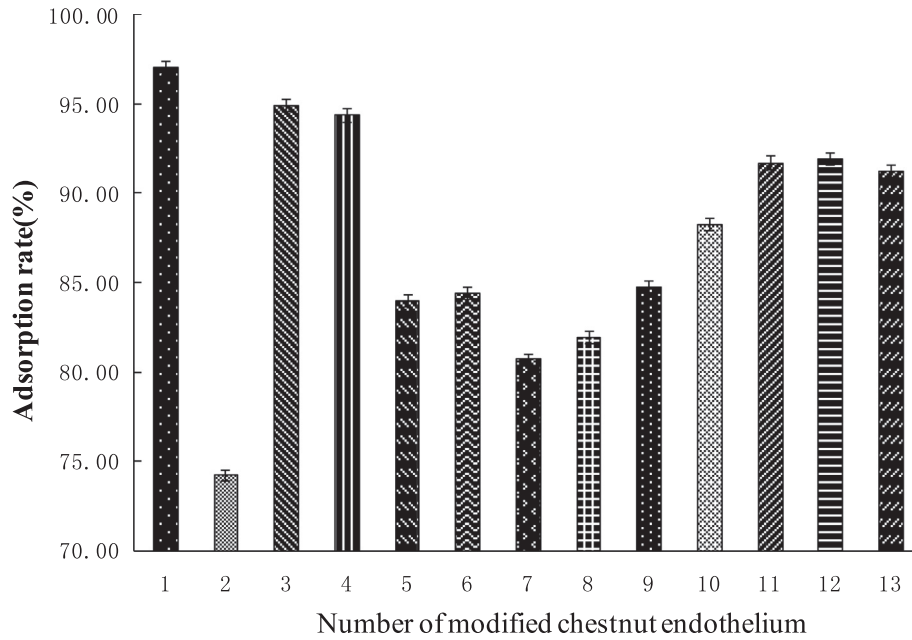


Fig. 2. The adsorption rate of Cd²⁺ onto different modification chestnut endothelium.

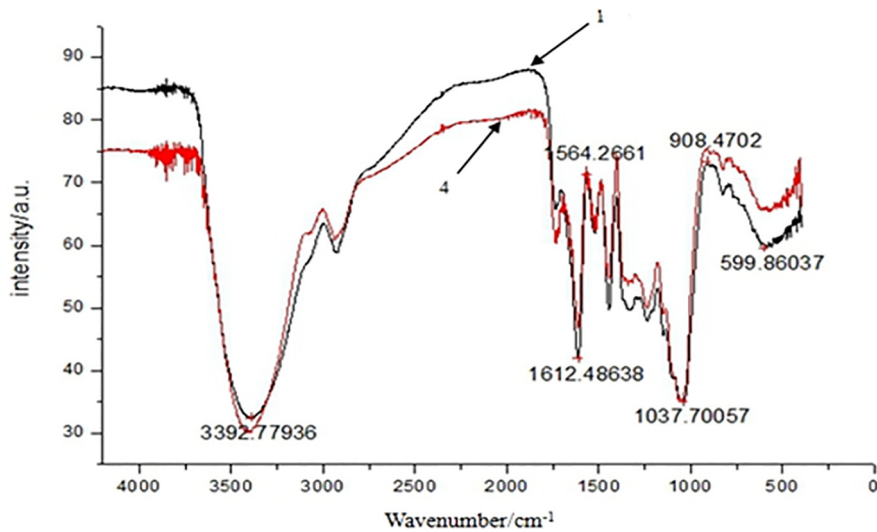


Fig. 3. FTIR spectrum of before and after modified chestnut inner shells.

2008), 1250 cm⁻¹ (deformation vibration of C–O and stretching formation of OH), 1000 cm⁻¹ (stretching formation of NH). Hence, it can be inferred that the functional groups in pretreated chestnut endothelium, such as C–O, O–H and C–H, could interact with Pb and Cd ions.

1, The discolored chestnut endothelium; 4, pre-treated chestnut endothelium

4, pre-treated chestnut endothelium; 5, Pb²⁺ loaded pre-treated chestnut endothelium; 6, Cd²⁺ loaded pre-treated chestnut endothelium

3.3. Single-factor experiments

3.3.1. Effect of initial pH

The pH of solution was an important parameter by directly influencing the active sites on adsorbent surface and the solution chemistry of the heavy metal ions. The effect of pH on the

adsorption of Pb²⁺ and Cd²⁺ on chestnut endothelium was presented in Fig. 5. The removal of both metal ions from solution is strongly affected by the pH of the medium. The adsorption efficiency increased with the increases of pH. When the pH was increased from 1 to 7 (the metal ions would precipitate when pH is higher than 7), the adsorption rate of Pb²⁺ was increased from 93.53 to 99.65% for Pb²⁺ and from 89.35 to 97.96% for Cd²⁺, respectively. The adsorption rate of Pb²⁺ and Cd²⁺ onto modified chestnut endothelium was significantly higher than that onto natural chestnut endothelium at low pH value (pH < 3). When the pH value is 1, the adsorption rate of Pb²⁺ onto modified chestnut endothelium was 93.53%, which was 4.2 times higher than that (22.25%) on to natural chestnut endothelium. And the adsorption rate of Cd²⁺ onto modified chestnut endothelium (89.35%) was 3.8 times higher than that (23.35%) on natural one. Hence, the modified chestnut endothelium could effectively work at highly acidic environment.

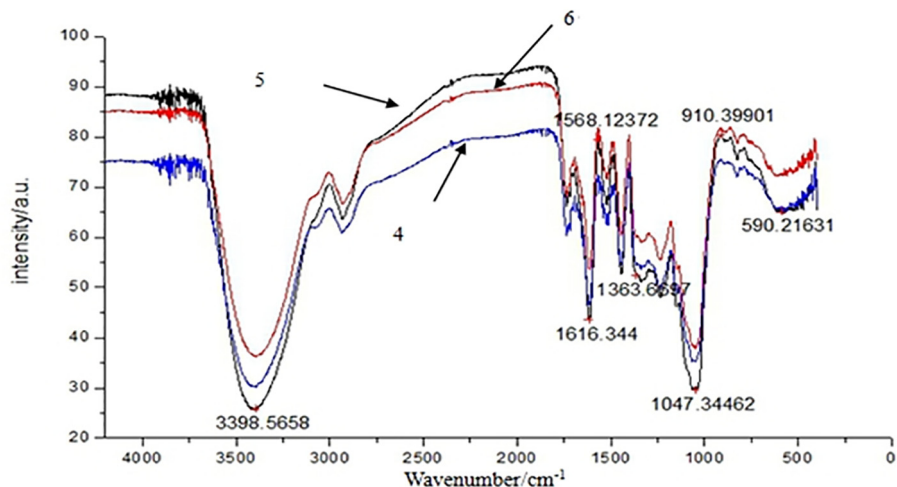


Fig. 4. FTIR spectrum of before and after adsorbed modified chestnut inner shells.

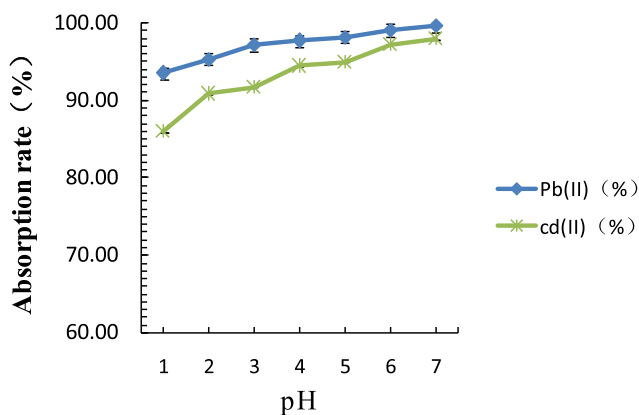


Fig. 5. The effect of different pH on adsorption of Pb²⁺ and Cd²⁺ in aqueous solution by modified Chestnut endothelium.

3.3.2. Effect of temperature

The results of effect of temperature were showed in Fig. 6. As the Fig. 4 presented, with temperature increasing, the adsorption rates of Pb²⁺ and Cd²⁺ onto modified adsorbents were increased apparently. When the temperature was increased from 30 to 50 °C, the adsorption rate was increased from 91.31 to 98.29% for Pb²⁺, and from 87.96 to 95.49% for Cd²⁺, respectively.

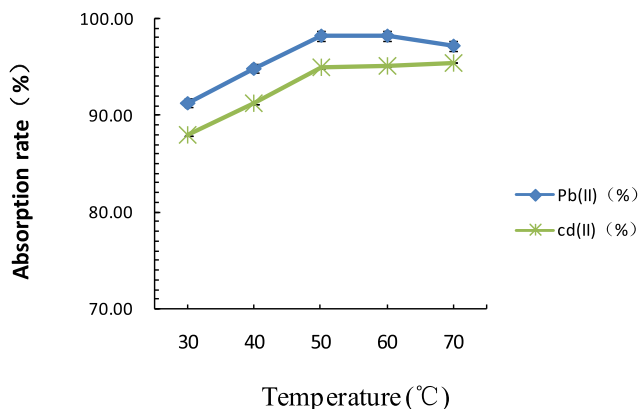


Fig. 6. The effect of different temperature on adsorption of Pb²⁺, Cd²⁺ by modified Chestnut endothelium.

The adsorption rate of Pb²⁺ was decline slightly when the temperature was increased from 50 to 70 °C, and the adsorption rate of Cd²⁺ was increased gently. The results were in accordance with those previously obtained in the analysis of adsorption thermodynamics experiment.

3.3.3. Effect of contact time

Fig. 7 showed the effect of adsorption time on absorption rate. It is observed that in the range from 0.5 to 1 h, both of the adsorption rates of Pb²⁺ and Cd²⁺ were more than 90%, which indicated that the adsorption was quite rapid initially. Further increase in contact time from 1 to 5 h, the adsorption rate of Pb²⁺ was increased slowly from 93.06 to 98.26%, and attained an equilibrium time of around 5 h. The adsorption rate of Cd²⁺ reached peak on 94.96% at 5 h, and decreased after 6 h. Hence, a contact time of 5 h was chosen for Pb²⁺ and Cd²⁺ in the following experiments.

3.3.4. Effect of the initial concentration of heavy metal ion

The effect of the initial concentration of heavy metal ion was showed in and Fig. 8. As With the increase of metal ion concentration in solution, the adsorption rate of Pb²⁺ and Cd²⁺ onto modified chestnut endothelium was decreased significantly. The adsorption was decreased from 98.31 to 42.14% for Pb²⁺, and from 95.25 to 39.21% for Cd²⁺, respectively. This decrease is due to the fact that all adsorbents have a fixed number of active sites, and the active

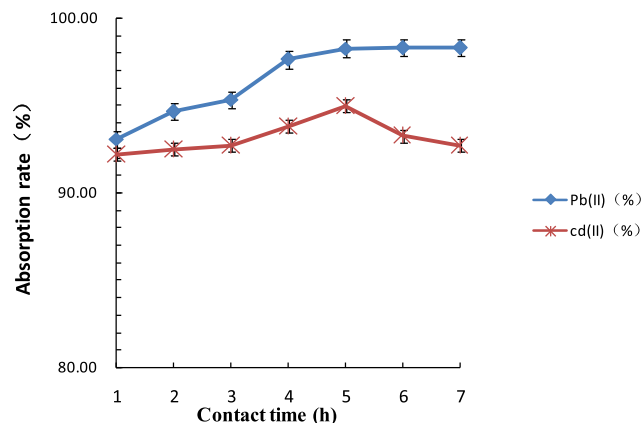


Fig. 7. The effect of contact time on adsorption of Pb²⁺ and Cd²⁺ in aqueous solution by modified Chestnut endothelium.

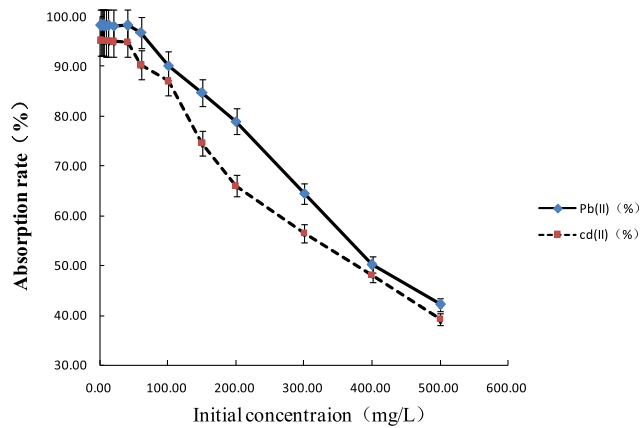


Fig. 8. The effect of different concentrations on adsorption of Pb^{2+} and Cd^{2+} in aqueous solution by modified Chestnut endothelium.

sites become saturated at higher metal ion concentrations (Martinez et al., 2006).

3.4. Response surface methods and designs

Two multivariate quadratic regression equations by regression fitting were obtained as following Eqs. (7) and (8):

$$Y(Pb^{2+}) = 98.23 + 2.02A + 3.05B + 1.47C - 0.13A * B + 0.035A * C + 0.058B * C - 1.69A^2 - 3.25B^2 - 2.09C^2 \quad (7)$$

$$Y(Cd^{2+}) = 97.74 + 4.03A + 0.96B - 0.058C - 0.12A * B - 0.24A * C - 0.45B * C - 3.88A^2 - 1.91B^2 - 0.28C^2 \quad (8)$$

The analysis of dependent variance of the two models was presented in Tables 4 and 5. In Table 4, all variance in the models of adsorption of Pb^{2+} were considered statistically significant of solutions, contact time and adsorption temperature had significant effect on the adsorption of Pb^{2+} onto modified chestnut endothelia. In Table 5, pH in the models of adsorption of Cd^{2+} reached significant level. Hence, the pH of solutions was significant variance on the adsorption of Pb^{2+} and Cd^{2+} on modified chestnut endothelium. The mathematical models of Pb^{2+} and Cd^{2+} were extremely significant ($p < 0.0001$), and the determination coefficients were 0.9952 and 0.9887, respectively, indicating that these two models can explain of the change of response values, and provided a perfect fit of response surface.

Table 4
The analysis of variance table of Pb^{2+} adsorption by modified chestnut endothelium.

Resources of variance	Sum of squares	Degree of Freedom	Mean square	f value	P Value
model	207.3614	9	23.0402	159.7863	<0.0001
A-pH	32.6028	1	32.6028	226.1045	<0.0001
B-T	74.4200	1	74.4200	516.1118	<0.0001
C-t	17.3166	1	17.3166	120.0928	<0.0001
AB	0.0702	1	0.0702	0.4870	0.5078
AC	0.0049	1	0.0049	0.0340	0.8590
BC	0.0132	1	0.0132	0.0917	0.7708
A ₂	12.0755	1	12.0755	83.7454	<0.0001
B ²	44.5011	1	44.5011	308.6203	<0.0001
C ²	18.4537	1	18.4537	127.9783	<0.0001
Residual	1.0094	7	0.1442		
lack of fit	1.0077	3	0.3359	799.7421	0.7851
Error	0.0017	4	0.0004		
total variation	208.3708	16			
R ²	0.9952	Adj R ²	0.9889		

The impact significance order of the effect of 3 factors on the adsorption was pH > adsorption temperature > contact time. As the result, the adsorption rate of Pb^{2+} onto modified chestnut endothelium was 99.78% at 59.23 °C, 5.72 h of contact time and 6.16 of pH. And the adsorption rate of Cd^{2+} onto modified chestnut endothelium was 98.98% at 55.99 °C, 4.43 h of contact time and 6.06 of pH. To confirm the theoretical results, three parallel experiments were carried out under those optimized conditions. The experiment value of the adsorption of Pb^{2+} and Cd^{2+} onto modified chestnut endothelium was 99.76% and 98.90%, respectively, which was close to the predicted value.

3.5. Adsorption kinetics of modified chestnut endothelium

With the adsorption kinetic model, the rate and the mechanism of adsorption can be deduced. The applicability of Pseudo-first-order and Pseudo-second-order kinetic equation was tested, and the rate constant and the correlation coefficient were obtained.

The adsorption of both heavy metals ions onto chestnut endothelium agreed well with Pseudo-second-order kinetic model according to correlation coefficients, which reached 0.9999 and 0.9997, for Pb^{2+} and Cd^{2+} , respectively. On the other hand, the coefficients of determination for the pseudo-first-order kinetics were low, and the plots of $\ln(q_e - q_t)$ vs. t for the pseudo-first-order model were not shown as figure. The pseudo-second order kinetic model was based on the premise that the adsorption rate was controlled by chemical sorption (Lodeiro et al., 2006; Ding et al., 2011). Initially, the sorption sites at the surface of chestnut shell was unoccupied and could easily bind with Pb^{2+} or Cd^{2+} . As time went on, the adsorption site gradually became saturated with heavy metal ions, and the sorption rate decreased correspondingly (Kim et al., 2005).

3.6. Isothermal adsorption curve

Langmuir model and Freundlich isotherms were applied to describe the equilibrium between adsorbed heavy metal ions and heavy metal ions in solution. The Freundlich and Langmuir constants which are concluded from these plots were summarized in Table 6 along with the determination coefficients. The adsorption constant showed that both models describe well the adsorption of Pb (II) and Cd (II) ion onto chestnut endothelium, and both the simulated linear correlations could reach 0.92. However, Langmuir isothermal adsorption model provided better fit to the equilibrium data, implying that adsorption occurred at finite number of identical homogeneous sites within the adsorbent.

Table 5The analysis of variance table of Cd²⁺ adsorption by modified chestnut endothelium.

Resources of variance	Sum of squares	Degree of freedom	Mean square	f value	P Value
model	222.3419	9	24.7047	67.7717	<0.0001
A-pH	130.1320	1	130.1320	356.9882	<0.0001
B-T	7.3272	1	7.3272	20.1006	0.0029
C-t	0.0266	1	0.0266	0.0731	0.7947
AB	0.0609	1	0.0609	0.1671	0.6949
AC	0.2296	1	0.2296	0.6299	0.4535
BC	0.8040	1	0.8040	2.2057	0.1811
A ₂	63.3819	1	63.3819	173.8741	<0.0001
B ²	15.3374	1	15.3374	42.0749	0.0003
C ²	0.3299	1	0.3299	0.9051	0.3731
Residual	2.5517	7	0.3645		
lack of fit	0.3529	3	0.1176	0.2140	0.8821
Error	2.1988	4	0.5497		
total variation	224.8936	16			

Table 6Adsorption isotherm constants for the adsorption of Pb²⁺ and Cd²⁺ by modified Chestnut endothelium.

Heavy metals	T (K)	Langmuir model			Freundlich model		
		q _m (mg/g)	K _L	R ²	K _F	n	R ²
Pb ²⁺	303	44.44	0.0699	0.9983	2.84	1.7756	0.9544
	323	52.91	0.1462	0.9971	3.34	1.9083	0.9229
	343	52.08	0.1486	0.9980	3.17	1.9980	0.9403
Cd ²⁺	303	43.48	0.0423	0.9812	2.10	1.7071	0.9744
	323	50.25	0.0692	0.9913	3.86	1.7050	0.9414
	343	51.28	0.0790	0.9937	3.19	1.6852	0.9285

Table 7Removal effect of Pb²⁺ and Cd²⁺ by several adsorbents.

Biomaterials	Heavy metal ions	Maximum Adsorption Capacity (mg/g)	Source
Saw dust of Pinussylvestris	Pb ²⁺	9.78	Taty-Costode et al. (2003)
Phaseolus aureus hulls	Pb ²⁺	25.5	Rao et al. (2009)
Rice Husk	Pb ²⁺	20.24	Kumar and Bandyopadhyay (2006)
almond shells	Pb ²⁺	9.0	Mehrasbi et al. (2009)
endothelium	Pb ²⁺	52.91	In this paper
Chestnut shell	Pb ²⁺	8.5	Vázquez et al. (2009)
Saccharomyces cerevisia	Cd ²⁺	15.36	Gao et al. 2007
wheat straw	Cd ²⁺	14.612	Dang et al. (2009)
almond shells	Cd ²⁺	7.0	Mehrasbi et al. (2009)
Peanut husk	Pb ²⁺	29.14	Li et al. (2006)
Chestnut shell	Cd ²⁺	51.28	In this paper
Chestnut shell	Pb ²⁺	9.9	Vázquez et al. (2012)

The K_L in Langmuir formula represents the adsorption stability between the adsorbate and adsorbent under given conditions. The increase in adsorption temperature resulted in an increase in K_L of the adsorption about Pb²⁺ and Cd²⁺ on modified adsorbent, which mean that high temperature would promote the uptake of Pb²⁺ and Cd²⁺ ions, so the adsorption was an endothermic process in nature. Because only chemical reaction could be an endothermic process (physical adsorption and partial exothermic chemical reaction are exothermic process), the adsorption of Pb²⁺ and Cd²⁺ onto modified adsorbent accounted for the chemical reaction process.

The maximum adsorption amount of Pb²⁺ and Cd²⁺ on modified adsorbent is 52.91 mg/g and 51.28 mg/g, respectively. Comparing to some biomaterial that had been researched (refer to Table 7), the adsorption capacity of modified endothelium was raised obviously.

The uptake of Pb²⁺ Kumar and Bandyopadhyay (2006), Zhang et al. (2016) and Cd²⁺ ions onto modified endothelium is favorable adsorption, when the value of n in Freundlich isotherm is more than 1. The adsorption constant K_F indicated the adsorption affinity between metal ions and adsorbent. In the adsorption of Pb²⁺ and Cd²⁺ onto modified adsorbent, both the Freundlich model

constants n are more than 1, and K_F was initially increasing and then decreasing with the increase of temperature, which indicated that the adsorption affinity between modified adsorbent and heavy metal ions become stronger at first and then turn weaker with rising temperature. Therefore, the desorption of heavy metal ions would happen if the adsorption process was overheating. Hence, an appropriate temperature range was needed to increase the adsorption capacity. The result would be proved and the temperature would be obtaining in the following experiment.

4. Conclusion

The chestnut endothelium modified by 0.5 mol/L cis-butene dioic acid was the effective way to enhance the capacity for removing Pb²⁺ and Cd²⁺ from the waste water. Under the optimized condition, the experiment value of the adsorption of Pb²⁺ and Cd²⁺ was 99.76% and 98.90%, respectively. Comparing to other modified waste biomaterial sources which had been reported, the modified chestnut endothelium has high adsorption capacity in high acid environment (pH < 3). The maximum adsorption of Pb²⁺ and Cd²⁺

were 52.91 mg/g and 51.28 mg/g, respectively. The proposed adsorption kinetics of Pb^{2+} and Cd^{2+} fit second-order kinetic model better. According to all the result, it can be concluded that the modified discolor chestnut endothelium is an excellent potential bio sorbent material for removing heavy metal ions coming from aqueous solutions. The FTIR showed that C–O, O–H and C–H groups were involved in Pb^{2+} and Cd^{2+} adsorption process.

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Further reading

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