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Original Research

Adsorptive Removal of Hg(II) Ions from Aqueous Solutions Using Chemical-Modified Peanut Hull Powder

Zhuhong Ding[1]*, Rui Yu[1], Xin Hu[2], Yijun Chen[2]

[1]School of Environment, Nanjing University of Technology,
200 Zhongshanbei Road, Nanjing 210009, P.R. China
[2]State Key Laboratory of Analytical Chemistry for Life Science,
Center of Material Analysis and School of Chemistry and Chemical Engineering,
20 Hankou Road, Nanjing University, Nanjing 210093, P.R. China

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Abstract

Peanut hull powders were chemically modified using mercaptoacetic acid to develop a convenient, low-cost, and highly efficient adsorbent for the removal of Hg(II) from aqueous solutions. A pseudo-second-order rate equation fitted the kinetic data better than a pseudo-first-order rate equation did for both the raw and the mercapto-modified peanut hull powder. The equilibrium data for both the raw and the mercapto-modified peanut hull powder fitted well with the Langmuir, Freundlich, and Temkin isotherm models. Mercapto-modification improved the adsorption capacity of Hg(II) onto peanut hull powder. Fourier-transform infrared spectra revealed that mercapto groups, together with hydroxyl and carboxyl groups, were the main function groups of Hg(II) biosorption onto chemical-modified peanut hull powder.

Keywords: bioadsorption, mercapto-modification, equilibrium, kinetic, Hg(II)

Introduction

Mercury is one of the heavy metals of most concern with regard to the environment because of its toxicity. For example, mercury and its compounds can cause dermatitis by skin contact. Fever, chemical tracheal bronchitis, pneumonia, respiratory failure, and kidney failure can be caused by inhalation of mercury steam. Therefore, effluents containing mercury may pose serious threats to environmental quality and to human health. The removal of mercury from wastewaters has received much attention worldwide.

Adsorption has been widely used in the removal of metal ions from aqueous media. However, the development of convenient, low-cost, highly efficient, and practical adsorbents for metal ions in aqueous media is still a challenge. Low-cost biosorbents have been used to adsorb heavy-metal ions from aqueous solutions. For example, rice husks [1], corn cobs [2], cashew nut shells [3, 4], prunus amygdalus shells [5], rose waste biomass [6], and coconut shells [7] have been used to adsorb metal ions such as Pb(II), Cu(II), Ni(III), Cr(III), and Hg(II) in aqueous solutions. In recent years, chemical modification of biosorbents has been investigated to improve the removal efficiency of heavy metals from aqueous solutions [8-11]. Generally, biosorbents contain abundant alcoholic hydroxyl, phenolic hydroxyl, and carboxyl groups. These groups can be chemically modified to form new compounds with changed properties to improve adsorption capacity [8-10, 12].

Peanut hulls are common agricultural waste and are mainly combusted or discarded in China, which may cause

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*e-mail: dzhuhong@njtech.edu.cn

secondary pollution. For example, the cultivation area for peanuts in China is more than 500 million ha. Peanut hulls containing abundant cellulose have been investigated as a low-cost adsorbent to remove heavy metals such as Cu(II), Ni(III), and Cr(III) from aqueous solutions [13-15]. Can chemical modification enhance its metal adsorption capacity? As a soft-acid heavy-metal with high polarization, Hg(II) can combine with mercapto groups, which are soft alkali species. Therefore, we have explored a simple means of chemical modification of peanut hull powder using mercaptoacetic acid. The equilibrium and kinetic adsorptions of Hg(II) from aqueous solutions using chemically modified and raw peanut hulls were compared. This study is helpful for increasing the use of peanut hulls as a resource.

Materials and Methods

Adsorbent Preparation

Peanut hulls were washed in running tap water, and then transferred to an oven at 65ºC to dryness. The dried peanut hulls were milled and sieved using an 80-mesh sieve. The sieved peanut hull powder was divided into two sub-samples. One was washed by deionized water several times and dried. Then the raw hull powder was obtained, which was abbreviated as P in the present study. The other was soaked in 17.5% NaOH solution for 48 h to remove coloration and impurities, and washed with distilled water several times until the pH value of supernatant was approximately 7.0, then freeze-dried.

Mercapto-group modification of the peanut hulls was carried out according to the method of synthetic thiol cotton fiber [16] with some modifications. Mercaptoacetic acid (200 mL), acetic anhydride (120 mL), acetic acid (36%, 80 mL), and concentrated sulfuric acid (0.6 mL) were added in turn to a 1-L wide-mouthed bottle. The mixture was stirred thoroughly and cooled to room temperature, followed by the addition of 60 g of the peanut hull powder, which had been treated using 17.5% NaOH solution. The bottle was covered with a lid and put in an oven at 40ºC for 2-4 d. After removal from the oven, the mixture was washed thoroughly with deionized water until it was approximately neutral, and spread out in a freeze-drying apparatus. Finally, the mercapto-modified peanut hulls (denoted by MP in the present study) were obtained. The product was kept in a refrigerator at 4ºC.

The C, H, N, and S contents of P and MP were determined using an elemental analyzer (EA) (Vario MICRO, Elementar) via high-temperature catalyzed combustion followed by thermal conductivity detection of the resulting CO_2, H_2O, N_2, and SO_2 gases.

Morphological analyses of P and MP were performed using scanning electron microscopy (SEM) (model S-3400N II, Hitachi Co., Tokyo, Japan) with an accelerating voltage of 20 kV. The sample was fixed on an aluminum holder and sputtered with platinum. Representative micrographs of the P and MP were obtained at 500× magnification with a secondary electron detector.

Batch Adsorption Experiments

Batch adsorption experiments were carried out at room temperature (20±2ºC) by adding 0.05 g of adsorbent to 100-mL conical flasks containing 50 mL of Hg(II) solution of desired concentrations. The solution pH was adjusted using 0.01 $mol \cdot L^{-1}$ NaOH and 0.01 $mol \cdot L^{-1}$ HCl. The mixture was shaken in a rotary shaker.

The effects of solution pH on the equilibrium adsorption of Hg(II) were examined from pH 2.0 to pH 7.0. In the kinetic experiments, the contact time was varied between 1 and 360 min, and solutions containing 50 $mg \cdot L^{-1}$ of Hg(II) were used. In the isotherm experiments, 0.05 g of adsorbent was added into 50 mL of Hg(II) solutions of concentrations between 0.05 and 200 $mg \cdot L^{-1}$. All the adsorption experiments were conducted in duplicate, and the mean values are reported.

When the preset contact time was reached, the samples were removed and centrifuged at 4,000 rpm for 5 min. Then Hg(II) in the supernatant was determined using inductively coupled plasma mass spectrometry (ICP-MS, ELAN9000, Perkin-Elmer Co.) as soon as possible. The internal standard added online during analysis was 209Bi at 20 $\mu g \cdot L^{-1}$ in 2% HNO_3. Au solution (10 $mg \cdot L^{-1}$) was used to eliminate the memory effect. The adsorption rate (Q%) and the amount of adsorbed Hg(II) (q_t) per unit sorbent mass were calculated using the following equations:

$$Q(\%) = [(C_0 - C_t)/C_0] \times 100 \quad (1)$$

$$q_t = [(C_0 - C_t) \times V]/m \quad (2)$$

...where C_0 and C_t are the initial Hg(II) concentration and equilibrium Hg(II) concentration at time t ($mg \cdot L^{-1}$), respectively; q_t is the amount adsorbed ($mg \cdot g^{-1}$) at time t; V is the volume of the solution (L); and m is the mass of the adsorbent (g).

Fourier Transform Infrared Spectrophotometer (FTIR) Analysis

Infrared spectra of the P, MP, and Hg(II)-MP were recorded using a Fourier-transform Infrared Spectrometer (FT-IR, NEXUS870, NICOLET Co., USA) in the range of 4,000-500 cm^{-1} with a resolution of 0.2 cm^{-1}, using a KBr disc containing 1% of finely ground sample produced using a bench press.

Results and Discussion

Characterization of Sorbent

The contents of C, H, N, and S in the raw peanut hulls (P) were 42.0%, 8.03%, 0.54%, and 0.35%, respectively, and the modified peanut hulls (MP) contained 45.5% C, 8.02% H, 0.41% N, and 0.49% S. Compared with P, the contents of C and S increased in MP. The S content in MP increased from 0.35% to 0.49%, indicating that mercapto groups might be grafted onto the cellulose in the peanut hulls.

SEM micrographs of P and MP are shown in Fig. 1. Fig. 1(a) shows that P had a smooth surface, large particles, a compacter configuration, low porosity, and an inconspicuous cellulose structure. In contrast, MP had a rougher surface, smaller particles, a looser structure, higher porosity, and an obvious cellulose structure; these characteristics signified that MP was suitable for adsorption (Fig. 1b).

Effects of pH

The pH of the aqueous solution is important in the adsorption of metals on adsorbents. As is well known, the pH can affect protonation of the functional groups on the adsorbent surface, such as carboxyl, phosphate, and amino groups, as well as the chemical characteristics of the metal ions, such as solubility [17]. Fig. 2(a) shows the effects of pH on the removal of Hg(II). The removal efficiency of Hg(II) by P and MP tended to increase with increasing pH value between 2.0 and 4.0. The maximum equilibrium adsorption of Hg(II) by P occurred in the pH range of 4.0-6.0, whereas that for MP was about pH 4.0.

Adsorption Kinetics of Hg(II)

The time-dependent behavior of Hg(II) removal was evaluated for different equilibrium time intervals from 1 to 360 min at 20ºC with an initial Hg(II) concentration of 50 mg·L^{-1} at pH 4.5. The adsorption rate was initially fast (Fig. 3 (a)), and the adsorption capacity increased quickly with contact time. The rapid adsorption of Hg(II) in the first 30 min may be the result of there being larger numbers of active adsorption sites available on the adsorbent surface at the beginning, thus Hg(II) could interact easily with these sites [18]. Both P and MP achieved adsorption equilibrium at 90 min.

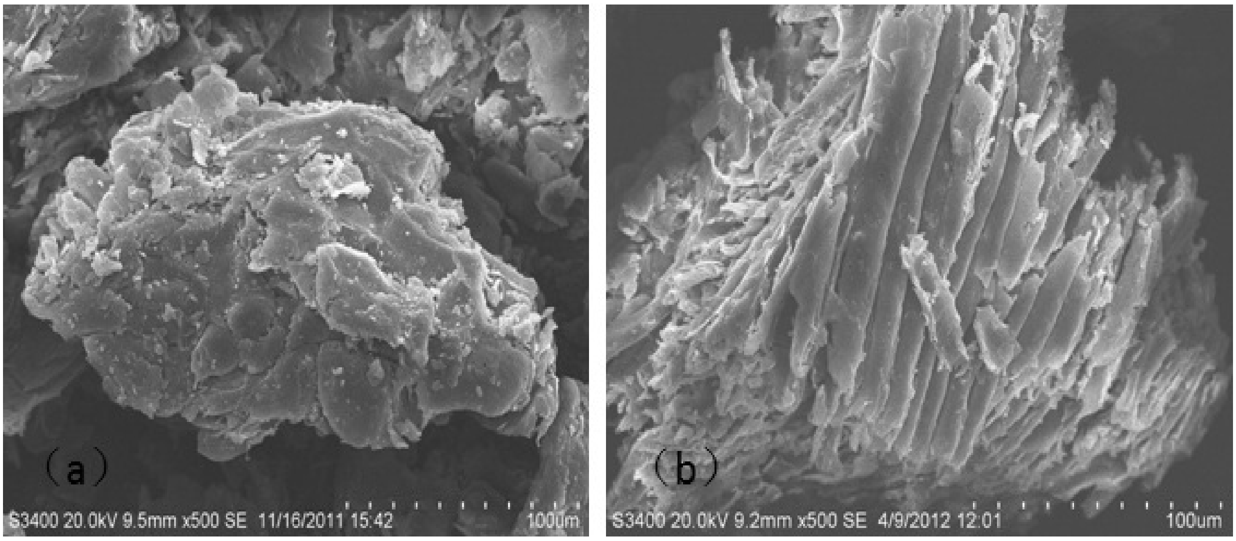
(a)
S3400 20.0kV 9.5mm x500 SE 11/16/2011 15:42
100um
(b)
S3400 20.0kV 9.2mm x500 SE 4/9/2012 12:01
100um

Fig. 1. Images of the raw and the mercapto-modified peanut hull powder (a: P and b: MP) performed using scanning electron microscopy.

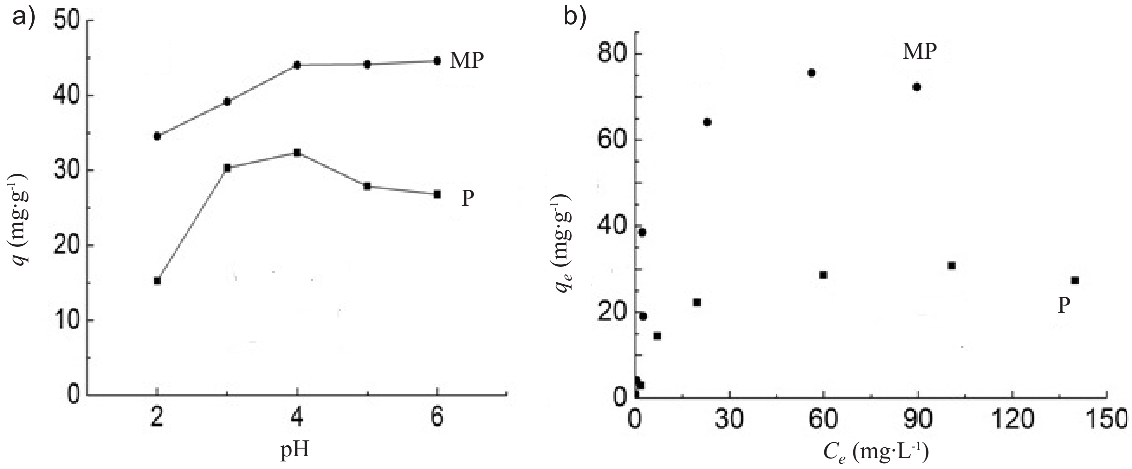

Fig. 2. Effects of pH (a) and initial concentration (b) on the adsorption of Hg(II) onto the raw and the mercapto-modified peanut hull powder (a – P and b – MP).

Table 1. Kinetic model parameters for Hg(II) adsorption onto raw and chemically modified peanut hulls.

	Experimental	Pseudo-first-order			Pseudo-second-order		
	q_{exp}	q_e	k_1	R^2	q_e	k_2	R^2
	($mg·g^{-1}$)	($mg·g^{-1}$)	($mg·g^{-1}·min^{-1}$)		($mg·g^{-1}$)	($mg·g^{-1}·min^{-1}$)	
P	32.7	26.2	0.691	0.637	32.6	0.003	0.996
MP	43.9	36.5	1.38	0.830	44.4	0.003	0.998

Adsorption kinetics is one of the best characteristics for representing adsorption efficiency. Generally, pseudo-first-order (Eq. 3) and pseudo-second-order (Eq. 4) rate equations were fitted to the experimental data to predict the adsorption process:

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e t} \qquad (3)$$

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

...where q_e is the amount of Hg(II) adsorbed at equilibrium ($mg·g^{-1}$), k_1 is the pseudo-first-order rate constant for adsorption ($mg·g^{-1}·min^{-1}$), t is the reaction time (min), and k_2 is the pseudo-second-order rate constant for adsorption ($mg·g^{-1}·min^{-1}$).

In order to analyze the adsorption abilities of the adsorbents to Hg(II), pseudo-first-order and pseudo-second-order kinetic equations were fitted to the experimental data to determine the relevant parameters (Figs. 3b and c). A comparison of the pseudo-first-order and pseudo-second-order model parameters is presented in Table 1. For the pseudo-first-order model, the correlation coefficient was 0.798 for P, lower than that (0.911) for MP. The correlation coefficients for P and MP for the linear plots of t/q against t for the pseudo-second-order equation are close to 1 (Table 1). In addition, the experimental and theoretical values of qe obtained from the pseudo-second-order model are similar to each other (Table 1); the qe value for P was higher than that for MP, suggesting that MP had higher adsorption ability. The results suggested that the pseudo-second-order kinetic model gives a better fit than the pseudo-first-order model does for the adsorption processes of P and MP.

Adsorption Isotherm of Hg(II)

Fig. 2c shows the relationship between the equilibrium concentration and the equilibrium adsorption capacity of Hg(II) at 20°C. In the present work, the initial Hg(II) concentrations were in the range 0.05-200 $mg·L^{-1}$. The initial pH values of the Hg(II) solutions were adjusted to 4.5, and the reaction time was 3 h. The equilibrium concentration increased from 0.0042 to 140 $mg·L^{-1}$ for P and 0.0025 to 89.7 $mg·L^{-1}$ for MP, and the adsorbed content increased from 0.02 to 30.8 $mg·g^{-1}$ for P and 0.02 to 75.6 $mg·g^{-1}$ for MP. The adsorbed content of Hg(II) on both P and MP increased with increasing equilibrium concentration of Hg(II) in the aqueous solution. The saturation adsorption occurred and adsorption did not increase with increasing initial concentration of the aqueous solution once a certain adsorption capacity was achieved. Fig. 2(c) shows that the adsorption capacity of MP for Hg(II) was higher than that of P.

Adsorption isotherm models are significant methods for understanding the mechanism of adsorption. Three important isothermic equations are used in this study, namely the Langmuir, Freundlich, and Temkin models.

The Langmuir isothermic equation is represented as follows:

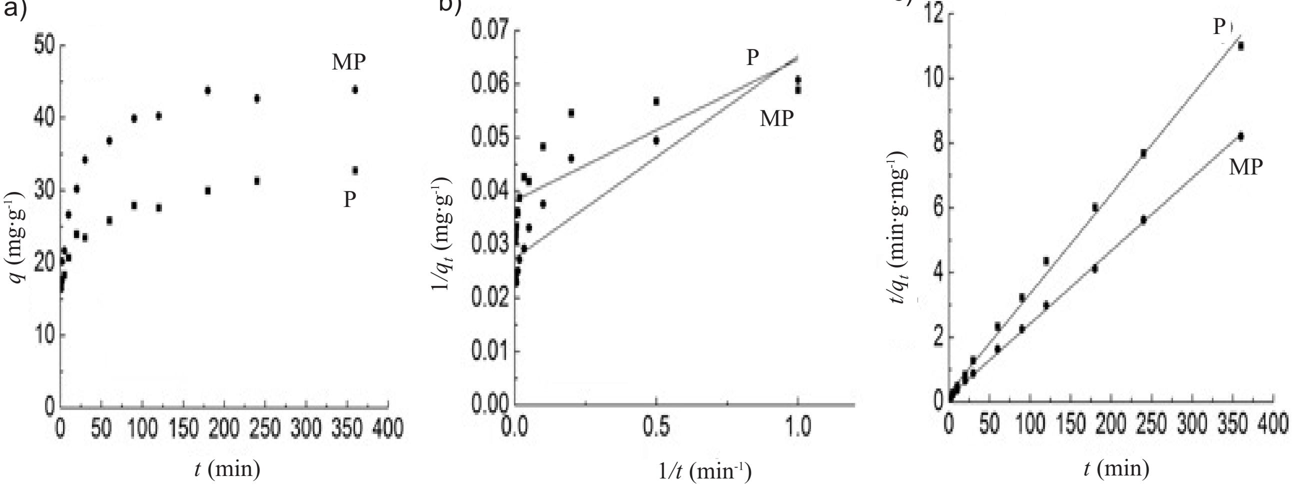

Fig. 3. Adsorption kinetics of Hg(II) onto the raw and the mercapto-modified peanut hull powder (a) and the fitting curve of the experimental data using pseudo-first-order (b) and pseudo-second-order (c) models.

Table 2. Isotherm model parameters for Hg(II) adsorption onto raw and chemically modified peanut hulls.

Langmuir			Freundlich			Temkin		
	P	MP		P	MP		P	MP
q_m (mg·g^{-1})	30.3	83.3	K_f (mg g·g^{-1})	2.50	6.89	B	3.0	3.08
b (l·mg^{-1})	0.15	0.16	$1/n$	0.60	0.69	A (l·g^{-1})	0.062	0.14
R^2	0.98	0.99	R^2	0.88	0.89	b (J·mol^{-1})	812	792
R_L	0.03-0.99	0.03-0.99				R^2	0.84	0.84

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \tag{5}$$

...where C_e is the Hg(II) equilibrium concentration (mg·L^{-1}), q_m is the maximum adsorption capacity of the sorbent when the surface is completely covered with Hg(II) (mg·g^{-1}), and b is the adsorption constant representing the affinity between the sorbent and Hg(II) ions (mg·g^{-1}). Based on further analysis of the Langmuir model, the dimensionless parameter of the equilibrium or adsorption intensity (RL) can be expressed as follows [19]:

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

There are four possible R_L values:

(i) for favorable adsorption, $0 < R_L < 1$
(ii) for unfavorable adsorption, $R_L > 1$
(iii) for linear adsorption, $R_L = 1$
(iv) for irreversible adsorption, $R_L = 0$ [20].

The linear form of the Freundlich equation is as follows [21]:

$$\lg q_e = \lg K_f + \frac{1}{n}\lg C_e \tag{7}$$

...where K_f is a constant related to adsorption capacity (mg·g^{-1}) and $1/n$ is an empirical parameter related to adsorption intensity. K_f and $1/n$ are determined by the adsorbent properties. The value of $1/n$ varies with the sorbent heterogeneity and provides a criterion for determining the favorability of the adsorption process. There are four possible values for $1/n$ [22]:

(i) for favorable adsorption, $0 < 1/n < 1$
(ii) for unfavorable adsorption, $1/n > 1$
(iii) for linear adsorption $1/n = 1$
(iv) for irreversible adsorption $1/n = 0$.

The Temkin isotherm model is used to explore the energy distribution. The linear form is as follows [23]:

$$q_e = B\ln A + B\ln C_e \tag{8}$$

$$B = \frac{RT}{b} \tag{9}$$

where A is the equilibrium binding constant corresponding to the maximum binding energy (L·g^{-1}), T is the solution temperature (K), and B is the Temkin constant related to the heat of adsorption (J·mol^{-1}).

The relevant equilibrium data obtained from the adsorption of Hg(II) onto P and MP were respectively fitted using the Langmuir, Freundlich and Temkin isothermic models (Fig. 4). All the isothermic constants and correlation coefficients were calculated from the corresponding linear equations (Fig. 4), and are listed in Table 2. The correlation coefficients of these models were all greater than 0.9, showing good fitting trends. The Langmuir isothermic model showed that the saturated monolayer adsorption of MP for Hg(II) was higher than that of P, demonstrating that Hg(II) ions were better adsorbed onto the MP surface than onto the surface of P. For the initial Hg(II) concentration range of 0.05 to 200 mg·L^{-1}, the RL values ranged from 0.03 to 0.99

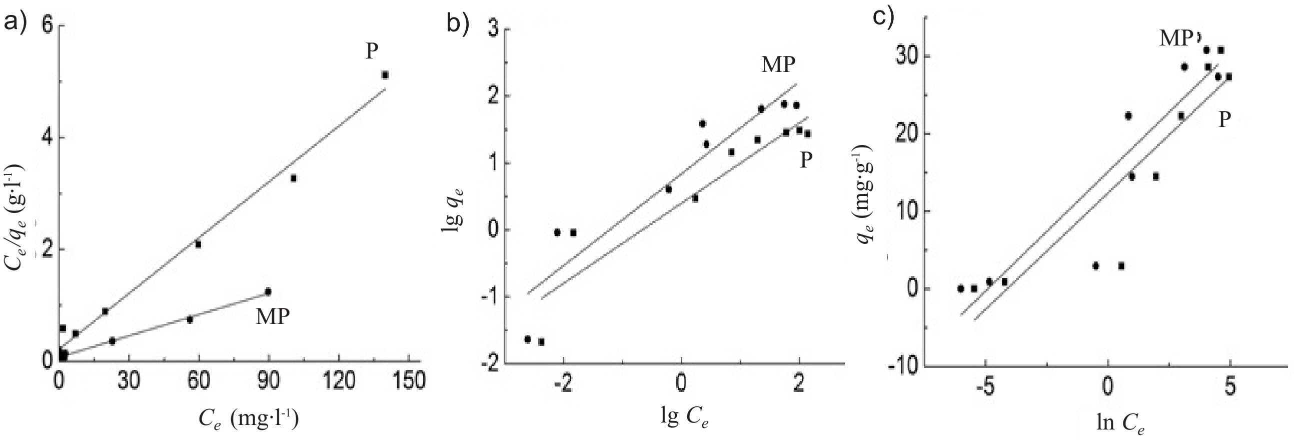

Fig. 4. Fitting of the isothermic experimental data using Langmuir isotherm (a), Freundlich isotherm (b), and Temkin isotherm (c) models.

for both P and MP, indicating that Hg(II) adsorption onto P and MP are favorable under the studied conditions. The 1/*n* values, calculated using the Freundlich isothermic model, were between 0.1 and 1, which supported the favorability of the adsorption process.

Adsorption Mechanism Analysis

The form of metal ions adsorbed onto plant materials depends on the active groups and bonds located on the adsorbent surface. Fig. 5 shows the FTIR spectra of P, MP and Hg(II)–MP. The broad and intense absorption peak at 3,349.8 cm^{-1} can be attributed to the O–H stretching vibration (Fig. 5a). The peak observed at 2,932.6 cm^{-1} corresponds to the C–H stretching vibration of alkyl (–CHn) groups. The peak observed at 1,736.6 cm^{-1} is the stretching vibration of the C=O bonds from non-ionic carboxyl groups (–COOH, –OOCH$_3$), and may be from carboxylic acids or their esters [24]. The peak observed at 1,646.7 cm^{-1} is the asymmetric stretching vibration of the C=O bonds of ionic carboxyl groups (–COO–). The peak observed at 1,510.8 cm-1 is the stretching vibration of the aromatic ring skeleton. The absorption at 1,373.0 cm^{-1} corresponds to the deformation vibration absorption peak of C–H from celluloses and hemicelluloses. The peak at 1,265.5 cm^{-1} is ascribed to vibrations including the deformation vibration of C=O and the stretching vibration of –OH from carboxylic acids and phenols. The peak at 1,034.4 cm^{-1} can be assigned to the C–O stretching vibration of celluloses and hemicelluloses [25-27].

The characteristic absorption peak of the sulfydryl group appears at 2,500-2,600 cm^{-1}. In Fig. 5(b), the appearance of a new peak at 2,562.4 cm^{-1} demonstrated the grafting of sulfydryl groups onto the peanut hull powder. The spectrum displayed a strong band of the C=O from carboxyl groups at 1,731.6 cm^{-1}, and a shift from the value of 1,736.6 cm^{-1} in Fig. 5a showed the presence of ester carbonyl groups. This band indicated that mercaptoacetic acid esterified the hydroxy groups of the peanut hulls and generated an ester peak, with the consequent release of a carboxylic acid functional group. The peaks at 1,373.0 cm^{-1}, 1,265.5 cm^{-1}, and 1,034.4 cm^{-1} clearly shifted and suggested the aromatic nuclei and C–O bonds had been removed in the modification process.

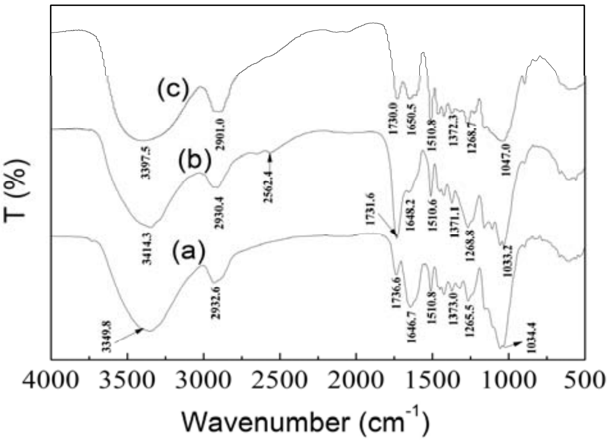

Fig. 5. FT-IR spectra of the raw and the mercapto-modified peanut hull powder ((a: P and b: MP) and the mercapto-modified peanut hull powder after adsorption of Hg ions (c: MP–Hg(II)).

Compared with FTIR spectra before and after biosorption of Hg(II) onto MP, there were clear band shifts and disappearances, and an intensity decrease at some bands. Fig. 5c showed the disappearance of the peak at 2,562.4 cm^{-1} in Fig. 5b, suggesting that the sulfydryl groups had reacted with Hg(II). As a soft-acid heavy-metal with high polarization, Hg(II) can combine with mercapto groups, which are soft alkali species [28, 29]. The O–H stretching vibration at 3,414.3 cm^{-1} moved to 3,397.5 cm^{-1}, and become less speculate. This may qualitatively be attributed to adsorption by the O–H of peanut hull powder. What's more, the peaks at 1,731.6 cm^{-1} and 1,648.2 cm^{-1} in Fig. 5b had shifted to 1,730.0 cm^{-1}, and 1,650.5 cm^{-1}, respectively. These shifts may be attributed to the changes in counter-ions in relation to carboxylate and hydroxylate anions, demonstrating that the hydroxyl and carboxyl groups also contributed to Hg(II) adsorption [30-32]. Similarly, the intensity at 1,268.7 cm^{-1} in Fig. 5c) was weakened sharply compared by 1,268.8 cm^{-1} (Fig. 2b). Thus, except for sulfydryl groups, the shifts of peaks may qualitatively indicate that the surface functional groups such as hydroxyl and carboxyl groups on peanut hull powder also participated to the adsorption process.

Conclusions

Peanut hull powder was chemically modified using mercaptoacetic acid. The adsorption kinetics showed that the removal of Hg(II) by raw and chemically modified powder was rapid, and sorption equilibrium was achieved at 90 min. Batch adsorption experiments confirmed that the adsorption capacity of modified powder for Hg(II) was about twice that of raw powder. Hg(II) removal by raw and chemically modified powder followed pseudo-second-order kinetics. The equilibrium data obtained from the adsorption of Hg(II) onto raw and chemically modified powder fitted well with the Langmuir, Freundlich, and Temkin isothermic models. The FTIR spectra and S contents of raw and chemically modified powder showed that mercapto groups were grafted onto the cellulose in the peanut hulls. FTIR spectra also revealed that mercapto groups, together with hydroxyl and carboxyl groups, were the function groups of Hg(II) biosorption onto chemically modified peanut hull powder. Therefore, chemical modification of raw peanut hull powder was an effective way to improve the removal efficiency of Hg(II) ions from aqueous solutions. This is helpful for increasing the use of peanut hulls as a resource.

Acknowledgements

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