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Adsorption of Hg^{2+} and Cd^{2+} by ethylenediamine modified peanut shells

Yong Liu, Xiaomei Sun, Buhai Li*

Key Laboratory of Analytical Chemistry, The State Ethnic Affairs Commission, College of Chemistry and Materials, South-Central University for Nationalities, Wuhan, Hubei 430074, PR China

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ABSTRACT

In this study, an absorbent material was prepared using peanut shells modified with epichlorohydrin and ethylenediamine. Peanut shells were modified by mixing with 10 mL ethylenediamine, 100 mL water and 1 g $NaCO_3$ per 10 g shells at 60 °C for 2 h. Factors affecting the adsorption behavior of Hg^{2+} and Cd^{2+}, such as pH, initial metal concentration and adsorption time, were then investigated. Results suggested that optimal Hg^{2+} adsorption by modified peanut shells can be obtained by adding 0.2 g modified peanut shells per 25 mL of 10 mg/L Hg^{2+} and mixing at a fixed pH of 3.0 for 30 min. The adsorption rate was merely 37%, while after modification the adsorption rate can reach 100% for Hg^{2+}. Data also suggested that separation of Hg^{2+} and Cd^{2+} can be achieved by maintaining the solution acidity to less than pH 2.5.

1. Introduction

With the rapid increase of global industrial activities, heavy metal pollution has seriously damaged the environment and endangered human health (Chen & Wang, 2004). Typical heavy metal pollutants, such as Hg^{2+} and Cd^{2+}, come from various industrial sources including electroplating, metal finishing, textile, storage batteries, lead smelting, mining, plating, ceramics and glass manufacturing. Due to their harmful effects to human and the ecosystem, research on removal of Hg^{2+} and Cd^{2+} from wastewater has become one of the hot topics in recent years. A plethora of methods for heavy metal removal have been reported, e.g. chemical precipitation, membrane filtration, ion exchange, liquid extraction and electrodialysis (Sitting, 1981; Patterson, 1985). However, none of these methods has been widely used due to the relatively high cost and low feasibility for small-scale industries. In contrast, the adsorption technique has become one of the most preferred methods for removal of heavy metals due to its high efficiency and low cost.

China ranks first in peanut production in the world and a potential of 4.5 million tons of peanut shells are produced annually (Tao & Liu, 2008). As an agricultural waste, most of the peanut shells were either sludged for fuel or abandoned, resulting in a tremendous waste of natural resources. The comprehensive utilization of peanut shells also has direct impact on the value of peanuts. Recently, interests in developing peanut shells for wastewater treatment have been reported by several studies (Brown, Atly Jefcoat, Parrish, Gill, & Graham, 2000; Johnsona, Watsona, Browna, & Jefcoatb, 2002; El-Shafey, 2007). Other agricultural wastes had directly been used as sorbents for heave metal adsorption from wastewater, which included soybean hull (Laszlo & Dintzis, 1994), olive cake (Doyurum & Elik, 2006), wheat straw (Kumar, Rao, & Kaul, 2000), maize cob (Abia & Igwe, 2005), rice husk (Wong, Lee, Low, & Haron, 2003), barley straw (Pehlivan, Altun, & Parlay, 2009), bagasse pith (Krishnan & Anirudhan, 2003), coconut husk (Babarinde, 2002), Cocoa shells (Meunier, Laroulandie, Blais, & Tyagi, 2003), and tee leaves (Tee & Khan, 1988), orange peel and banana peel (Annadurai, Juang, & Lee, 2002). But few researches had been done about the removal of Hg^{2+} on to agricultural wastes, especially for peanut shells. In this research, we compared the performance of unmodified and modified peanut shells as absorbents to remove Hg^{2+} and Cd^{2+} from the wastewater.

2. Materials and methods

2.1. Materials

The peanut shells used in this study were obtained from the suburban area of Wuhan, China. The collected biomaterial was extensively washed with tap water to remove soil and dust, sprayed with distilled water and then dried in an oven at 50 °C to a constant weight. Dry biomass was crushed into powder, sieved into 100–120 meshes.

The Hg^{2+} stock solution (500 mg/L) was prepared by dissolving $HgCl_2$ in deionized water and acidified with concentrated HCl to prevent hydrolysis. The Cd^{2+} stock (500 mg/L) was prepared by

* Corresponding author. Tel.: +86 276 784 1306; fax: +86 276 784 1306.
E-mail address: Sunxm311@yahoo.com.cn (B. Li).

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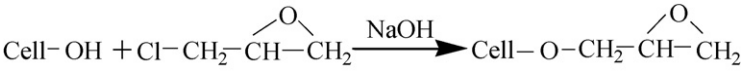
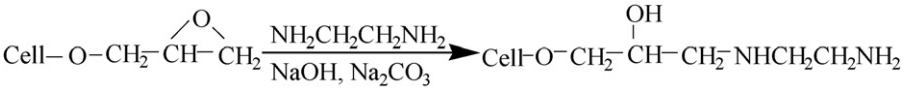
dissolving $Cd(NO_3)_2$ in deionized water and acidified with concentrated HNO_3 to prevent hydrolysis. The two stock heavy metal solutions were diluted with deionized water to various working concentrations for adsorption test.

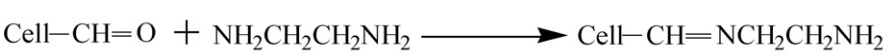
2.2. Preparation of adsorbent

Ten grams of peanut shells were mixed with 80 mL of NaOH solution (1.25 mol/L) and 30 mL of epichlorohydrin at 40 °C for 1 h. The mixture was then filtered, rinsed with water, oven-dried and stored in a desiccator (Li, Zhang, & Fan, 2008). During the mixing, the hydroxyl groups of cells in the peanut shells reacted with epichlorohydrin. The chemical equation is shown below:



Modified peanut shells (MPS) were prepared by adding 10 mL ethylenediamine solution, 100 mL water and 1 g $NaCO_3$ to each 10 g peanut shells modified with epichlorohydrin. The mixture was then mixed by agitation at 60 °C for 2 h. Modified peanut shells were oven-dried and stored in a desiccator (Wang & Song, 2009). The following chemical equations show the reactions occurred during the modification.





2.3. Equipments and characterization method

A fluorescent electron microscope (Nikon SMZ1500, Nikon, Japan) was employed to study the surface morphology of peanut shells. Infrared spectra of unmodified and modified peanut shells were obtained from a FT-IR spectrophotometer (Nicolet NEXUS 470, Nicolet Co., Ltd., USA) with KBr disks. A systronic microprocessor pH meter (pHS-3C, Shanghai Leizi Instrument Factory, China) was used for pH measurements. A temperature controlled water bath flask shaker (SHZ-03, Shanghai Kanxin Instrument Factory, China) was used for mixing of all solutions. Concentration of Cd^{2+} in all solutions was determined with an AA-6300 atomic absorption spectrophotometer (AAS, Shimadzu, Japan). Concentration of Hg^{2+} in all solutions was determined with a UV–vis spectrophotometer (Liu, Huang, & Dong, 1999) (LAMBDA B10 35, PerkinElmer, USA).

2.4. Adsorption assay

Batch adsorption experiments of Hg^{2+} and Cd^{2+} by peanut shells were performed in closed flasks inside a water bath flask shaker at room temperature. In this study, 0.2 g adsorbent was put into a 50 mL flask containing 25 mL heavy metal solution of predetermined initial Hg^{2+} and Cd^{2+} concentrations and various pH (1.0–7.0). The initial pH of the solution was adjusted to the desired value by addition of small amount of 0.1 N HCl or NaOH. The mixture was shaken at 150 rpm at desired temperature before it was centrifuged. Cd^{2+} and Hg^{2+} concentrations of the supernatants were then determined.

2.5. Adsorption kinetic model

In an attempt to present the kinetic equation representing adsorption of heavy metals on unmodified and modified peanut shells, second-order equation was used to test the experimental data.

Kinetics data were calculated with the following second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_i q_e^2} + \frac{t}{q_e} = \frac{1}{q_0} + \frac{t}{q_e} \quad (1)$$

where k is the rate constant of the second-order equation (g mg/min); v_0 is the initial rate of adsorption; q_t (mg/g) is the amount of adsorption at time t (min); q_e is the amount of adsorption at equilibrium (mg/g).

2.6. Adsorption isotherms

The adsorption isotherm is based on the assumptions that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not adjacent sites are occupied. An adsorption process is usually described by the following two widely used isotherms:

(a) Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{b_i q_m} + \frac{C_e}{q_m} \quad (2)$$

where C_e is the equilibrium concentration (mg/L); q_e is the amount adsorbed at equilibrium (mg/L); q_m (mg/L) and b (L/mg) are Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively.

(b) Freundlich isotherm:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where q_e is the amount of metal ions adsorbed per unit mass of the adsorbent, C_e the equilibrium solution concentration, K_F and n are Freundlich equilibrium coefficients. For favorable adsorption, $0 < 1/n < 1$, while $1/n > 1$ represents unfavorable adsorption, and $1/n = 1$ indicates linear adsorption. If $n = 0$, the adsorption process is irreversible.

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. FT-IR spectra

Infrared spectroscopy provides information on the chemical structure of the adsorbent material. As shown in Fig. 1, the most characteristic change in peanut shells after modification was observed in the range of 1720–3360/cm. The 3360/cm band is attributed to the stretching vibrations of hydroxyl group (OH); the band centered at 1740/cm is due to the stretching vibrations of carboxyl groups (C=O). As expected, the C=O band at 1740/cm disappeared and the relative intensity of OH band decreased in the FI-IR spectra of MPS. This result indicated that MPS had gone through the modification reactions mentioned earlier in the method section.

3.1.2. X-ray photoelectron (XP) spectra

To better understand the surface chemical characteristics of MPS, X-ray photoelectron spectroscopy was employed for high resolution spectra (Fig. 2). Deconvolution of the N(1s) spectra yielded three main peaks: peak 1 (399.3 eV), —NH or —NH_2; peak

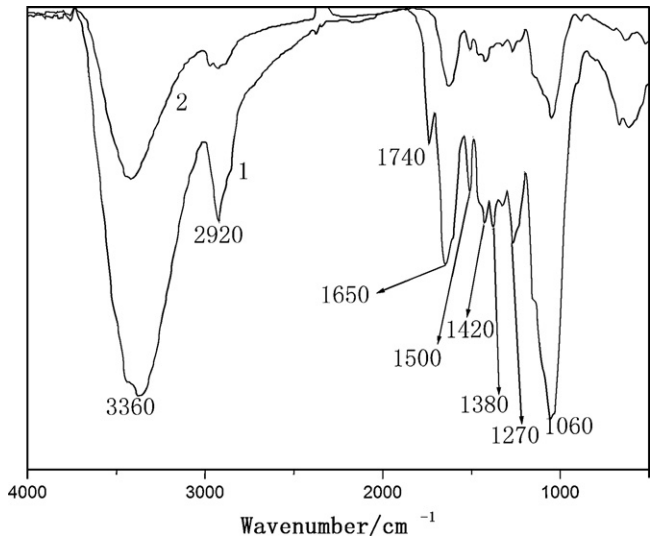


Fig. 1. FTIR spectra of the peanut shell before (1) and after (2) modification.

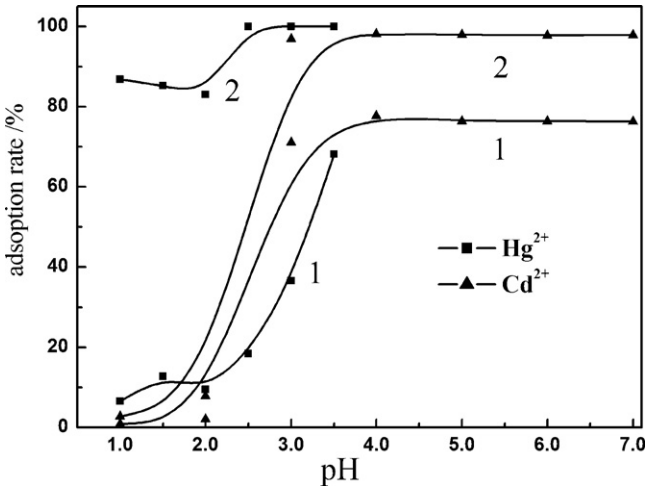


Fig. 3. Effect of pH on the adsorption rate of Hg^{2+} and Cd^{2+} by peanut shells before (1) and after (2) modification. (Adsorption time 60 min, adsorption amount 0.2 g, initial metal ions10 mg L^{-1}.)

2 (400–401 eV), —N=; peak 3 (401–402 eV), $—NH_2^+$ or $—NH_3^+$. Protonation of the amine groups may explain why the modified peanut shells have improved adsorption of Hg^{2+} under low pH conditions.

3.2. Adsorption experiments

3.2.1. Effect of pH on metal ion removal

PH of the aqueous solution is one of the most important controlling parameters in the adsorption process. It not only affects the surface properties of the adsorbent, but also influences the form of metal ions in a solution. Based on calculation, in order to prevent the hydrolysis of metal ions, pH of the adsorption solution containing Hg^{2+} should be between 1.0 and 3.5. For Cd^{2+}, it should be between 1.0 and 7.0. In this study, the removal rates of Hg^{2+} and Cd^{2+} by PS and MPS were tested in the pH range of 1.0–7.0 (Fig. 3). As shown, the adsorption rates of both peanut shells increased as the solution pH increased. Absorption rate of PS was more easily affected by acidity, while lower pH had smaller impact on MPS adsorption. When pH was less than 2.5, mercury forms chloro-complexes due to high chloride concentration. At lower pH, the Hg^{2+} removal rate by MPS was over 85%, while it was almost negligible by PS, suggesting that the electrostatic attraction mechanism might be involved in the uptake of mercury chloro-complexes by the protonated amine groups of the modified peanut shells (Chassary, Vincent, Marcano, Macaskie, & Cuibal, 2005). When pH was higher than 2.5, the increased adsorption of Hg^{2+} by MPS might be due to the electrostatic attraction of chloro-anionic species by the protonated amine groups and simultaneous chelation of metals by Schiff base groups. Data showed that the modified peanut shells can be applied to a wider range of acidity of the water body. When pH was less than 2.5, Hg^{2+} had much higher adsorption rate, while it was almost negligible for Cd^{2+}. Therefore, Hg^{2+} and Cd^{2+} can be selectively separated from the solution by MPS.

3.2.2. Effect of adsorption time

Fig. 4 illustrates effect of the adsorption time on Hg^{2+} and Cd^{2+} uptake by PS and MPS. Adsorption of Hg^{2+} and Cd^{2+} showed an increasing trend up to a reaction time of 30 min beyond which adsorption appeared to have approached equilibrium. After 1 h, the adsorption capacity of Cd^{2+} by PS and MPS was still increasing. After

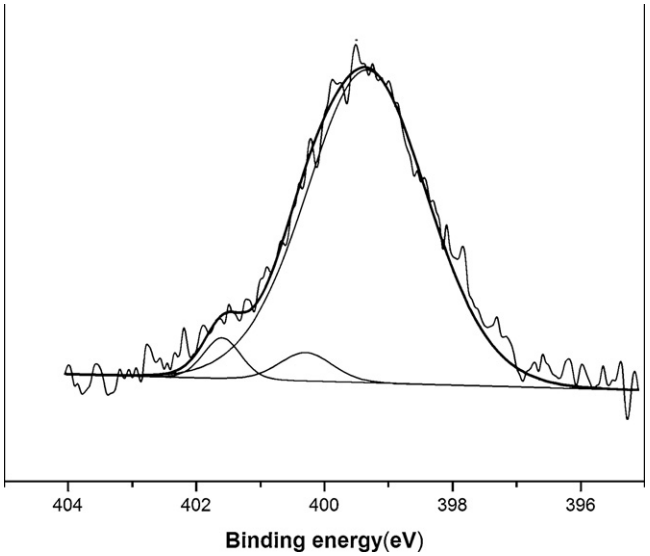


Fig. 2. N(1s) spectra of the modified peanut shell after adsorption of Hg^{2+}.

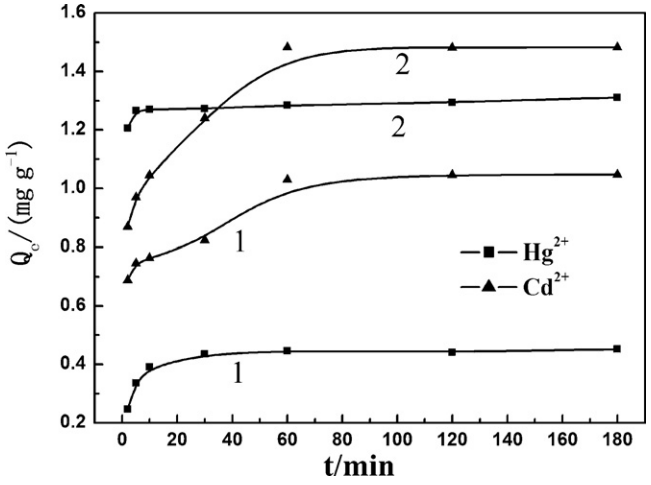


Fig. 4. Effect of time on the adsorption rate of Hg^{2+} and Cd^{2+} by unmodified (1) and modified (2) peanut shells. (Initial metal ions10 mg L^{-1}, adsorption amount 0.2 g, pH 3.0 (Hg^{2+}), pH 4.0 (Cd^{2+}).)

Table 1
Kinetic parameters in the pseudo-second-order equations for Cd^{2+} and Hg^{2+} adsorption by unmodified (PS) and modified (MPS) peanut shells.

Absorbent	Adsorbate	q_e (mg/g)	v_0 (mg/g min)	$q_{e,c}$ (mg/g)	R^2
PS	Cd^{2+}	1.066	0.277	1.077	0.9998
MPS	Cd^{2+}	1.483	0.509	1.502	0.9997
PS	Hg^{2+}	0.452	0.279	0.454	0.9998
MPS	Hg^{2+}	1.312	2.352	1.310	0.9999

Table 2
Langmuir and Freundlich isotherm constants for Cd^{2+} and Hg^{2+} adsorption by unmodified and modified peanut shells (MPS).

Absorbent	Adsorbate	Langmuir coefficient			Freundlich coefficient		
		b (L/mg)	q_m (mg/g)	R^2	K_F	$1/n$	R^2
PS	Cd^{2+}	0.541	6.00	0.9996	2.752	0.1807	0.6360
MPS	Cd^{2+}	0.3608	14.17	0.9987	5.799	0.2006	0.6494
PS	Hg^{2+}	0.058	1.90	0.9977	0.3340	0.3242	0.9313
MPS	Hg^{2+}	0.011	30.72	0.9904	0.6099	0.6822	0.9743

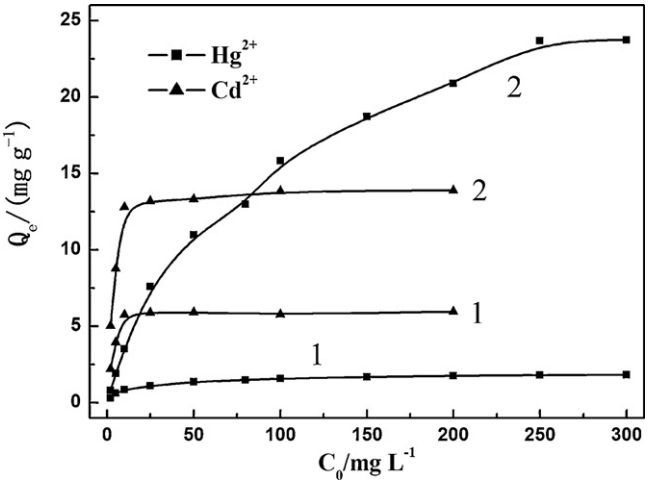


Fig. 5. Hg^{2+} and Cd^{2+} adsorption isotherms of peanut shells before (1) and after (2) modification. (Adsorption time 60 min, adsorption amount 0.2 g, pH 3.0 (Hg^{2+}), pH 4.0 (Cd^{2+}).)

2 h, two of them got equilibrium. The rate of uptake of Hg^{2+} by PS and MPS was faster than Cd^{2+}.

3.2.3. Effect of initial concentration

Fig. 5 shows the adsorption isotherm of Hg^{2+} and Cd^{2+} by PS and MPS at 298 K. The adsorption rate of peanut shells increased when the initial concentration of Hg^{2+} and Cd^{2+}increased. Thereafter, the adsorption capacity gradually reached equilibrium.

3.2.4. Adsorption kinetic model

Table 1 compares values of q_e, v_0, the calculated amount of adsorption at equilibrium ($q_{e,c}$) and the determined coefficient (R^2) of the two peanut shell types. The second-order equation appeared to be a good fitting model, as the calculated amount of adsorption at equilibrium ($q_{e,c}$) was similar to the actual amount of adsorption at equilibrium (q_e). The adsorption rate varied due to different metal concentrations at different activated sites on the surface of the adsorbent.

3.2.5. Adsorption isotherms

Langmuir equation was applied for the adsorption equilibrium of both PS and MPS. Equilibrium data obtained from the two adsorbents were fitted to the Langmuir isotherm equation. As presented in Table 2, the high values of correlation coefficient (R^2) for both PS and MPS indicated good agreement between experimental and predicted data using the Langmuir equation. q_m and b were determined from the Langmuir plots and listed in Table 2. It is worth mentioning that the ratio of q_m values of MPS over PS was 12.9 for Hg^{2+}, indicating a significantly improved adsorption capacity of the MPS.

3.3. Test with simulated wastewater

Feasibility of heavy metal removal by MPS was demonstrated by applying MPS to a simulated wastewater. The polluted water sample (25 mL tap water containing 10 mg/L Hg^{2+}) was found to be Hg^{2+} free after treated with 0.2 g of MPS at pH 3.0 for 30 min.

4. Conclusion

Hg^{2+} and Cd^{2+} can be adsorded rapidly by peanut shells modified with epichlorohydrin and ethylenediamine. FT-IR spectra of MPS showed that amine and hydroxyl groups were involved in the modification reactions. Separation of Hg^{2+} and Cd^{2+} can be achieved by controlling the solution pH (<2.5). The optimal condition of Hg^{2+} adsorption by MPS is pH 3.0 and 30 min of shaking. Under this condition, 25 mL of 10 mg/L Hg^{2+} can be absorbed by 0.2 g modified peanut shells. The maximum mercury adsorption rate by PS was merely 37%, while the adsorption rate of MPS can reach 100%. The isothermal data were in agreement with the Langmuir equation for the present system. High efficiency and low cost of this system suggested that peanut shells can not only be modified for heavy metal removal in waste water and many other polluted environments, but be utilized to improve the overall economic efficiency of peanut agriculture.

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