

# Longan Shell as Novel Biomacromolecular Sorbent for Highly Selective Removal of Lead and Mercury Ions

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Strongly selective adsorbability of natural longan (*Euphoria longan*) shell as a biomacromolecular sorbent toward heavy metal ions from aqueous solutions has been discovered and successfully optimized by facilely controlling the shell dosage, sorption time, pH value, and ion concentration. The sorption well-fits the Langmuir isotherm and obeys the pseudo-second-order kinetics. The maximum adsorptivity of Pb(II) and Hg(II) is 99.3 and 99.1%, respectively, with short equilibrium sorption time. The redox sorption mechanism of Pb(II) and Hg(II) ions onto longan shell was proposed on the basis of IR and X-ray diffraction analyses. In particular, a slow but durative redox interaction between Pb(II) ions and longan shell was revealed even at a solid state, resulting in the formation of Pb(syn) crystals onto longan shell. Competitive sorption suggested that the shell demonstrated a preferential sorption to Pb(II) over Hg(II) in their mixture solution, despite higher adsorptivity of Hg(II) than Pb(II) in corresponding pure solutions. The shell displayed highly selective sorption to Pb(II) over light metal ions with an adsorbability order of Pb(II) > Hg(II)  $\gg$  Zn(II) > Cu(II) > Ca(II) > Mg(II)  $\gg$  Fe(III,II), indicating that the shell could efficiently purify drinking water and nutritious liquids by just eliminating the harmful metal ions and still retaining the nutritious metal ions. The printery sewage and polluted river water both meet the discharge standard after being treated once with longan shell, and even satisfy the standards for irrigation/fishery and drinking water, respectively, after being treated twice. A large amount of functional groups like hydroxyl, ether, and carbonyl in the longan shell, as well as its intrinsic hydrophilicity, are responsible for the strong adsorbability toward the heavy metal ions. Not only does the longan shell have low cost and have inherent environmental friendliness in contrast to all synthetic and even seminatural sorbents but it also has stronger adsorbability toward Pb(II) and particularly Hg(II) ions than the most natural sorbents reported, making longan shell attractive as a highly cost-efficient sorbent for the selective removal of hazardous heavy metal ions.

## Introduction

With the rapid development of industrialization, heavy metals, as important materials, play an increasingly vital role in industrial production. Unfortunately, most of them, such as mercury, lead, and so on, are among the most feared contaminants in water sources that are beginning to cause severe public health problems nowadays.<sup>1–5</sup> Heavy metal ions are being released into the environment thus affecting ecological life because they tend to accumulate in organisms and exhibit a high toxicity when adsorbed into the body. Therefore, serious water pollution from hazardous heavy metals is becoming one of the toughest problems which have attracted rather considerable attention. The removal of heavy metal ions from aqueous solution has traditionally been carried out by several techniques, such as reverse osmosis, neutralization–precipitation, and ion exchange,<sup>6</sup> among which sorption<sup>7–9</sup> has shown to be an effective and economically feasible alternative method. Natural sorbents may have a potential marketing advantage in the wastewater treatment over other sorbents including synthetic sorbents, because natural biomass is much cheaper, more

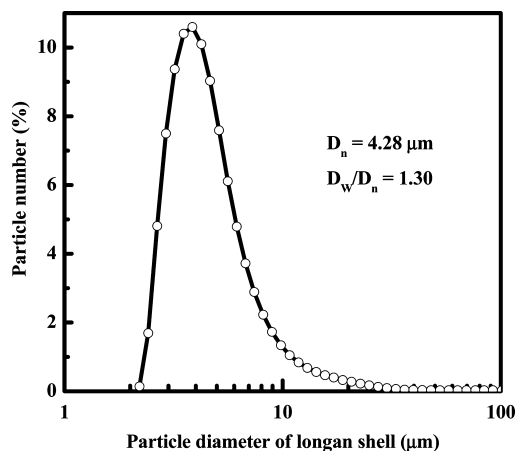
biosafe, and much more environmentally friendly than traditional activated carbon, and ion exchange resins.<sup>5,10</sup>

In recent years, the research of waste biomass from our daily life and production has aroused much attention. As a sorbent of heavy metal ions, the waste biomass is not only inexpensive and harmless but also able to powerfully adsorb the heavy metal ions from aqueous solution. Most of the natural biomacromolecular sorbents include cellulose and lignin or chitin and chitosan, which can strongly adsorb the heavy metal ions. At present, egg shell, millet shell, wastepaper, sawdust, straw, and nonliving algal biomass are all used for the removal of the heavy metal ions. It is reported that the highest adsorptivity of mercury ions at initial concentration of 200 mg L<sup>−1</sup> on natural chitosan is 55%.<sup>11</sup> A condensation product between glutaraldehyde–chitosan and sulfhydryl alanine exhibits the maximal sorption capacity of mercury ions of up to 1600 mg g<sup>−1</sup> at an initial Hg-ion concentration of 290 mg L<sup>−1</sup>.<sup>12</sup> It appears that the chemically modified chitosan would be one of the best seminatural sorbents of mercury ions, but with an accompanying loss of an advantage of low cost as compared with the purely natural sorbents. Similarly, a time-consuming process of pretreatment also largely increases the utilization cost of the nonliving algal biomass *Oedogonium* sp. and *Nostoc* sp. as sorbents.<sup>13,14</sup>

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**Figure 1.** Size distribution of the longan shell particles used in this study.

In this study, longan shell was used as an environmental friendly sorbent of the metal ions for the first time in order to satisfactorily remove toxic heavy-metal ions from the aqueous solution by making full use of daily waste with very low cost. Longan, as a kind of tropical fruit belonging to the soapberry family (*Sapindaceae*), is native to Southern Asia and has been introduced into other warm regions of the world. Regrettably, many longan shells are wasted without any reasonable utilization every year. Longan shell includes plenty of cellulose, lignin, and a few flavonoids, which favorably endow longan shell with excellent ability to strongly and efficiently remove the heavy-metal ions from their aqueous solutions.

## Experimental Section

**Chemical Reagents.**  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{CuSO}_4$ ,  $\text{FeCl}_3$ ,  $\text{ZnSO}_4$ , and other chemicals of analytical reagent grade were commercially obtained and used as received. Fresh longan, dried longan, and dried litchi were bought from a Shanghai supermarket, China. Further these materials were washed with distilled water, dried, and crushed before sorption. The size distribution of the longan shell used in this study was shown in Figure 1. A stock  $\text{Pb}(\text{II})$  solution of  $1000 \text{ mg L}^{-1}$  was prepared by dissolving  $\text{Pb}(\text{NO}_3)_2$  in demineralized water. The other metal-ion solution was prepared in a similar way. For the sorption experiments, a  $10 \text{ mM}$  standard solution of ethylenediaminetetraacetic acid (EDTA) was prepared and calibrated with anhydrous sodium carbonate. The various concentrations needed in the experiments can be obtained by diluting the standard solutions. The pH of the solution was adjusted by adding  $\text{NaOH}$  or  $\text{HNO}_3$  solutions as required.

**Sorption Experiments.** A typical sorption procedure is as follows: after the longan shell particles of  $300 \text{ mg}$  were added to  $25 \text{ mL}$  of lead-ion aqueous solution, the suspension was stirred for  $2 \text{ h}$  in a water bath at  $30^\circ\text{C}$ . The particles were filtered from the aqueous solution, and then the concentration of  $\text{Pb}(\text{II})$  ions in the filtrate was measured by a direct complex titration based on EDTA.<sup>15</sup>

**Real Water Sample Treatment.** To purify practical environmental wastewater,  $25 \text{ mL}$  of water of a tributary (Zou-Ma-Tang near Tongji University) of the Huangpu River, Shanghai, China, was treated for  $2 \text{ h}$  at  $30^\circ\text{C}$  with  $300 \text{ mg}$  of longan shell as the sorbent after a simple filtration in order to remove solid waste.

The real wastewater from Printing House in Fudan University, Shanghai, China, was also purified so as to further confirm the

**TABLE 1: Adsorptivity of  $\text{Pb}(\text{II})$  Ions on Three Typical Shells in  $25 \text{ mL}$  of  $\text{Pb}(\text{NO}_3)_2$  Solution at the Initial  $\text{Pb}(\text{II})$  Concentrations from  $100$  to  $400 \text{ mg L}^{-1}$  under the Sorption Conditions of  $30^\circ\text{C}$  and  $2 \text{ h}$**

initial $\text{Pb}(\text{II})$ concentration ( $\text{mg L}^{-1}$ )	$\text{Pb}(\text{II})$ adsorptivity (%)		
	dried longan shell	fresh longan shell	dried litchi shell
100	84.2	84.5	79.3
200	83.3	83.0	78.4
400	79.8	80.2	71.6

applicability of longan shell as a powerful biosorbent. The wastewater was collected from washing water for a printing machine and consequently contained some oil. Therefore, the real water sample was filtered three times before the same treatment by longan shell for the removal of oil. The concentration of various residual ions in the real water was simultaneously analyzed by inductively coupled plasma (Hitachi P-4010 ICP) mass spectrometry.

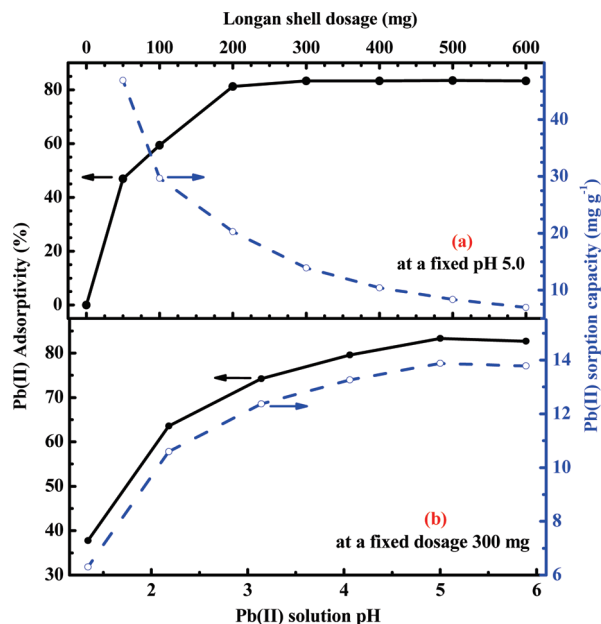
**Characterization.** The size and its distribution of the longan shell particles in water were analyzed by a Beckman Coulter LS230 laser particle-size analyzer (LPA). The concentration of  $\text{Pb}(\text{II})$ ,  $\text{Fe}(\text{III})$ , and  $\text{Zn}(\text{II})$  ions in the filtrate was measured by a direct complex titration based on EDTA,<sup>15</sup> but the mercury-ion concentration was measured by the same method but based on  $\text{NaSCN}$ .<sup>16</sup> The  $\text{Cu}(\text{II})$  concentration in the filtrate was measured by a back-titration based on EDTA. When the lead- and mercury-ion concentrations in the filtrate are less than  $50 \text{ mg L}^{-1}$ , a Hitachi P-4010 ICP technique was used instead. IR spectra of the longan shell particles were recorded on a Nicolet Magna 550 FTIR spectrometer at  $2 \text{ cm}^{-1}$  resolution. Wide-angle X-ray diffractograms were gained by a D/max 2550 model X-ray diffractometer with  $\text{Cu K}\alpha$  radiation of X-ray wavelength of  $1.5418 \text{ \AA}$  over a  $2\theta$  range from  $5$  to  $70^\circ$ .

## Results and Discussion

**Longan Shell as Environmental Friendly Sorbents.** The  $\text{Pb}(\text{II})$  sorption results were summarized in Table 1 to investigate the possibility of different kinds of fruit shells as environmental friendly sorbents. The fresh and dried longan shells at an initial  $\text{Pb}(\text{II})$  concentration of  $200 \text{ mg L}^{-1}$  have a similar adsorptivity that is larger than the dried litchi shell. Because the fresh longan shell is preserved with difficulty and not obtained at any time as expected, the dried longan shell simply called longan shell for the following investigation was carefully chosen as the sorbents in this work.

Note that the color of the filtrate after sorption changed from colorless clear to light yellow. To investigate whether the water-soluble part of the longan shell contributes to the sorption of heavy-metal ions, the longan shell prewashed in distilled water at  $30^\circ\text{C}$  for  $2 \text{ h}$  was used in the sorption. Almost the same adsorptivity as those in Table 1 was observed, confirming that the water-soluble fraction of the longan shell does not contribute to the sorption. Therefore, the longan shell powder pretreated with distilled water was used in the following study.

**Sorption of  $\text{Pb}(\text{II})$  Ions onto Longan Shell. Effect of Longan Shell Dosage.** The effect of longan shell dosages was carefully analyzed and shown in Figure 2a. The adsorptivity augments rapidly with increasing dosage from  $0$  to  $200 \text{ mg}$  and then reaches a plateau of up to  $83.3\%$  at the dosage above  $200 \text{ mg}$ . However, unilaterally increasing the shell dosage leads to a monotonic decrease of the sorption capacity and thus to a waste of sorbent. Nonliving algal biomass *Oedogonium* sp. and *Nostoc* sp.<sup>14</sup> and orange peel cellulose adsorbents<sup>17</sup> demonstrate



**Figure 2.** Effect of the longan shell dosage (a) and the solution pH value (b) on sorption of Pb(II) ions at 30 °C in 25 mL of Pb(NO<sub>3</sub>)<sub>2</sub> solution at an initial Pb(II) concentration of 200 mg L<sup>-1</sup> for 2 h.

similarly decreased sorption capacity with increasing dosage. Because the longan shell is a kind of waste material, the cost hardly ever rises with an increase in the longan shell dosage. Therefore, we do not have to balance sorption capacity and adsorptivity for the optimization of the dosage. As a result, 300 mg of the longan shell has been chosen as optimal dosage in the following investigation. This is different from synthetic sorbents and some graft copolymers, such as poly(diaminonaphthalene),<sup>18</sup> cross-linked chitosan with epichlorohydrin,<sup>19</sup> and poly(vinyl pyridine)-poly(ethylene glycol methacrylate-co-dimethacrylate) beads.<sup>20</sup> Compared with other natural adsorbents, including olive stone waste<sup>21</sup> and pomegranate peel,<sup>22</sup> the longan shell has lower optimal dosage and hence is a more efficient natural sorbent.

Contrastive experiments were carefully performed to investigate why the adsorptivity does not increase with further increasing longan shell dosage. Longan shell powder of 200 mg was added into Pb(II) solution of 25 mL and stirred for 2 h, and the filtrate obtained thus was again retreated with another longan shell powder of 200 mg for another 2 h. The whole Pb(II) adsorptivity discovered thus can reach up to 94.0%, which is apparently larger than that (83.3%) in one-portion sorption shown in Figure 2a. When much shell powder was used in one portion, a particle conglomeration would cause an incomplete exposition of the active sites of the particle surface. As a result, when longan shell is used to adsorb the heavy-metal ions from the real wastewater, multiple-low-dose addition of longan shell powder may be the best way.

**Effect of Solution pH.** The pH of the solution seems to be an important parameter in the sorption process.<sup>13</sup> In this study, the initial pH of the Pb(NO<sub>3</sub>)<sub>2</sub> solution was adjusted between pH 1.0 and 6.0 by adding various concentrations of HNO<sub>3</sub> or NaOH. When the value is higher than pH 6.0, Pb(OH)<sub>2</sub> precipitates can be observed, which strongly interfere in the sorption process. The variation of Pb(II) sorption with the pH value of Pb(NO<sub>3</sub>)<sub>2</sub> solution was studied at an initial Pb(II) concentration of 200 mg L<sup>-1</sup> at 30 °C for 2 h. The results presented in Figure 2b showed that the optimum uptake of Pb(II) ion by the longan shell appeared at pH 5.0. It is observable

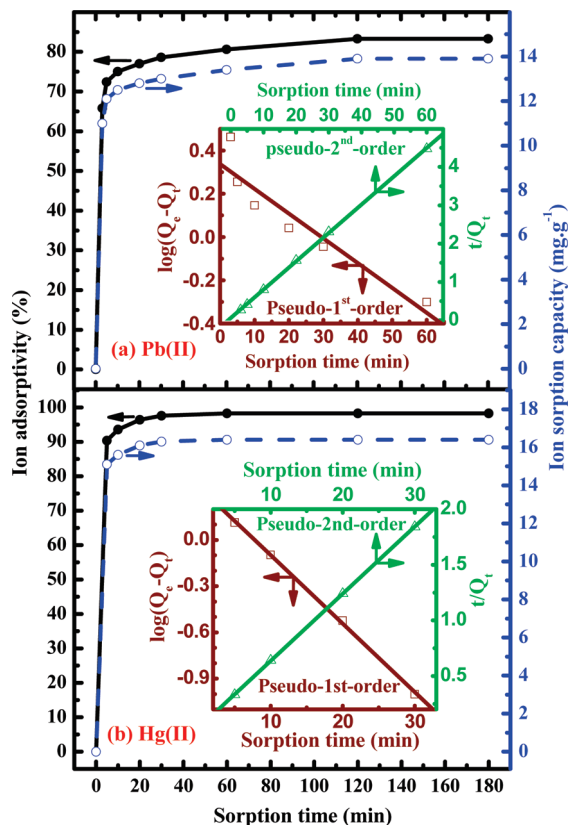
that the sorption capacity and adsorptivity of Pb(II) ions both tend to increase with augmenting pH from 1.3 to 5.0, but their increasing rate declined gradually. Consequently, both the sorption capacity and adsorptivity slightly diminished when the pH further rose to 5.9. Similar phenomena have been earlier recorded for the nonliving algal biomass *Oedogonium* sp. and *Nostoc* sp. as a kind of heavy-metal-ion sorbent.<sup>14</sup> As a result, the following sorption experiments were all performed at an optimized solution pH of 5.0.

The pH value can affect the existence form of metal ions and the activity of the functional groups on the longan shell sorbents. At low pH, the Pb(II) ions competed with the protons on the binding sites of the surface functional groups, which is disadvantageous for the approach of the Pb(II) ions.<sup>23</sup> As pH rises, the competing effect of proton decreases and then positively charged metal ions have more opportunity to take up the free binding sites, resulting in an improved Pb(II) uptake capacity. However, at a very high value of up to pH 5.9, the Pb(II) ions will begin to hydrolyze and hence form a small amount of PbOH<sup>+</sup>, Pb(OH)<sub>2</sub>, or Pb(OH)<sub>3</sub><sup>-</sup> varieties via combination with OH<sup>-</sup>. Compared with free Pb<sup>2+</sup> ions, these ion varieties are disadvantageous for sorption, especially for anion hydrolysate, which accounts for the slight decline in approximately neutral Pb(II) solution. Accordingly, there were maximal sorption capacity and adsorptivity of Pb(II) ions at pH 5.0. Apparently, pH 5.0 was chosen as the best pH for the Pb(II) sorption onto the longan shell sorbent.

**Effect of Sorption Time and Sorption Kinetics.** One of the most important parameters that significantly describe sorbent characteristics is sorption time. The effect of contact time on the sorption of Pb(II) ions onto the longan shell particles at an initial Pb(II) concentration of 200 mg L<sup>-1</sup> at 30 °C is displayed in Figure 3a. The sorption capacity and adsorptivity of Pb(II) ions onto the shell both augment extremely rapidly in the initial 5 min, but augment only slightly in the sorption time from 5 to 120 min. The highest sorption capacity and adsorptivity of up to 13.9 mg g<sup>-1</sup> and 83.3%, respectively, appear at the sorption time of 120 min. Obviously, the sorption process can be divided into two steps: a primary rapid step and a secondary slow step. The initial rapid step lasts for only 5 min but surprisingly contributes 87% to the adsorbability maximum. The fast step of Pb(II) sorption may occur on the particle surface due to an immediate interaction. The sorption reached the equilibrium at the sorption time of 120 min, which is slightly longer than some synthetic sorbents such as poly(phenylenediamine)<sup>18</sup> and poly(2-hydroxyethyl methacrylate-methacryloylamidohistidine).<sup>24</sup>

Batch kinetics analysis of Pb(II) removal can be used to predict the practical applicability of sorbent. Several kinetic models are available to examine the controlling mechanism of sorption, which is important for the efficiency evaluation of the sorption process. The rate constant of metal-ion sorption from solution onto the longan shell was determined using the pseudo-first-order and pseudo-second-order equations. The curves of  $\log(Q_e - Q_t)$  and  $t/Q_t$  versus  $t$  based on the data during the contacting time from zero to 60 min in Figure 3 provide the corresponding parameters, as listed in Table 2. It can be seen that the application of the pseudo-second-order model correlates better with the experimental data because of higher correlation coefficient and smaller difference between theoretical  $Q_e$  (13.5 mg g<sup>-1</sup>) and experimental  $Q_e$  (13.9 mg g<sup>-1</sup>) than the pseudo-first-order model. Besides, both the sorption capacity and adsorptivity of the Pb(II) rise extremely rapidly in the initial sorption time of 5 min in Figure 3, which is completely coincident with the much faster initial sorption rate (16.1 mg



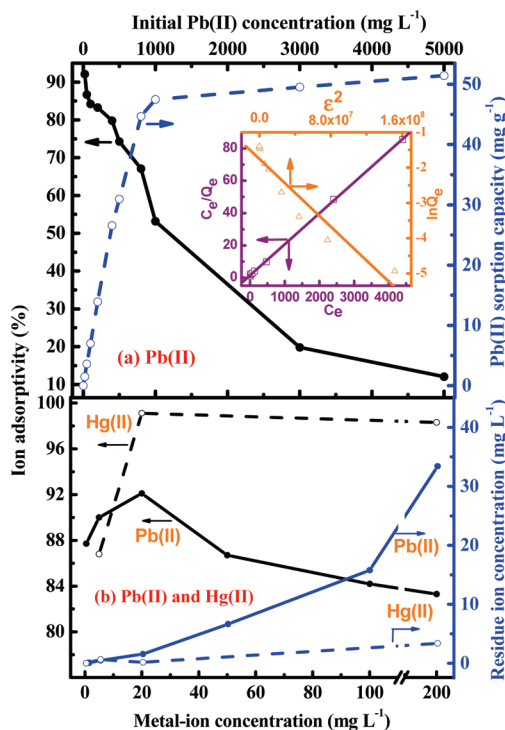


**Figure 3.** Effect of sorption time on Pb(II) sorption (a) and Hg(II,I) sorption (b) onto the longan shell at 30 °C in 25 mL of Pb(NO<sub>3</sub>)<sub>2</sub> (a) and Hg(NO<sub>3</sub>)<sub>2</sub> (b) solutions with a shell dosage of 300 mg at an initial Pb(II) (a) or Hg(II) (b) concentration of 200 mg L<sup>-1</sup> at pH 5.0. Inset: The pseudo-first-order and pseudo-second-order plots of the sorption data.

g<sup>-1</sup> min<sup>-1</sup>) calculated by the pseudo-second-order equation. Thus the sorption is more appropriately described by a pseudo-second-order kinetics model based on the assumption that the rate-limiting step may be chemical sorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate. The IR and X-ray analyses of the Pb(II)-adsorbing longan shell indeed testify to a chemically reactive redox sorption of Pb(II) ions onto longan shell, as discussed below. Particularly, the initial sorption rate of Pb(II) ions onto the longan shell is 16.1 mg g<sup>-1</sup> min<sup>-1</sup> that is higher than that onto other natural sorbents listed in Table S1 of the Supporting Information and even polymer-grafted banana (*Musa paradisical*) stalk<sup>37</sup> but lower than that onto some synthetic sorbents such as poly(phenylenediamine).<sup>22</sup> Many functional groups on the longan shell should be responsible for the fast initial sorption of Pb(II).

**TABLE 2: Kinetics and Isotherm Model Equations for Pb(II) and Hg(II,I) Sorption onto Longan Shell Based on the Data in Figures 3 and 4**

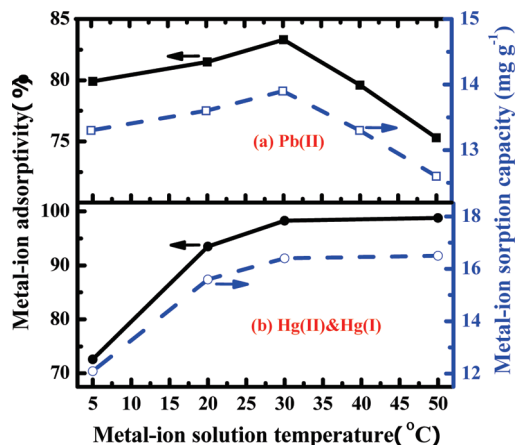
mathematical model	equation	correlation coefficient	$Q_e$ or $Q_m$ (mg g <sup>-1</sup> )	$k'$ (min <sup>-1</sup> ), $h$ (mg g <sup>-1</sup> min <sup>-1</sup> ), $K_a$ (L mg <sup>-1</sup> ), or $E$ (kJ mol <sup>-1</sup> )
Pb(II) Sorption				
pseudo-first-order	$\log(Q_e - Q_t) = -0.0115t + 0.3375$	0.8824	$Q_e = 2.18$	$k' = 0.026$
pseudo-second-order	$t/Q_t = 0.0739t + 0.0623$	0.9998	$Q_e = 13.5$	$h = 16.1$
Hg(II,I) Sorption				
pseudo-first-order	$\log(Q_e - Q_t) = -0.0444t + 0.3457$	0.9991	$Q_e = 2.22$	$k' = 0.10$
pseudo-second-order	$t/Q_t = 0.0603t + 0.0339$	1	$Q_e = 16.6$	$h = 29.50$
Pb(II) Sorption				
Langmuir	$C_e/Q_e = 0.0192C_e + 1.5685$	0.9997	$Q_m = 52.1$	$K_a = 0.0122$
Freundlich	$\log Q_e = 0.4475 \log C_e + 0.3198$	0.8747	$Q_m = 1.38$	
Dubinin–Radushkevich (D–R)	$\ln Q_e = -2 \times 10^{-8}\epsilon^2 - 1.7531$	0.9079	$Q_m = 35.9$	$E = 5$



**Figure 4.** (a) Effect of initial Pb(II) concentration on the Pb(II) sorption onto the longan shell at 30 °C in 25 mL of Pb(NO<sub>3</sub>)<sub>2</sub> solution with a shell dosage of 300 mg at pH 5.0 for 2 h. Inset: Langmuir and D–R plots of the sorption data in the concentration range from 0 to 5000 mg L<sup>-1</sup>. (b) Sorption of Pb(II) and Hg(II) ions at low concentrations onto 300 mg of longan shell at 30 °C for 2 h.

**Effect of Initial Pb(II) Concentration and Sorption Isotherm.** Sorption of Pb(II) ions onto the longan shell is given as a function of initial Pb(II) concentration in Figure 4a. It is found that the sorption capacity rises significantly with increasing Pb(II) concentration from 20 to 1000 mg L<sup>-1</sup>, while the Pb(II) adsorptivity reduces gradually. Thereby, both the sorption capacity and adsorptivity of the Pb(II) ions reach a high level simultaneously at the optimal initial Pb(II) concentration of around 800 mg L<sup>-1</sup>. When the initial Pb(II) concentration is 20 mg L<sup>-1</sup>, the adsorptivity can reach up to 92.1%. The results reveal that at high initial Pb(II) concentration, the available sorption active sites become insufficient, hence resulting in reduced adsorptivity.

To establish a quantitative relationship between Pb(II) concentration and the sorption process, two linear mathematical models proposed by Langmuir and Freundlich were utilized to describe and analyze the sorption isotherm and equilibrium. The Langmuir isotherm based on an assumption of monolayer



**Figure 5.** Effect of metal-ion solution temperature on the sorption of (a) lead and (b) mercury ions on the longan shell in 25 mL of solution with a shell dosage of 300 mg at an initial metal-ion concentration of 200 mg L<sup>-1</sup> for the sorption time of (a) 2 h and (b) 1 h, respectively.

sorption on a surface containing a finite number of sorption sites is the simplest for revealing sorption characteristics. The free energy of sorption is considered to be independent of coverage so that no other interaction is assumed. This model is useful when there is a strong specific interaction between the surface and the adsorbate. As a result, a single sorption layer forms and no multilayer sorption occurs. The most popular sorption model for a single-solute system, the Freundlich model, is an empirical equation based on the distribution of solute between the solid phase and aqueous phase at equilibrium. The Freundlich isotherm model assumes heterogeneous surface energy in which the energy term in the Freundlich equation varies as a function of surface coverage. The Dubinin–Radushkevich (D–R) isotherm equation is more generally applied to distinguish between physical and chemical sorptions on the basis of the potential theory assuming heterogeneous surface. The D–R constant can give the valuable information regarding the mean energy of sorption. The parameters and correlation coefficients listed in Table 2 show that the sorption behavior of Pb(II) ions onto the longan shell particles is best described by the Langmuir isotherm in the three isotherm models because the Langmuir isotherm yields the highest correlation coefficient and smallest difference between theoretical  $Q_m$  (52.1 mg g<sup>-1</sup>) and experimental  $Q_m$  (51.5 mg g<sup>-1</sup>). The maximal sorption capacity,  $Q_m$ , 52.1 mg g<sup>-1</sup>, of longan shell calculated from the Langmuir isotherm is higher than that of other sorbents, such as cross-linked chitosan with epichlorohydrin,<sup>19</sup> pomegranate peel,<sup>22</sup> and seven natural sorbents in Table S1. The mean sorption energy was involved in the transfer of free energy of 1 mol of solute from infinity to the surface of adsorbent. The mean sorption energy of 1–8 and >8 kJ mol<sup>-1</sup> might be used to predict the physical and chemical sorption, respectively.<sup>38</sup> Therefore, the mean energy of 5 kJ mol<sup>-1</sup> in this study revealed that the sorption is dominated by a physical process.

**Effect of Pb(NO<sub>3</sub>)<sub>2</sub> Solution Temperature.** To find the optimal sorption temperature, the effect of Pb(NO<sub>3</sub>)<sub>2</sub> solution temperature on the Pb(II) sorption in a temperature range of 5–50 °C was studied. As shown in Figure 5a, the sorption capacity and adsorptivity of Pb(II) ions on the longan shell both demonstrate the maximum at 30 °C, which is different from that on some synthetic sorbents just like poly(phenylenediamine).<sup>15</sup> At low temperature, the activity of the functional groups in the longan shell is weak, thereby leading to low sorption capacity and adsorptivity. It is well-known that

chemical sorption is endothermic, suggesting that high temperature would be advantageous to the sorption, whereas high temperature would be disadvantageous to the process for the physical sorption as an exothermic process. It can be seen from Figure 5a that the sorption has two steps: the first step at lower temperature is a chemical sorption control, and the second step at higher temperature is a physical sorption control. A simultaneous reduction of the sorption capacity and adsorptivity is possibly attributable to enhanced molecular vibration at elevated temperature, which may partly desorb the Pb(II) ions physically adsorbed on the longan shell.

**Sorption of Mercury Ions onto Longan Shell. Effect of Sorption Time and Sorption Isotherm.** Like the Pb(II) sorption discussed above, the effect of contacting time on the Hg-ion sorption onto the longan shell at an initial Hg(II) concentration of 200 mg L<sup>-1</sup> at 30 °C was illustrated in Figure 3b. Note that the formation and stable existence of Hg<sub>2</sub><sup>2+</sup> in the filtrate after the sorption were verified by the milky deposition (Hg<sub>2</sub>Cl<sub>2</sub>) and its turning into black precipitates (HgNH<sub>2</sub>Cl and Hg)<sup>16</sup> if respectively adding 0.1 mM NaCl and some ammonia into the filtrate. That is to say, some of Hg(II) ions have been reduced to Hg(I) ions, suggesting that both the Hg(II) and Hg(I) ions were adsorbed onto the longan shell at the same time. Therefore, the behavior of Hg(II) and Hg(I) sorption is different from the Pb(II) sorption. The sorption capacity and adsorptivity of Hg(II) and Hg(I) ions onto the longan shell both augment dramatically in the initial sorption time of 5 min, but augment only slightly in the time range from 5 to 60 min, and reach a sorption equilibrium with the sorption capacity of 16.4 mg g<sup>-1</sup> and adsorptivity of up to 98.3% at the sorption time of longer than 60 min that is much shorter than the equilibrium time (120 min) of the Pb(II) sorption in Figure 3a. It could be concluded that the longan shell has stronger adsorbability toward Hg(II) and Hg(I) ions than Pb(II) ions.

Sorption kinetics were also elaborated to understand the sorption behavior of the longan shell toward mercury ions. The pseudo-first-order and pseudo-second-order equations are very useful to examine the controlling mechanism of sorption based on the data during the contact time between 0 and 30 min, as listed in Table 2. Because the theoretical  $Q_e$  (16.6 mg g<sup>-1</sup>) calculated by the pseudo-second-order equation is very close to the experimental  $Q_e$  (16.4 mg g<sup>-1</sup>), it can be concluded that the pseudo-second-order model correlates even better with the experimental data than the pseudo-first-order model regardless of their simultaneously high correlation coefficients, signifying a chemically reactive redox sorption of Hg(II) ions onto longan shell. The initial sorption rate of Hg(II) and Hg(I) ions onto the longan shell is 29.50 mg g<sup>-1</sup> min<sup>-1</sup> that is much higher than that (16.05 mg g<sup>-1</sup> min<sup>-1</sup>) of Pb(II) ions. This may be the reason why the adsorptivity of Hg(II) and Hg(I) ions is higher than that of Pb(II) ions.

**Effect of Hg(NO<sub>3</sub>)<sub>2</sub> Solution Temperature.** The effect of Hg(NO<sub>3</sub>)<sub>2</sub> solution temperature on the Hg(II,I) sorption onto the longan shell in a temperature range of 5–50 °C was shown in Figure 5b. Unlike the Pb(II) sorption, the sorption capacity and adsorptivity of mercury ions rise monotonically with elevating temperature, finally reaching the highest values of 16 mg g<sup>-1</sup> and 98.8% at 50 °C. It seems that chemical sorption mainly predominates the mercury-ion sorption process onto the longan shell because of an additional redox sorption from Hg(II) to Hg(I) onto the longan shell by contrast with Pb(II) sorption.

**Sorption of a Trace Amount of Heavy-Metal Ions.** The concentration of heavy metal ions in the environmental wastewater is usually low. To investigate the practical applicability

**TABLE 3: Theoretical Sorption Selectivity of Five Metal Ions onto 300 mg of Longan Shell at 30 °C in 25 mL of Metal-Ion Solution at Initial Ion Concentration of 200 mg L<sup>-1</sup> for 2 h**

metal-ion solution	sorption capacity (mg g <sup>-1</sup> )	adsorptivity (%)	theoretical selectivity coefficient	
			Pb(II)	Hg(II,I)
FeCl <sub>3</sub>	0.24	1.44	57.8	68.3
CuSO <sub>4</sub>	0.99	5.92	14.1	16.6
ZnSO <sub>4</sub>	2.67	16.0	5.2	6.1
Pb(NO <sub>3</sub> ) <sub>2</sub>	13.9	83.3	1.0	1.2
Hg(NO <sub>3</sub> ) <sub>2</sub>	16.4	98.3	0.8	1.0

**TABLE 4: Competitive Sorption of Pb(II) and Hg(II,I) Ions onto 300 mg of Longan Shell at 30 °C in 25 mL Solution at Initial Ion Concentration of 20 mg L<sup>-1</sup> for Each Metal Ion for 2 h**

metal ion	adsorptivity (%)		adsorptivity difference (%)
	separated solution	mixed solution	
Pb(II)	92.1	95.0	2.9
Hg(II)	99.1	86.4	-12.7

of the longan shell in purifying the ambient wastewater, the sorption of Pb(II) and Hg(II,I) ions at trace concentration onto the longan shell was actualized. It is seen from Figure 4b that the adsorptivity can reach at least 86.8% in the heavy-metal-ion concentration of 20 mg L<sup>-1</sup> or lower. Especially, when the initial Hg(II) concentration was 20 mg L<sup>-1</sup>, the adsorptivity could be as high as 99.1% together with a very low residue Hg-ion concentration of 0.18 mg L<sup>-1</sup>, implying that the longan shell particles have a great potential for the purification treatment of the wastewater containing a trace amount of heavy metal ions. Note that the adsorptivity of the heavy-metal ions onto the sorbents decreases rather than increases as the initial ion concentration declines from 20 to 0.5 mg L<sup>-1</sup>.

**Competitive Sorption of Heavy-Metal Ions over Nutrition Ions onto Longan Shell.** The selective sorption of the several common metal ions onto the longan shell is important for its further practicability. The results in Table 3 suggest that the sorption capacity and particularly adsorptivity of Zn(II), Cu(II), and Fe(III) ions are both much lower than those of Pb(II) and Hg(II). That is to say, the theoretical selectivity coefficients of hazardous Pb(II) and Hg(II) ions over innocuous or nutritious Zn(II), Cu(II), and Fe(III) ions onto the shell are 5.2 or even up to 68.3. It is apparent that longan shell has well predominant sorption toward the heavy-metal ions in metal-ion mixtures. A certain amount of Cu(II), Zn(II), and Fe(III) ions remaining in the water are not only innocuous for the environment and creature but also very good for farmland irrigation.

The competitive sorption between Pb(II) and Hg(II) ions onto the longan shell particles was further explored and summarized in Table 4. It can be found that the Pb(II) adsorptivity was higher when the Pb(II) and Hg(II) ions were mixed than in pure Pb(II) solution, while the mercury-ion adsorptivity was lower than in pure mercury-ion solution. It seems that the sorption sites on the longan shell are more active for Pb(II) ions than Hg(II,I) ions under the circumstances of Pb(II) and Hg(II,I) ion coexistence. This signifies that a competitive sorption between Pb(II) and Hg(II,I) ions onto the longan shell did happen, demonstrating a preferential sorption to the Pb(II) ions rather than the Hg(II) ions if in the Pb(II) and Hg(II) mixture solution. The presence of competitive sorption lowers the Hg(II) adsorbability,<sup>39</sup> but enhances the Pb(II) adsorbability. One of the possible reasons is that some Hg(II) ions were surrounded by the Pb(II)

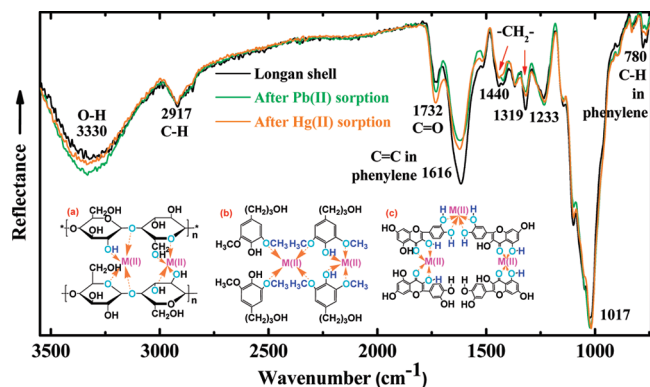
ions, consequently leading to the Hg(II) inaccessibility for sorption. However, the real reason for this, which is an important topic in heavy metal ion sorption, still needs further investigation.

**Performance Comparison of Longan Shell with Other Natural Biosorbents.** As discussed above, the longan shell, as a kind of environmentally friendly biosorbent, possesses a powerful selective adsorbability toward the heavy metal ions rather than nutritious metal ions. Although it is hard to directly compare the performance of the longan shell with other natural sorbents because of different sorption conditions, a possible comparison has been summarized in Table S1. It can be seen that most of the purely natural sorbents have similar equilibrium sorption time of Pb(II) except for olive stone waste, *Fraxinus* and *Ulmus* tree leaves. The longan shell has higher maximal sorption capacity of Pb(II) ions than the other natural sorbents but *Fraxinus excelsior* and *Ulmus carpinifolia* leaves. In particular, the longan shell has the highest initial sorption rate of Pb(II) ions in all natural sorbents but formaldehyde-modified orange peels in Table S1. Furthermore, it is surprisingly discovered that the longan shell has more rapid equilibrium sorption, much higher adsorptivity, and more rapid initial sorption of mercury ions than all the natural sorbents in Table S1. For instance, the longan shell can achieve higher than 90% mercury-ion adsorptivity in only 5 min. This strongly implies that longan shell is a very promising sorbent of Pb(II) and especially mercury ions because of its fast, durable, and efficient adsorbability toward Pb(II) and mercury ions. Besides, a very simple pretreatment decides its extremely low cost in contrast to the synthetic sorbents.

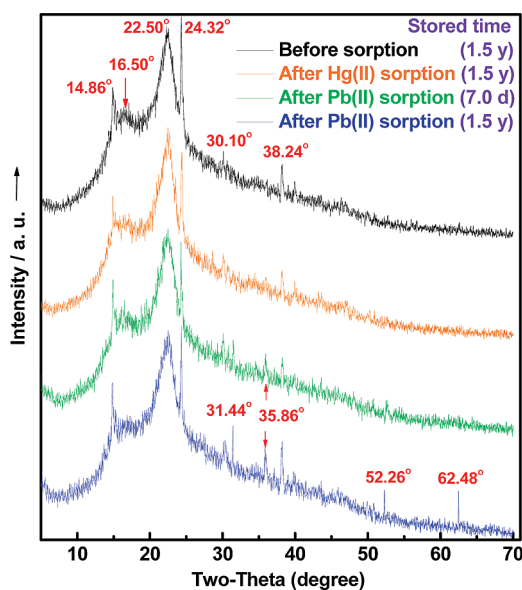
**Sorption Mechanism of Pb(II) and Hg(II) onto Longan Shell.** The basic biomacromolecular components of the longan shell are cellulose, lignin, and hemicellulose. Cellulose is a polysaccharide consisting of linear macromolecular chains of several hundred to over ten thousand  $\beta$ 1 $\rightarrow$ 4 linked D-glucose units that are good for sorption. Lignin in its natural unprocessed form is complex, amorphous, three-dimensional, and racemic macromolecules with molecular weight of 15000 or higher that comprise various types of substructures including a phenylpropane structure, that is, a benzene ring with a tail of three carbons such as *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol units. Hemicellulose has a random amorphous supramolecular structure. The functional groups present in these macromolecules, involving carbonyl, phenolic, carboxyl, and methoxyl groups as well as structural polysaccharides, have the intrinsic affinity for heavy-metal ions. Besides, it is reported that the longan shell also includes quercetin, methylgallate, 6-methoxy-7-methylcoumarin, and fridin, whose characteristic structures can reversibly chelate with some heavy-metal ions. Generally, the main sorption sites for the heavy metal ions locate at the characteristic oxygen-containing groups because the oxygen atom has a lone pair of electrons that can efficiently bind a metal ion through sharing an electron pair to form a metal complex, as illustrated in Figure 6 (inset).

To identify the possible sorption sites of Pb(II) and Hg(II,I) ions bonded to the longan shell, IR spectra were obtained in Figure 6 for longan shell before and after the metal ion sorption. Although the O—H band at 3330 cm<sup>-1</sup> could not be used to quantitatively confirm the O—H content in the samples because this band is also very sensitive to water content, a significant variation of other functional groups after binding metal ions onto the longan shell can be used to well reveal the possible sorption mechanism. The three bands at 1616/780 and 1319 cm<sup>-1</sup> due to C=C/C—H bonds in phenylene and -CH<sub>2</sub>- units become weaker, while a characteristic band at 1732 cm<sup>-1</sup> due





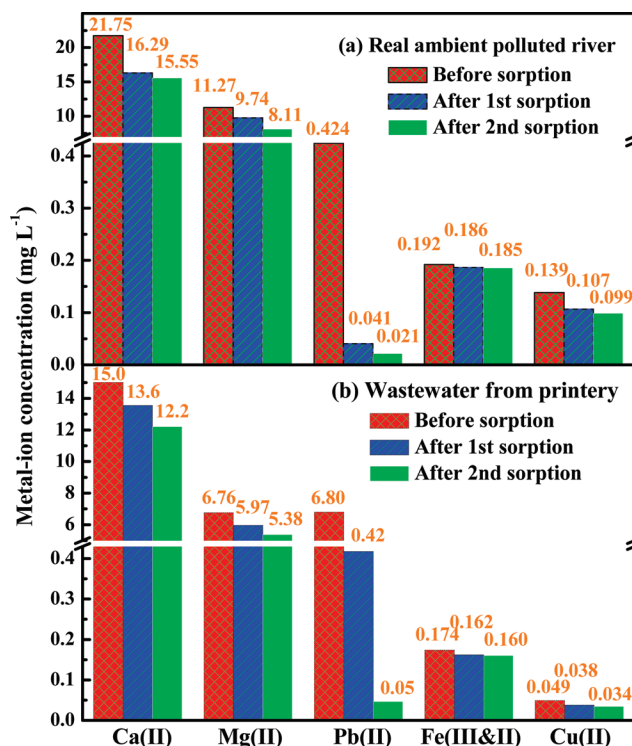
**Figure 6.** IR spectra of the longan shell before and after Pb(II) or Hg(II,I) sorptions. Inset: Possible complex structure of heavy metal ion [M(II)] on (a) cellulose, (b) lignin, and (c) quercetin.



**Figure 7.** Wide-angle X-ray diffractograms of longan shell adsorbing Pb(II) and Hg(II,I) ions. Pb<sup>2+</sup> was adsorbed on 100 mg longan shell in 50 mL of Pb<sup>2+</sup> solution at an initial Pb<sup>2+</sup> concentration of 200 mg L<sup>-1</sup> for 2 h at 30 °C. Hg ions were adsorbed on 300 mg of longan shell in 25 mL of Hg-ion solution at an initial Hg-ion concentration of 200 mg L<sup>-1</sup> for 1 h at 30 °C.

to the stretch of C=O bond becomes stronger after adsorbing Pb(II) and Hg(II) ions, but other bands change a little or hardly ever change. These may be attributable to increased C=O bonds and thus decreased C=C/C-H bonds in phenylene and -CH<sub>2</sub>-units because of redox interaction between -O-H groups and the metal ions. The redox interaction between -O-H groups and Pb(II) ions has been further verified by the wide-angle X-ray diffraction below. Note that the Hg(II,I)-adsorbing longan shell exhibits the strongest C=O band at 1732 cm<sup>-1</sup>, signifying the strongest redox sorption of Hg(II) ions onto the longan shell.

All of the samples in Figure 7 show the strongest broad peak at  $2\theta = 22.50^\circ$  ( $d_{(200)} = 0.3946$  nm) and a weak broad peak at  $2\theta = 16.50^\circ$  ( $d_{(101)} = 0.5368$  nm) due to low crystalline cellulose, as well as the sharpest strong peak at  $2\theta = 24.32^\circ$  and the sharp moderate peaks at  $2\theta = 14.86^\circ$ ,  $38.24^\circ$ , and  $30.10^\circ$  due to water-insoluble low molecular weight crystalline substance including quercetin, methylgallate, 6-methoxy-7-methylcoumarin, and fridin. It is of interest that the longan shell adsorbing Pb(II) demonstrates two or even four weak but sharp diffraction peaks at  $31.44^\circ$ ,  $35.86^\circ$ ,  $52.26^\circ$ , and  $62.48^\circ$  that are very close to the four strongest diffraction peaks at  $31.31^\circ$



**Figure 8.** Removal efficiency of Pb(II) from real ambient polluted river (a) and the wastewater from printery (b) by using longan shell as a biomacromolecular sorbent.

(strongest,  $d_{(111)} = 0.2855$  nm),  $36.27^\circ$  (second strongest,  $d_{(200)} = 0.2475$  nm),  $52.23^\circ$  (fourth strongest,  $d_{(220)} = 0.1750$  nm), and  $62.12^\circ$  (third strongest,  $d_{(311)} = 0.1493$  nm) in the wide-angle X-ray diffraction database of 99.999% Pb(syn) crystals (radiation = Cu K $\alpha$ 1,  $\lambda = 1.54056$  Å, filter = Ni).<sup>40</sup> This signifies that some Pb(II) ions in the sorption solution have been reduced into Pb(syn) crystals by the longan shell, only their diffraction peaks are weak because the content of Pb(syn) crystals in the final longan shell is low. However, the diffraction peaks from the Pb(syn) crystals in the longan shell tend to become more intense with increasing stored time in ambient environment. The fact that a 1.5 year stored sample exhibits two apparent changes, (1) strong diffraction peaks at  $31.44^\circ$  and  $35.86^\circ$  and (2) two additional diffraction peaks at  $52.26^\circ$  and  $62.48^\circ$  compared with 7 day stored sample, implies that the redox reaction between Pb(II) ions and -OH groups in the longan shell adsorbing Pb(II) ions progresses continually even at a solid state. Thus it can be seen that longan shell has a reducibility from Pb(II) ions to Pb(syn) crystals, accompanying with the oxidation of the -CH<sub>2</sub>-OH/>CH-OH/>C-OH into -CHO/>C=O/>C=O, respectively. This well-confirms a significant redox sorption between Pb(II) and -OH groups in longan shell particles. By the way, the X-ray diffractogram does not seem to change after adsorbing Hg ions, implying that no crystalline sorption products formed on the longan shell.

**Applicability of Longan Shell for the Purification of Real Water.** The main ions and their concentrations in the Zou-Ma-Tang tributary of the Huangpu River, Shanghai, China, before and after sorptions are collected in Table S2 and Figure 8a. After sorption twice, the Pb(II) concentration decreased remarkably while other ion concentrations slightly declined. This strongly indicates that the longan shell has very satisfactory selectivity of adsorbing Pb(II) ions in real metal-ion mixture from ambient polluted river. After the first sorption, the Pb(II) concentration reduced to  $40.5 \mu\text{g L}^{-1}$  which meets the discharge

standard of pollutants for municipal wastewater treatment plant (GB18918-2002), standards for irrigation water quality (GB5084-92), and standards for fisheries water quality (GB11607-89) of China. After the second sorption, the Pb(II) concentration reduced to  $21.4 \mu\text{g L}^{-1}$ , approaching to standards for drinkable water GB5749-2006 of China.

The real wastewater from Printing House in Fudan University China contains  $6\text{--}8 \text{ mg L}^{-1}$  Pb(II) ions, which is much higher than that in the ambient polluted river, but fortunately the Pb(II) concentration was dramatically reduced to  $0.4181 \text{ mg L}^{-1}$  after the first sorption cycle by the longan shell (Table S2 of the Supporting Information). And the Ca(II) and Mg(II) ions of high concentrations were slightly adsorbed and their existence would not affect the strong Pb(II) sorption, which can be seen intuitively from Figure 8b. The treated water by the longan shell can be let out in the drainer as it meets the Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant (GB18918-2002) of China. After the second sorption cycle by the longan shell, the Pb(II) concentration further reduced to  $0.0462 \text{ mg L}^{-1}$ , suggesting that the quality of the water is greatly improved and can be used for agriculture and aquaculture industry since the twice-treated water satisfies the Standards for Irrigation Water Quality (GB5084-92) and Standards for Fisheries Water Quality (GB11607-89) of China. In other words, the twice-treated water can be allowed to afflux farmland, pond, and river. In particular, the shell will not cause secondary pollution, while most synthetic adsorbents containing -SH, -NH<sub>2</sub>, -NH-, -OH, or -COOH functional groups and even chemically modified natural sorbents including glutaraldehyde or epichlorohydrin cross-linked chitosan and formaldehyde-modified orange peels would probably cause other pollution due to their high reactivity and slight water solubility regardless of their strong adsorbability toward the heavy or even common metal ions.

Upon the basis of the results above, the shell displays highly selective sorption to Pb(II) over light metal ions in real environmental water, with an adsorbability order of Pb(II) > Hg(II) > Zn(II) > Cu(II) > Ca(II) > Mg(II) > Fe(III,II), further indicating that the shell has a great potential to be used for perfect purification of the drinking water and nutritious liquids by just removing the harmful heavy-metal ions but still retaining the nutritious metal ions.

## Conclusion

Longan shell, as a waste biomacromolecular substance, demonstrates very high selectivity of Pb(II) and Hg(II) over relatively light metal ions. The shell will not cause secondary pollution, while most synthetic adsorbents and chemically modified natural sorbents would probably cause unexpected pollution. The longan shell has not only incomparable environmental benignity and low-cost advantage compared with all synthetic and seminatural sorbents but also simpler pretreatment and stronger adsorbability toward Pb(II) and particularly Hg(II) than most natural sorbents. Redox sorption mechanism of Pb(II) and Hg(II) ions onto longan shell was revealed. The successful elimination of the hazardous Pb(II) ions from both environmentally polluted rivers and industrial wastewater demonstrates that longan shell is the most promising in practical wastewater treatment. The efficient utilization of longan shell waste for the removal of harmful metal ions and retainment of the nutrition ions represents a new form of using trash as treasure. Besides, the entire pretreatment of the shell, which does not involve any organic solvents or even acids or alkalis, achieves zero emission and follows the principles of green chemistry. The shell should

be an attractive and highly cost-efficient natural sorbent toward heavy metal ions from their aqueous solutions with or without light metal ions. It is anticipated that longan shell would find important application across a wide spectrum of wastewaters.

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**Supporting Information Available:** Tables for a comparison<sup>25–36</sup> of Pb(II) and Hg(II) sorption onto the longan shell with other natural sorbents and removal efficiency of Pb(II) from real ambient water by the longan shell. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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