

## Preparation and modification of peanut shells and their application for heavy metals adsorption

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Peanut shells are a test adsorption material, the influences of key factors (pH, reaction duration, initial concentration and adsorption dosage) on its adsorption of heavy metal ions including  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  were studied. The results showed that: the adsorption rate of the above mentioned heavy metal ions increased gradually with the pH increase. We also noticed that the adsorption of heavy metal ions by unmodified peanut shells performed well under acidic conditions, while the best results for modified peanut shells were obtained under alkaline conditions. Meanwhile, the adsorption rate reached about 88% of the maximum adsorption rate after treatment for a 15 min reaction and tended to balance after 50 min; with increasing initial ion concentration, the adsorption rate increased gradually, and reached the maximum adsorption rate at 30 mg/L. However, it was gradually reduced when over 30 mg/L. The results revealed that adsorption rate increased with the adsorbent dosage. The dynamic behaviors of both modified and unmodified peanut shells well fit the Lagergren (II) order chemical reaction kinetics model. Additionally, compared with unmodified peanut shells, the adsorption effect for modified shells was significant.

**Keywords:** Peanut Shell, Adsorption, Heavy Metals, Modification, Dynamics.

### INTRODUCTION

The heavy metals,  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ , are harmful to the environment. They accumulate in the living organisms by adsorption and thus pose a serious threat to public health. Excessive accumulation of copper *in vivo* could lead to many diseases like diarrhea, skin diseases and even death [1, 2]. Lead is a cumulative poison acting on various systems and organs of the human being [3], such as the hematopoietic and cardiovascular system, the central nervous systems and the reproductive organs [4]. There are many technical methods used to treat contamination by heavy metals, such as ion exchange resin, activated carbon adsorption, chemical precipitation and electrochemical treatment [5]. These methods have some effect, but their cost compared with biotechnology, is much larger and may cause secondary pollution.

In recent years, the biomass material, as an adsorbent applied for controlling heavy metals contamination, is becoming a hot research topic. Biomass materials have the advantage of widespread-sources, convenience, low-cost, directly-treated and thus greatly reduce the cost of

the treatment of heavy metals. Therefore biomass materials find good application prospects [6, 7]. Different from the traditional process, the biological assay has the following advantages: metal ions can be selectively removed with low concentrations of heavy metals; energy-efficiency, cost-effectiveness; easy separation and recovery of heavy metals; the sustainability-adsorbent is easily regenerated and recycled.

As the increasing lack of non-renewable resources such oil and coal, the preparation of new industrial products with agricultural and forestry waste together with other renewable resources as raw materials gradually draws attention from all over the world. The common agricultural and sideline products include bark, cotton shells, peanut shells, sawdust, orange peel and others. A large number of peanut shells are discarded in the natural environment or burned, which not only cause serious environmental pollution, but also are a waste of resources. Peanut hull carbide (PHC), commonly used as a bio-adsorbent produced from piles of peanut shells, is similar to the activated carbon structure in appearance. According to the research, PHC may contain polar functional groups such as aldehydes, ketones, acids and phenolic compounds, which can be involved in the formation

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of chemical bonds and can adsorb heavy metal ions [9]. In China, peanut shells are cheap and have a wide range of sources. In this paper, peanut shells are used as an adsorbent and therefore the mechanism of heavy metal ions in solution adsorption laws are discussed.

Peanut shells are an abundant inexpensive adsorbent and can be applied to govern heavy metal pollution after modifying its structural characteristics [10]. Up until now, many researchers [11, 12] have removed heavy metal ions from the wastewater using peanut shells as an adsorbent or using peanut shells as a raw material for activated carbon preparation [13], which had a great practical significance for recycling and application of such a large quantity of cheap agricultural and forestry waste in environmental pollution. However, these studies only focus on the effects of polluted water following the adsorption of heavy metals together with characteristics, such as the adsorption temperature, pH, amount of adsorbent and the initial ion concentration. However, these do not fully explore the best adsorption conditions of modified peanut shells. This paper mainly studied the optimum conditions of adsorption. In this paper, we modified peanut shells with 0.1 mol/L of hydrochloric acid and applied modified peanut shells to process the simulated industrial wastewater containing copper, lead and zinc ions, which provided a new thought as regards the utilization of peanut shells and the treatment for heavy metal ions.

## MATERIALS AND METHODS

### *Preparation of solutions and samples*

The peanut shells used in this study were derived from fresh peanuts. All the chemical reagents used were analytical grade. A stock solution with 100 mg/L  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  respectively was prepared by deionized water,  $Pb(NO_3)_2$ ,  $Cu(NO_3)_2$  and  $Zn(NO_3)_2$ . Working solutions were obtained by appropriate dilution. Peanut shells were smashed and screened through a mesh of size 80. Then the samples were soaked with deionized water for 24 hours and the fine suspended material was removed as well as the soluble matter. The samples were stored in a desiccator after being dried at 80°C the modified peanut shells were prepared as follows: 200 g of peanut shells were placed in a 2.5 L beaker, 500mL 1 mol/L hydrochloric acid was added in the beaker. After being stirred for 1 h, the liquid portion was removed by filtration. The solid fraction was washed with deionized water until neutral and dried at 80°C. Infrared spectrum samples were prepared by

potassium bromide tableting. Unmodified or modified peanut shells powder and potassium bromide powder were thoroughly ground. The mixed powder was made into a transparent sheet with about 1 mm thickness by a pneumatic tableting machine. Then the samples were analyzed by a Fourier transform infrared spectrometer at 400 - 4000  $cm^{-1}$ .

### *Peanut shells adsorption of simulated industrial wastewater*

The ion mixed solution was made from 50 mg/L  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ . 60 mL of ion mixed solution was added in an 100 mL Erlenmeyer flask, the pH of which was adjusted. The initial concentration of  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  was measured by an atomic absorption spectrophotometer. Unmodified or modified peanut shells were placed in an Erlenmeyer flask and cultured in the constant temperature incubator shaker with an oscillation rate of 120 r/min at 32°C. Thereafter, 10 mL of solution in a centrifugal tube was centrifuged to remove the impurities in the solution. The concentration of  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  after adsorption was measured by an atomic absorption spectrophotometer. The adsorption rate was used to determine the optimum adsorption conditions.

### *Single factor experiment and orthogonal test*

The adsorption rate is an evaluation index, four factors including the adsorption reaction duration (A), the initial ion concentration (B), dosage of the samples (C), pH value (D) were selected to be the testing factors of the adsorption efficiency of the peanut shells. According to the results of the single factor experiment, an orthogonal test with four-factors and three-levels was applied to optimize the adsorption condition of the peanut shells.

### *Kinetics experiments*

50 mL, 40 mg/L or a 50 mg/L mixed ion solution was added into a 100 mL Erlenmeyer flask with a pH adjusted to  $5.00 \pm 0.01$ . 0.50 g unmodified peanut shells powder was added in the solution. Then the solution was shaken for 10, 20, 30, 40, 60, 80 min, separately at 32°C. The concentration of  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  were assayed and plotted after being filtered and centrifuged. Characterization of the dynamic mechanism of the data in the figure was analyzed using the following two models.

### *Lagergren apparent first-order kinetic model*

$$\ln(1-q/q_e) = -k_1 t \quad (1)$$

In which:  $q_t$ ,  $q_e$  (mg/g) are the  $\text{Cu}^{2+}$  adsorption at  $t$  (min) time,  $\text{Cu}^{2+}$  equilibrium adsorption. Respectively;  $k_1$  (g/(mg·min)) is the adsorption rate constant of first order which can be obtained by a plot using  $\ln(1 - q_t/q_e)$  and  $t$ .

Lagergren apparent second-order kinetic model

$$t/q_t = (1/k_2 q_e^2) + (t/q_e) \quad (2)$$

In which:  $k_2$  (g/(mg·min)) is the adsorption rate constant of apparent second order which can be obtained by a plot using  $t/q_t$  and  $t$ ;  $k_2 q_e^2$  (mg/(g·min)) is the initial adsorption rate.

## RESULTS AND DISCUSSION

### Effect of pH on the adsorption

As shown in Fig. 1, the metal ions adsorption rate of peanut shells increased gradually with the increase of pH at a range of 3-5. Unmodified peanut shells reached a maximum value when the pH was 5 and reduced when the pH was 7. However, modified peanut shells continued to increase gradually under given alkaline conditions. Thus, the optimum pH of unmodified peanut shells was acidic and the optimum pH of modified peanut shells was alkaline. Moreover, the maximum adsorption rate of modified peanut shells was higher than that of unmodified peanut shells. The maximum adsorption rates of unmodified peanut shells for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  were 93.3%, 77.6%, 71.5%, respectively, while the adsorption maximum of modified peanut shells for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  were 96.2%, 87.0%, 74.0%, respectively. Generally, the absorption efficiency of modified peanut shells was better than the unmodified one and the adsorption of peanut shells on  $\text{Pb}^{2+}$  was the most obvious.

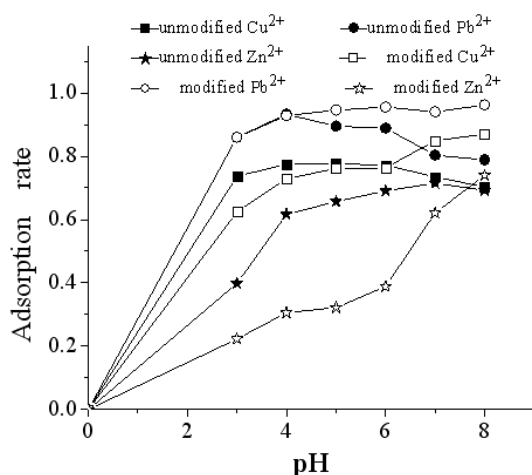


Fig. 1. The influence of pH on adsorption

### Effect of the adsorption reaction duration on adsorption

Fig. 2 showed that the adsorption rate of peanut shells for metal ions increased with time and reached a balance after a reaction duration of 50 minutes. The adsorption rate reached 88% of the maximum adsorption rate after 15 min, which showed that the adsorption by peanut shells of metal ions was terminated in a short space of time. The adsorption of modified and unmodified peanut shells and metal ions at the interface between the liquid and solid was mainly physical adsorption. In theory, the longer the reaction duration the more the adsorbent dosage, the more thorough the adsorption removal is. The maximum adsorption rates of unmodified peanut shells for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  were 94.3%, 69.3%, 16.7%, respectively, while the adsorption maximums of modified peanut shells for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  were 68.9%, 48.9%, 16.4%, respectively. Overall, the absorption efficiency of unmodified peanut shells was better than the modified one and the adsorption of peanut shells on  $\text{Pb}^{2+}$  was the most obvious.

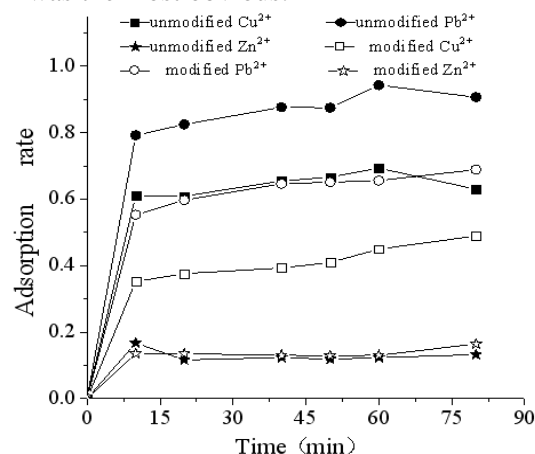


Fig. 2 The influence of reaction duration on adsorption

### Effect of the initial ion concentration on adsorption

The absorption rate increased with the initial ion concentration and reached a maximum with the initial ion concentration being 30 mg/L and then reduced gradually. When the initial ion concentration in the solution was much higher, the adsorption sites of the peanut shells for metal ions on the surface were saturated so the adsorption rate gradually decreased. In Fig. 3, when the concentration of metal ions was low, the adsorption rate was relatively high, while the adsorption rate became lower with the higher metal ion concentration, which indicated that the peanut shells were suitable for the adsorption of low metal ion concentrations. The maximum adsorption rates of unmodified peanut shells for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$

were 90.1%, 69.9%, 69.1%, respectively, while the adsorption maximums of modified peanut shells for  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  were 85.9%, 77.6%, 78.1%. In total, the absorption efficiency of modified peanut shells was better than the unmodified one and the adsorption of peanut shells on  $Pb^{2+}$  was the most obvious.

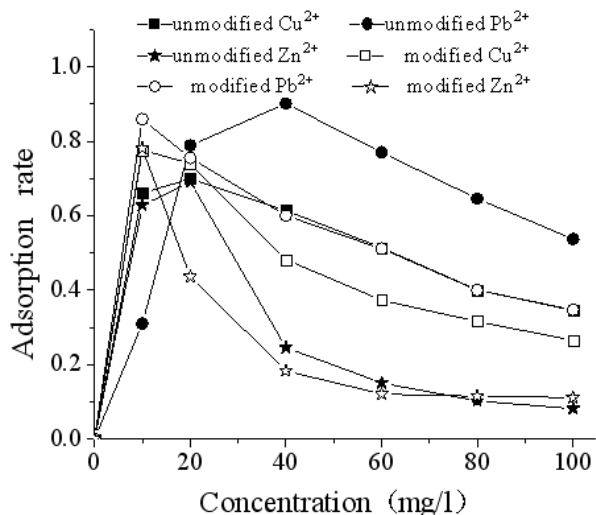


Fig. 3 The effect of the initial concentration on adsorption

#### Effect of the pH value on the adsorption

As manifested in Fig. 4, the metal adsorption range of unmodified peanut shells were 0.2-0.6g and the adsorption rate increased with the adsorbent dosage.

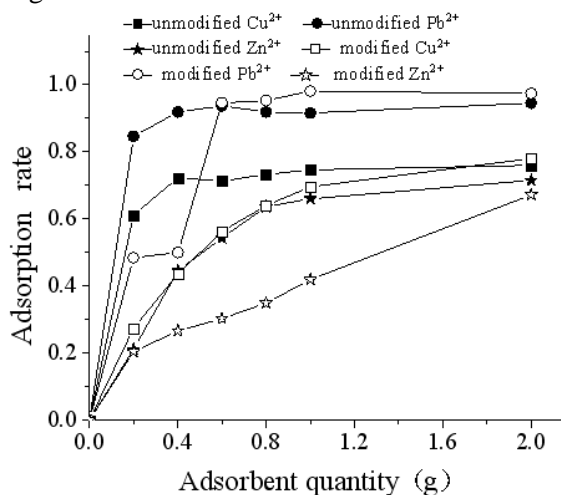


Fig. 4 The effect of the adsorbent dosage on adsorption

The maximum adsorption rates of unmodified peanut shells for  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  were 94.5%, 76.0%, 71.5%, respectively. The adsorption rate of modified peanut shells was also increased with the adsorbent dosage and reached the maximum when the dosage of samples was 2.0 g. The adsorption maximums of modified peanut shells for  $Pb^{2+}$ ,  $Cu^{2+}$ ,

$Zn^{2+}$  were 98.1%, 78.0%, 67.2%. Increasing the amount of peanut shells increases the surface area of the peanut shells in the metal solution and the effective adsorption sites, therefore the adsorption rate increases. But when the adsorption rate of the heavy metal ions reach an equilibrium, the increasing adsorbent dosage would reduce the adsorption capacity of the per unit mass adsorbent which means non-saturation of the adsorption capacity and results in a waste of adsorbent. In total, the absorption efficiency of the modified peanut shells was better than that of the ones unmodified and the adsorption efficiency on  $Pb^{2+}$  was more obvious.

#### Analysis of the orthogonal results

##### Orthogonal results assay of the unmodified peanut shells

The most obvious factor was the initial ion concentration for  $Cu^{2+}$  and  $Zn^{2+}$  while the most significant factor was the pH value of  $Pb^{2+}$  by the Anova and range analysis in Table 1 and Table 2. Based on the K value, the best combinations of  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Pb^{2+}$  were  $A_2B_3C_1D_1$ ,  $A_3B_3C_3D_2$  and  $A_1B_2C_1D_3$  respectively, which meant that the optimum condition for  $Cu^{2+}$  was the reaction duration for 60min, the initial ion concentration being 40 mg/L, the 0.5 g of adsorbent at pH 5; the optimum condition for  $Pb^{2+}$  lasted for 80min, the initial ion concentration being 40 mg/L, the 0.7 g of adsorbent at pH 6; the optimum condition for  $Zn^{2+}$  lasted for 40min, the initial ion concentration being 30 mg/L, the 0.5 g of adsorbent at pH 7.

##### Orthogonal results analysis of modified peanut shells

According to the Anova and range analysis in Table 3 and Table 4, the most obvious factor was the adsorption reaction duration for  $Pb^{2+}$  and  $Zn^{2+}$ , while the most significant factor was the initial ion concentration for  $Cu^{2+}$ . Based on the K value, the best combination of  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Pb^{2+}$  were  $A_3B_3C_2D_1$ ,  $A_3B_3C_3D_3$  and  $A_1B_2C_3D_3$ , respectively, which, in detail, means that the optimum condition for  $Cu^{2+}$  was a reaction lasting for 80 min, the initial ion concentration being 30 mg/L, the 1.5 g adsorbent at pH 6; the optimum condition for  $Pb^{2+}$  was a reaction lasting for 80 min, the initial ion concentration was 30 mg/L, the 2.0 g adsorbent at pH 8; besides, the optimum condition for  $Zn^{2+}$  was a reaction lasting for 60 min, the initial ion concentration was 20 mg/L, the 2.0 g adsorbent at pH 8.

**Table 1.** Orthogonal experimental results of unmodified peanut shells.

Factors	Adsorption Rate								
	K1			K2			K3		
A	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	0.700	0.966	0.709	0.711	0.965	0.695	0.704	0.969	0.691
B	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	0.653	0.953	0.711	0.710	0.955	0.715	0.753	0.992	0.669
C	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	0.719	0.957	0.704	0.681	0.954	0.681	0.715	0.988	0.703
D	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	0.733	0.981	0.689	0.708	0.983	0.698	0.675	0.935	0.708
Best Group	Cu <sup>2+</sup>			Pb <sup>2+</sup>			Zn <sup>2+</sup>		
	A <sub>2</sub> B <sub>3</sub> C <sub>1</sub> D <sub>1</sub>			A <sub>3</sub> B <sub>3</sub> C <sub>3</sub> D <sub>2</sub>			A <sub>1</sub> B <sub>2</sub> C <sub>1</sub> D <sub>3</sub>		

**Table 2.** Anova table of unmodified peanut shells.

Variance Source	Factors											
	A			B			C			D		
SS	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	0.000	0.000	0.001	0.015	0.003	0.004	0.003	0.002	0.001	0.005	0.005	0.001
Df	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	2	2	2	2	2	2	2	2	2	2	2	2
MS	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	0.000	0.000	0.571	2.609	1.200	2.286	0.522	0.800	0.571	0.870	2.000	0.571
F-value	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	4.460	4.460	4.460	4.460	4.460	4.460	4.460	4.460	4.460	4.460	4.460	4.460
Significance	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	\	\	\	\	\	\	\	\	\	\	\	\
Note	Error: Cu <sup>2+</sup> : 0.02, 8; Pb <sup>2+</sup> & Zn <sup>2+</sup> : 0.01, 8; \—non-significance.											

**Table 3.** Orthogonal experiment results of modified peanut shells

Factors	Adsorption Rate								
	K1			K2			K3		
A	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	0.602	0.595	0.731	0.646	0.847	0.702	0.651	0.906	0.655
B	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	0.418	0.633	0.665	0.738	0.792	0.731	0.744	0.923	0.692
C	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	0.599	0.783	0.704	0.659	0.769	0.675	0.642	0.873	0.708
D	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	0.649	0.736	0.689	0.611	0.769	0.671	0.639	0.843	0.728
Best Group	Cu <sup>2+</sup>			Pb <sup>2+</sup>			Zn <sup>2+</sup>		
	A <sub>3</sub> B <sub>3</sub> C <sub>2</sub> D <sub>1</sub>			A <sub>3</sub> B <sub>3</sub> C <sub>3</sub> D <sub>3</sub>			A <sub>1</sub> B <sub>2</sub> C <sub>3</sub> D <sub>3</sub>		

**Table 4.** Anova table of modified peanut shells

Variance Source	Factors											
	A			B			C			D		
SS	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	0.004	0.164	0.009	0.209	0.127	0.007	0.006	0.049	0.002	0.002	0.018	0.005
Df	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	2	2	2	2	2	2	2	2	2	2	2	2
MS	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	0.072	1.832	1.565	3.783	1.419	1.217	0.109	0.547	0.348	0.036	0.201	0.870
F-value	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
	4.460	4.460	4.460	4.460	4.460	4.460	4.460	4.460	4.460	4.460	4.460	4.460
Significance	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>
Note	Error: Cu <sup>2+</sup> : 0.22, 8; Pb <sup>2+</sup> : 0.36, 8; Zn <sup>2+</sup> : 0.02, 8; \ —non-significance.											

**Table 5.** Reaction kinetics parameters of unmodified peanut shells

Adsorbent	Initial ion concentration	Apparent first order		Apparent second order	
		k1	r1	k2	r <sup>2</sup>
Unmodified peanut shells	Pb <sup>2+</sup> (40mg/L)	0.0257	0.3769	0.4277	0.9947
	Cu <sup>2+</sup> (40mg/L)	0.0397	0.6709	0.4630	0.9987
	Zn <sup>2+</sup> (40mg/L)	0.0319	0.2885	0.1145	0.9976
	Pb <sup>2+</sup> (50mg/L)	0.0527	0.7279	0.1304	0.9993
	Cu <sup>2+</sup> (50mg/L)	0.0524	0.3590	0.4402	0.9932
	Zn <sup>2+</sup> (50mg/L)	0.0234	0.2510	0.3375	0.9867

**Table 6.** Reaction kinetics parameters of modified peanut shells

Adsorbent	Initial ion concentration	Apparent first order		Apparent second order	
		k1	r1	k2	r <sup>2</sup>
Modified peanut shells	Pb <sup>2+</sup> (30mg/L)	0.0361	0.7412	0.1264	0.9707
	Cu <sup>2+</sup> (30mg/L)	0.0289	0.7508	0.0423	0.9715
	Zn <sup>2+</sup> (30mg/L)	0.0321	0.5385	0.1465	0.8934
	Pb <sup>2+</sup> (50mg/L)	0.0922	0.9178	0.0613	0.9961
	Cu <sup>2+</sup> (50mg/L)	0.0423	0.8610	0.1645	0.9863
	Zn <sup>2+</sup> (50mg/L)	0.0276	0.5499	0.1096	0.9615

### Dynamics analysis

The process and dynamical behavior of adsorption of metal ions (Pb<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>) by peanut shells was consistent with the Lagergren apparent second-order kinetic model as shown in Table 5 and Table 6, which indicated that the physical adsorption and the biological adsorption of heavy metals happened simultaneously which coincided with many previous reports. Under the optimum condition, the average absolute deviation rate of the equilibrium adsorption amount from the Lagergren apparent first-order kinetic model ( $q_e$ , cal) and experiments ( $q_e$ , exp) was relatively large, while the one from Lagergren apparent second-order kinetic model ( $q_e$ , cal) and experiments ( $q_e$ , exp) was much smaller. Therefore, the apparent second-order adsorption dynamics model better

describes the adsorption process under the optimum condition. Moreover, the apparent second-order adsorption dynamics model was more suitable for the system when reached equilibrium after a much longer time with  $q_e$  unknown.

### Infrared spectrum (IR) analysis

As stated in Fig. 5 and Fig. 6, the infrared absorption spectra of unmodified and modified peanut shells is similar, which indicates that the hydrochloric acid modification does not have a great influence on the chemical properties of peanut shells.

The absorption peak of modified peanut shells broadened at 3420 cm<sup>-1</sup> and 1050 cm<sup>-1</sup> and the absorption intensity increased at 1640 cm<sup>-1</sup> and 1510 cm<sup>-1</sup>.

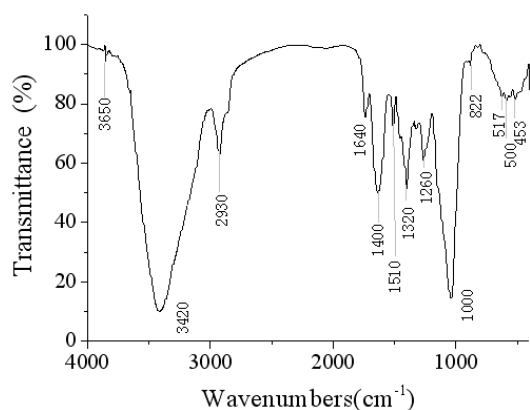


Fig. 5. Infrared spectrum of unmodified peanut shells

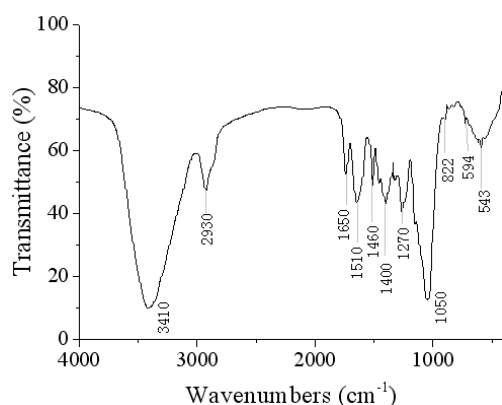


Fig. 6. Infrared spectrum of modified peanut shells.

A strong absorption peak at  $3420\text{ cm}^{-1}$  was stretching the vibration absorption peak of unsaturated hydrocarbon together with a small amount of the amino group; the peak at  $2930\text{ cm}^{-1}$  was an asymmetric stretching vibration of methylene; the peak at  $1640\text{ cm}^{-1}$  was a stretching vibration absorption peak of carbonyl; the peak at  $1510\text{ cm}^{-1}$  was likely to be an anti-symmetric stretching vibration absorption peak of the ester group from carboxylate; the peak at  $1270\text{ cm}^{-1}$  was a plane vibration absorption peak of hydroxy from cellulose; the peak at  $1050\text{ cm}^{-1}$  was a vibration absorption peak of polysaccharide backbone, which is mainly caused by stretching the vibration of C-OH from sugars or P-O-C.

## CONCLUSION

Peanut shells have the ability to adsorb  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions which could be influenced by factors such as the adsorption reaction duration, the initial ion concentration, dosage of the samples and the pH value. The adsorption rate grew with the increase of the pH value, the reaction duration and the adsorbent dosage, while the adsorption rate decreased with the initial rise in ion concentration. The study indicated that the adsorption of metal ions by peanut shells is completed within a short time. The effect of the recommended factors on the

adsorption was not obvious and the dynamical behavior of unmodified and modified peanut shells was more suitable for the Lagergren second-order kinetic model. The maximum adsorption rates of unmodified peanut shells for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  were 99.8%, 77.6%, 72.3%, respectively, while the maximum adsorption rates of modified peanut shells for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  were 97.6%, 80.3%, 77.1%, respectively. In a word, the absorption efficiency of modified peanut shells was higher than that of unmodified shells. Meanwhile, the adsorption efficiency of modified peanut shells was increased and further optimized.

So far, enormous progress has been made in the study of the adsorption of heavy metal ions. The experiments showed that the adsorption by agricultural and forestry waste is an effective method for removing heavy metals from wastewater, but its industrial introduction was slow and the study and development of the adsorption carriers need more hard work. There were various factors affecting the adsorption efficiency which should be further discussed, such as the modification methods and characteristics of the absorbing materials, desorption conditions of the adsorption materials and the recycling of heavy metal ions together with the regeneration and repeated utilization of the adsorbent. The influence of the coexisting cations on the adsorption process should be taken into consideration if the solution is a mixture of metals. In order to put adsorption of heavy metals into applications more efficiently, we should focus on the adsorption mechanism, the regeneration of biological adsorbent, reuse of industrial sewage, and establishment of a better adsorption technical process in the next stage.

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## МОДИФИЦИРАНЕ НА ШЛЮПКИ ОТ ФЪСТЪЦИ И ТЯХНОТО ПРИЛОЖЕНИЕ ЗА АДСОРБЦИЯ НА ТЕЖКИ МЕТАЛИ

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(Резюме)

Шлюпките от фъстъци са пробен материал за адсорбция. Изследвана е способността им да адсорбират тежки метали ( $Pb^{2+}$ ,  $Cu^{2+}$  и  $Zn^{2+}$ ) в зависимост от различни фактори (рН, времетраене на пиролизата, начална концентрация, доза). Резултатите показват, че адсорбцията на тежките метали расте с повишаването на рН. Беше установено, че адсорбцията на йоните на тежки метали върху не-модифицирани шлюпки протича добре в кисела среда, докато при модифицираните това е в алкална среда. Степента на адсорбция достига 88% от максималната след 15 минути с тенденция към равновесие след 50 мин. Степента на адсорбция расте с нарастване на концентрацията на металните йони, като максимумът се достига при 30 mg/L, а след това тя намалява.

Динамичното отнасяне както на модифицираните, така и на не-модифицираните шлюпки добре се описват от модела на Lagergren за химична кинетика на реакция от 2-ри порядък. Адсорбционният ефект на модифицираните шлюпки е много по-добър от не-модифицираните.