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Study on the adsorption of lead(II)in wastewater by hazelnut shell powder

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ABSTRACT

In order to study the adsorption mechanism of hazelnut shell powder on Pb^{2+},This work studied on kinetic adsorption properties and isothermal adsorption property of Pb^{2+} in hazelnut shell powder, and the thermodynamic analysis was carried out. The results show that the Pseudo-second-order model is suitable for the adsorption of Pb^{2+} on HS, the maximum adsorption capacity obtained by Langmuir model is very close to the actual value, and maximum adsorption capacities were 65.66mg/g. The process of hazelnut shell powder adsorbent of Pb^{2+} was an exothermic process.

KEYWORDS

Hazelnut shell powder;
Biosorption;
pb(II);
Kinetics;
Isothermal adsorption.

INTRODUCTION

Heavy metal pollution is irreversible,they do not likely organic pollutants after a period of time can be achieved by biological degradation,and they can never be automatically reduced to a safe concentration range. The only effective way to reduce the pollution of heavy metal ions is to remove the heavy metal ions from water. Domestic and foreign scholars have focused on the research of forestry and agricultural residues such as straw, peel, bark, nut shell to prepare the adsorbent for the adsorption of heavy metal ions[1-5]. The hazelnut shell waste rich in cellulose, hemicellulose, lignin is very suitable for the adsorption of metal elements in the water. In this work,the adsorption mechanism of systematic removal of Pb^{2+} of hazelnut shell adsorbent was studied and the effects of pH, temperature, adsorption time and adsorbate concentration on the adsorption were investigated. The adsorption behavior of Pb^{2+} in water was analyzed by using Langmuir, Freundlich isothermal adsorption model, thermodynamic model, pseudo-first-order kinetic model and pseudo-second-order kinetic model.

EXPERIMENTS

Instrumentation and reagents

Hazelnut shell produced in Liaoning Xiuyan, 70 °Cdry and crushed 80 mesh sieve,later put in the dryer. The product was named HS.

Atomic absorption spectrophotometer (AAnalyst 200, PerkinElmer)ÿgas-bath Constant temperature oscillator (THZ-92AÿSH1717).

Adsorption experiment method

A certain amount of hazelnut shell powder was added in the 100ml erlenmeyer flask, then add 20ml a certain concentration of Pb^{2+} standard solution, adjusting pH value, adsorption of a certain time in a certain temperature (30°C, 40°C 50°C, 60°C) oscillated adsorption. The Pb^{2+} concentration in the filtrate was determined by the flame atomic absorption spectrophotometer,and calculate the adsorption capacity (1) and adsorption rate (2).

$$q = \frac{(c_0 - c_e)V}{m} \quad (1)$$

$$Adsorption\% = \frac{c_0 - c_e}{c_0} \quad (2)$$

Where c_0 and c_e are the initial concentration and equilibrium concentration (mg/L) ; m was the mass of the adsorbent used for adsorption experiment(mg); V was the volume of adsorbate solution(mL).

RESULTS AND DISCUSSION

The effect of pH on adsorption property

From the data in Figure 1, when the initial pH increased from 2 to 4, the adsorption rate of HS to pb^{2+} was increased from 20.87% to 98.12%. When pH>4, the adsorption tends to be stable. This is due to the hazelnut shell containing - NH, - OH, R-C-NH_2, C=O, COO^- groups. The adsorption activity is surrounded by proton, and in high pH value of the solution, adsorption activity is exposed,so when the solution pH was high up, HS on pb^{2+} adsorption performance improved significantly.

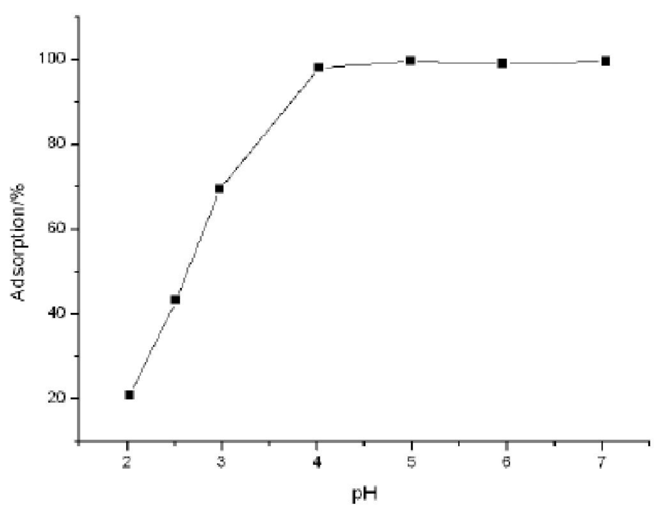

Figure 1 : Effect of pH on the adsorptivity

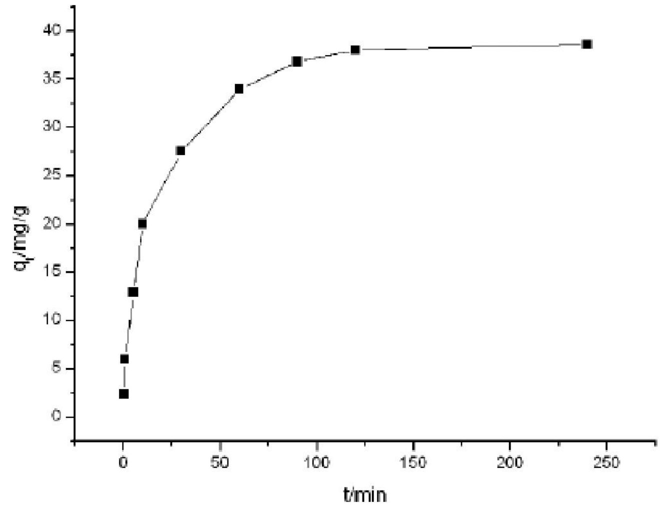

Figure 2 : Effect of time on adsorption

Adsorption kinetics

Kinetic and equilibrium models were employed to analyse the data of the complete adsorption process to better understand the Pb^{2+} sorption characteristics by HS. From Figure 2,we can see that the adsorption rate of HS on pb^{2+} is very fast, and 120 min contact time was considered to be adequate for the adsorption. We used pseudo-first-orde kinetic model (3), pseudo-second-order kinetic model (4), the adsorption process was simulated to analyze the relationship between adsorption time and adsorption capacity, fitting results are shown in Figure 3, the corresponding parameters are listed in TABLE 1.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

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

Where q_e represents the calculated values of the adsorption capacity of HS at equilibrium (mg/g); q_t (mg/g)was the adsorption amount at time t (min) ; K_1 (min^{-1}), K_2 (g/ (mg·min)are the rate constants of pseudo-first-order and pseudosecond-order kinetics equations, respectively.

It can be seen that the correlation between the pseudo-second-order kinetic model fitting results is higher than that of the pseudo-first-order kinetic model, and the linear correlation coefficient is more than 0.999. And the saturated adsorption capacity

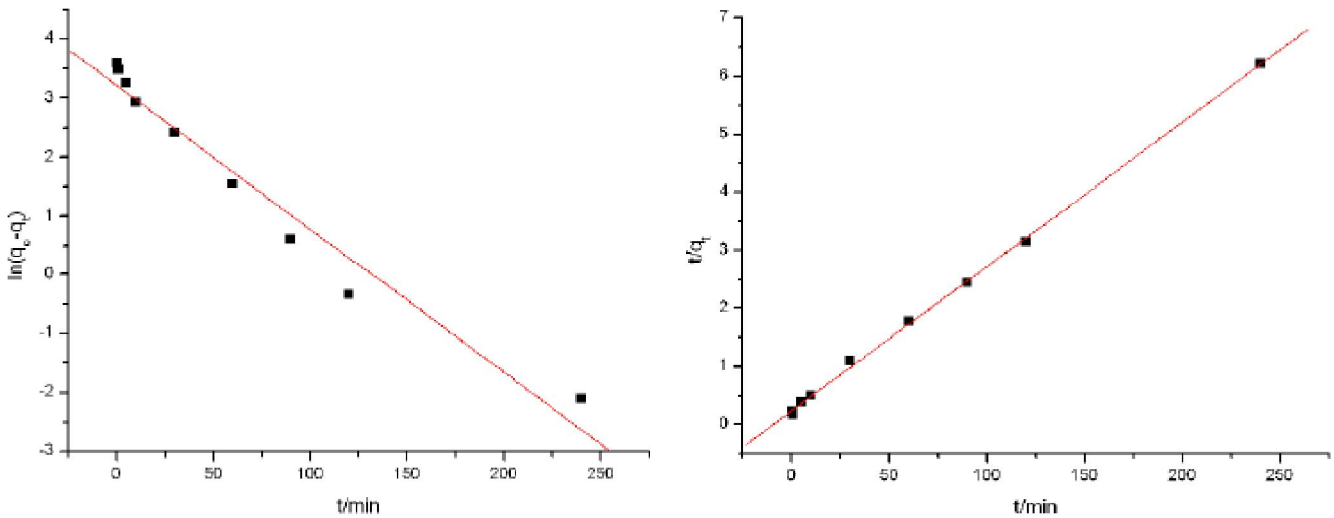

Figure 3 : a. Pseudo-first-order kinetics plots for the adsorption of pb^{2+} on HSÿb Pseudo-second- order kinetics plots for the adsorption of pb^{2+} on HS

TABLE 1 : Kinetic parameters for the removal of MG by HS

		Quasi first order equation				Quasi two order equation		
qe, exp	k_1	$q_{e,cal}$	Relative error/%	R^2	k_2	$q_{e,cal}$	Relative error/%	R^2
38.57	0.024	24.98	35	0.9625	0.0026	40.2	-4	0.9991

obtained by the pseudo-second-order kinetic model is very close to the experimental saturated adsorption capacity. The relative error is -4%, which indicates that the pseudo-second-order kinetic model can describe the adsorption process.

Adsorption isothermal

It can be seen that the adsorption capacity increases with the increase of pb^{2+} concentration in solution, and the final equilibrium is reached. The experimental data were analyzed by using different isothermal adsorption models, and the theoretical basis of HS adsorption on pb^{2+} could be provided. In this study, the data were fitted to the Langmuir isotherm model (5), Freundlich isothermal adsorption model (6), and the data from Figure 4a. The results are shown in Figure 4 and TABLE 3.

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m} \quad (5)$$

$$\lg q_e = \lg k_F + \frac{1}{n} \lg c_e \quad (6)$$

Where q_e represents the calculated values of the adsorption capacity of HS at equilibrium (mg/g); q_m was the maximum adsorption capacity (mg/g); c_e was adsorbed at equilibrium when the concentration (mg/L), and b was Langmuir the isothermal adsorption equation constant (L/mg); k_F was the Freundlich constant (mg/L),and n was related to the adsorption capacity.

From the linear correlation coefficient, Langmuir isothermal adsorption model was more suitable for describing the adsorption process of HS on pb^{2+}. The saturated adsorption capacity and the measured values were very close to the Langmuir isothermal adsorption model, and the relative error was -0.7%, which indicated that the adsorption of pb^{2+} on the HS was a single molecular layer adsorption.

Thermodynamic analysis

Investigated the effect of temperature on the adsorption properties, and according to the formula (7) (8) (9) calculation of the value of HS on adsorption of Pb^{2+} on ΔG^0, ΔH^0, ΔS^0

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

$$\ln k = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (8)$$

$$k = \frac{c_a}{c_e} \quad (9)$$

Where R was a gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$); T was the thermodynamic temperature (K); k was the

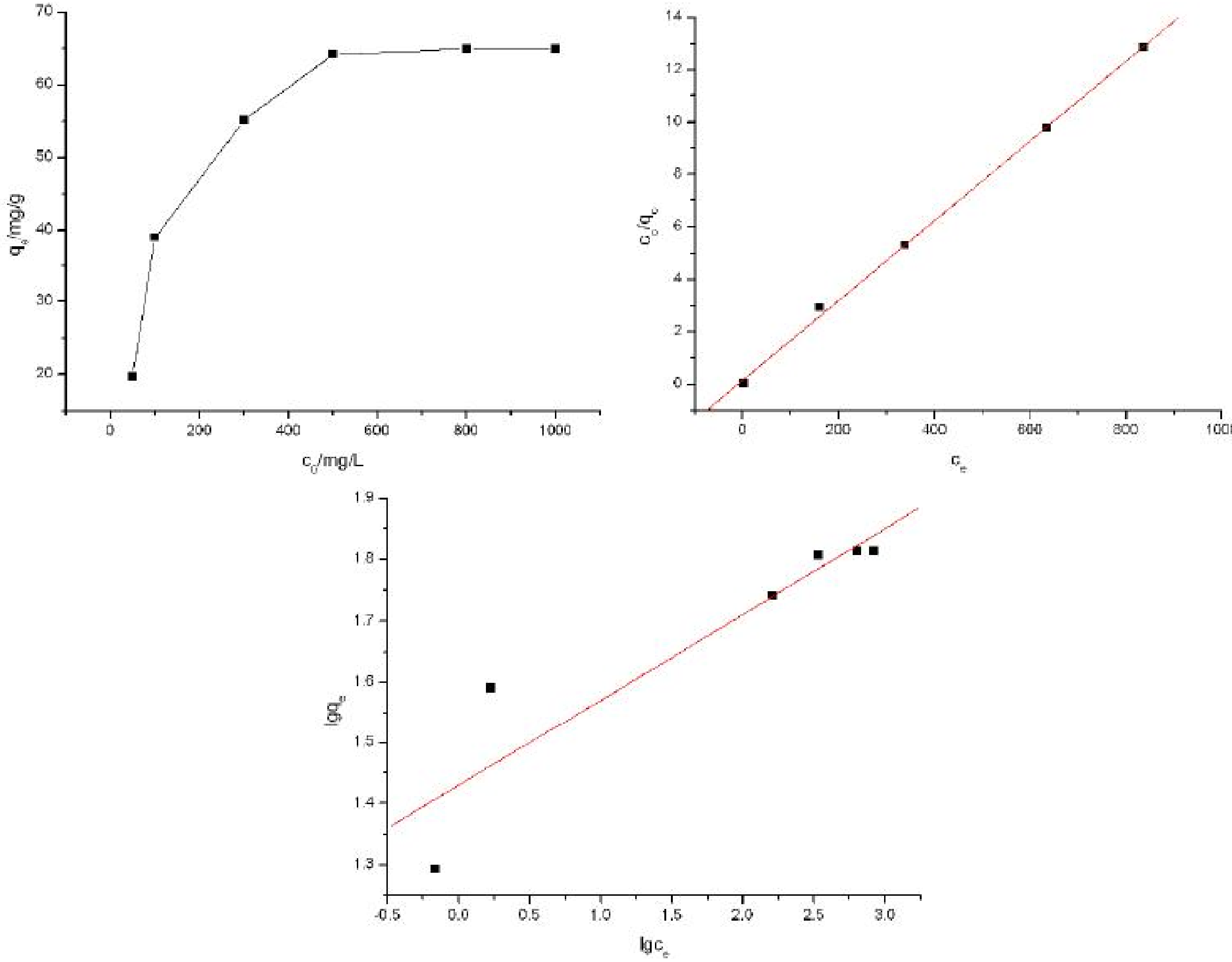

Figure 5 : a Influence of initial concentrations on the absorption capacity of HS; b Langmuir adsorption isotherm plots of HS; c Freundlich adsorption isotherm plots of HS

TABLE 2 : Langmuir, Freundlich parameters for adsorption isotherms of pb^{2+} by HS

		Langmuir				Freundlich	
$q_{m,\ exp}$/mg/g	qm/mg/g	b/L/mg	R^2	Relative error/%	K_F	n	R^2
65.02	65.66	0.108	0.9990	-0.7	26.91	7.12	0.8552

TABLE 4 : Thermodynamic parameters of pb^{2+} adsorption of HS

Temperature (K)	Concentration mg/L	ΔG^0/KJ/mol	ΔH^0/KJ/mol	ΔS^0/J/mol·K
303		-10.2253		
313	100	-8.6066	-2.001	0.024
323		-6.3861		
333		-3.7360		

thermodynamic constant; c_a was metal ion concentrations on the adsorbent at equilibrium and c_e was the equilibrium concentration of metal ions in solution (mg/L).

The experimental results show that the $\Delta G^0<0$, which means that the adsorption process of HS adsorbent for pb^{2+} is a spontaneous process. Temperature from 30°C increased to 60°C, the ΔG^0 values increased with the increase of temperature, which indicates that the high temperature is not conducive to the hazelnut shell powder adsorption of Pb^{2+}. The adsorption reaction $\Delta H^0<0$, also shows that the adsorption was exothermic process.

CONCLUSIONS

HS has very good adsorption performance, can adsorb pb^{2+} in water, and it can reach the adsorption equilibrium within two hours. The saturated adsorption capacity of pb^{2+} by Langmuir adsorption model is 65.66mg/g. In summary, HS can be used in the treatment of real waste-water, and it has achieved good results.

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