Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(6):649-653

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Removal of cadmium ions from aqueous solution using chemically modified peanut shell

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ABSTRACT

The efficiency of chemically modified peanut shell (CMPS) on adsorbing cadmium ions was evaluated in this paper. The kinetic, isothermal and thermodynamic models were applied to study adsorption properties and characteristics in a batch system. The pH, adsorption time and initial concentrations were followed. The results indicated that under the indoor temperature (25 ℃), when pH was 8 and adsorption time was 40min, the adsorption capacity reached the maximum, 40.10mg/g. The kinetic adsorption was better described by pseudo-second-order rate model; Equilibrium experimental data were both fitted to linear Langmuir and Freundlich models, but Langmuir model provided a better coefficient of determination value; the theoretical maximum adsorption capacity calculated by Langmuir equation were 95.24, 105.26, 109.89mg/g at 283K, 298K and 308K respectively.

Keywords: chemically modified peanut shell, adsorption, cadmium ions, kinetics

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INTRODUCTION

With the rapid industry development in China, water resource pollution by heavy metals has become increasingly severe. Because heavy metals are toxic, non-degradable and therefore persistent in the environment [1], and can enter the food chain through the water channels [2], the water pollution by heavy metals causes a lot of disease problems such as renal kidney disease, nervous system damages, cancer and mental retardation [3]. Especially, the cadmium ions pollution of waters could create severe problems to environment and human health. According to the reports: in 1931, in Toyama Japan, the water pollution by cadmium resulted that the rice did not grow and most residents caught itai-itai disease; in 2006, Bac Giang located in Guangdong China, was polluted by cadmium, the content exceeded 20 times of the limit for standard, contributing to 100 thousand people lack water.

Recently years, the removal of cadmium ions from aqueous solution using agricultural wastes is popular with easy-to-operate, low price, high efficience and non-secondary pollution. The abundant and low-price agricultural wastes are available, because China is a big agricultural country, producing 1.0×10^9t agricultural wastes every year[4]. However the most of them are burned rather than being resource utilized, which caused severe air and soil pollution. So, agricultural wastes can be utilized to dispose pollution, it must create favorable environment benefits.

The previous work of removing cadmium ions from aqueous solution by agricultural wastes has proved that some agricultural wastes are effective in absorbing cadmium ions in aqueous solution. For instance, Xiao-bao Gong used rape straw to remove cadmium ions, at pH 6.0 the adsorption capacity was maximum, 17.7mg/g [5]. Yang Ding, et al, did the work on adsorption of cadmium ions onto rice straw, the results show that 0.5% (w/v) rice straw absorbed 50mg/mL $CdSO_4$ solution for 3h, the content of cadmium ions in rice straw reached 8-10 mg/g [6].

However, there is still dearth of the study on adsorbents' performance on adsorption of cadmium ions. In this study, the agricultural waste peanut shell was chemically modified, and employed for evaluating the efficiency of absorbing cadmium ions in aqueous solution. An attempt was made to explore the optimum adsorption conditions and adsorption properties. This paper aims for providing more documents and theoretical basis for adsorption of cadmium ions with agricultural wastes.

EXPERIMENTAL SECTION

Preparation of chemically modified peanut shell (CMPS)
Peanut shells were purchased from a farmer's market in Jilin (Jilin, China), were washed with tap water to remove soil and debris, and washed three times using deionized water. The cleaned peanut shells were dried at 60℃ to constant weight. After that, the dried samples were crushed with a stainless blender, passed through a 100-mesh sieve and stored in a jar.

The raw material was soaked in 50*wt*% $ZnCl_2$aq at 1:1 ratio for 24h and activated by 640W microwave for 4min. When cooled to indoor temperature, washed with deionized water till the filtrate was neutral [7]. Then the filter paper and chemically modified peanut shell were dried at 80℃ to constant weight and separated. Then the chemically modified peanut shell was kept in jars.

Bath adsorption experiment
Batch adsorption experiments were performed by adding 0.2g CMPS to 250mL conical flasks containing 100mL solutions with 100mg/L cadmium ion concentrations. The effect of pH on adsorption was studied in the range of 2.0-8.0 (when pH was above 8.0, the precipitation was generated in the solutions), and pH was adjusted with 0.1M NaOH and 0.1M HCl. Then, the samples were agitated on a concussion incubator at 150rpm for a certain time. The experiments were carried out at indoor temperature (25℃). The concentrations of cadmium ions were determined by flame atomic absorption spectrometer (FAAS).

The adsorption time was studied for building adsorption kinetic models. At the optimum pH and indoor temperature, 0.2g CMPS was used to absorb 100mL solutions with 100mg/L cadmium ion concentrations. The samples were collected at 5, 10, 20, 30, 40, 60, 90, 120min respectively and filtered for analyzing residual cadmium ion concentrations.

At the optimum pH and saturated adsorption time, the isothermal adsorption models were set up with the solutions with different initial concentrations. The study initial concentrations ranged from 100mg/L to 600mg/L. The experiments were carried out at 10℃, 25℃, 35℃ respectively.

Each analysis was carried out in triplicate for quality control and statistical purposes.

Measurement of adsorption capacity
The adsorption capacity of CMPS absorbing cadmium ions for each sample was calculated by following equation:

$$Q_e = \frac{(C_0 - C_t)V}{M} \tag{1}$$

where V is the sample volume (L), C_0 is the initial cadmium ion concentration (mg/L), C_t is the cadmium ion concentration at equilibrium (mg/L), M is dry weight of CMPS (g) and Q_e is the adsorption capacity of cadmium ions onto CMPS (mg/g).

RESULTS AND DISCUSSION

Effect of pH on adsorption
The pH is an important factor to affect the adsorption of metal ions onto the liquid/solid interface. Because of the existence of anionic groups on the surface of CMPS, such as carboxylic and hydroxide groups, pH could control the adsorption of the surface charge, the degree of ionization and speciation of metals in solutions [8].

The adsorption amount increases with the rise of pH. The the strongest adsorption was obtained at pH 8, whereas the adsorption was the weakest when pH was 2.

Kinetic Modeling
The experimental data obtained were used to set up adsorption kinetic models. The kinetic parameters for CMPS were calculated by pseudo-first-order and pseudo-second-order kinetic equations [9]. The equations were expressed as following:

The pseudo-first-order kinetic equation:

$$\lg(q_1 - q_t) = \lg q_1 - \frac{k_1 t}{2.303} \tag{2}$$

where q_1 is the adsorption capacity of cadmium ions onto the CMPS at equilibrium (mg/g), q_t is the adsorption capacity of cadmium ions onto the CMPS at t min (mg/g), and k_1 is the pseudo-first-order rate constant (min^{-1}).

The pseudo-second-order kinetic equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \tag{3}$$

Where q_2 is the adsorption capacity of cadmium ions onto the CMPS at equilibrium (mg/g), q_t is the adsorption capacity of cadmium ions onto the CMPS at *t* min (mg/g), k_2 is the pseudo-second-order rate constant (g/mg min).

The parameters of adsorption kinetics calculated by equations (2) and (3) are represented in Table 1. It can be seen, the pseudo-second-order kinetic model provided a better coefficient of determination value (R^2), indicating that it could better describe the kinetic adsorption, correspondingly, it also provided a better agreement between calculated value and the experimental value of adsorption capacity. However, the obtained data for kinetic adsorption were not well fitted by pseudo-first-order kinetic model, the calculated coefficient of determination value (R^2) was just 0.7574. It was concluded that the kinetic adsorption of CMPS absorbing cadmium ions followed the pseudo-second-order kinetic model.

Table 1 Parameters of adsorption kinetics

Experimental value q(mg/g)	pseudo-first-order kinetic equation			pseudo-second-order kinetic equation		
	q_1(mg/g)	K_1(min^{-1})	R^2	q_2(mg/g)	K_2(min^{-1})	R^2
40.10	65.13	0.1237	0.7574	50.00	0.001505	0.9427

Effect of initial concentration and isotherm studies

The adsorption isotherms were studied by varied initial concentrations (100mg/L-600mg/L) at different temperatures (283, 298 and 308 K). As seen in Figure 1, the adsorption capacity increases with the increasing initial concentrations. When the initial concentration was above 400mg/L, the adsorption capacity was more or less constant. Because the increase in initial cadmium ion concentration strengthened the driving force of overcoming the barrier between solid/aqueous phases, but when the initial concentration of cadmium ions was high enough, the surface of CMPS was fully covered by cadmium ions, resulting the rate of adsorption dramatically slowed down.

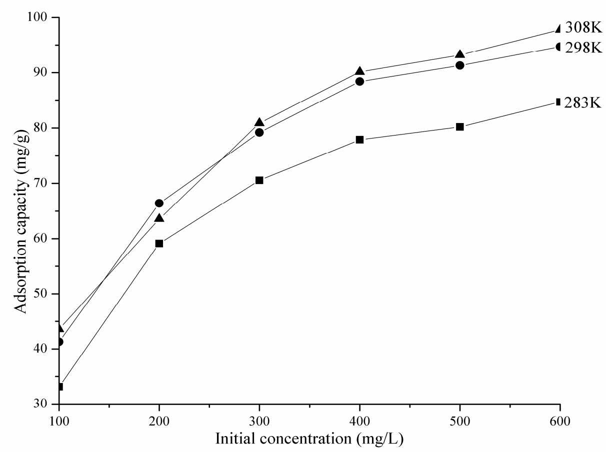

Figure 1 Effect of initial concentration on adsorption of cadmium irons onto CMPS

The Langmuir and Freundlich isothermal models were applied to experimental data. Langmuir isotherm assumes monomolecular layer formation without interaction between the adsorbed molecules during the adsorption process [10]. The Langmuir equation is expressed as following:

$$\frac{C_e}{q_e} = \frac{1}{aQ_m} + \frac{C_e}{Q_m} \tag{4}$$

where C_e is concentration of cadmium ions at equilibrium (mg/L), q_e is adsorption capacity of cadmium ions onto CMPS at equilibrium (mg/g), Q_m is the theoretical maximum adsorption capacity (mg/g), and a is the Langmuir constant [11].

The Freundlich isotherm assumes the adsorption occurred on the heterogeneous surface sites [12]. The linearized form of Freundlich isotherm is represented as following:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \quad (5)$$

where C_e is concentration of cadmium ions at adsorption equilibrium (mg/L), q_e is adsorption capacity of cadmium ions onto CMPS at equilibrium (mg/g), K and n is the Freundlich constants [12].

According to the R^2 as shown in Table 2, both Langmuir and Freundlich models could give a good fit to experimental data at all study temperatures. However, the R^2 fitted by Langmuir model were higher than by Freundlich model at all study temperatures. It was indicated that the adsorption was not only onto monomolecular layer, but also heterogeneous surface sites, but mainly occurred on the monomolecular layer. The theoretical maximum adsorption capacity Q_m calculated by Langmuir equation increased with the elevation of temperature. It was proved that higher temperature was advantageous to adsorption and the process was endothermic in nature. In addition, a calculated by Langmuir equation were all above zero, revealing the adsorption process was spontaneous.

Table 2 Parameters of isothermal adsorption equations

	Langmuir			Freundlich	
Temperature (K)	*Qm*	*a*	R^2	*n*	R^2
283	95.24	0.0176	0.9987	2.8563	0.9122
298	105.26	0.0197	0.9997	3.1526	0.9372
308	109.89	0.0180	0.9994	3.1476	0.9675

Evaluation of CMPS as an adsorbent absorbing cadmium ions

The previous work on adsorption of cadmium ions from aqueous solution onto adsorbents was shown in Table 3. Compared with the unmodified peanut shell, the adsorption capacity elevated greatly after modification; the adsorption was more effective by chemically modified by $ZnCl_2$aq than by phosphoric acid; the adsorption effect of CMPS was better than chemically modified radish cake. That could be explained by that, peanut shells were rich in cellulose, but the cellulose was most crystallinity form, however the activating agent Zinc Chloride could make the activation temperature low and effectively dissolved cellulose, decreased crystallinity, therefore the heavy metal ions could be removed by producing chemical reaction with cellulose.

Table 3 Comparison of adsorbents absorbing cadmium ions

Adsorbents	TMAC[4] (mg/g)	pH	References
CMRK[1]	64.10	6.9	Rita F.L. Ribeiro, et al., 2012[13]
CMPSPC[2]	37.50	4	Guoqiang Xiang, et al., 2009[14]
PS[3]	28.50	neutral	Yongmei Liu, et al., 2011[15]
CMPS	109.89	8	This study

[1] *chemically modified radish cake (CMRK)*

[2] *Chemically modified peanut shell with phosphoric acid (CMPSPC)*

[3] *Peanut shell (PS)*

[4] *Theoretical maximum adsorption capacity (TMAC)*

CONCLUSION

In this study, CMPS was employed to remove cadmium ions from aqueous solution. The result showed that pH and adsorption time were important factors for CMPS absorbing cadmium ions, the adsorption capacity was the highest at pH 8. The kinetic adsorption for CMPS absorbing cadmium ions followed pseudo-second-order kinetic model, and provided a better agreement between calculated value and experimental value of adsorption capacity. At all the study temperatures, Langmuir and Freundlich isothermal adsorption models both well fitted to experimental data, but Langmuir model gave a better fit than Freundlich, indicating that the adsorption was not only onto monomolecular layer, but also heterogeneous surface sites, but mainly onto monomolecular layer. The theoretical maximum adsorption capacity increased with the elevation of temperature, revealing higher temperature was favorable to adsorption. In addition, the adsorption process was a spontaneous and endothermic in nature proved by thermodynamic study.

Acknowledgements
This work was supported by Jilin University Of Chemical Technology, all the experiments were carried out in the lab of Biotechnology, School of chemical engineering and Biotechnology.

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