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Kinetics Study of Cd^{2+} Adsorption on Modified Rice Husks

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Abstract

Kinetics model of Cd^{2+} adsorption by modified rice husks was discussed in this paper. The results showed that the entire adsorption process is in accordance with pseudo-second-order kinetics equation. Equilibrium adsorption amount and reaction rate constant of kinetics equation increased with increase of temperature.

Keywords

Modified rice husk; Adsorption; Cadmium.

1. Introduction

With the development of industrial technology, a large number of heavy metal ions are discharged into water body [1], causing serious environmental pollution. Agricultural wastes as adsorbent materials have attracted much attention due to their rich sources and low prices [2]. Rice husks are rich in hydroxyl groups with a tubular structure, huge specific surface area, and high mechanical strength. They can be chemically modified to introduce one or more active functional groups that have strong adsorption capacity. Therefore rice husks can be used as adsorbent to adsorb heavy metal ions from wastewater [3, 4].

In this paper, rice husk was modified as a adsorbent material to adsorb Cd^{2+} from wastewater in order to explore its adsorption kinetics and resource utilization of agricultural waste for solving metal contamination problems.

2. Materials and methods

2.1 Preparation of modified rice husks

2.1.1 Pretreatment of rice husks

Rice husks were from the Environmental Protection Monitoring Institute of the Ministry of Agriculture. Rice husks were added to a 250 mL screw-top bottle, and then sodium hydroxide solution was poured into the screw-top bottle. The screw-top bottle was put in a water bath shaker with temperature of 85℃ and speed of 150r / min. After 4 hours, the screw-on bottle was taken out, and rice husks were washed to neutral with deionized water, and then dried [5].

2.1.2 Modification of rice husks

0.5g of ethylene diaminetetraacetic dianhydride powder was put in a 250mL screw-top bottle containing 50mL of N, N-dimethylformamide solution, then 0.5g of pretreated rice husk was added. The screw-top bottle was put in a water bath shaker with temperature of 85℃ and peed of 150 r / min. After 4 hours, the screw-on bottle was taken out. The rice husks were washed by N, N-dimethylformamide and sodium hydroxide solution in turn, and finally washed to neutral with deionized water and dried. Thus, modified rice husks were obtained [6].

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2.2 Adsorption experiment

0.1g of modified rice husk was added to a screw-top bottle containing 100 mL of Cd^{2+} solution. Then the bottle was put in water bath oscillator to oscillate and adsorb, afterwards the solution was filtered through 0.45μm filter membrane. The Cd^{2+} concentration in the filtrate was measured by flame atomic absorption spectrometry. The initial concentration of Cd^{2+} solution was 100 mg / L. The reaction temperature range was 15-35℃, and the reaction time range was 0-3 h.

2.3 Adsorption kinetic model

The pseudo-first order dynamic model expressions are shown in formula (1) and (2):

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

$$\ln(q_e - q_t) = \ln q_e - k_t \quad (2)$$

Where q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t is the mass of metal adsorbed at time t (mg/g), k_1 is the first-order reaction rate constant (min-1), t is the adsorption time (min).

The pseudo-second order dynamic model expressions are shown in formula (3) and (4).

$$\frac{dq_t}{dt} = k_2(q_e - q_t) \quad (3)$$

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

Where k_2 is the second-order reaction rate constant (g/mg min)

3. Results and discussion

3.1 Adsorption equilibrium curve

Adsorption equilibrium curve of Cd^{2+} by modified rice dusks at different temperatures was showed in Fig.1.

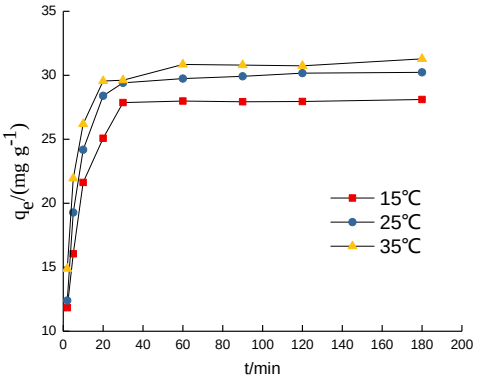

Fig.1 Adsorption equilibrium curve of Cd^{2+} by modified rice dusks

From the figure 1, Cd^{2+} adsorption by modified rice husk reached basically equilibrium in 30 minutes. During the same reaction time, the adsorption capacity of Cd^{2+} by the modified rice husks increased with increase of temperature, which indicated that the adsorption reaction by modified rice husks was an endothermic reaction. Meanwhile, the amount of exposed active groups on the modified rice husk increased because of increase of temperature, so the adsorption reaction was more likely to occur.

3.2 Adsorption kinetics equation

The pseudo-first-order kinetics and pseudo-second-order kinetic models were used to fit experimental data to explore the kinetic characteristics of Cd^{2+} adsorption by modified rice husks at different temperatures [7]. The experimental data was showed in Fig.2, Fig.3 and Table 1.

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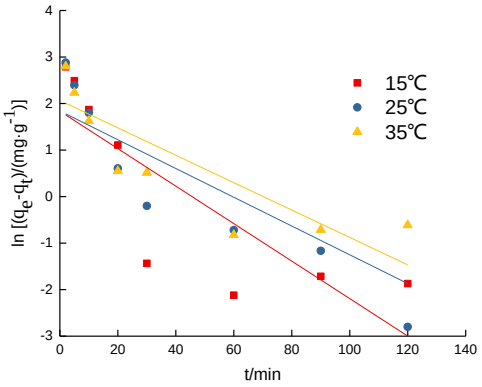

Fig.2 Pseudo-first equation of Cd^{2+}adsorption by modified rice husk

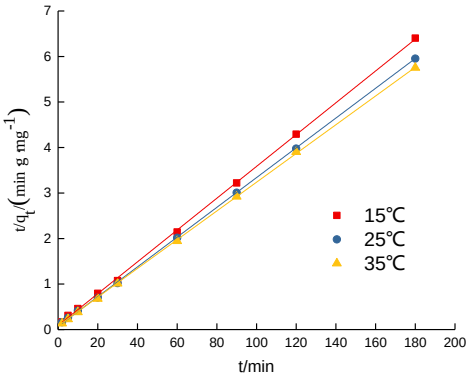

Fig.3 Pseudo-second equation of Cd^{2+}adsorption by modified rice husk

Table 1 Kinetics model parameters

T/K	q_e /(mg g^{-1})	pseudo-first order			pseudo-second order		
		q_{c1} /(mg g^{-1})	k_1 /min^{-1}	R^2	q_{c2} /(mg g^{-1})	k_2 /min^{-1}	R^2
288	28.11	6.28	0.0403	0.6862	28.57	0.0136	0.9997
298	30.23	8.32	0.0420	0.8904	30.67	0.0143	0.9999
308	31.28	6.30	0.0272	0.7182	31.55	0.0161	0.9999

In table 1, T is the absolute temperature; q_e is the equilibrium adsorption amount measured experimentally; qc_1 and qc_2 are respectively the equilibrium adsorption amounts calculated by the pseudo-first-order kinetic equation and pseudo-second-order kinetic equation at theoretical equilibrium; k_1 and k_2 are respectively reaction rate constant of the pseudo-first-order kinetic and the pseudo-second-order kinetic.

From figure 2, the adsorption process of Cd^{2+} by modified rice husk does not fit the pseudo-first-order kinetic equation well. As the adsorption time increased, experiment data gradually deviates from the fitting curve. But the pseudo-second-order kinetics can well describe the adsorption process from figure 3. Similarly, the result can also be found in the table 1. The correlation coefficient R^2 of the pseudo-second-order kinetic equation is above 0.999 at different temperatures, which is much greater than the correlation coefficient of the pseudo-first-order kinetic equation. The obtained equilibrium adsorption amount (qc_2) is much closer to the experimentally measured equilibrium adsorption amount (q_e). Therefore, the adsorption process is more in accordance with the pseudo-second-order kinetic model. It is speculated that the adsorption of Cd^{2+} by modified rice husk is

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mainly chemical adsorption. Reaction rate constant k_2 gradually increases with increase of temperature, which indicates that increasing temperature is beneficial to adsorption reaction and the reaction is an endothermic reaction [8].

4. Summary

The adsorption equilibrium is basically reached within 30 minutes. The adsorption of Cd^{2+} by the modified rice husk conforms to the pseudo-second-order kinetic model (R^2> 0.999), and the reaction is mainly chemical adsorption.

Acknowledgments

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References

[1] Zhu Dandan, Zhou Qixing. A review on the removal of heavy metals from water using nanomaterials. Journal of Agro-Environment Science, Vol. 37(2018), No.8, p.1551-1564.

[2] Li Dongwei, Yang Ke, Fan Meng. Research progress on heavy metal pollution control and remediation. Research Journal of Chemistry and environment, Vol. 17(2013), No.2, p.76-83.

[3] Li Yuan. Microwave modified rice husk for Pb (II), Cd (II) adsorption performance research. Industrial water treatment, Vol. 4(2016), No.3, p.62-65.

[4] Du Z L, Chen H A, An Y, Guo X Y. Advances in the preparation of lignocellulose-based heavy metal adsorbents. Journal of agro-environmental science, Vol. 38(2019), No.12, p.2659-2671.

[5] Kumar P, Barrett D M, Delwiche M J, et al. Methods for pretreatment of lingo cellulosic biomass for efficient hydrolysis and biofuel production. Industrial & Engineering Chemistry Research, Vol. 48(2009), No.8, p.3713-3729.

[6] Qi Yafeng: Adsorption behavior of modified bagasse on heavy metal ions. (Master, Wuhan University of Technology, China, 2012). p.84.

[7] Wang Yanxia, Du Zhaolin, Zheng Tong, et al. Preparation of modified jute and its adsorption on copper ions. Journal of environmental engineering, Vol. 9(2015), No.4, p.1593-1598.

[8] Shao Aiyun, Cheng Deyi, Dai Jingyu, et al. Adsorption properties of thiol modified rice hull carbon on Cd2+ in water. Chinese journal of ecology and rural environment, Vol. 35(2019), No. 8, p.1071-1079.