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Kinetics and Thermodynamics of Cr^{3+} Adsorption on Modified Palm Thread

WENGANG LV[1,2], BING HE[1,2], YANBO ZHOU[1,2], HAIBING QIU[1,2] and JUN LU[1,2,*]

College of Resource and Environmental Engineering, East China University of Science and Technology, No. 130, Meilong Road, Shanghai, 200237, P.R. China

Key Laboratory of Coal Gasification & Energy Chemical Engineering of Ministry of Education, East China University of Science & Technology, Shanghai 200237, P.R. China

*Corresponding author: Tel: +86 13764365741, E-mail: shimily666@163.com; lujun@ecust.edu.cn

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Adsorption of Cr^{3+} from aqueous was studied by using a novel adsorbent *i.e.* (NaOH-PT), palm thread (PT) modified with sodium hydroxide. The electron microscopy, infrared spectroscopy and X-ray diffraction were used to analyze the sorbents before and after modification. The effects of initial pH and contact time on the adsorption were examined. The results showed that the adsorption capacity reached the maximum at pH of 6.0 and the adsorption reached the equilibrium about 8 h. At different temperatures, the adsorption kinetics was better meet the Lagergren pseudo second kinetic model. And the whole adsorption process was controlled by liquid film diffusion and particle diffusion. The adsorption isotherms were better fitted Langmuir adsorption model. According to the calculations of thermodynamic equation, $\Delta G < 0$, $\Delta H = 35.4584$ kJ mol^{-1}, $\Delta S = 139.9828$ J mol^{-1}, those indicated that the adsorption was spontaneous, endothermic, entropy increase and belonged to chemical adsorption.

Key Words: Adsorption, Modified palm thread, Chromium(III).

INTRODUCTION

The heavy metal ions, one of the most important pollutants in waste water. In recent decades, due to the rapid development of industry, heavy metals pollution has attracted the world's attention. Heavy metals such as chromium, zinc, copper, nickel, lead, mercury and cadmium can be detected in the wastewater. These wastewater containing heavy metals mainly comes from electroplating, metallurgy, mining, battery manufacturing, oil refining, leather production, pesticide, printing and dyeing, paint production and photography and other industries[1,2]. Heavy metals in environment can be accumulated in living tissue and even have the effect on the cause of cancer. For this reason, this wastewater must be processed before discharge. The traditional treatment methods of heavy metal wastewater contain[3] chemical precipitation, ion exchange, electrolytic flotation method, membrane separation technology (ultrafiltration, nanofiltration, reverse osmosis, electrodialysis) and solvent extraction method, *etc*. But these methods generally applies to waste water with high concentration of heavy metal ions. But for the low concentration (< 100 mg L^{-1}) wastewater[4], the traditional methods are not suited and high cost.

In recent years, the adsorption method[2,3], suitable for treatment of the wastewater of low concentration of heavy metal ions, has been greatly developed. Activated carbon is one of the most commonly used absorbents, but its cost is more expensive[5]. In order to find low-cost adsorbents, many researches on materials have been studied, such as chitosan, clay, montmorillonite, fly ash, zeolite, algae and agricultural wastes[6]. The results showed that the agricultural wastes were the ideal material. The agricultural wastes[2,4,7-16] were studied including peanut hulls, sawdust, corn cobs, palm kernel shell, modified cellulose materials, coconut shells, bagasse, masson pine bark, modified lignin, tea, banana peel, orange peel, coffee residue, sugar beet pulp.

Sawdust[8], peanut shells, corn cobs[9], straw[17] have been studied on adsorbing Cr^{3+} from wastewater, but the palm thread was less researched. In this paper, the palm thread (PT) was modified with sodium hydroxide and used for the adsorbent to adsorbing Cr^{3+} from wastewater. Many parameters those affected the sorption were investigated such as the solution pH, the initial concentration, temperature, reaction time and adsorption kinetics and thermodynamic behaviour were studied. These all had the theoretical and practical value on the using of palm thread to treat wastewater of heavy metals.

EXPERIMENTAL

Palm thread (PT) was obtained from local palm trees (Shanghai, China). The palm thread was washed several times with deionized water to remove dust and soluble impurities.

Then it was dried for 12 h in an oven at 65 ºC and cut into pieces of length of 1-3 mm. The palm thread, only washed by the deionized water, was labeled as palm thread. $CrNO_3 \cdot 9H_2O$, NaOH are of analytical grade and were purchased from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China). The standard solutions and HNO_3 for AAS were guaranteed reagent and were purchased from Alfa Aesar A Johnson Matthey Company (NJ, USA).

Palm thread modified with NaOH (NaOH-PT): Modified steps were as follows 1: 20 g of palm thread and 400 mL of 3 % (w/w) NaOH solution were mixed together in flask (1000 mL). The flask was shaken with 120 rpm by water bath oscillator for 5 h at 25 ºC. Then the liquid was discharged and the modified palm thread was washed with deionized water until the pH was neutralized (pH 6-7). Then it was dried for 12 h at 65 ºC and was labeled as NaOH-palm thread.

Characterization of sorbent: The surface configuration of palm thread and NaOH-PT was showed by scanning electron microscope JSM-6360LV(JEOL, Japan). Specific surface area was measured by time methylene blue adsorption method[18]. Natural biomass materials contain rich organic functional groups, like hydroxyl, carboxyl, phenol and carbonyl. In the modification and adsorption process, these functional groups can play important roles. These were analyzed by fourier transform infrared spectroscopy Nicolet 5700 (Thermo Electron, USA) and X-ray diffractometer Ultima IV (Rigaku, Japan).

Batch mode sorption for Cr^{3+}: The palm thread and NaOH-PT to adsorb Cr^{3+} were examined by measuring the initial and equilibrium concentrations of Cr^{3+} in a batch system. Batch mode adsorption studies were carried out by shaking 60 mL screw cap vials with polytetrafluoroethylene sealer containing 0.2 g of sorbents and 50 mL of Cr^{3+} solutions of desired concentration on an orbital shaker equipment at 120 rpm, 25 ºC and at an initial pH 5. At the end of the adsorption period, the supernatant solution was separated by centrifugation at 3000 rpm for 10 min.

Analysis: After equilibrium was reached, the residual of Cr^{3+} concentration was analyzed using Jena650P atomic absorption spectrophotometer (Jena, Germany) at wavelengths of 425.4 nm. The Cr^{3+} uptake (q) was calculated from the mass balance as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where q_e is the equilibrium sorption capacity (mg g^{-1}); V is the experimental solution volume (L) and m is the amount of adsorbent (g) used; C_0 and C_e are the initial and equilibrium concentrations of Cr^{3+} (mg L^{-1}), respectively.

RESULTS AND DISCUSSION

Analysis of surface configuration: The SEM photos of palm thread and NaOH-PT were shown in Fig. 1(a)-(b). As shown in Fig. 1(a), palm thread had a complete fiber structure and the structure of these fibers formed the skeleton of palm thread, therefore it had certain mechanical strength. The fiber structures of NaOH-PT remained intact, indicating that NaOH did not damage the fiber backbone, keeping good mechanical strength. Comparing to the palm thread, NaOH-PT became more rough and its microtubule structure expanded. These features could be due to the formation of alkali cellulose as a result of the reaction of NaOH with cellulose[19].

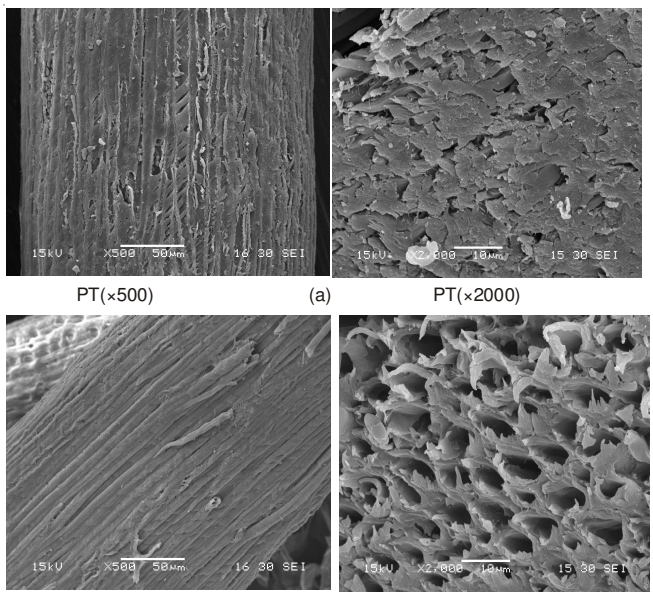


Fig. 1. SEM micrographs of PT (a) and NaOH-PT (b)

Analysis of specific surface area: The specific surface areas of palm thread and NaOH-PT were shown in Table-1. The results showed that comparing to palm thread, specific surface area of NaOH-PT greatly improved 230 %. This proved that NaOH modification can effectively increase the specific surface area of the adsorbent, thereby increasing the contact area and contact probability of the adsorption material and heavy metal ions.

TABLE-1
SPECIFIC SURFACE AREA OF PALM THREAD AND NaOH-PT

Adsorbent	Specific surface area ($m^2 \cdot g^{-1}$)
Palm thread	0.57
NaOH-PT	1.88

Analysis of fourier transform infrared spectroscopy: The FTIR spectrum of palm thread and NaOH-PT were shown in Fig. 2.

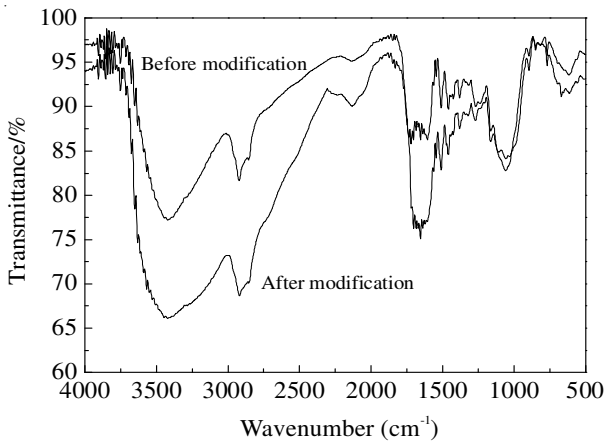
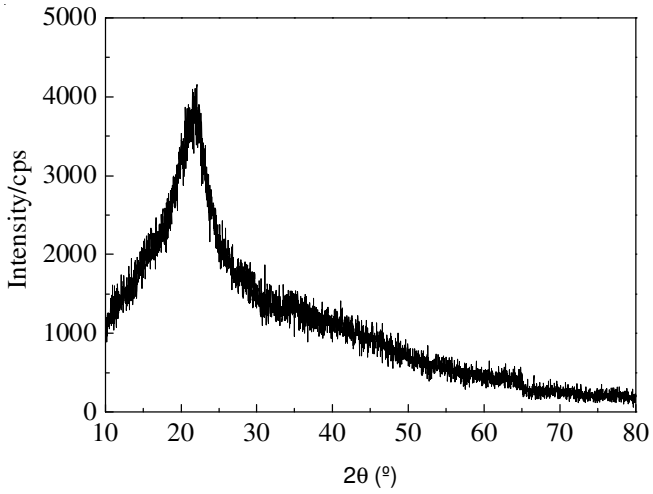


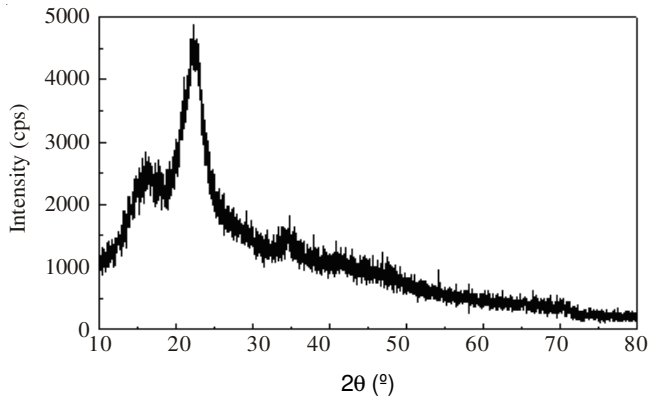
Fig. 2. FT-IR spectra of palm thread before and after modification

Peaks at 3396, 2919, 1706 and 1076 cm^{-1} are observed in the spectrum. The broad and strong band at 3396 cm^{-1} is attributed to the overlapping of O-H and N-H. Peak at 2919 cm^{-1} is the C-H stretching vibration. The peaks at 1706 and 1076 cm^{-1} can be separately assigned to C=O and C-O stretching vibration. As shown in Fig. 2, after modification with NaOH, the peaks at 3396, 2919, 1706 and 1076 cm^{-1} all strengthened. As for the reasons: that the components of hemicellulose and lignin were reduced in the process of NaOH modification made the relative content of cellulose greatly increased, thereby increasing the phenolic hydroxyl group (O-H) and the unsaturated aldehyde carbonyl (C = O).

Analysis of X-ray diffraction: XRD spectra of NaOH-PT and Cr^{3+}-laden NaOH-PT were shown in Fig. 3. After contact with Cr^{3+} (Fig. 3b), the XRD peaks for NaOH-PT after absorbing Cr^{3+} (b) were observed to be strengthened at 2θ values 16.42º and 34.64º and they both were characteristic peaks of Cr^{3+}. This suggested that the Cr^{3+} were adsorbed on to the adsorbent.



(a) NaOH-PT before adsorbing Cr^{3+}



(b) NaOH-PT after adsorbing Cr^{3+}

Fig. 3. X-ray diffraction analysis on palm thread before and after Cr^{3+} adsorption

Effect of initial pH on Cr^{3+} adsorption: At pH > 6.10[20], temperature 298 K and concentration of Cr^{3+} 50 mg/L, the precipitate would appear, so the maximum pH of experiment was designed as 6.0. Effect of pH is shown in Fig. 4.

As shown in Fig. 4, the effect of pH on adsoption was soobvious. When pH increased from 1 to 6, the capacity increased rapidly from 1.45 mg g^{-1} to 24.25 mg g^{-1}. The reason[8] of this result was considered as followed: at low pH, due to the high concentration of H^+, the H^+ would compete with Cr^{3+} adsorbing on to the the active sites of the adsorbent surface and made the capacity of Cr^{3+} less. At high pH, the concentration of H^+ was down, the ability of H^+ competing adsorption reduced.

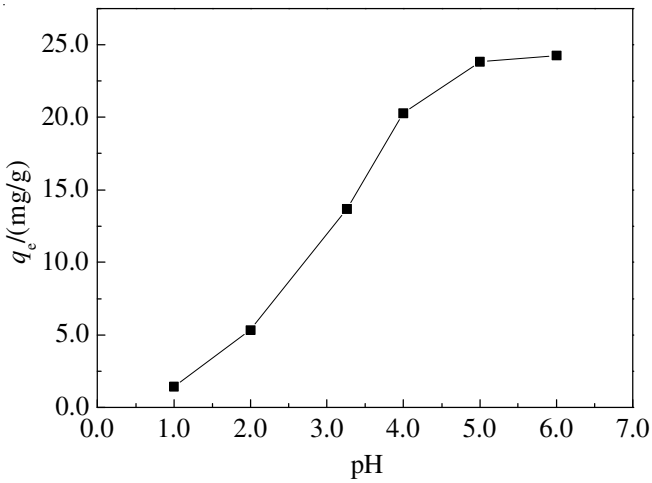


Fig. 4. Effect of pH on adsorption of Cr^{3+} by NaOH-PT

Effect of contact time on Cr^{3+} sorption: As shown in Fig. 5 sorption amount of Cr^{3+} increased with the increasing contact time. All curves have similar tendency and appear to be governed by two transport stages. During the first stage (0-3 h), the sorption rate was very high. Sorption amounts of Cr^{3+} increased rapidly and all exceeded 80 % of the equilibrium sorption capacity, which indicates a quick partitioning of Cr^{3+} from aqueous solution to active sites on NaOH-PT surface. During the second stage (3-24 h), the sorption rate became much lower. The sorption amount increased slowly but gradually and approached equilibrium in about 8 h. This may be explained as: at the initial adsorption stage, the adsorbents (NaOH-PT) had a lot of active sites and Cr^{3+} ions could be combined with these active sites rapidly, so the adsorption rate was faster; A large number of Cr^{3+} were accumulated on the NaOH-PT surface, that hindered the molecular motion of Cr^{3+}, resulting in a nonlinear adsorption[21].

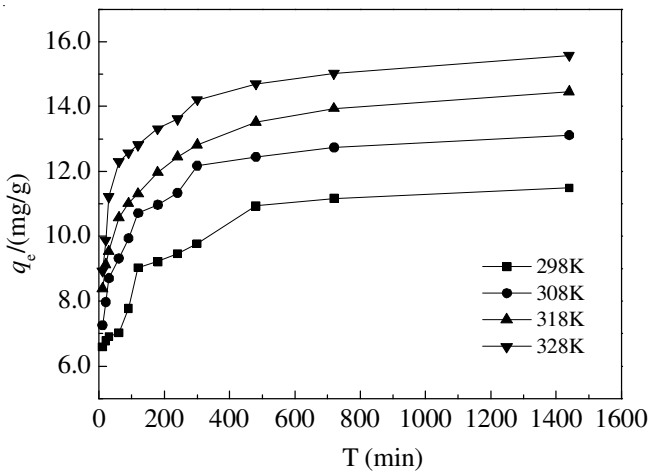


Fig. 5. Kinetic curves of Cr^{3+} adsorption by NaOH-PT at different temperatures

TABLE-2
FIRST-ORDER AND SECOND-ORDER KINETIC MODEL CONSTANTS

T/K	$q_{e,exp}$	Pseudo-first- order model			Pseudo-second-order model		
		k_1 (min^{-1})	q_{e1} (mg g^{-1})	R^2	k_2 g (mg^{-1} min^{-1})	q_{e2} (mg g^{-1})	R^2
298	11.8598	2.0036×10^{-3}	4.2580	0.8877	2.4418×10^{-3}	11.6959	0.9985
308	13.4212	2.0957×10^{-3}	4.0077	0.8764	2.9636×10^{-3}	13.2626	0.9994
318	14.6886	2.2800×10^{-3}	4.6045	0.9526	2.4793×10^{-3}	14.5985	0.9991
328	15.7731	2.3260×10^{-3}	4.3106	0.9382	2.8379×10^{-3}	15.6740	0.9994

$q_{e,exp.}$ equilibrium sorption capacity from experimental results; q_{e1} and $q_{e2.}$ equilibrium sorption capacity calculated from model

Sorption kinetics of Cr^{3+}: Various models have been suggested to express the kinetics of adsorption of solute molecules onto a sorbent. We tested the probabilities of two kinetic models to describe the processes of Cr^{3+} adsorption onto NaOH-PT. These models were a pseudo-first-order model and a pseudo-second-order model.

The pseudo-first-order kinetic model[22] used is:

$$\ln(q_e - q_t) = \ln q_1 - k_1 t \quad (2)$$

The pseudo-second-order kinetic model used is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \quad (3)$$

In these models, k_2 (g mg^{-1} h^{-1}) is the rate constant for the pseudo-second-order model, a, b are the constants related to surface coverage and activation energy, k_1(h^{-1}) is the rate constant for the pseudo-first-order model, q_e(mg g^{-1}) is the amount of solute adsorbed at equilibrium and q_t(mg g^{-1}) is the amount of solvent adsorbed at time t(h). The initial adsorption rate in the pseudo-second-order kinetic model is $h = k_2 q_2^2$.

As shown in Table-2, the R^2 of fitted curve using the pseudo-first-order kinetic model was between in 0.87 to 0.96. It indicates that this model could not give a suitable description of the sorbent NaOH-PT to Cr^{3+}. The R^2 of fitted curve using the pseudo-second-order model were all above 0.99 and the q_e^2 values calculated from the model were close to the values obtained from the experimental results. It suggests that the sorption of Cr^{3+} onto NaOH-PT follows the pseudo-second-order model.

By calculation from Table-2, the initial adsorption rates($k_2 q_e^2$) were 0.3340, 0.5213, 0.5284, 0.6972 mg g^{-1} min^{-1} and equilibrium adsorption capacities (q_e^2) were 11.6959, 13.2626, 14.5985, 15.6740 mg g^{-1},while temperatures increased from 298 K to 328 K. This indicated that the temperature is to help improve the response of the initial adsorption rate and equilibrium adsorption capacity.

Sorption isotherm of Cr^{3+}: The equilibrium sorption isotherm was used to quantify the sorption of Cr^{3+} on NaOH-PT.

Langmuir model[23] was also examined to describe the sorption isotherms:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (4)$$

where K_L is Langmuir adsorption constant (L mg^{-1}); q_{max} is monolayer adsorption capacity (mg g^{-1}); C_e is equilibrium concentrations of Cr^{3+} (mg L^{-1}).

Freundlich model[23] was used to describe the sorption isotherms:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

where K_F is the sorption capacity coefficient [(mg g^{-1}) (L mg^{-1})$^{1/n}$]; n is the Freundlich exponent that describes the nonlinearity degree of sorption; C_e is equilibrium concentrations of Cr^{3+} (mg L^{-1}).

Sorption coefficients and parameters of Langmuir and Freundlich model of NaOH-PT are shown in Table-3. All the sorption isotherms better-fit to the Langmuir than to Freundlich model and due to R^2 values the processes of NaOH-PT could not use the Freundlich model to describe the kinetic involved. And the maximum adsorption capacities increased with the temperature increasing. This also indicated that the adsorption process was endothermic.

TABLE-3
CONSTANTS OF ADSORPTION ISOTHERMS OF Cr^{3+} ON NaOH-PT AT DIFFERENT TEMPERATURES

T (K)	Langmuir Model			Freundlich Model		
	K_L(L mg^{-1})	q_m (mg g^{-1})	R^2	K_F (mg·g^{-1})	n	R^2
298	0.2288	13.5870	0.9988	4.0132	3.3179	0.8305
308	0.4237	14.3472	0.9993	5.4929	4.0274	0.8649
318	0.5609	15.6250	0.9942	6.5328	8.0710	0.8151

Thermodynamics constant calculation of Cr^{3+}: The following formula (6) and (7) were used to calculate the Gibbs free energy change (ΔG), the adsorption enthalpy change (ΔH), entropy change (ΔS), when the adsorption reaction reached adsorption equilibrium[24].

$$\Delta G = -RT \ln K_L \quad (6)$$

$$\ln K_L = -\Delta H/(RT) + \Delta S/R \quad (7)$$

where K_L is adsorption equilibrium constant (L mmol^{-1}); R is gas constant (8.314 J mol^{-1} K^{-1}); ΔG(kJ mol^{-1}).

As shown in Table-4, at all experimental temperatures the ΔG were less than 0 kJ mol^{-1}. This indicated that the adsorption process was spontaneous. And with increasing temperature, the absolute values of ΔG increased, indicating that elevated temperature could increase the spontaneity of the adsorption process. The ΔH of the adsorption was 35.4584 kJ mol^{-1} more than 0 kJ mol^{-1}, indicating the adsorption process was endothermic and elevated temperature was conducive to adsorption. When ΔH was between in 20.9 to 418.4 kJ mol^{-1}, the adsorption was chemisorption; so the adsorption of Cr^{3+} on NaOH-PT was chemisorption[25]. The ΔS was 139.98 J mol^{-1} was more than 0, meaning that the state of Cr^{3+} dissolved in the solution to the NaOH-PT adsorbed state is the increase in disorder.

Conclusion

This study investigated the effect of NaOH modification palm thread on the surface properties and sorption performance for Cr^{3+} adsorption. At pH 1 to 6, adsorption capacity of Cr^{3+} on NaOH-PT rapidly increased with pH increasing. And at

TABLE-4
THERMODYNAMIC PARAMETERS OF Cr^{3+} ON NaOH-PT AT DIFFERENT TEMPERATURES

T/K	K_L (L mmol^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1})
298	11.8967	-6.1351		
308	22.0307	-7.9188	35.4584	139.98
318	29.1646	-8.9176		

pH = 6, the adsorption capacity reached the maximum, 24.25 mg g^{-1}. At different temperatures, the process of adsorption divided into two stages, the fast adsorption stage and the gradual adsorption stage. The adsorption kinetics better fitted to the Lagergren pseudo second kinetic model. The adsorption process was an endothermic reaction, indicating that the higher temperature, the better initial adsorption rate and adsorption capacity. At different temperatures, the adsorption isotherm better fitted to Langmuir adsorption model. The adsorption capacity increased with temperature increasing. The thermodynamic studies showed that the adsorption process was a spontaneous endothermic reaction. the adsorption process was chemisorption.

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REFERENCES

1. W.S.W. Nagh and M.A.K.M. Hanafiah, *Bioresour. Technol.*, **99**, 3935 (2008).
2. A. Demirbas, *J. Hazard. Mater.*, **157**, 220 (2008).
3. F.L. Fu and Q. Wang, *J. Environ. Manage.*, **92**, 407 (2011).
4. Q.F. Zhang, G.D. Yang and X.Q. Kong, *Chem. Bioeng.*, **25**, 29 (2008).
5. P. Marzal, A. Seco and C. Gabaldon, *J. Chem. Technol. Biotechnol.*, **66**, 279 (1996).
6. S. Babel and T.A. Kurniawan, *J. Hazard. Mater.*, **B97**, 219 (2003).
7. C.S. Zhu, T. Wei and W.B. Chen, *Environ. Pollut. Cont.*, **30**, 14 (2008).
8. J. Zhou, J.P. Zhai and H.F. Lu, *Tech. Equip. Environ. Pollut. Cont.*, **7**, 122 (2006).
9. Y. Song and Y. Y. Song, *West Leather*, **30**, 28 (2008).
10. B.Q. Zhen, *Yunnan Chem. Technol.*, **32**, 20 (2005).
11. W.H. Wang, Y.M. Feng and X.L. Chang, *Technol. Water Treat.*, **30**, 95 (2004).
12. G. Vazquez, J. Gonzalez-Alvarez and S. M. Freire, *Bioresour. Technol.*, **82**, 247 (2002).
13. B. Acemioglu and M.H. Alma, *J. Colloid Interf. Sci.*, **243**, 81 (2001).
14. G. Annadurai, D.J. Lee and R.S. Juang, *Water Sci. Technol.*, **47**, 185 (2003).
15. F.Q. Li and Z.M. Wu, *J. Anhui Agric. Sci.*, **37**, 16445 (2009).
16. Z. Reddad, C. Gerente and Y. Andres, *Carbohyd. Polym.*, **49**, 23 (2002).
17. P. Miretzky and A.F. Cirelli, *J. Hazard. Mater.*, **180**, 1 (2010).
18. H.T. Xia, Harbin Institute of Technology Press, Haerbin, China, pp. 222-226 (2003).
19. W.S. Wang, *Tianjin Chem. Ind.*, **18**, 10 (2004).
20. J. Rivera-Utrilla and M. Sanchez-Polo, *Water Res.*, **37**, 3335 (2003).
21. B.Y. Liu, Z. Yao and Z. Zhou, *Chinese J. Process Eng.*, **9**, 865 (2009).
22. Y. Jiang, H. Pang and B. Liao, *Acta Scient. Natur. Univ. Sunyatseni*, **47**, 32 (2008).
23. C.H. Fan, Y. Zhang and Y.C. Zhang, *Spectros. Spect. Anal.*, **30**, 2345 (2010).
24. N. Diban, G. Ruiz and A. Urtiaga, *J. Food Eng.*, **84**, 82 (2008).
25. M. Kilic, H. Yazici and M. Solak, *Bioresour. Technol.*, **100**, 2130 (2009).