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Removal of Fe^{3+} in Citric Acid with Macroporous Amidoxime Chelating Resin

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Macroporous amidoxime chelating resin was prepared in order to remove Fe^{3+} from citric acid. The key influence factors, kinetics, thermodynamics, mechanism of adsorption were analyzed with macroporous amidoxime chelating resin which was prepared by chemical modification of acrylonitrile polymer. Results indicated that adsorption amount of Fe^{3+} significantly decreased with the increase of citric acid concentration and the saturated adsorption time prolonged with the increase of concentration of citric acid. The adsorption equilibration of macroporous amidoxime chelating resin achieved after 2.5 h in solution without citric acid and the adsorption amount could reach to 14.01 mg/g. Moreover, the absorption isotherm followed the Freundlich model well. ΔH and ΔS were more than zero in the range of 303-323 K, whereas ΔG was less than zero and the adsorption of Fe^{3+} by macroporous amidoxime chelating resin was a spontaneous and decalescence adsorption process. This research will be helpful for providing new methods to deal with organic acid solution containing Fe^{3+}.

Keywords: Fe^{3+}, Adsorption, Macroporous amidoxime chelating resin, Citric acid.

INTRODUCTION

As one of the most important chemical products, citric acid is widely applied in food, medicine, daily chemical and other industries[1-5]. It is mainly produced by fermentation of sucrose, starch or subsidiary agricultural products with *Aspergillus niger*[6-9]. However, the existence of Fe^{3+} affects the quality and the yield of citric acid in the production process. Thus, it is very important and urgent to remove the Fe^{3+} either in the fermentation process or in the citric acid product. Various separation processes (such as ion exchange, precipitation, adsorption) have been developed for the removal of Fe^{3+} from industrial wastewater[10]. Meanwhile, there are many ways to remove the impurities of citric acid , such as crystallization, ion exchange[11]. Thus the ion exchange method may be used to remove Fe^{3+} in citric acid solution.

The chelating agent with hydroxyimino group is found to have higher adsorption capacity for Fe^{3+} ions[12,13]. However it is probably unsuitable for removal of Fe^{3+} from citric acid solution because of contaminating citric acid product, which easily results in decline in the quality of citric acid. The chelating resin is widely used for the removal of heavy metal in wastewater, which have higher selective adsorption, chemical stability, adsorption capacity, mechanical strength, *etc*.[14-17]. Moreover, the chelating resin has higher mechanical resistance against attrition and excellent replicability, thus it is feasible to remove the Fe^{3+} from citric acid solution. The macroporous amidoxime chelating resin, which contains the amidoxine functional group[18]. Unfortunately, the Fe^{3+} absorbed by macroporous amidoxime chelating resin has not been investigated in the citric acid solution, thus the adsorption of Fe^{3+} by macroporous amidoxime chelating resin in citric acid solution is still unknown.

In this paper, the macroporous amidoxime chelating resin is prepared by the suspension polymerization and the graft modification. The objectives of this study are as follows: (i) examining the effect of several factors on the absorption of Fe^{3+} by macroporous amidoxime chelating resin in the citric acid solution; (ii) analyzing the adsorption isotherm of Fe^{3+} by macroporous amidoxime chelating resin; (iii) elucidating the characteristics of adsorption thermodynamics. This research will be helpful for removing Fe^{3+} from citric acid and it will also be helpful for providing new methods to deal with organic acid solution containing Fe^{3+}.

EXPERIMENTAL

Acrylonitrile/divinylbenzene (AN-DVB) bead (cross-linking degree, 6 %; 70-100 mesh) was provided by Wuxi Institute of green separation (China). All reagents are analytical grade and purchased from Sinopharm chemical Reagent Co. (China) and the deionized water was used in the experiment.

Preparation of macroporous amidoxime chelating resin: The AN-DVB bead was swelled in the anhydrous methanol solution for 3 h. After that, 1 mol/L hydroxylamine hydrochloride and 1 mol/L sodium hydrate were added into the suspension. The AN-DVB bead was reacted with hydroxylamine at 338 K for 5 h and the suspension was stirred with magnetic stirrers (80 rpm). The modified resin (namely macroporous amidoxime chelating resin) was obtained by filtrating the suspension after reaction. And then the macroporous amidoxime chelating resin was washed with deionized water until the wash water without hydroxylamine, dried in vacuum at 45 °C for 24 h.

Adsorption experiment

Saturated adsorption: One gram macroporous amidoxime chelating resin was added to 90 mL of the mixed solution containing Fe^{3+} and citric acid and the mixture was shaken in the thermostated water bath (30 °C, 100 rpm). At intervals, an amount of solution was taken by pipette and then the concentration of Fe^{3+} was detected by means of improved Tiron spectrophotometry[19]. The adsorption amount of Fe^{3+} is calculated as follows:

$$Q = \frac{V(C_0 - C)}{W} \quad (1)$$

where Q is the adsorption amounts (mg/g), C_0 and C are the initial and the final concentrations of Fe^{3+} in solution (mg/mL) respectively, V is the volume of the aqueous ions solution (mL), W is the weight of dry macroporous amidoxime chelating resin (g).

Adsorption isotherms: Adsorption isotherm was studied in the thermostat water bath (303-323 K). In the experiment, the solution was prepared with 20 % citric acid and Fe^{3+} (50-250 mg/mL), the solution was transferred into Erlenmeyer flask and then the Erlenmeyer flask was shaken in the thermostat water bath (100 rpm). The sample was taken from the Erlenmeyer flasks after reaction and then the concentration of Fe^{3+} was determined by the improved Tiron spectrophotometry[19].

Effect of citric acid: The macroporous amidoxime chelating resin (1 g) was placed in the Erlenmeyer flasks containing citric acid (5-30 %, mass fraction) and Fe^{3+} (100-300 mg/L). The mixture was shaken for 24 h at 30 °C, the concentration of Fe^{3+} was determined by the improved Tiron spectrophotometry[19].

Contact time: The macroporous amidoxime chelating resin (1 g) was placed in the Erlenmeyer flasks containing citric acid (0-30 %, mass fraction) and Fe^{3+} (300 mg/L). The mixture was shaken at 30 °C, the samples were taken from the Erlenmeyer flasks at required intervals and then the concentration of Fe^{3+} was determined by the improved Tiron spectrophotometry[19].

Detection method: The UV spectrophotometer (Beijing Purkinje General Instrument Co., China) was used to determine the concentration of Fe^{3+} in citric acid solution and the wavelength is 480 nm[19]. The AN-DVB bead and the macroporous amidoxime chelating resin are characterized with FTIR spectrophotometer (ABB, Canada) and TGA (Mettler-Toledo State Trading Co., China) respectively. The operation condition of TGA: heating rate, 10 °C × min^{-1}; N_2 flow rate, 60 mL/min; range of raising temperature, 50-550 °C.

RESULTS AND DISCUSSION

The FTIR spectra of AN-DVB bead and macroporous amidoxime chelating resin are shown in Fig. 1. The characteristic adsorption peaks of AN-DVB bead appear at 2937 cm^{-1} and 1455 cm^{-1} respectively, this may arise from the C-H stretching and the bending vibration. The adsorption peak of C-N stretching vibration is 2243 cm^{-1}. Moreover, the characteristic adsorption peaks of macroporous amidoxime chelating resin are 1654 and 914 cm^{-1}, this is assigned to the C=N and N-O of the amidoxime groups, respectively. Additionally, the intensity decrease of the C-N adsorption peak (2240 cm^{-1}), which indicates that the nitrile is transformed into the amidoxime group. Therefore, the synthetic method of macroporous amidoxime chelating resin used in the experiment is feasible and the macroporous amidoxime chelating resin could be used to absorb Fe^{3+} ion in the following reaction.

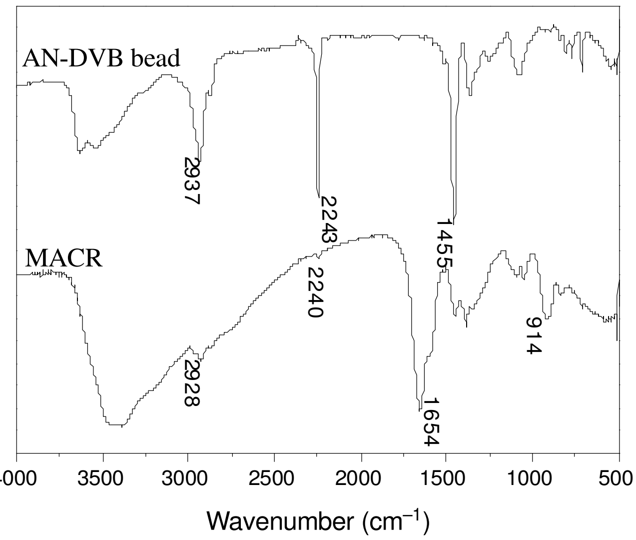

Fig. 1. FTIR spectra of AN-DVB bead and macroporous amidoxime chelating resin

Furthermore, the TG analysis of AN-DVB bead and macroporous amidoxime chelating resin were performed in order to analyze the functional group of two resins. As shown in Fig. 2a and b, the initial weight loss temperatures of two resins are different and the initial decomposition temperatures of AN-DVB and macroporous amidoxime chelating resin are 280 and 80 °C respectively, indicating that the thermal stability of macroporous amidoxime chelating resin decreases after the grafting reaction of AN-DVB bead. Moreover, the AN-DVB resin has a weightlessness step and the macroporous amidoxime chelating resin has three weightlessness steps, the difference in the DTG curve indicates that the amidoxime group is grafted to the AN-DVB resin and the structure and composition of AN-DVB bead is changed.

Effect of citric acid on adsorption of Fe^{3+}: Citric acid concentration is an important impact factor for adsorption of Fe^{3+} in citric acid solution by macroporous amidoxime chelating resin. Fig. 3 showed the adsorption capacity of macroporous

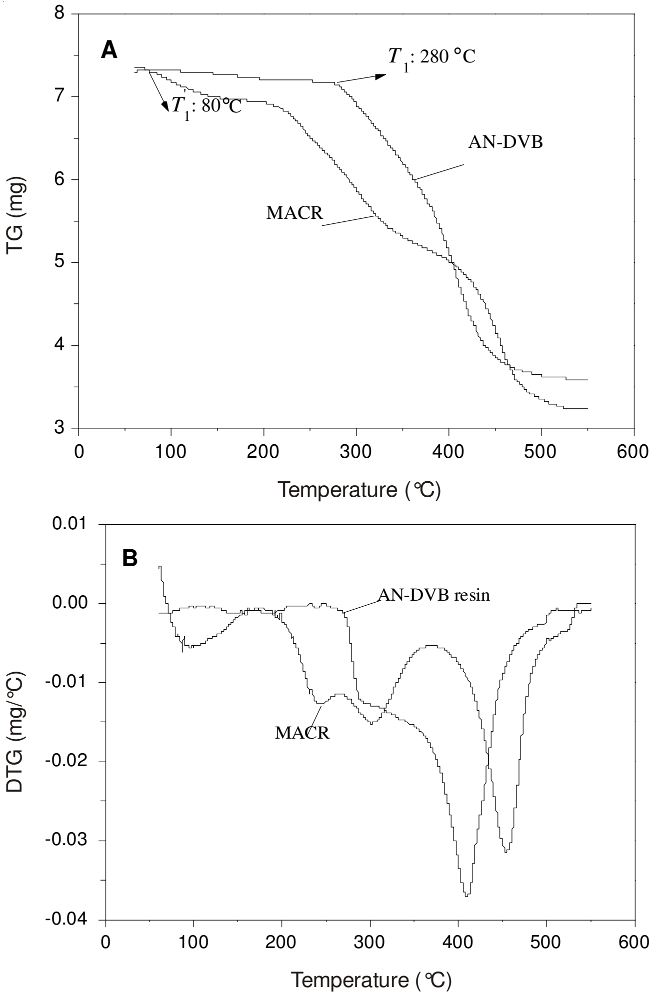

Fig. 2. TGs (a) and DTGs (b) of AN-DVB bead and macroporous amidoxime chelating resin

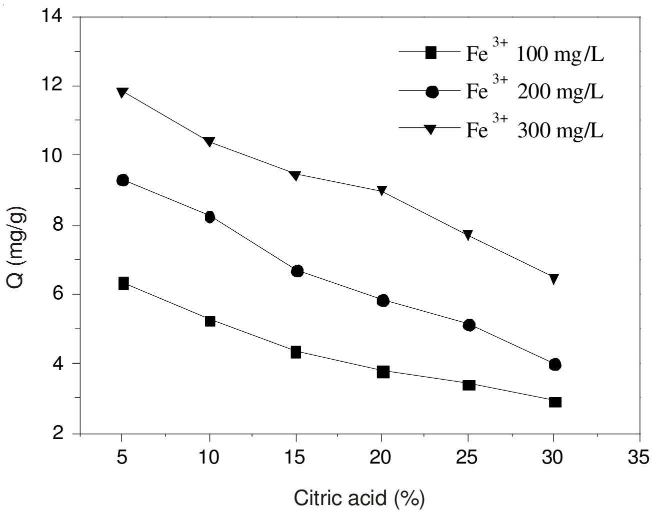

Fig. 3. Effect of citric acid on adsorption of Fe^{3+} at 30 °C and 24 h

amidoxime chelating resin decreased with increase of citric acid concentration. When the concentrations of Fe^{3+} were 100, 200 and 300 mg/L, the adsorption capacities of macroporous amidoxime chelating resin in 30 % citric acid solution were reduced by 58.5, 56.7 and 45.1 % in compare to that in 5 % citric acid solution respectively (calculating data). Moreover, the adsorption capacity of macroporous amidoxime chelating resin increased with the increase of concentration of Fe^{3+} under condition of same concentration of citric acid. The adsorption amount of macroporous amidoxime chelating resin wer 6.34 mg/L and 11.83 mg/L when the concentration of Fe^{3+} were 100 and 300 mg/L in 5 % citric acid solution respectively. Indicating that the increase in Fe^{3+} concentration is useful for the enhancement of adsorption capacity of macroporous amidoxime chelating resin. Similarly, the change trend of adsorption amount of macroporous amidoxime chelating resin in 30 % citric acid solution was similar to that in 5 % citric acid solution. This phenomenon may arise from that part of the functional group of the macroporous amidoxime chelating resin are occupied by citric acid molecule, thus there have some loss of citric acid during adsorption of macroporous amidoxime chelating resin.

Effect of contact time on adsorption of Fe^{3+}: The influence of contact time was studied in the range of 0-30 % citric acid solution. As shown in Fig. 4, a rapid adsorption rate achieved within 1 h and the adsorption equilibration achieved after 2.5 h. When the concentration of citric acid increased, the saturated adsorption time was prolonged. When the citric acid concentration increased from 0 to 30 %, the saturated adsorption time was prolonged from 2.5 to 9 h and the adsorption capacity of macroporous amidoxime chelating resin decreased from 14.01 to 6.87 mg/g. This phenomenon may arise from higher concentration of citric acid which affects the mass transfer process of Fe^{3+}, thus the adsorption saturation time of macroporous amidoxime chelating resin must be prolonged. Additionally, higher concentration of citric acid is diluted to lower concentration of citric acid, which may be better for Fe^{3+} absorbed by macroporous amidoxime chelating resin.

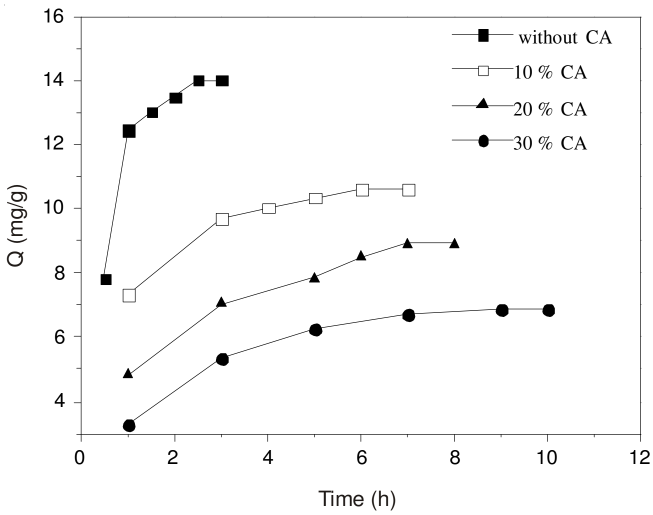

Fig. 4. Effect of contact time on adsorption of Fe^{3+} at 30 °C and 300 mg/L Fe^{3+} with and without citric acid (CA)

Adsorption isotherm: The adsorption isotherm of Fe^{3+} onto macroporous amidoxime chelating resin was studied in order to understand the mechanism of adsorption of Fe^{3+} in citric acid solution. The adsorption of Fe^{3+} at different temperature was showed in Fig. 5. It was found that the adsorption amount of macroporous amidoxime chelating resin proportionally increased with the increase of absorption temperature.

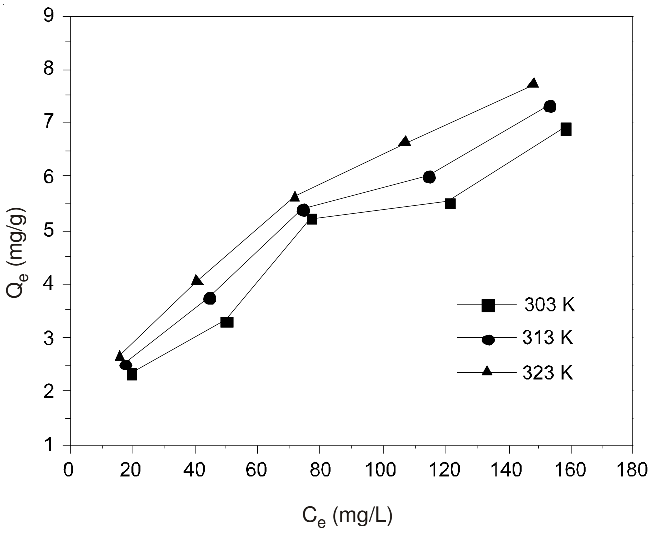

Fig. 5. Adsorption isotherms of Fe^{3+} for macroporous amidoxime chelating resin

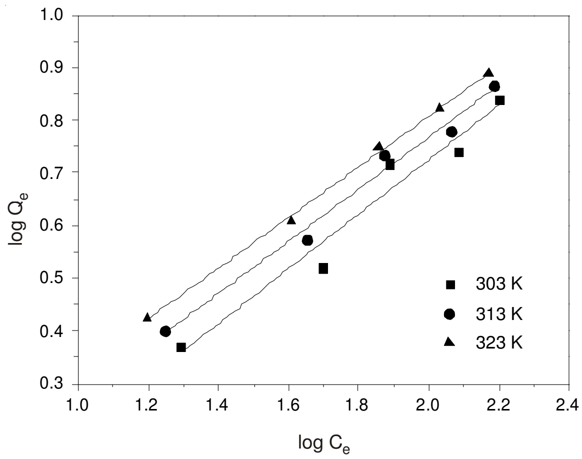

Fig. 6. Linearized Freundlich isotherm model for Fe^{3+} adsorption on macroporous amidoxime chelating resin

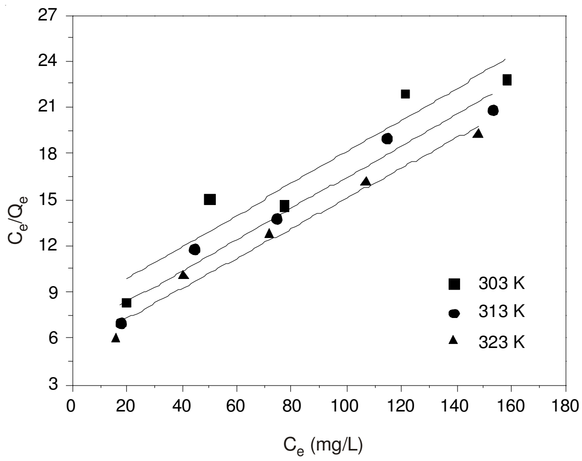

Fig. 7. Linearized Langmuir isotherm models for Fe^{3+} adsorption on macroporous amidoxime chelating resin

Meanwhile, the result confirms that the macroporous amidoxime chelating resin adsorption process is endothermic and the endothermic nature of process may be due to the fact that high temperatures increase the free volume in the adsorbent pores and the movement of solute[20,21].

The Freundlich model[22] and the Langmuir model[23] are used to analyze the absorption equilibration data of Fe^{3+}. The Freundlich model is a commonly used equation and suitable for a heterogeneous surface. The linear form of the Freundlich equation is given as:

$$\lg Q_e = \lg K_F + \frac{1}{n}\lg C_e \qquad (2)$$

where Q_e is the adsorption amounts (mg/g); C_e, the equilibration concentration of Fe^{3+} (mg/L); K_F and n, the Freundlich constants. K_F and n are indicative of the adsorption capacity and the adsorption intensity, respectively. Linear plot of lg Q_e *vs*. lg C_e is given in Fig. 6.

The Langmuir model assumes that the surface of the resin is homogeneous, a site is only occupied by an adsorbed molecule and there is no interaction force between the molecules. The Langmuir isotherm is given as:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_L} + \frac{1}{K_L Q_L} \qquad (3)$$

where Q_e is the adsorption amounts (mg/g); Ce, the equilibration concentration of Fe^{3+} (mg/L); Q_L is the maximum adsorption capacity (mg/g); K_L is the adsorption equilibrium constant (L/mg). Linear plot of C_e /Q_e *vs*. C_e at different temperatures is given in Fig. 7.

R_L is a dimensionless constant as separation factor or equilibrium parameter, which indicates the essential features of the Langmuir model. R_L is defined by:

$$R_L = \frac{1}{1 + C_0 K_L} \qquad (4)$$

where C_0 is the initial concentration of the Fe^{3+} (mg/L) and K_L is the Langmuir constant described above.

Then isotherm model parameters are listed in Table-1. At different temperature, the values of $R_L < 1$ and $n > 1$ indicate that the adsorption of Fe^{3+} onto macroporous amidoxime chelating resin is a favorable process. The values of the correlation coefficient for Freundlich model are greater than that of Langmuir model and it is greater than 0.9. This result indicates that the Freundlich model is more suitable to describe the relationship between the adsorption capacities of Fe^{3+} and its equilibration concentration in 20 % citric acid solution.

TABLE-1
PARAMETERS OF FREUNDLICH MODEL AND LANGMUIR MODEL

T (K)	Freundlich			Langmuir			
	K_F	n	R^2	Q_m	K_L	R_L	R^2
303	0.4869	1.9260	0.9430	9.7087	0.0132	0.6024-0.2326	0.8875
313	0.5997	2.0198	0.9842	9.8619	0.0160	0.5556-0.2000	0.9529
323	0.7008	2.0786	0.9973	10.2564	0.0183	0.5222-0.1794	0.9739

TABLE-2
THERMODYNAMIC PARAMETERS

Q_e (mg/g)	ΔH (kJ/mol)	ΔG (kJ/mol)			ΔG (kJ/mol)		
		303 K	313 K	323 K	303 K	313 K	323 K
3	19.89				0.079	0.081	0.079
5	16.65	-4.85	-5.26	-5.58	0.071	0.070	0.069
7	14.51				0.064	0.063	0.062

Adsorption thermodynamics: Thermodynamic parameters such as the change in Gibbs free energy (ΔG), enthalpy (ΔH), entropy (ΔS) are calculated by using the following equations:

$$\ln \frac{1}{C_e} = \ln K_0 + (-\Delta H / RT) \quad (5)$$

where C_e is the equilibrium concentration (mg/L), Q_e is the definitive adsorption amounts (mg/g), K_0 is the constant, R is the gas constant (8.314 J/(k mol)). When the equilibrium adsorption amounts is defined at different temperature (303, 313 and 323 K), the equilibrium concentration is calculated from the Freundlich equation. ΔH is obtained from the slope of van't Hoff plot of ln $(1/C_e)$ *vs.* 1/T (Fig. 8).

$$\Delta G = -nRT \quad (6)$$

where n is the constant of Freundlich equation.

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

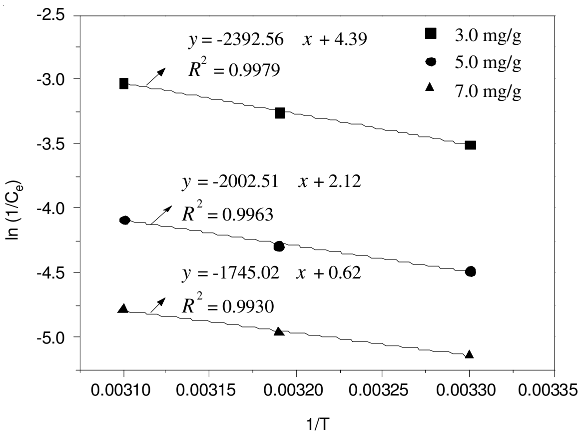

Fig. 8. Fitting curve of ln C_e and 1/T

Table-2 shows the thermodynamic parameters at different adsorption amounts. The positive ΔH indicates that the adsorption process of Fe^{3+} on the amidoxime resin is endothermic at 303-323 K and higher temperature is more favorable for the adsorption efficiency of macroporous amidoxime chelating resin. The value of ΔH decreases with increase of definitive adsorption amounts, which could be due to the surface irregularity and hole filling action of resin.

The value of ΔG reflects the driving force of the adsorption. The negative ΔG implies that the adsorption process is a spontaneous nature. Furthermore, it indicates that Fe^{3+} is easily adsorbed by macroporous amidoxime chelating resin . The solvent exchange process leads to the change of entropy. The positive value of ΔS indicates the increased randomness at the solid solution interface during the adsorption process.

Conclusion

Macroporous amidoxime chelating resin was successfully synthesized and characterized with the FTIR spectroscopy and TGA. Macroporous amidoxime chelating resin could be used for the removal of ferric ion in citric acid solution and the adsorption effects were related to temperature, absorption time and citric acid concentration. Moreover, the adsorption amount of macroporous amidoxime chelating resin decreased with the increase of citric acid concentration, the concentration of citric acid increased, the saturated adsorption time was prolonged and the increase of temperature could enhance adsorption capacity of macroporous amidoxime chelating resin. The maximum adsorption capacity for macroporous amidoxime chelating resin was 14.01 mg/g in solution without citric acid. Finally, the Freundlich model was demonstrated to provide a better correlation between the adsorption capacities of Fe^{3+} and its equilibration concentration. The ferric ion adsorbed on macroporous amidoxime chelating resin was spontaneous and endothermic process.

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REFERENCES

1. B. Duarte, M. Delgado and I. Cacador, *Chemosphere*, **69**, 836 (2007).
2. K.C. Poh, H.S. Lim, H. Pan, J. Lin and J.Y. Lee, *J. Power Sources*, **176**, 70 (2008).
3. Y.M. Jiang, L.T. Pen and J.R. Li, *J. Food Eng.*, **63**, 325 (2004).
4. R.A. Angumeenal and D. Venkappayya, *LWT-Food Sci. Technol.*, **50**, 367 (2013).
5. X.Y. Chen, Q. Lin, M.Y. Luo, Y.F. He, S.J. Zhen, Y.L. Yu, G.M. Tian and M.H. Wong, *Chemosphere*, **50**, 807 (2003).
6. M.Y. Lu, I.S. Maddox and J.D. Brooks, *Bioresour. Technol.*, **54**, 235 (1995).
7. I.-U. Haq, S. Ali and J. Iqbal, *Process Biochem.*, **38**, 921 (2003).
8. S.Y. Mostafa and A.S. Alamri, *Saudi J. Biol. Sci.*, **19**, 241 (2012).
9. D. Kumar, K.V. Jain, G. Shanker and A. Srivastava, *Process Biochem.*, **38**, 1731 (2003).
10. S.M. Lee and J.M. Nicol, *Hydrometallurgy*, **86**, 6 (2007).
11. Z. Liu and X. Wang, *Chinese J. React. Eng.*, **7**, 87 (1998).
12. B.R. Liu, Chelating Flotation Agent, Metallurgical Industry Press, Beijing, p. 80 (1982).
13. A.M. Rahman, H. Hasegawa, K. Kadohashi, T. Maki and K. Ueda, *Chemosphere*, **77**, 207 (2009).
14. H.S. Choi, S.M. Choi, T.Y. Park, K. Lee and H. Kang, *Radiat. Phys. Chem.*, **67**, 387 (2003).
15. M. Nogami, Y.S. Kim, N. Asanuma and Y. Ikeda, *J. Alloys Comp.*, **374**, 269 (2004).
16. G. Zong, H. Chen, R. Qu, C. Wang and N. Ji, *J. Hazard. Mater.*, **186**, 614 (2011).
17. X. Liu, H. Chen, C. Wang, R. Qu, C. Ji, C. Sun and Q. Xu, *Polym. Adv. Technol.*, **22**, 2032 (2011).
18. X. Liu, H. Chen, C. Wang, R. Qu, C. Ji, C. Sun and Y. Zhang, *J. Hazard. Mater.*, **175**, 1014 (2010).
19. L. Fan, J. Zhang and Q. Peng, *Appl. Chem. Ind.*, **41**, 1263 (2012).
20. S.Y. Ho and G. Mckay, *Process Biochem.*, **38**, 1047 (2003).
21. S. A. Özcan, B. Erdem and A. Özcan, *Colloids Surf. A*, **266**, 73 (2005).
22. V.B.H. Dang, H.D. Doan, T. Dang-Vu and A. Lohi, *Bioresour. Technol.*, **100**, 211 (2009).
23. J. Romero-Gonzalez, J.R. Peralta-Videa, E. Rodriguez, S.L. Ramirez and J.L. Gardea-Torresdey, *J. Chem. Thermodyn.*, **37**, 343 (2005).