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Amino-modified Hydrogen-Bonding Resin and Its Adsorption on Berberine

SHAN Yongping[1a], ZENG Ping[1b], SONG Yonghui[1c*], Guo Yuting[1,2], GALARNEAU Anne[3], MANERO Marie-Helene[4,5]

[1] Department of Urban Water Environmental Research, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

[2]College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266510, China

[3]Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM2-ENSCM-UM1, ENSCM, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France

[4] Université de Toulouse ; INPT, UPS ; Laboratoire de Génie Chimique ; 4, Allée Emile Monso, F-31432 Toulouse, France

[5] CNRS ; Laboratoire de Génie Chimique ; F-31432 Toulouse, France

[a]shanyp@yeah.net, [b]zengping71@hotmail.com, [c]songyh@craes.org.cn

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Abstract. A hydrogen-bond donor resin HX was obtained by modifying resin H103 . The adsorption effect of resin HX on berberine was determined. The adsorbing kinetic and dynamic mechanisms of resin HX and resin H103 was compared. The results showed that, after modification, resin HX could form hydrogen-bond with berberine molecules. In the adsorption process, two C-O groups on berberine molecules became the electron acceptor of hydrogen-bond and the N-H group on resin molecules became the electron donor of hydrogen-bond. The existence of hydrogen-bond enhanced the adsorption force, and led to bigger amount of adsorption.

Introduction

Berberine is one of the important isoquinoline alkaloids, which has been widely used as an anti-inflammatory medicine. As the research in recent years, berberine could also be used in anti-hyperlipidemic[1], antidepressive[2], anticancer[3], and so on.

As the increase of demand, more and more berberine should be synthetized, and the amount of wastewater during berberine production has become a serious environmental problem. Berberine wastewater is a challenging work because of its high acidity, high concentration of organics and antibacterial characteristics. Research shows that bioreactors as UASB-MBR[4], SBBR[5], as well as physico-chemical processes like UV-O_3 [6], could decrease the concentration of berberine under certain conditions. But these processes also manifested shortages: wildly fluctuate of wastewater quality would be fatal to UASB-MBR and SBBR as the antibiotic character of berberine could damage microorganisms in bioreactors, and the high energy-consumption features would limit the application of UV-O_3 process.

In recent years, resin adsorption processes have been applied in many important fields. Macroporous resin of polystyrene skeleton is widely used in wastewater treatment due to its large specific surface area, strong adaptability of poor water quality. H103 is one important type of macroporous resins of polystyrene skeleton, and it has excellent acid- and alkali-resistant and heat-resistant. Considering it's characteristic, it was select to treat berberine wastewater with high concentration and low pH.

In this paper, resin H109 was modified, in order to obtain a hydrogen-bonding adsorbent which could lead to significant improvement of berberine adsorption.The berberine adsorption mechanism on resin H103 was studied as well as resin HX. Resin HX was synthesized by adding ammonia functional group to H109, the skeleton resin of resin H103.

Experimental Set-up

Modification of resin with hydrogen-bonding donor. The modification mechanism was shown in Fig.1

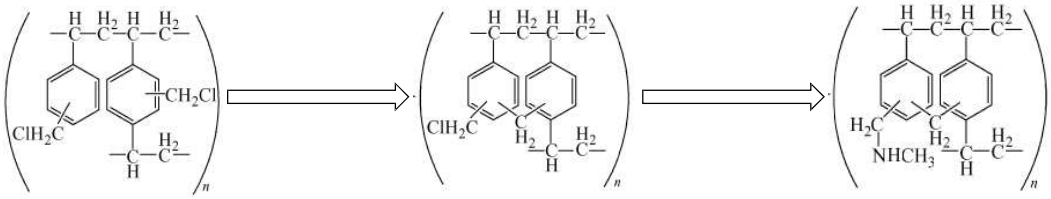

Fig.1 Modification of polystyrene resin with protonated amino groups

Analyses. The berberine concentration in solution was determined by Agilent 1260 HPLC at a wavelength of 345 nm, employing a 0.05M KH_2PO_4/ acetonitrile 30/70 (v/v) solution as mobile phase. FTIR spectra were determined using a Thermo Scientific Nicolet 6700 instrument. The mesopore size and the specific surface area of resins were determined using a TRISTAR II3020 apparatus.

Kinetic experiments. In typical adsorption experiments, 1.0 g resin HX or resin H103 was added in 200 mL berberine solution (without pH adjustment, the pH value was 3.92) of different concentrations from 500 to 900 mg/L in a 250 mL flask and kept in an incubator shaker at 150 rpm and 25℃. 1mL of solution were taken and filtered with 0.22 μm filter membrane at the time of 24 h.

Adsorption Mechanism experiments. To evaluate the influence of the temperature on berberine removal from a solution, 1.0 g of resin H103 was added in five conical flasks containing 200 mL of berberine solutions (without pH adjustment, the pH value was 3.92) at concentrations of 500 to 900 mg/L, and kept in an incubator shaker at 150 rpm and temperatures of 10, 30, 50 and 70℃.

Results and Discussion

Properties of new protonated polystyrene resin HX. As can be seen by FTIR in Fig.2, the presence of a N-H bond is revealed by the band at 1110 cm^{-1}. The existence of N-H proved that the modification of resin with hydrogen-bonding donor has been successful, and the rest functional groups of resin H109 did not change.

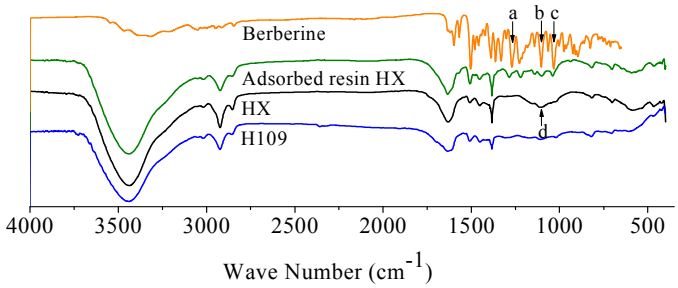

Fig.2 FTIR of berberine and resins

Berberine adsorption. The amount of berberine adsorbed on resin HX was significantly higher than that of resin H109 (Fig. 3). After 1 h, the berberine amount adsorbed on resin HX was 21.4 mg/g higher than that on resin H109. This value then decreased with time. The adsorption reached equilibrium after 8 h, and resin HX adsorbed 7.9 mg/g more berberine than resin H109. In the first hour, the adsorption of berberine on resin HX was much faster than on resin H109, mainly due to hydrogen bonds forming between berberine and resin HX, which is an interaction much stronger than Van der Waals force promoting berberine adsorption on the pure polystyrene resin as H109. Hydrogen-bond interactions between N-H and the two -OCH_3 functional groups on benzene could be the main cause of the increase amount of berberine adsorption and the rate of adsorption.

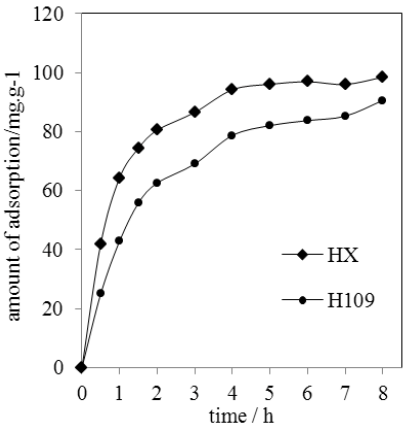

Fig.3 Amount of berberine adsorbed on resin HX and resin H109 at an initial berberine concentration of 1000 mg/L

Kinetics of adsorption. In order to characterize the mechanisms of the adsorption, the adsorption processes were fitted with: (a) Intraparticle diffusion model, (b) Film diffusion model, (c) Modified pseudo-first order model and (d) Pseudo-second order model.

Tab.1. Correlation coefficient of the different equations on kinetic analysis of resins

	Correlations			
	Equation (a)	Equation (b)	Equation (c)	Equation (d)
H103	0.996	0.994	0.926	0.792
HX	0.788	0.773	0.948	0.997

As shown in Tab.1, for polystyrene resin H103, the two equations (a) and (b) well fitted the adsorption isotherm of berberine as correlation coefficients are over 0.99, and both of fitting curves are not zero crossing. It means that intragranular diffusion and liquid film diffusion are the control steps of adsorption at the same time. This indicated that the main reaction of adsorption with resin H103 was physical adsorption.

For resin HX，the correlation coefficient of pseudo secondary dynamics equation (d) was much higher than for the other equations. This indicates that another effect than just physical adsorption is governing the adsorption and could certainly be H-bonding interactions. Kinetic mechanism of adsorption is therefore more complicated on the new HX resin in comparison with on the commercial polystyrene resin H103. Hydrogen-bond affected the kinetic mechanism of resins.

Adsorption mechanisms. In order to better characterize adsorption mechanism of resin H103, thermodynamic analysis was carried out using the Freundlich equation and the Van't Hoff equation.

Freundlich adsorption isotherm, originally proposed as an empirical equation, is used to describe the data for heterogeneous adsorbents.

$Q_m = K_a C_e^{1/n}$

Q_m is the equilibrium adsorption capacity (mg/g), K_a and n are Freundlich characteristic parameters, C_e is the equilibrium concentration (mg/L).

The Freundlich equation is consistent with the thermodynamics of heterogeneous adsorption. According to the fitting results of adsorption process performed at different temperatures (Fig. 3), the adsorption isotherms of berberine on resin H103 could be well described by the Freundlich equation. Freundlich adsorption intensity parameter n increased with the increase of temperature, which means that the adsorbate was more active at higher temperature. The adsorption intensity parameter $n > 2$ indicated that H103 was a good adsorbent of berberine[7-9].

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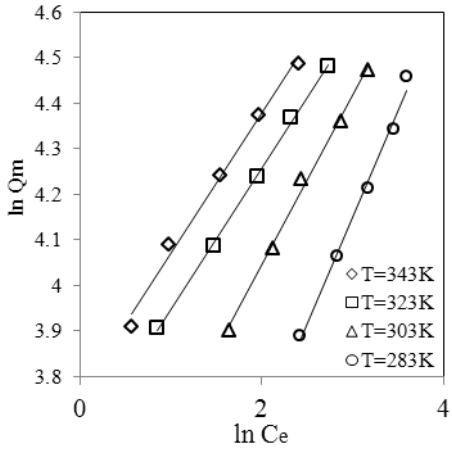

Fig.4 Freundlich equation to simulate the berberine adsorption process on H103 resin

To characterize the thermodynamic properties of berberine adsorption on H103, isosteric adsorption enthalpy was calculated with the Van't Hoff equation:

$[\ln (C_e)]_q = -\ln(K_0) + \Delta H/RT$

Ce is the equilibrium concentration and K_0 is the constant.

Tab.2 Adsorption enthalpy under different amount of adsorption

q_e（mg/g）	slope	ΔH (KJ/mol)	R^2
40	6536	20.76	0.995
50	6983	23.56	0.997
60	7499	26.80	0.998
70	8109	30.62	0.999
80	8855	35.31	0.999

The calculated adsorption enthalpy for berberine adsorption on polystyrene resin H103 was less than 40 kJ/mol (Tab.2), and this confirms that the adsorption was mainly physical adsorption. It indicated that there was no hydrogen bonding, chelating or other chemical adsorption.

FTIR spectra were taken to elucidate the berberine adsorption mechanisms on resin HX. According to Fig.2, the FTIR spectrum of berberine molecule showed two infrared absorption peaks at 1290~1240 cm^{-1} and 1050~1000 cm^{-1} corresponding to the two C-O bonds and the 1150~1085 cm^{-1} band corresponding to the C-O-C bond. After the adsorption of berberine on resin HX, the two C-O bands moved to higher wavelength for 16 and 10 cm^{-1}, respectively, which proved the existence of H-bond between berberine molecule and the protonated nitrogen of the resin HX and evidenced that the H-bond acceptor in berberine molecule was the two CH_3-O bonds (Fig. 5). Furthermore, as the N-H bond of the resin at 1110 cm^{-1} disappeared after the berberine adsorption, this indicates that the proton of the resin HX is moving close to the C-O bond of the berberine molecule. The electron cloud of N-H moved much closer to oxygen atom, and led to the disappearance of N-H infrared absorption peak. In the hydrogen-bonding mechanism of berberine adsorption on modified-polystyrene resin, the berberine molecule was the electron acceptor and resin HX was the electron donor.

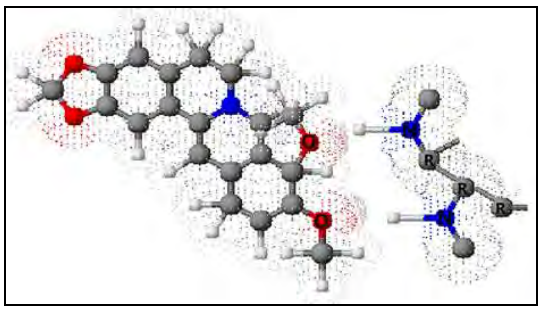

Fig.5 The adsorption mechanism of berberine molecule on resin HX

Conclusions

The modification of a resin with a hydrogen-bonding donor characteristic was successfully realized with a commercial polystyrene resin. The amount of berberine adsorption on this resin was significantly increased. The kinetic mechanism analysis indicated that hydrogen bonding was the cause of the increase of adsorption. The thermodynamic analysis and FTIR spectrum analysis proved the existence of hydrogen bonding between the berberine molecules and the resin. The H-bonding interaction was identified with a proton transfer between the N-H bond of the resin to the O-CH_3 bonds of the berberine molecule.

Acknowledgement

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