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Adsorption Characteristics of Benzoic Acid from Aquatic System by Hypercrosslinked Resin Modified with Benzoyl Group

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In this paper, a hypercrosslinked polymeric adsorbent (ZH-03) was employed to remove benzoic acid and its static and kinetic adsorption were investigated within the temperature range 288-318 K. Freundlich and Langmuir models give perfect fitting to the isotherm data. The results show that the adsorbent is superior to Amberlite XAD-4 for removing benzoic acid in aqueous solutions, which is contributed to microporous structure and the polar groups on the network of ZH-03 resin. The kinetics data were fit for the first-order equation and the secondary-order equation on ZH-03. The results showed that the hypercrosslinked polymeric adsorbent (ZH-03) was better than the Amberlite XAD-4 for removing the benzoic acid in aqueous solutions.

Keywords: Hypercrosslinked resins, Benzoic acid, Adsorption, Kinetics, Freundlich model, Langmuir model.

INTRODUCTION

As a result of human activities, numerous hazardous organic compounds are introduced into environmental waters. Benzoic acid, as one of the most important preservatives, is widely used for the manufacture of food. As a result, more and more benzoic acid wastewater has been introduced into water bodies. For their high toxicity, the efficient removal of these organic compounds from water has draw significant concern[1].

Presently, various methods of wastewater treatment have been developed such as catalytic oxidation, liquid membrane separation, biological degradation and adsorption[2]. Due to the high concentration ability of typical adsorbents, adsorption is proved to be one of the most attractive and effective techniques for purification and separation in wastewater treatment[3]. We have previously prepared a new hypercrosslinked adsorbent ZH-03 modified by benzoyl functional group[4] and investigated the static and the kinetic adsorption of benzoic acid on Amberlite XAD-4 and ZH-03.

EXPERIMENTAL

Acetone, ethanol, zinc chloride, 2-chloromethane, hydrochloric acid, nitrobenzene, phthalic anhydride, benzoic acid were used in this study. All these chemicals are of analytical grade and were purchased from Shanghai Chemical Reagent Plant (Shanghai, China). Styrene and divinylbenzene (purity: 50.4 %) were purchased from Dongda Chemical Co. Ltd, (Shandong province, China). Chloromethyl methylether was obtained from Langfang Chemical Co. Ltd. (Hebei province, China). The spherical Amberlite XAD-4 resin was purchased from Rohm & Haas Company (Philadelphia, USA). Benzoic acid used in this study was analytical grade reagents of 99.5 % purity (Shanghai Chemical Reagent Plant, China). The reagent was used to prepare the stock solution with a concentration of 500 mg/L, which was kept in sealed ground-glass-stoppered brown bottles and stored in a refrigerator at 4 °C.

Synthesis of ZH-03 resin: ZH-03 was synthesized according to literature[4]. In a 500 mL round-bottomed flask, 50 g of chloromethylated poly(styrene-divinylbenzene) beads (chlorine content 19.5 %) were swollen in 600 mL nitrobenzene. Under mechanical stirring, 5 g of zinc chloride were added slowly at room temperature. The mixture was further stirred for 8 h at 408 K. After cooled, 10 g phthalic anhydride was added to the above mixture at 383 K and stirred for another 15 h. Finally, the mixture was poured into an acetone bath, which contained 1 % hydrochloric acid. The filtered polymers were extracted with ethanol for 8 h in a Soxhlet apparatus and dried under vacuum at 333 K for 8 h. The properties of ZH-03 and XAD-4 resins are given in Table-1.

Analytic method: An Agilent gas chromatograph equipped with a HP-5 column (30 m × 0.35 mm × 0.25 μm) was used to separate and determine the level of benzoic acid in water

TABLE-1
TYPICAL PROPERTY OF THE POLYMERIC RESINS

Property	XAD-4	ZH-03
Polarity	Nonpolar	Moderate polar
Specific surface area (m^2/g)	880	883.4
Average diameter (nm)	5.8	1.33
Micropore area (m^2/g)	3	492.6
Average particle size (mm)	0.5	0.5
Porosity (mL/g)	1.0	0.224
Residual chlorine content (%)	0	4.4
Color	White	Brown

samples. Of course, all samples were filtered with a 0.45 μm membrane and benzoic acid was extracted with 2-chloromethane for analysis. The oven temperature was programmed as follows: 80 °C for 1 min, increasing to 150 °C at 15 °C/min and holds for 1 min, then increasing to 250 °C at 10 °C/min, hold for 1 min. The injector and detector temperatures were kept at 250 and 280 °C, respectively. Nitrogen (99.999 %) was used as carrier gas and make-up gas.

Adsorption experiments: Equilibrium adsorption of benzoic acid was performed at three difference temperatures: 288, 303 and 318 K. Dry ZH-03 resin (0.1g) was weighed accurately and introduced into a 250 mL conical flask directly, while the XAD-4 resin should be wetted in 0.5 mL methanol and rinsed with deionized water for more than three times before use. Then, 100 mL aqueous solution of the adsorbates of certain concentration (C_0, mg/L) ranging from 80 to 400 was added to each flask. The flask were completely sealed and shaken in a ZD-880D model incubator shaker (Taichang, bolate Scientific Co. Inc.) at a presettled temperature under 130 rpm until equilibrium reached. The concentration (C_e, mg/L) of the residual aqueous phase was determined using the above method. Thus, the concentration of the adsorbent-phase solute, Q_e (mmol/g), is calculated as below:

$$Q_e = V_1 (C_0\text{-}C_e)/M\,W \quad (1)$$

where V_1 is the volumn of solution (L), W is the weight of dry resin (g) and M is the molecular weight of corresponding adsorbate.

RESULTS AND DISCUSSION

Static equilibrium adsorption: Equilibrium data concerning the adsorption of the benzoic acid from aqueous solutions onto the two adsorbents were shown in Figs. 1 and 2. It is well known that increasing temperature was disadvantageous for a physical adsorption process. The equilibrium adsorption capacities of benzoic acid on ZH-03 and Amberlite XAD-4 decreased with the increase of temperature, which are the characteristic of physical adsorption process. The adsorbing capacities for benzoic acid on the ZH-03 is significantly higher than that on Amberlite XAD-4, which may be contributed to its high micropore area and benzoyl functional groups on the networks[5-8].

Freundlich model was used to fit the equilibrium adsorption data. The model was rearranged and expressed as below.

$$\text{Freundlich equation: } \ln Q_e = \ln K_F + 1/n \ln C_e \quad (2)$$

where Q_e is the equilibrium adsorption capacity (mmol/g), C_e the equilibrium concentration (mmol/L), K_F and n the characteristic constants. The evaluated constants for the isotherms are shown in Tables 2 and 3.

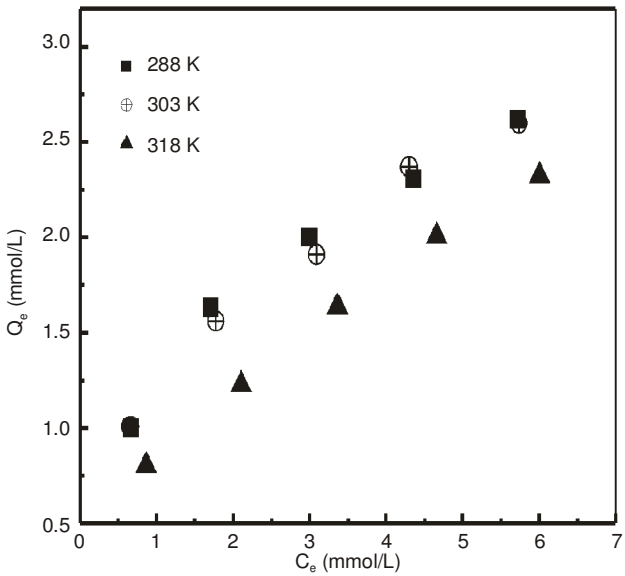

Fig. 1. Equilibrium adsorption isotherms for benzoic acid on ZH-03 at different temperature

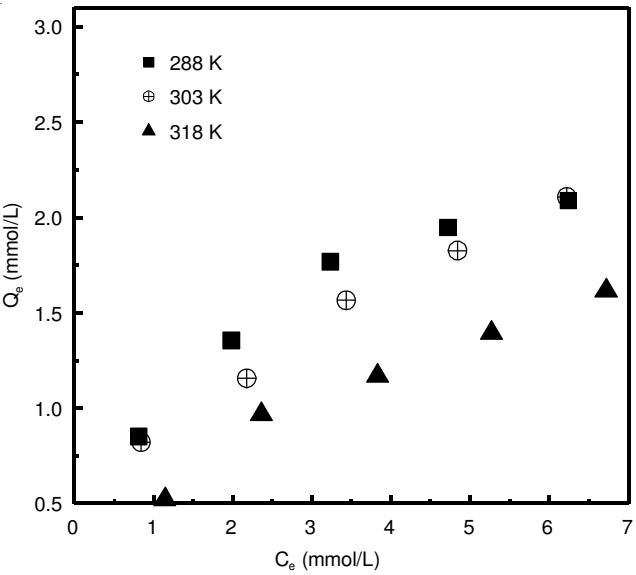

Fig. 2. Equilibrium adsorption isotherms for benzoic acid on XAD-4 at different temperature

TABLE-2
REGRESSION EQUATION OF log Q_e *vs.* log C_e FOR FREUNDLICH ISOTHERMS ON THE ZH-03 AND XAD-4 RESINS

Adsorbents	T (K)	Regression equation	K_f	n	R^2
ZH-03	288	log Q_e = 0.4854 log C_e + 0.0849	1.2159	2.0602	0.9913
	303	log Q_e = 0.4263 log C_e + 0.065	1.1614	2.3458	0.9905
	318	log Q_e = 0.5477 log C_e - 0.0726	0.8472	1.8258	0.9909
XAD-4	288	log Q_e = 0.5111 log C_e - 0.0579	0.8752	1.9566	0.9932
	303	log Q_e = 0.5335 log C_e - 0.1002	0.7940	1.8744	0.9903
	318	log Q_e = 0.6063 log C_e - 0.2174	0.6062	1.6494	0.9924

TABLE-3
REGRESSION EQUATION OF lg Q_e *vs.* lg C_e FOR LANGMUIR ISOTHERMS ON THE ZH-03 AND XAD-4 RESINS

Adsorbents	T (K)	Langmuir equation	q_m	K_L	R^2
ZH-03	288	$C_e/Q_e = 0.2741\ C_e + 0.5547$	3.648	0.5547	0.9901
	303	$C_e/Q_e = 0.3338\ C_e + 0.5315$	2.995	0.5315	0.9979
	318	$C_e/Q_e = 0.3110\ C_e + 0.9110$	3.215	0.9110	0.9990
XAD-4	288	$C_e/Q_e = 0.3321\ C_e + 0.8582$	3.011	0.8582	0.9956
	303	$C_e/Q_e = 0.3339\ C_e + 0.9946$	2.994	0.9946	0.9943
	318	$C_e/Q_e = 0.3327\ C_e + 1.4262$	3.005	1.4262	0.9913

Langmuir model was used to fit the equilibrium adsorption data. The model was rearranged and expressed as below.

$$\text{Langmuir equation: } C_e/Q_e = C_e/q_m + K_L \quad (3)$$

where q_m is the saturated adsorption capacity (mmol/g), K_L is the characteristic constants.

The Freundlich and Langmuir adsorption models can give a perfect fitting for all the correlative factors $R^2 > 0.98$. The correlative parameters of Freundlich and Langmuir adsorption isotherm equations for benzoic acid at different temperatures are listed in Tables 2 and 3, respectively. Based on the Freundlich and Langmuir theory, coefficient K_f and K_L are indication of the adsorbing capacity and R^2 denotes the degrees of deviation from isotherm linearity. According to K_f and K_L in Tables 2 and 3, the obviously higher adsorbing capacities toward benzoic acid on ZH-03 can be expected. The specific surface area of ZH-03 is larger than that of Amberlite XAD-4, so the adsorbing capacities for benzoic acid on ZH-03 is higher than that on Amberlite XAD-4 within the temperature range 288-318 K and the saturated adsorption capacity (q_m) for benzoic acid on ZH-03 are higher than that on Amberlite XAD-4, which further proved that besides specific surface area, adsorption capacity will be effected by several other factors, including adsorbent polarity, active groups and pore structures, *etc*. Tables 2 and 3 show the consistency using the above isothermal model that ZH-03 will exhibit its potential at even higher concentrations for column operations.

Adsorption kinetic studies: The influence of contact time on benzoic acid removal by Amberlite XAD-4 and ZH-03 were presented in Figs. 3 and 4. All the adsorbents showed their ability to adsorb benzoic acid with various efficiencies.

The kinetics adsorption data was processed to understand the dynamics of the adsorption process in terms of the rate constant. All the data were fit for the first-order equation form as follows[9]:

$$\ln [Q_e/(Q_e - Q_t)] = k_t \text{ or } -\ln (1-F) = kt \quad (4)$$

where Q_e was the equilibrium adsorption capacity (mmol/g), Q_t was the adsorption capacity at the contact time t (mmol/g), F was the fractional attainment of the equilibrium and k was the overall rate constant (min^{-1}), which showed the intraparticle diffusion would not be the rate limiting for the straight line did not pass through the origin. The values of the rate constant k was calculated from the slope of the plots obtained from -ln(1-F) *vs.* the contact of benzoic acid time t are given in Table-4. At the same time, the resins of adsorption for benzoic acid by fitting equation in different temperatures on ZH-03 and XAD-4 resins are shown in Tables 5 to 7. From Tables 5 to 7, the adsorption for benzoic acid on ZH-03 resin are fitting

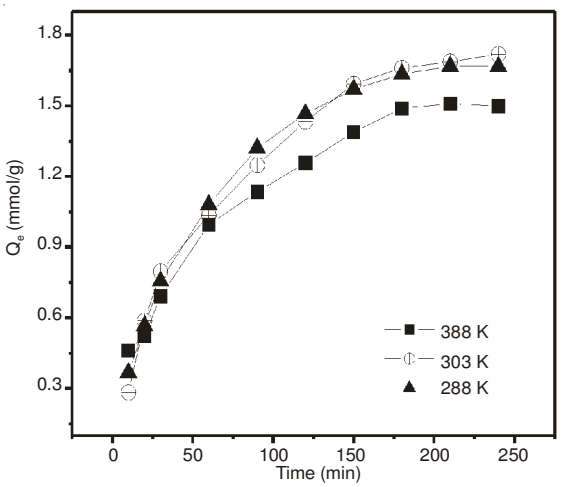

Fig. 3. Influence of Contact time on benzoic acid removal by amberlite ZH-03 at different temperature

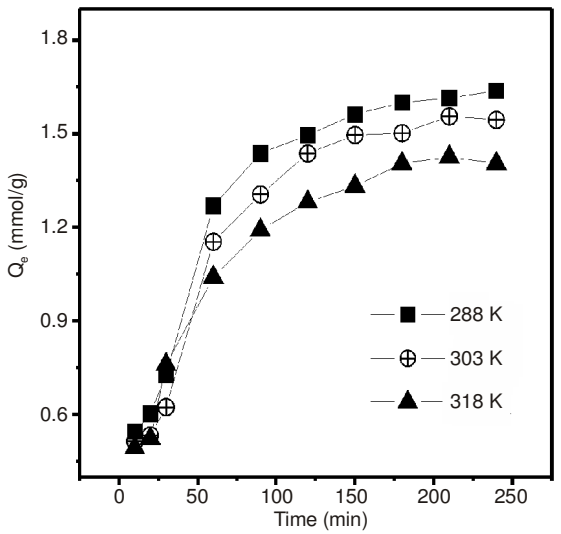

Fig. 4. Influence of contact time on benzoic acid removal by XAD-4 at different temperature

TABLE-4
RESULTS OF THE FIRST-ORDER DYNAMIC EQUATION ON THE ZH-03 AND XAD-4 RESINS

Adsorbents	T (K)	First-order dynamic equation	R^2	$K\times10^3$
ZH-03	288	$\ln (Q_e/(Q_e-Q_t)) = 0.0036t + 0.1674$	0.9391	3.6
	303	$\ln (Q_e/(Q_e-Q_t)) = 0.0043t + 0.1533$	0.9560	4.3
	318	$\ln (Q_e/(Q_e-Q_t)) = 0.0047t + 0.1865$	0.9499	4.7
XAD-4	288	$\ln (Q_e/(Q_e-Q_t)) = 0.0052t + 0.3863$	0.6756	5.2
	303	$\ln (Q_e/(Q_e-Q_t)) = 0.004t + 0.3256$	0.7012	4.0
	318	$\ln (Q_e/(Q_e-Q_t)) = 0.0077t + 0.4337$	0.7350	7.7

TABLE-5
RESULTS OF THE SECONDARY-ORDER DYNAMIC EQUATION ON THE ZH-03 AND XAD-4 RESINS

Adsorbents	T(K)	Secondary-order dynamic equation	R^2
ZH-03	288	$t/Q_t = 0.6025t + 17.76$	0.9820
	303	$t/Q_t = 0.5154t + 20.667$	0.9657
	318	$t/Q_t = 0.5522t + 17.66$	0.9814
XAD-4	288	$t/Q_t = 0.5825t + 13.774$	0.9406
	303	$t/Q_t = 0.6924t + 9.6177$	0.9929
	318	$t/Q_t = 0.6476t + 18.061$	0.8932

TABLE-6
RESULTS OF THE ELOVICH DYNAMIC EQUATION ON THE ZH-03 AND XAD-4 RESINS

Adsorbents	T (K)	Elovich dynamic equation	R^2
ZH-03	288	$Q_t = 3.4041 \ln t + 1.8283$	0.9391
	303	$Q_t = 2.8499 \ln t + 0.7649$	0.8593
	318	$Q_t = 3.0766 \ln t + 0.5752$	0.9178
XAD-4	288	$Q_t = 2.8614 \ln t + 0.5185$	0.7731
	303	$Q_t = 3.6237 \ln t + 0.1238$	0.9472
	318	$Q_t = 3.3122 \ln t + 0.4935$	0.8234

TABLE -7
RESULTS OF THE DOUBLE CONSTANT RATE DYNAMIC EQUATION ON THE ZH-03 AND XAD-4 RESINS

Adsorbents	T (K)	Double constant rate dynamic equation	R^2
ZH-03	288	$\ln Q_t = 0.4246 \ln t - 1.8283$	0.9906
	303	$\ln Q_t = 0.4042 \ln t - 1.6972$	0.8384
	318	$\ln Q_t = 0.4146 \ln t - 1.7285$	0.9499
XAD-4	288	$\ln Q_t = 0.3501 \ln t - 1.3711$	0.8174
	303	$\ln Q_t = 0.4169 \ln t - 1.7385$	0.9409
	318	$\ln Q_t = 0.3529 \ln t - 1.5323$	0.7671

to the first-order kinetics equation and the secondary dynamic equation. In accordance with the first order kinetics equation fitting, the rate constant is little change for adsorption of benzoic acid on ZH-03 resin with the different temperature. The adsorption for benzoic acid on XAD-4 resin is fitting to the first-order kinetics equation and the rate constant change is obvious in the different temperature[10,11]. With the temperature 303 K, the adsorption for benzoic acid on XAD-4 are fitting to the first-order kinetics equation, the secondary kinetics equation, Elovich equation, double constant rate equation and so on. The absorption rate of benzoic acid on ZH-03 is higher than on XAD-4' at the same temperature. The adsorption kinetics equation can be relatively satisfied with the result of the dynamic adsorption, the process of master steps was showed that liquid film diffusion for the adsorption.

Conclusion

A hypercrosslinked polymeric adsorbent (ZH-03) for adsorbing and removing benzoic acid compound from their aqueous solutions has been studied and the equilibrium adsorption capacity for benzoic acid on ZH-03 are markedly higher than that on XAD-4, which can be attributes to its high micropore area and the benzoyl functional group. Thermodynamics study draws a conclusion for adsorbing benzoic acid compounds on ZH-03 that there is physical adsorption processes.

All the isotherm data for the benzoic acid on the XAD-4 and ZH-03 can be satisfactorily fit for the Freundlich and Langmuir equation.

The adsorption for benzoic acid on ZH-03 resin is fitting to the first-order kinetics equation and the secondary dynamic equation. Accordance with the first order kinetics equation fitting, the rate constant is little change for adsorption of benzoic acid on ZH-03 resin at the different temperature. The adsorption for benzoic acid on XAD-4 resin is fitting to the first-order kinetics equation and the rate constant change is obvious at the different temperature. The absorption rate of benzoic acid on ZH-03 is higher than the XAD-4' at the same temperature. The adsorption kinetics equation can be relatively satisfied with the result of the dynamic adsorption; The process of master steps was showed that liquid film diffusion for the adsorption.

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REFERENCES

1. A.M. Li, C. Long, Y. Sun, Q.X. Zhang, F.Q. Liu and J.L. Chen, *Sep. Sci. Technol*., **37**, 3211 (2002).
2. F. Zhenghao, X. Mingfang, W. Lin, C. Jinlong, G. Yunlan, L. Aimin and Z. Quanxing, *Adsorpt. Sci. Technol*., **23**, 225 (2005).
3. Z.H. Fei, Z.T. Liu, F.Q. Liu, A.M. Li, J.L. Chen and Q.X. Zhang, *Acta Chimi. Sin*., **65**, 1515 (2007).
4. F. Zhenghao, X. Mingfang, W. Lin, C. Jinlong, G. Yunlan, L. Aimin and Z. Quanxing, *Adsorpt. Sci. Technol*., **22**, 439 (2004).
5. W.H. Tao, A.M. Li, C. Long, Z.C. Fan and W.W. Wang, *J. Hazard. Mater*., **193**, 149 (2011).
6. W.H. Tao, A.M. Li, C. Long, H.M. Qian, D.J. Xu and J. Chen, *J. Hazard. Mater*., **175**, 111 (2010).
7. J.P. Wang and Z.H. Fei, *Chinese J. Polym. Sci*., **24**, 545 (2006).
8. J.P. Wang, S.H. Tang, Z.H. Fei, J. Chen and Y.F. Sun, *Chinese J. Polym. Sci*., **28**, 241 (2010).
9. Z.H. Fei, J.L. Chen, J.G. Cai, Y.P. Qiu, A.M. Li and Q.X. Zhang, *Chinese J. Polym. Sci*., **22**, 531 (2004).
10. J.P. Wang, J. Chen, Y.F. Sun, J.T. Dai and Y.Y. Wei, *Asian J. Chem.*, **25**, 6209 (2013).
11. J.P. Wang, J.T. Dai, J. Chen, Y.F. Sun, J. Yin and D.M. Chen, *Asian J. Chem.*, **25**, 10485 (2013).