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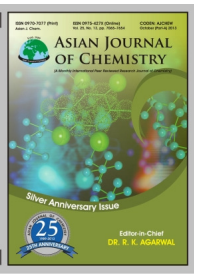

Adsorption Behaviours of Sorbic Acid onto Polymeric Adsorbent Modified with 2-Carboxybenzoyl Group

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In the present study, a hypercrosslinked polymeric adsorbent (ZH-01) was employed to remove sorbic acid. The study focuses on the static equilibrium adsorption behaviours and the adsorption thermodynamics. Freundlich and Langmuir model give perfect fitting to the isotherm data. The adsorbing capacities for sorbic acid on ZH-01 is higher than on Amberlite XAD-4 within the temperature range 288-318 K, which is contributed to microporous structure and the polar groups on the network of ZH-01 resin. The changes of enthalpy, free energy, entropy were indicative of an exothermic, a spontaneous and disorder decreasing process. The data of the kinetics were fit for the first-order equation. The results showed that the hypercrosslinked polymeric adsorbent (ZH-01) was better than the Amberlite XAD-4 for removing the sorbic acid in aqueous solutions.

Key Words: Hypercrosslinked resins, Sorbic acid, Adsorption.

INTRODUCTION

Sorbic acid, as one of the most important preservative, is widely used for the manufacture of food. As a result, more and more sorbic 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].

The present work aimed at investigation of the adsorption behaviours of sobic acid from their aqueous solutions onto ZH-01 adsorbent containing 2-carboxybenzoyl group. In comparison with Amberlite XAD-4, ZH-01 has higher adsorption capacity for sorbic acid, because it is high micropore area and the presence of 2-carboxybenzoyl functional group.

EXPERIMENTAL

Acetone, ethanol, zinc chloride, 2-chloromethane, hydrochloric acid, nitrobenzene, phthalic anhydride, sorbic 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 and Haas Company (Philadelphia, USA). Sorbic 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-01 resin: ZH-01 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 were 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-01 and XAD-4 resins are given in Table-1.

TABLE-1
TYPICAL PROPERTY OF THE POLYMERIC RESINS

Property	XAD-4	ZH-01
Polarity	Non-polar	Moderate polar
Specific surface area (m^2/g)	880	1118
Average diameter (nm)	5.8	1.2
Micropore area (m^2/g)	3	686
Average particle size (mm)	0.5	0.5
Porosity (mL/g)	1.0	0.69
Residual chlorine content (%)	0	2.8
Colour	White	Brown

Analytical 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 sorbic acid in water samples. Of course, all samples were filtered with a 0.45 μm membrane and sorbic 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 hold 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 °C and 280 °C, respectively. Nitrogen (99.999 %) was used as carrier gas and make-up gas.

Adsorption experiments: Equilibrium adsorption of sorbic acid was performed at three difference temperatures: 288 K, 303 K and 318 K. Dry ZH-01 resin (0.1 g) 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 flasks 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 method above. 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 sorbic acid from aqueous solutions onto the two adsorbents were shown in Fig. 1 and 2. It is well known that increasing temperature was disadvantageous for a physical adsorption process. The equilibrium adsorption capacities of sorbic acid on ZH-01 and Amberlite XAD-4 decrease with the increase of temperature, which are the chracteristic of physical adsorption process. The adsorbing capacities for sorbic acid on the ZH-01 is significantly higher than that on Amberlite XAD-4, which may be contributed to its high micropore area and 2-carboxybenzoyl functional groups on the networks.

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

$$\ln Q_e = \ln K_F + 1/n \ln c_e \quad (2)$$

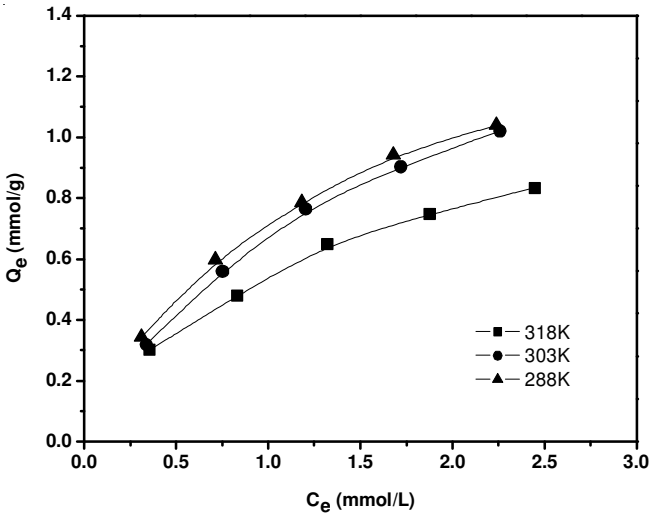

Fig. 1. Equilibrium adsorption isotherms for sorbic acid on ZH-01 at different temperature

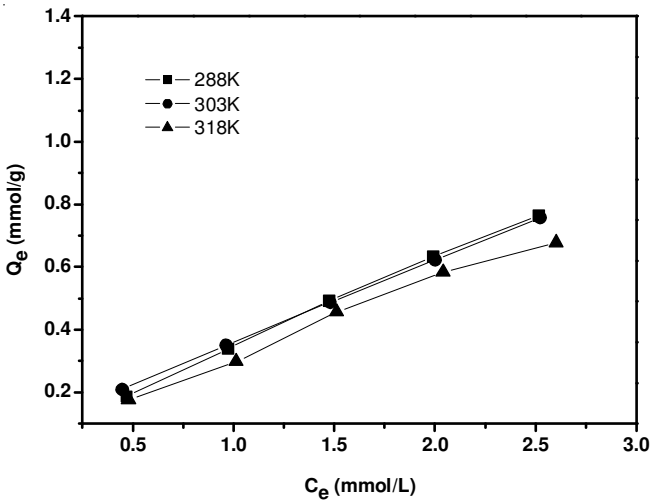

Fig. 2. Equilibrium adsorption isotherms for sorbic acid on XAD-4 at different temperature

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 Table-2 and Table-3.

Langmuir model was used to fit the equilibrium adsorption data. The model was rearranged and expressed as below. 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 model 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 sorbic acid at different temperatures are listed in Table-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 Table-2 and 3, the obviously higher adsorbing capacities toward sorbic acid on ZH-01 can be expected. The specific surface area of ZH-01 is larger than that of Amberlite XAD-4, so the adsorbing capacities for sorbic acid on ZH-01

TABLE-2
REGRESSION EQUATION OF log Q_e *versus* log c_e FOR FREUNDLICH ISOTHERMS ON THE ZH-01 AND XAD-4

Adsorbents	T (K)	Regression equation	K_f	n	R^2
ZH-01	288	$\log Q_e = 0.52673 \log C_e - 0.15503$	0.6998	1.8985	0.9891
	303	$\log Q_e = 0.52363 \log C_e - 0.18361$	0.6552	1.7432	0.9900
	318	$\log Q_e = 0.51519 \log C_e - 0.2704$	0.5365	1.9410	0.9919
XAD-4	288	$\log Q_e = 0.3754 \log C_e - 0.45304$	0.3523	1.1849	0.9997
	303	$\log Q_e = 0.4017 \log C_e - 0.45304$	0.3661	1.2904	0.9982
	318	$\log Q_e = 0.4896 \log C_e - 0.49994$	0.3163	1.2238	0.9934

TABLE-3
REGRESSION EQUATION OF lgQ_e *VERSUS* lgc_e FOR LANGMUIR ISOTHERMS ON THE ZH-01 AND XAD-4

Adsorbents	T (K)	Langmuir equation	q_m	K_L	R^2
ZH-01	288	$C_e/Q_e = 0.81853C_e + 0.96025$	1.1731	1.2217	0.9961
	303	$C_e/Q_e = 0.59692C_e + 0.86884$	1.4555	1.6752	0.9993
	318	$C_e/Q_e = 0.63982C_e + 0.72328$	1.1304	1.5629	0.9993
XAD-4	288	$C_e/Q_e = 0.63036C_e + 0.61715$	0.9790	1.5863	0.9983
	303	$C_e/Q_e = 0.62464C_e + 0.46441$	0.7466	1.6009	0.9960
	318	$C_e/Q_e = 0.60167C_e + 0.37642$	0.6256	1.6620	0.9979

is higher than that on Amberlite XAD-4 within the temperature range 288-318 K and the saturated adsorption capacity (q_m) for sorbic acid on ZH-01 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-01 will exhibit its potential at even higher concentrations for column operations.

Isosteric enthalpies for sorbic acid adsorption: The isosteric enthalpies of adsorption were calculated with a derivative van't Hoff equation[5,6].

$$\ln(1/C_e) = \ln(K_0) + (\Delta H/RT) \quad (4)$$

where ΔH is the isosteric enthalpy change of adsorption reaction (kJ/mol) when Q_e is a fixed value, R is the ideal gas constant and C_e is equilibrium concentration of solute in mol/L at the absolute temperature T. At different temperatures (288 K, 303 K and 318 K), C_e is obtained from the Freundlich isotherms when Q_e equals to 1.0 mmol, 1.5 mmol and 2.0 mmol. ΔH was calculated from the slope of line plotted by ln c_e *versus* 1/T. A summary of the calculated values for enthalpy about ZH-01 adsorbing sorbic acid is listed in Table-4. The H values imply that the adsorption of sorbic acid by ZH-01 is an exothermic process and almost all the values are less than 42 kJ/mol. It shows a physical adsorption process for sorbic acid on ZH-01 and XAD-4.

Free energies and entropies of adsorption for sorbic acid compound: The free energies of adsorption were calculated with a derivative Gibbs equation[7,8].

$$\Delta G = -nRT \quad (5)$$

where n is a coefficient of Freundlich equation. The entropies change of adsorption was calculated with Gibbs-Helmholtz equation.

$$\Delta G = \Delta H - T^*S \quad (6)$$

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

A summary of the calculated values for enthalpy, free energy, entropy about ZH-01 and XAD-4 adsorbing sorbic acid are listed in Table-4.

Little change in enthalpy at different Q_e shows homogeneous nature of the adsorbent surface once again. The absolute heat quantities for ZH-01 are larger than XAD-4's. So, the adsorption abilities of ZH-01 for sorbic acid is stronger than XAD-4's. Due to the adsorbate molecular after adsorption can orderly cover the surface of adsorbent, the disorder and entropy are almost decreasing. Changes in enthalpy, free energy and entropy (always negative) are indicative of an exothermic, spontaneous and disorder process for sorbic acid. All the data on ZH-01 and XAD-4 show that they belong to physical adsorption process.

Adsorption kinetic studies: The influence of contact time on sorbic acid removal by Amberlite XAD-4 and ZH-01 were presented in Figs. 3 and 4. All the adsorbents showed their ability to adsorb sorbic 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]:

$$\ln[Q_e/(Q_e - Q_t)] = kt \quad \text{or} \quad -\ln(1-F) = kt \quad (8)$$

TABLE-4
ESTIMATED THERMODYNAMIC PARAMETERS OF THE SYSTEMS TESTED

Adsorbents	Q_e (mmol/g)	-ΔH (KJ/mol)	-ΔG (KJ/mol)			-ΔS (J/mol)		
			288 K	303 K	318 K	288 K	303 K	318 K
ZH-01	1.0	13.3	4.55	4.39	5.13	30.36	30.61	27.68
	1.5	13.7						
	2.0	13.9						
XAD-4	1.0	4.36	2.84	3.25	3.24	5.28	5.07	5.84
	1.5	4.79						
	2.0	5.09						

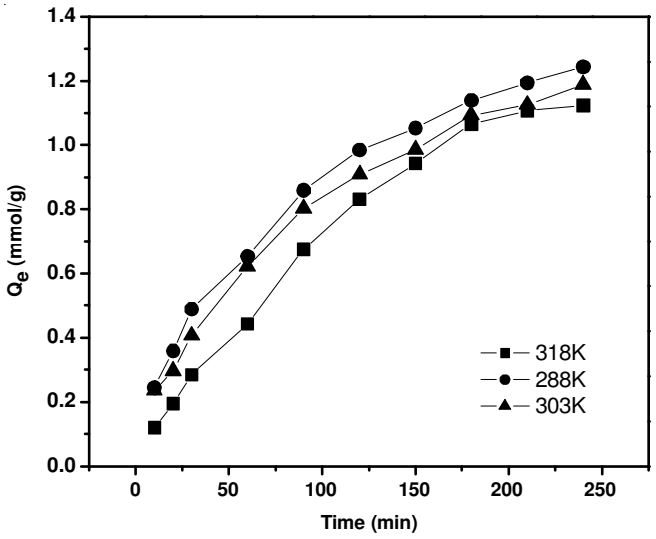

Fig. 3. Influence of contact time on sorbic acid removal by Amberlite ZH-01 at different temperature

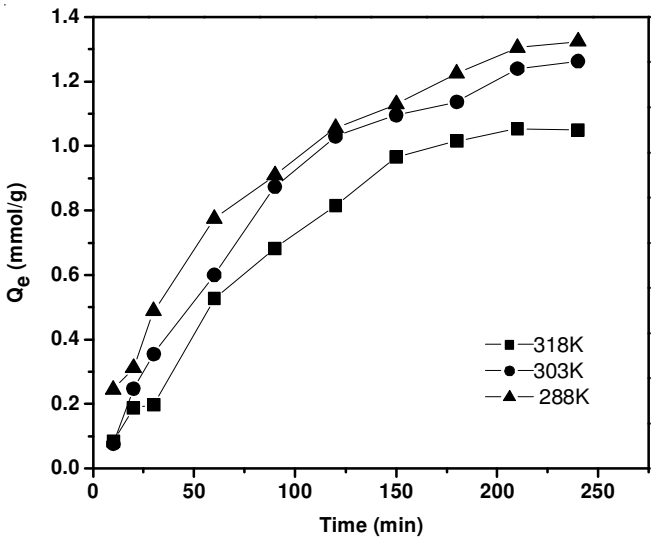

Fig. 4. Influence of contact time on sorbic acid removal by XAD-4 at different temperature

where Q_e was the equilibrium adsorption capacity (mmol/g), Q_t was the adsorption capacity when 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 sorbic acid time t were 0.0156 min^{-1}, 0.0239 min^{-1} and 0.0250 min^{-1} for ZH-01 at 288 K, 303 K and 318 K, while 0.0123 min^{-1}, 0.0117 min^{-1} and 0.0076 min^{-1} for XAD-4 at 288 K, 303 K and 318 K, respectively.

Conclusion

A hypercrosslinked polymeric adsorbent (ZH-01) for adsorbing and removing sorbic acid compound from their aqueous solutions has been studied and the equilibrium adsorption capacity for sorbic acid compounds on ZH-01 are markedly higher than that on XAD-4, which can be attributes to its high microporous area and the 2-carboxybenzoyl functional group. The thermodynamics study draws a conclusion for adsorbing sorbic acid compounds on ZH-01 that there is physical adsorption processes. All the isotherm data for the sorbic acid compounds on the XAD-4 and ZH-01 can be satisfactorily fit for the Freundlich and Langmuir equation.

The hypercrosslinked Resins (ZH-01) could effectively remove the sorbic acid from aqueous solution. The new feasible measure for resolve sorbic acid was offered in groundwater micropollution.

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