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**Research Article** 

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# Cooperative effect and influence factors on simultaneous adsorption of phthalimide and anthranilic acid from aqueous solutions by hypercrosslinked polymeric adsorbents with multicarboxyl group

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## ABSTRACT

The hypercrosslinked polymeric adsorbents containing multicarboxyl groups and modified with phthalic anhydride, 1,2,4-benzenetricarboxylic anhydride or pyromellitic dianhydride (respectively named FZH12,FZH124,FZH1245) were prepared and characterized. The static adsorption of single or binary system, adsorption characteristics for phthalimide or anthranilic acid in aqueous solution at the temperature range of 288~318K on above self-prepared hypercrosslinked polymeric adsorbents were studied by using bottle point method and the influence of pH or inorganic salt on adsorption efficiencies were carried out. The results indicated that adsorption isotherms for phthalimide and anthranilic acid in both single and binary systems can be well fitted by the Langmuir equation, while the individual adsorbed amounts of phthalimide or anthranilic acid on above adsorbents in binary systems is higher than those in single systems because of the hydrogen bonding or weak acid base interaction between phthalimide and anthranilic acid towards the adsorption sites, and the existence of chemisorption effects at the proper temperature between adsorbents and adsorbates was confirmed and interpreted by the approximate orbital energy level difference between adsorbents and adsorbates calculated with the semiempirical molecular orbital method PM3. It is unobvious for adsorption efficiencies with low concentration inorganic salts but the change of pH value has an obvious influence on both adsorption systems.

Key words: hypercrosslinked polymeric adsorbent, phthalimide, anthranilic acid, chemical modification, cooperative adsorption

## INTRODUCTION

Anthranilic acid as a kind of important pesticide, medicine or dye intermediates is synthesized with phthalic anhydride and carbamide as initial raw materials in sequence by amidation, degradation, acidification and purification. In this process, phthalimide will be generated in wastewater with anthranilic acid and sodium chloride. Adsorption on granular activated carbon (GAC) is probably one of the best commercially proven methods for removing toxic organic chemicals from wastewater [1-3]. Although activated carbons exhibit an excellent adsorption capacity for organic removal from wastewater, the used activated carbon adsorbents are difficult to be regenerated and quite expensive to dispose. Therefore, it is essential to excavate alternative and economical adsorbents which are equally effective and easier to be regenerated. Consequently there has been a growing interest in developing and implementing various adsorption capacities for phthalimide and anthranilic acid in wastewater and newly resins having high adsorption efficiency for treating the wastewater containing phthalimide, anthranilic acid and sodium chloride have to be expounded.

Parikshit Gogoi et al[9]. provided an example for surface modification of the sorbent and effective design of adsorbents with high selectivity and capacity for adsorption of catechins from aqueous solution. the lower LUMO energy level of adsorbents for a specific donator adsorbate or the higher HOMO energy level of adsorbents for a specific acceptor adsorbate will contribute to the charge transfer in the process of adsorption, which will have the high chemisorption capacities at the right temperature. In this paper the hypercrosslinked polymeric adsorbents containing multicarboxyl groups, which has both the lower LUMO(lowest unoccupied molecular orbital)energy level and the higher HOMO(highest occupied molecular orbital) energy level, and modified with phthalic anhydride, 1,2,4-benzenetricarboxylic anhydride or pyromellitic dianhydride (respectively named FZH12, FZH124, FZH1245)were prepared and characterized. The static adsorption of single or binary system, adsorption characteristics for phthalimide or anthranilic acid in aqueous solution at the temperature range of 288~318K on above self-prepared hypercrosslinked polymeric adsorbents were studied. The influence of pH and inorganic salt on adsorption efficiencies were carried out and the mechanism of cooperative effect on simultaneous adsorption of phthalimide and anthranilic acid was investigated.

## EXPERIMENTAL SECTION

## 1.1. Materials

Styrene-divinylbenzene copolymer were purchased from Nanjing Maike Fei Co. LTD. phthalic anhydride, 1,2,4-benzenetricarboxylic anhydride and pyromellitic dianhydride were purchased from Element Mall. Ethanol, nitrobenzene, anhydrous aluminum chloride and hydrochloric acid were analytical grade, which were purchased from Shanghai Chemical Reagent. Ethanol, nitrobenzene, anhydrous aluminum chloride and hydrochloric acid were analytical grade, which were purchased from Shanghai Chemical Reagent. Ethanol, nitrobenzene, anhydrous aluminum chloride and hydrochloric acid were analytical grade, which were purchased from Shanghai Chemical Reagent.

DF-101S collector-type thermostat heating magnetic stirrer(Zhengzhou Great Wall Branch Co, Henan, China.); Pore surface area analyzer (Micromeritics, ASAP2010, USA); High-performance liquid chromatography (ULTIMATE 3000, Thermo-Fisher, USA); Infrared spectrometer (Broker company Vertex 80 Switzerland).

## 1.2. Synthesis of the resins

As shown in Figure 1, FZH series were prepared from the chloromethylated styrene-divinylbenzene copolymer (CLPs) through two continuous chemical reactions named self-Friedel–Crafts reaction and Friedel–Crafts acylation reaction. The chloromethylated styrene-divinylbenzene was dried in a vacuum oven at 333 K all night, and the solvent nitrobenzene was dehydrated using a molecular sieve desiccant. A known amount (30g) of chloromethylated poly(styrene–divinylbenzene) beads (chlorine content =19.5%) was placed in a 500 ml round-bottomed flask and swollen in 200ml nitrobenzene. Then, 5 g anhydrous aluminum chloride was added slowly at room temperature under mechanical stirring. The mixture was further stirred for 12h at 408K. After cooled, phthalic anhydride, 1, 2, 4-benzenetricarboxylic anhydride or pyromellitic dianhydride was added to the mixture at 343 K, and the mixture was stirred for 4h and an acetone bath containing 0.3 mol/L solution of hydrochloric acid for 2h and washed by de-ionized water until neutral pH. The filtered polymers were extracted by ethanol in a Soxhlet apparatus for 8 h and dried under vacuum at 333 K for 8 h, and the yield of all the FZH series resins is 28g or so. Reaction process as shown in Figure.1.

## 1.3. Adsorbent characterization and analytical methods

Pore volume, t-plot micropore volume, Brunauer–Emmett–Teller (BET) surface area, t-plot micropore surface area and pore diameter distribution of the FZH series adsorbents were calculated. The residual chlorine content of the resins and carboxyl group amounts was measured according to the Volhard method [10,11] and Boehm method (Boehm HP, 1966; Boehm HP, 1994), respectively.

## **1.4. Batch adsorption experiments**

The single-solute adsorption of phthalimide or anthranilic acid onto the adsorbents was performed by using batch experiments. A given amount of beads (100 mg) was added into phthalimide or anthranilic acid aqueous solution (100 ml) at a known concentration, constant temperature of 288~318K and constant rate 110rpm in a thermostat oscillator. The adsorption equilibrium time was predetermined by monitoring the concentration change via time change. After a desired period of sorption, the concentration of phthalimide or anthranilic acid was measured by HPLC. The adsorbance of phthalimide or anthranilic acid onto the adsorbents were calculated. 1.0 mol/L of hydrochloric acid or 1.0mol/L of sodium hydroxide was employed to adjust the solution pH. Sodium sulfate was used to investigate the salinity effect on the adsorption.



Figure. 1. The synthetic procedure of FZH series resins modified with phthalic anhydride, 1,2,4-benzenetricarboxylic anhydride or pyromellitic dianhydride

The adsorption isotherms for binary-solute system were conducted by above-mentioned procedures, except that primary concentration of one solute was at the constant level of 500 mg/L and the other varies at different levels.

### **RESULTS AND DISCUSSION**

## 1.5. Characterization of FZH series resins

The pore structural parameters were summarized in Table 1. Table 1 showed that the Specific surface area and microporous volume of FZH12 and FZH1245 were less than FZH124. In particular, the chlorine content of the hypercrosslinked polystyrene resins FZH12, FZH124 and FZH1245 sharply decreased from 19.5% to 3.78%, 3.30% and 3.25% respectively, implying that the chlorine of the macroporous crosslinked chloromethylated polystyrene was consumed in the first step and a longer reaction time lead to lower chlorine content. Meanwhile, carboxyl group amounts(mmol/g) of FZH12, FZH124 and FZH1245 was determined to be 2.24, 2.89 and 3.06 mmol/g, respectively, confirming that substitution of chlorine by carboxyl groups was successful Particularly. In addition, the chlorine methyl absorption peak at 676.6 cm<sup>-1</sup> was decreased significantly after the reaction (see Figure 2). Figure 2 shows that a new moderate vibrational band appears at 1716.4 cm<sup>-1</sup>,1706.8 cm<sup>-1</sup>,1729.4 m<sup>-1</sup> respectively, which can be assigned to the stretching of acid carbonyl groups [12,13] and this band is proven be caused by hindered vibrations of carbon–carbon bonds and valence angles in the aromatic fragments. The results show that the functional groups have been successfully modified.

Table 1	Surface	property	of FZH	series	adsorbents
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Properties	FZH12	FZH124	FZH1245
Specific surface area (m <sup>2</sup> / g)	1021	1081.3	998.5
Average pore radius (nm)	1.19	2.06	1.04
Microporous area (m <sup>2</sup> /g)	531.4	570.8	517.3
Microporous volume (mL/ g)	29.05	38.69	30.82
Residual chloride content (%)	3.78	3.30	3.25
Carboxyl group amounts(mmol/g)	2.24	2.89	3.06



Figure 2. IR spectra of resins and CLPS

 Table 2 Isotherm parameters for the adsorption of phthalimide or anthranilic acid on the FZH series resin with the temperature at 298 K, 303K, 318K according to Langmuir and Freundlich isotherm models

								-		
Resins T(K)		к) –	Langmuir isotherm model				Freundlich isotherm model			
resins	1 (	к)	$K_L/(L/g) = Qm/(mg/g)$		$\mathbf{R}^2$	K <sub>F</sub>	F n		$\mathbf{R}^2$	
288		88	20.98	322.6	322.6 0.9819		2 :	2.077	0.8880	
FZH12	30	03	30.00	303.0	0.9985	14.0	5	2.642	0.9773	
	3	18	8.534	400.0	0.9862	3.46	6	1.243	0.8858	
	23	88	23.11	400.0	0.9942	8.27	1 :	2.112	0.9893	
FZH124	30	03	23.38	370.4	0.9932	9.49	9	2.251	0.9927	
	3	18	7.482	434.8	0.9944	4.84	7	1.578	0.9844	
	23	88	17.92	333.3	0.9941	7.93	3	2.078	0.9182	
FZH1245	30	03	24.25.	322.6	0.9982	10.9	9	2.397	0.9680	
	3	18	10.67	370.4	0.9889	5.72	3	1.744	0.9612	
Deel		<b>T</b> ( <b>V</b>	, La	ngmuir isothe	erm model		Freund	lich isothe	erm model	
Kes	ins	I ( K	) K <sub>L</sub> /(L	/g) Qm/(mg	g/g) I	$R^2$	K <sub>F</sub>	n	$\mathbb{R}^2$	
		288	6.03	7 322.	6 0.9	994	5.348	1.676	0.9904	
FZH	[12	303	7.02	5 294.	1 0.9	811	6.255	1.833	0.9973	
		318	11.9	1 208.	3 0.9	924	10.11	2.313	0.9671	
		288	28.7	3 263.	1 0.9	972	11.97	2.482	0.9729	
FZH	124	303	13.4	9 312.	5 0.9	827	8.502	2.140	0.9656	
		318	10.6	7 277.	8 0.9	976	7.321	1.990	0.9788	
		288	13.8	4 222.	2 0.9	865	10.16	2.484	0.9874	
FZH1	245	303	15.0	9 217.4	4 0.9	988	11.99	2.319	0.9812	
		318	15.5	3 196.	1 0.9	950	10.74	2.319	0.9489	

#### 1.6. Adsorption isotherms of single-solute systems

Langmuir model parameters of phthalimide or anthranilic acid in single-solute adsorption systems are listed in Table 2. The experimental data are plotted in Figure 3. Langmuir model yields a good correlation for the single-solute adsorption systems. As presented in Table 2 and Figure 3, the affinity of phthalimide for FZH series containing carboxyl group is higher than for anthranilic acid, presumably due to the more hydrophobic nature and the thicker electron density phenyl ring of phthalimide[14,15]. The IR spectra indicate that the chemical structures of FZH series are weak polar which is believed to favour the adsorption of phthalimide or anthranilic acid due to acid-basic interaction between the amino or amide groups of adsorbates and the carboxyl group of the polymer matrix. The phthalimide or anthranilic acid uptakes increase with increasing of the equilibrium concentration and decrease with increment of the temperature, implying that the adsorption is an exothermic process[16,17]. the value of the correlation coefficient( $\mathbb{R}^2$ ) in the Langmuir isotherm model is more than 0.98, which suggested that the Langmuir isotherm model was more suitable to fit the adsorption equilibrium data. Langmuir was the first one proposing a coherent theory of adsorption on a flat surface based on a kinetic viewpoint, and the Langmuir isotherm assumes that the adsorption energy is constant over all adsorption sites, the adsorption on the surface is localized and each site can accommodate only one molecule. Its linear equation can be given as[18]:

 $Ce/Qe = 1/(K_L \times Qm) + Ce/Qm$ (1)

Where Qe is the equilibrium adsorption capacity(mg/g) with the equilibrium concentration Ce , Qm is the maximum monolayer adsorption capacity (mg/g) and  $K_L$  is a Langmuir constant related to adsorption energy (L/mg). The

Freundlich model can be rearranged as[19]:

 $\ln Qe = 1/n \ln Ce + \ln K_F$ (2)

where  $K_F [(mg/g)(L/mg)1/n]$  and n (dimensionless) are the characteristic constants.

The corresponding parameters  $K_L$ ,  $K_F$  and n, as well as the correlation coefficients  $R^2$  are summarized in Table 2.



Figure 3. Equilibrium adsorption isotherms of phthalimide or anthranilic acid on FZH series resins at 288K, 303K, 318K (the dotted line indicates phthalimide and the solid line indicates anthranili acid)

#### 1.7. Adsorption isotherms of binary-solute systems

In general, the presence of an adsorbate adsorbed on the surface of an adsorbent will diminish the uptake of the adsorbent for other solutes [20,21,22]. However, there are some unique systems in which adsorbate interactions can lead to enhanced adsorption. The generally accepted explanation for this "cooperative" type of adsorption is that on homogeneous surfaces lateral attractive interactions between adsorbate molecules can cause enhanced adsorption of some adsorbates. Figure 4 presents that the individual adsorbed amounts of phthalimide or anthranilic acid on above adsorbents is higher than those in single systems compared to the single-solute experiment at higher concentrations. Although there is the competitive adsorption of phthalimide or anthranilic acid is much greater than that[15]. Hence, considering both competitive and cooperative effect, the greater affinity enhancement of phthalimide or anthranilic acid to nonpolar adsorbents in the presence of co-solute is obviously observed.





Figure 4. Equilibrium adsorption isotherms of phthalimide or anthranilic acid on FZH series resins in single-solute and binary primary-co-solutes systems. S:phthalimide or anthranilic acid in single-solute adsorption system. C: primary solute with 500mg/L co-solute in binary primary-co-solutes adsorption systems

#### 1.8. Isosteric adsorption enthalpy of single-solute systems

The enthalpy change of adsorption and the adsorption capacity are closely related, When the adsorption capacity is fixed at a constant value, The adsorption enthalpy change is known as the equivalent enthalpy change. Following the Clausius-Clapeyron equation [23]:

$$lnCe=\Delta H/RT-lnK$$
 (3)

where Ce is the equilibrium concentration of the adsorbate (mg/L). Here Ce was obtained from the fitted isotherms by the Langmuir equation at a defined qe and temperature (298, 308 or 318 K). T is the absolute temperature (K),  $\Delta$ H is the isosteric enthalpy change of adsorption (kJ/mol), R is the ideal gas constant (8.314 J/mol K) and K is a constant.  $\Delta$ H was determined by plotting lnCe versus 1/T and could be calculated from the slope of the fitting line. Adsorption free energy can be calculated as[24]:

$$\Delta G = -RT ln K \tag{4}$$

Where  $\Delta G$  is the adsorption free energy (kJ/mol), R is the ideal gas constant (8.314 J/mol K) and T is the absolute temperature (K).

The adsorptive entropy change,  $\Delta S(J/mol \cdot k)$  were calculated using the Gibbs–Helmholtz equation:

(5)

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

Table 3 Thermodynamic parameters of phthalimide or anthranilic acid adsorption based on resins at different temperatures

Desing	AII(VI/mol)	$\Delta G(KJ/mol)$			$\Delta S(J/mol \bullet k)$		
Resilis	$\Delta \Pi(\mathbf{KJ}/\Pi 0\mathbf{I})$	288K	303K	318K	288K	303K	318K
FZH12	-37.79	-9.252	-8.833	-12.61	-99.09	-95.56	-79.18
FZH124	-38.40	-9.021	-9.416	-12.94	-102.0	-95.65	-80.06
FZH1245	-24.50	-9.630	-9.369	-12.01	-51.63	-49.93	-39.27
Pasing	AU(VI/mol)	$\Delta G(KJ/mol)$			$\Delta S(J/mol \cdot k)$		
Resilis	$\Delta H(KJ/III0I)$	288K	303K	318K	288K	303K	318K
FZH12	-13.570	-12.23	-12.49	-11.71	-4.652	-3.564	-5.849
FZH124	-22.98	-8.499	-10.31	-12.01	-50.28	-41.81	-34.49
FZH1245	-14.61	-10.25	-10.56	-11.01	-15.14	-13.36	-11.32

Tables 3 lists the  $\Delta$ H,  $\Delta$ G and  $\Delta$ S of FZH series resins towards phthalimide or anthranilic acid from aqueous solution. The value of  $\Delta$ H is negative, indicating an exothermic process[16]. The value of  $\Delta$ G is negative, indicating that the adsorption is a spontaneous process. The value of  $\Delta$ S is negative, revealing that a more ordered arrangement of phthalimide or anthranilic acid is shaped on the surface of FZH series resins after the adsorption.

## **1.9. Kinetic experiments**

Adsorption kinetic curves can describe the adsorption rate of the adsorbate on an adsorbent at a specific initial concentration and temperature, and the time required for the adsorption from the beginning to the equilibrium can be known from the kinetic curves. As can be seen in Figure.5, with the initial concentration of anthranili acid at 300.4 mg/L and the temperature at 288K. Adsorption capacity of the anthranilic acid on the resin increases rapidly with increasing of the time till the equilibrium and 600 min is enough for the adsorption reaching equilibrium on the three resins. The kinetic data in this study were analyzed by a pseudo first-order rate equation and pseudo second-order rate equation expressed as [25]:

$$\ln(\text{Qe} - \text{Qt}) = \ln\text{Qe} - \text{K}_1 \text{t} \tag{6}$$

where Qt is the amount of anthranilic acid adsorbed at time t(mg/g) and Qe is the amount of anthranilic acid adsorbed at equilibrium (mg/g).  $K_1$  is the rate constant of pseudo-first-order model  $(min^{-1})$ . The Qe and  $K_1$  values were calculated by plotting Qt versus t. The pseudo-second-order model can be written as follows<sup>[25]</sup>:

$$1/(Qe - Qt) = 1/Qe + K_2t$$
 (7)

where  $K_2$  is the rate constant of pseudo-second-order model (g/mg min). The Qe and  $K_2$  values were obtained by plotting Qt versus t.

 $k_{11}$ ,  $k_{12}$ , qe and  $R^2$  are listed in Table 4. It is found that the pseudo-first-order kinetic equation is more appropriate for the adsorption, due to the high correlation coefficients ( $R^2 > 0.98$ ) and the close equilibrium adsorption capacity between the experimental and the calculated, due to function of the liquid film diffusion or particle diffusion or both. The particle distribution was the main control step of entire absorption process because of the ln(Qe-Qt) and t showing a good linear relationship.

Table 4 Correlated parameters of the kinetic data for the adsorption of anthranilic acid on FZH series from aqueous solutions according to the pseudo-first-order rate and the pseudo-second-order rate equations

racin	ln(Qe-Qt)=lnQe-K <sub>1</sub> t			$1/(Qe-Qt)=1/Qe+K_2t$			
resin	K <sub>1</sub> ×10^2	R <sub>12</sub>	Qe(mg/g)	K <sub>2</sub> ×10^2	R <sub>22</sub>	Qe(mg/g)	
FZH12	0.3700	0.9878	153.0	0.0050	0.9703	188.6	
FZH124	0.7500	0.9919	184.9	0.0100	0.9344	500.0	
HZH1245	0.5000	0.9809	102.5	0.0090	0.9617	112.3	
	200 150 (50 (100 0 0 0 0 0	And the second		• FZH12 • FZH124 • FZH1245			

t(min) Figure 5. Kinetic adsorption curves of anthranilic acid on the FZH series resins

300 400

#### 1.10. Particle diffusion

In common, the intra-particle diffusion is the rate-limiting step for the adsorption of hyper-cross-linked resin towards aromatic compounds from aqueous solution. Therefore, the kinetic data are further dealt with by the intra-particle diffusion model as[26]:

$$q_t = k_d t^{1/2} + C$$
 (8)

where  $k_d$  is the intra-particle diffusion rate (mg/(g min 1/2)), and C is a constant.

If plots of qt versus  $t^{1/2}$  give a straight line and the straight line passes through the origin, the intra-particle diffusion is the rate-limiting step for the adsorption. While if it presents a multi-linear relationship or does not pass through the origin, two or more diffusion mechanisms affect the adsorption[27]. As shown in Figure 6, The fitting coefficient of the particle diffusion equation of anthranilic acid adsorption on three resins reached more than 0.98, which indicated that the adsorption rate of anthranilic acid were mainly controlled by the liquid film diffusion. But the three straight lines were not through the origin, indicating that the diffusion of external liquid film may also have a little effect on the adsorption.



Figure 6. Particle distribution curves of anthranilic acid on FZH series resins

#### 1.11. pH effect on the adsorption

The solution pH is one of the most important influencing factors for the adsorption of the polymeric adsorbents. The anthranilic acid uptakes on the FZH series resins as a function of the solution pH are displayed in Figure 7. It is evident that the equilibrium capacity of anthranilic acid on the FZH series resins is very sensitive to the solution pH and it reaches the largest at solution pH = 4.00.



Figure 7.The equilibrium adsorption capacity of anthranilic acid adsorbed on the FZH series resins on dependency of the solution pH from aqueous solutions

## 1.12.Effect of sodium chloride on the adsorption

NaCl is the coexistent inorganic salt in the industrial wastewater. Sometimes the concentration of the inorganic salts possesses a very high level, which may have a negative effect on the resin adsorption. Fine chemical wastewater not only contains a lot of organic pollutants, and also contains high concentrations of inorganic salt (such as NaCl, Na<sub>2</sub>SO<sub>4</sub>), which may have a negative effect on the resin adsorption[28]. Hence, the effect of NaCl on the adsorption ability of FZH series resins to adsorb anthranilic acid from aqueous solutions is measured in this study and the results are shown in Figure 8. It can be observed that NaCl affects the adsorption factors of inorganic salt on the adsorption, the adsorption of solvent is also present. Because of the increasing of the inorganic salt in the solution, the influence of the water clusters formed on the surface of the resin on the adsorption is gradually obvious, which this increasing will greatly weaken the adsorption increment caused by the salting out effect.



Figure 8. Effect of sodium chloride on the adsorption of anthranilic acid on the FZH series resins from aqueous solutions

#### CONCLUSION

In the present study, The hypercrosslinked polymeric adsorbents containing multicarboxyl group and modified with phthalic anhydride,1,2,4-benzenetricarboxylic anhydride or pyromellitic dianhydride (respectively named FZH12,FZH124,FZH1245) were prepared. The three resins have better adsorption properties and the affinity of phthalimide for FZH series containing carboxyl group is higher than for anthranilic acid. Both of nonlinear and linear fitting methods indicated that the Langmuir isotherm model was more suitable for fitting the equilibrium data than the Freundlich one, while the individual adsorbed amounts of phthalimide or anthranilic acid on above adsorbents in binary systems is higher than those in single systems. The value of  $\Delta$ H were all negative indicating an exothermic process. The kinetic data could be fit better by the pseudo first-order rate equation and Particle diffusion equation, indicating that the diffusion of external liquid film may also have a little effect on the adsorption. It is evident that the equilibrium capacity of anthranilic acid on the FZH series resins is very sensitive to the solution pH, while NaCl affects the adsorption slightly at different temperatures (288K, 303K, and 318K).

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