Adsorption of Acetamiprid and *p*-Cresol from Water in Single Component System and Binary Components System with the Adsorption Resin Modified with Proline

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The adsorption behavoiur of acetamiprid and *p*-cresol in water onto the resin of ZHP02 modified with proline based on NDA150 was investigated from static adsorption experiments at different temperatures in single component and binary components system. The adsorption capacities and adsorption selectivity for acetamiprid and *p*-cresol in water were tested. The results show that the adsorption is fitted well by Freundlich model and Langmuir model and the adsorption of acetamiprid or *p*-cresol on ZHP02 is an exothermic process by the negative adsorption enthalpy. Gibbs free energy, enthalpy change and entropy change have changed in binary components system, demonstrating the existence of the cooperative effect. A high removal efficiency of 61.18-85.85 % is obtained for acetamiprid and that of 32.77-49.45 % is for *p*-cresol in single component system,which are both higher than those in binary components system and the cooperative adsorption exists when the equilibrium concentration is higher. The adsorption of acetamiprid onto ZHP02 has little change in the presence of *p*-cresol, but the adsorption of *p*-cresol onto ZHP02 will be weakened significantly in the presence of acetamiprid. The adsorption selectivity index of acetamiprid on ZHP02 is larger than one,which can favour to apply ZHP02 for the successful separation and recovery of acetamiprid from the water containing *p*-cresol.

Key Words: Adsorption resin, Acetamiprid, *p*-Cresol, Binary components system, Cooperative adsorption, Competitive adsorption.

INTRODUCTION

Water pollution is mainly caused by the contaminants of human activities, including pesticides. Although pesticides are widely used to control the plant pests to produce higher yield, they exert an influence to human health and existence environment, even the whole ecosystem. Acetamiprid is a new type of high efficient-spectrum insecticides with high and fast effectiveness, has a persistent efficiency period for 20 days and better solubility under room temperature. The emission of polluting compounds into the environment should be strictly controlled. There is a serious need for the high-tech about the economic, efficient, feasible wastewater treatment, to protect the environment. The method of adsorption with resins is widely used in wastewater treatment[1], which makes the resin adsorption technology has irreplaceable characteristics in treating polluted water because of the designability and selectivity of resin's chemical or physical structures on practical application.

Now, studies on the resin adsorption of phenolic compounds are much more than those on the resin adsorption of the pesticides[2-6]. Compared with the single component adsorption, the adsorption rule is complicated and few papers were reported[7-13]. Due to the concomitant characteristic of organic pollutants in aqueous solution, this paper focuses on the adsorption of acetamiprid in aqueous solution on ZHP02 resin modified with proline[14] and the adsorption behaviour of bicomponent pollutants coexisting in water, where a modified adsorption resin ZHP02 as adsorbent and acetamiprid and *p*-cresol as adsorbate. **Schemes 1** and **2** are the structures of acetamiprid and ZHP02.
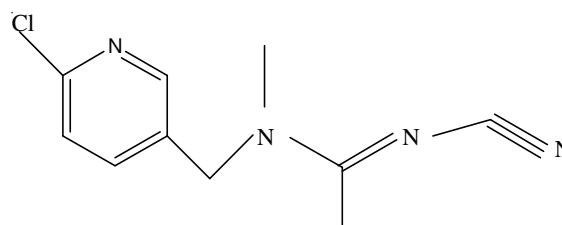
Scheme-I: Structure of acetamiprid
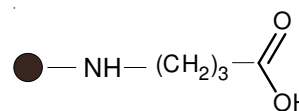
Scheme-II: ●-Functional group or structure model of resin ZHP02

EXPERIMENTAL

Static adsorption experiment: A bottle point isotherm procedure was used to conduct all the equilibrium studies in single component system. An accurate 0.1 g of ZHP02 was directly weighed. The adsorbents were contacted, in 250 mL stoppered conical flasks, with 100 mL of *p*-cresol or acetamiprid solution of certain concentration (C_0, mg/L) ranging from 400-800 mg/L. The flasks were completely sealed and then placed in an incubator shaker at different temperatures (288, 303 and 313 K) until equilibrium was achieved.

Experiments of binary solute isotherms were performed according to the above procedure. The main differences were that the initial concentrations of acetamiprid and *p*-cresol were equal to each other in the range of 200-400 mg/L. Other binary solute isotherms were also performed following the above procedure. The main differences were that the initial concentrations of acetamiprid were constant at 400 mg/L and those of *p*-cresol were in the range of 200-400 mg/L. Conversely, the initial concentrations of *p*-cresol were constant at 400 mg/L.

RESULTS AND DISCUSSION

Static adsorption in single component system

Static adsorption of acetamiprid and *p*-cresol in single component system: Equilibrium adsorption isotherms of the single solute of acetamiprid and *p*-cresol onto ZHP02 are, respectively presented in Fig. 1 (acetamiprid, *p*-cresol). The isotherm corresponding to lower temperature lies above, which shows the exothermic process with higher adsorption capacitis at lower temperature.

A high removal efficiency of 61.18-85.85 % was obtained for acetamiprid studied, as shown in Fig. 2, which may be attributed to the relatively stronger interaction between the acid groups on the adsorbent and the basic groups of the solute at the adsorption process. But with the increasing adsorption capacities there are some shields for the limited amount of adsorption sites or basic functional groups. But removal efficiency of 32.77-49.45 % was obtained for *p*-cresol studied (Fig. 2), which results from initial higher concentration.

Many theories, used to model the adsorption process with varying degrees of success, have been proposed to explain the adsorption phenomenon and to describe the adsorption isotherm relationships. Among them the Langmuir and Freundlich models have been widely used and their linear forms are given below, respectively[15].

$$\text{Langmuir model: } \frac{C_e}{q_e} = \frac{C_e}{M} + \frac{1}{(MK_L)} \qquad (1)$$

$$\text{Freundlich model: } \log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (2)$$

M, K_L, K_f and n are characteristic constants. The Langmuir constant M (mmol/g) is the maximum amount per weight of adsorbent to form a complete monolayer on the surface bound and K_L (L/g) is a constant related to the affinity of the binding sites. The Freundlich coefficient K_f (L/mmol) is an index of the sorption capacity of the resins and the Freundlich exponent
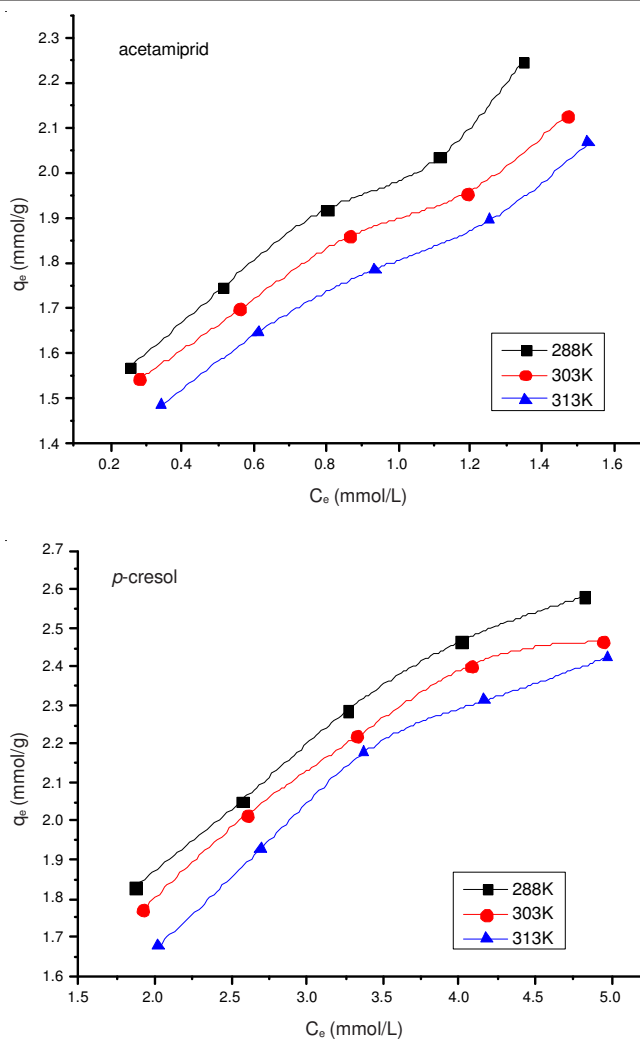

Fig. 1. Equilibrium adsorption isotherms of acetamiprid or *p*-cresol on ZHP02 in single component system

n (dimensionless) denotes the heterogeneity of the surface and the intensity of adsorption.

By a nonlinear least square routine, the regression equations corresponding to the above isotherms can be obtained and their constants along with the correlation coefficients r are presented in Table-1. The results clearly show that the adsorption data for the studied adsorption systems fit better to the Langmuir model for acetamiprid, but for *p*-cresol better to the Freundlich model.

As seen from the values of M and K_L (Table-1), the capacity of the adsorption decreases with the increasing temperature, indicating the predominant phenomena of "sorbent-motivated" effects caused mainly by the electrostatic interaction and ion change which are exothermic interactions. And the constant n and K_f are always more than 1 in present study range, both indicating a favourable type adsorption.

Thermodynamics: Thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS) for the adsorption of acetamiprid and *p*-cresol onto the resin ZHP02 are given in Table-2.

ΔG of *p*-cresol is calculated according to eqn. 3 the data onto the resin better fitted to the Freundlich model and ΔG of acetamiprid according to eqn. 4 for the data better to the

TABLE-1
FITTED RESULTS FOR LANGMUIR AND FREUNDLICH ISOTHERMS IN SINGLE COMPONENT SYSTEM

Regression equations	Parameters	Acetamiprid			*p*-Cresol		
		288 K	303 K	313 K	288 K	303 K	313 K
Langmuir	M	2.464	2.318	2.300	3.503	3.421	3.478
	K_L	0.190	0.183	0.229	0.663	0.636	0.523
	r	0.994	0.996	0.995	0.885	0.939	0.948
Freundlich	K_f	2.036	1.924	1.836	1.611	1.531	1.393
	n	4.899	5.362	4.750	2.666	2.761	2.402
	r	0.982	0.986	0.989	0.997	0.991	0.990

TABLE-2
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF ACETAMIPRID OR
p-CRESOL ONTO THE RESIN ZHP02 IN SINGLE COMPONENT SYSTEM

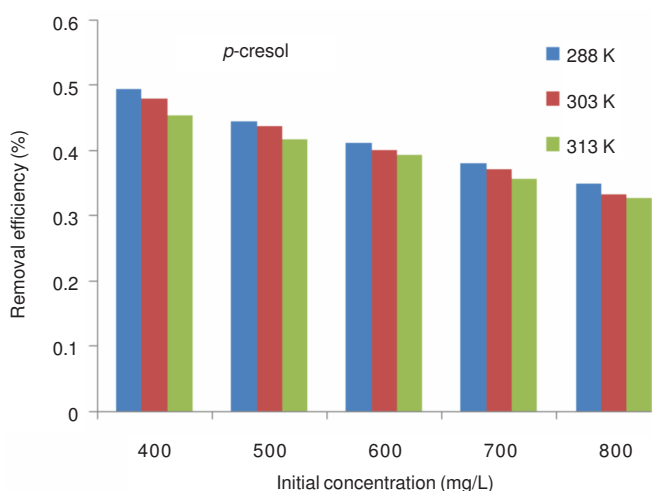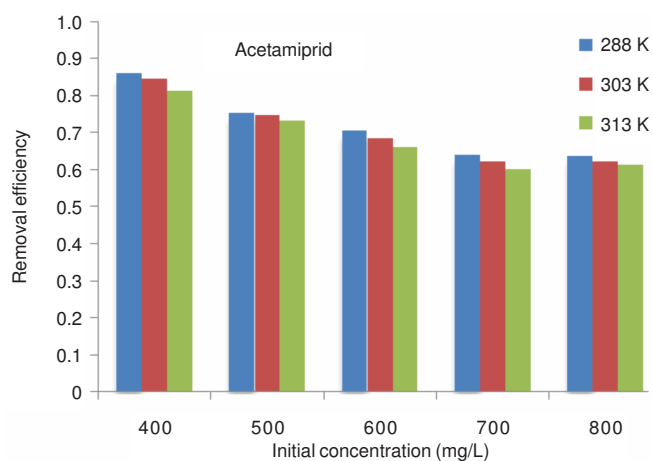| Adsorbate	q_e (mmol/g)	Temperature (K)	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)
Acetamiprid	1.0	288	-11.29	-34.30	-1.41
	1.0	303	-11.29	-33.20	-1.23
	1.0	313	-11.29	-30.19	-1.84
p-Cresol	1.0	288	-16.00	-33.40	-6.38
	1.0	303	-16.00	-29.87	-6.95
	1.0	313	-16.00	-31.15	-6.25

Fig. 2. Removal efficiency of acetamiprid or *p*-cresol by ZHP02 at different temperatures and initial solute concentrations in single component system

Langmuir model[16]. And so the calculation of ΔG in binary components system is the same as above in single component system.

$$\Delta G = -nRT \qquad (3)$$

$$\Delta G = -RT \ln\left(\frac{MK_L}{V_d}\right) \qquad (4)$$

where n is the Freundlich model characteristic constant, R is the gas constant (kJ/mol K) and T is the absolute temperature (K), M and K_L are the Langmuir constants. V_d is the micro porous volume of ZHP02, the value is 0.260 mL/g[14].

The following Gibbs-Helmholtz equation can be obtained to describe the relation between ΔG and the other two thermodynamic parameters.

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

Then, ΔH can be calculated, respectively from the Van't Hoff equation.

$$\ln\left(\frac{q_e}{C_e}\right) = -\frac{\Delta H}{RT} + \ln K_0 \qquad (6)$$

The estimated thermodynamic parameters of adsorption of acetamiprid or *p*-cresol onto ZHP02 are low and in the range of 10-40 kJ/mol where physical adsorption is expected to be the dominant mechanism. Values of enthalpy (always negative) indicate the adsorption process is an exothermic one, as generally expected.

It is well known that the free energy change value for a physical sorption, which is in the range of -20 to 0 kJ/mol, is less than that for a chemical sorption process, which is in the range of -400 to -50 kJ/mol. The free energy changes are small, shown in Table-2, further confirming the physical character of the adsorption. As expected they are negative in all cases because the solute is more concentrated on the surface of the adsorbents than in the bulk solutions. The magnitude of the free energy changes indicates the stronger adsorption force between ZHP02 and acetamiprid for the partially polar groups in its net work, with the results of equilibrium static adsorption.

The negative values of the adsorption entropy are consistent with the restricted mobility of the adsorbed *p*-cresol and acetamiprid molecules compared with those in solution. Thus

a more ordered arrangement of solute molecules for *p*-cresol is formed on the surface of ZHP02.

Static adsorption in binary components system

Same initial concentration of acetamiprid and *p*-cresol in binary components system: Equilibrium adsorption isotherms of acetamiprid and *p*-cresol onto ZHP02 in binary components system are, respectively presented in Fig. 3 (acetamiprid, *p*-cresol). For acetamiprid, temperature has little effect on the attachment. It shows good treatment efficiency in Fig. 4.
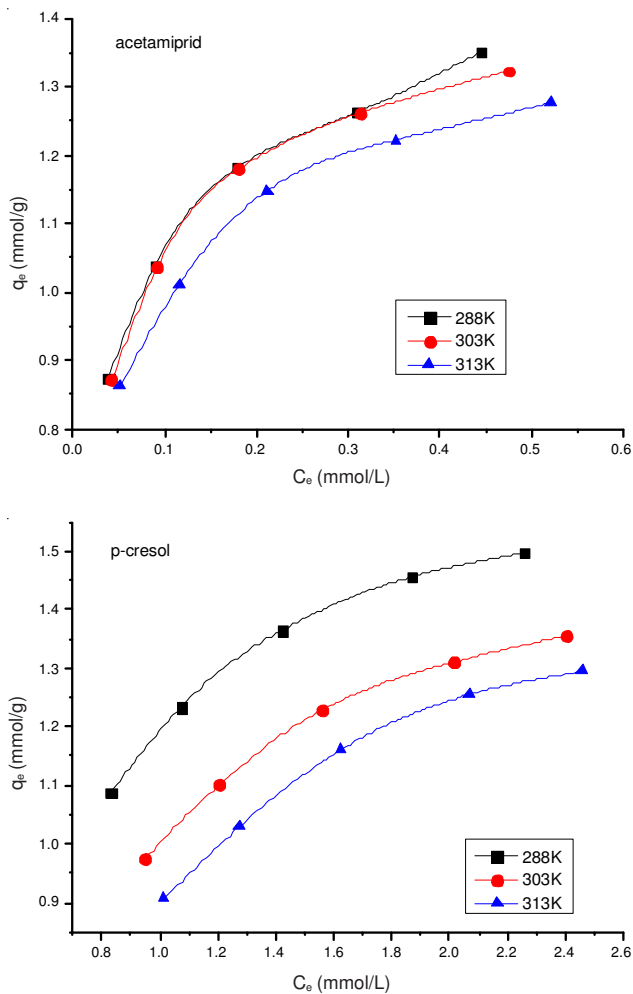
Fig. 3. Equilibrium adsorption isotherms of acetamiprid or *p*-cresol in binary components system on ZHP02
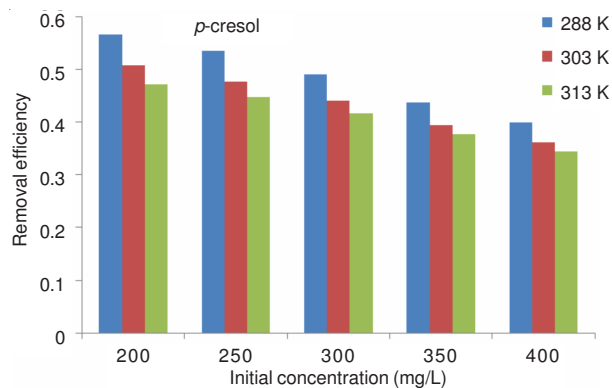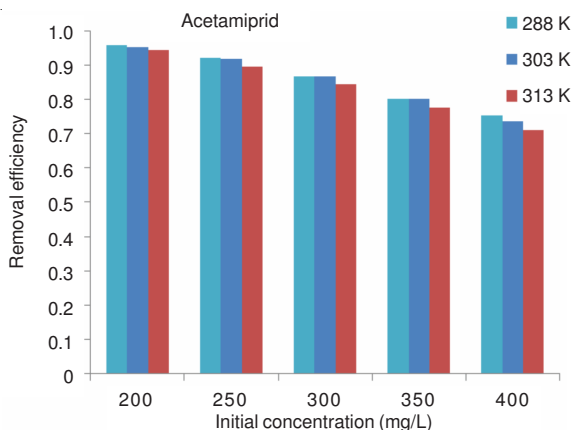

Fig. 4. Removal efficiency of acetamiprid or *p*-cresol by ZHP02 at different initial solute concentrations in binary components system

Higher removal efficiency was obtained for acetamiprid (Fig. 4), in the range of 71.03-95.81 %, but for *p*-cresol just in the range of 34.50-56.72 %. Compared with the results of the single component system, the absorbability of ZHP02 has been improved so much in binary components system, for acetamiprid and *p*-cresol.

Comparing of Figs. 5 and 6 of the binary components system with Fig. 1 of the single component system, the adsorption capacity of *p*-cresol and acetamiprid in binary components system were more than the adsorption capacity in single component system (acetamiprid or *p*-cresol) on ZHP02 at different initial concentrations, which is presumably due to the cooperative effect primarily arisen from the hydrogen bonding or acid-base interaction between acetamiprid and *p*-cresol. Further to prove this point (Table-3), in binary components system the equilibrium adsorption isotherms could also be fitted by the Langmuir and Freundlich equation, *n* value was larger than it in Table-1, r was greater than 0.981. Fig. 4 also provided data supporting for the cooperative effect, with higher removal yield.
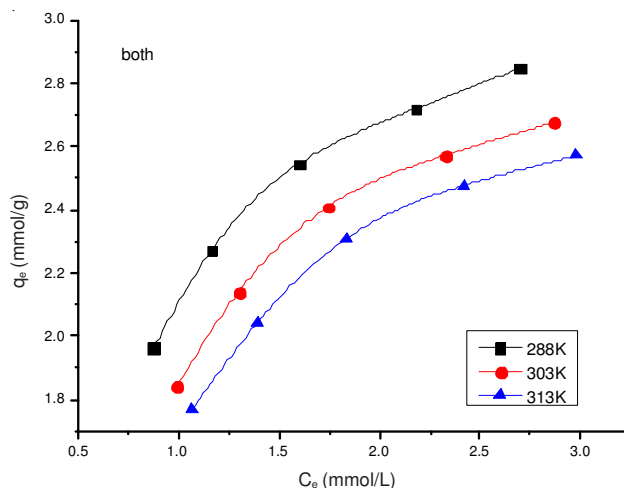

Fig. 5. Equilibrium adsorption isotherms of both acetamiprid and *p*-cresol on ZHP02 in binary components system

Thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS) for the adsorption of acetamiprid and *p*-cresol onto the resin ZHP02 with the same initial concentration of acetamiprid and *p*-cresol in binary components system are given in Table-4.

TABLE-3
FITTED RESULTS FOR LANGMUIR AND FREUNDLICH ISOTHERMS IN BINARY COMPONENTS SYSTEM

Regression equations	Parameters	Acetamiprid			*p*-Cresol		
		288 K	303 K	313 K	288 K	303 K	313 K
Langmuir	M	1.349	1.350	1.306	1.539	1.184	0.896
	K_L	46.338	42.079	36.467	1.960	1.861	1.861
	r	0.982	0.991	0.986	0.995	0.996	0.996
Freundlich	K_f	1.567	1.541	1.459	1.186	1.018	0.925
	n	5.718	5.800	5.800	3.155	2.827	2.459
	r	0.997	0.990	0.993	0.981	0.984	0.985

TABLE-4
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF ACETAMIPRID AND *p*-CRESOL ONTO
THE RESIN ZHP02 WITH THE SAME INITIAL CONCENTRATION IN BINARY COMPONENTS SYSTEM

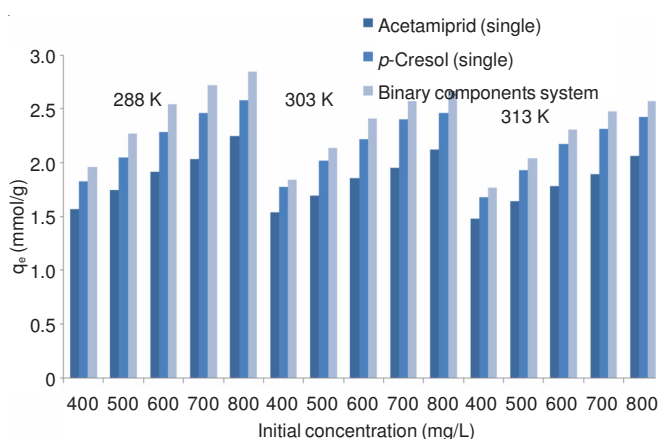| Adsorbate	q_e (mmol/g)	Temperature (K)	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)
Acetamiprid	1.0	288	-10.49	9.17	-13.13
	1.0	303	-10.49	10.16	-13.57
	1.0	313	-10.49	9.81	-13.56
p-Cresol	1.0	288	-11.61	-14.10	-7.55
	1.0	303	-11.61	-14.82	-7.12
	1.0	313	-11.61	-16.64	-6.40

Fig. 6. Contrast on the adsorption capacity of acetamiprid/*p*-cresol/ acetamiprid and *p*-cresol on ZHP02 at different initial concentrations in single and binary components system

Compared with the single component system (Table-2), there was variability in the thermodynamic parameters of binary components system (Table-4). The enthalpy change of acetamiprid and *p*-cresol decreased, but Gibbs free energy of both acetamiprid and *p*-cresol changed increased. Entropy change turned positive in Table-4 and randomness went up in the system, which could favour the adsorption process, further to demonstrate the existence of the cooperative effect.

Simultaneous adsorption in binary components system: The simultaneous binary components adsorption isotherms of the tested compounds from aqueous solutions could also be well described by both Langmuir and Freundlich models. For further testifying the above predominant competitive mechanism, the influence of initial concentration on the adsorption capacity is demonstrated in Fig. 6. Generally speaking, there is some drop in the adsorption amount of acetamiprid with the increase of the initial concentration of *p*-cresol, but larger distinction for *p*-cresol with the increase of the initial concentration of acetamiprid. In Fig. 7, with the initial concentration of *p*-cresol becoming larger, the absorbability of acetamiprid on ZHP02 decreases, competitive adsorption phenomenon
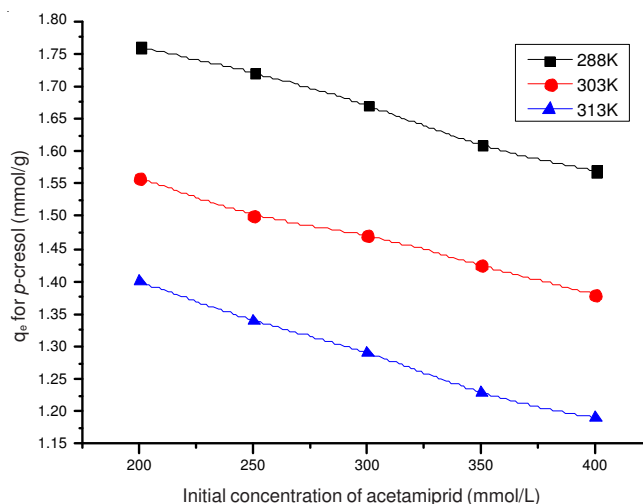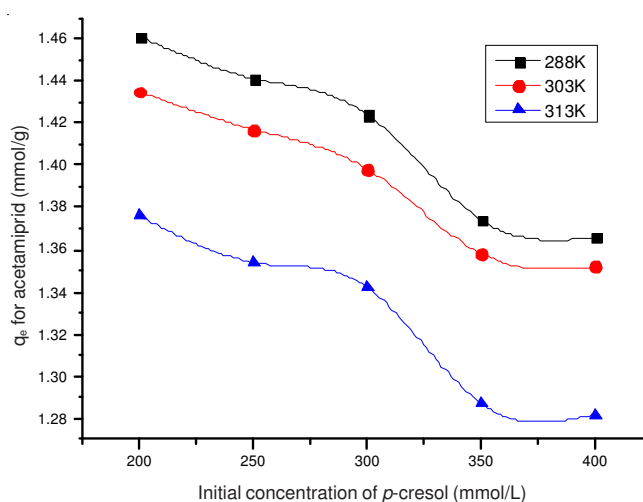

Fig. 7. Influence of initial concentration on the adsorption amount onto ZHP02 from the binary components adsorptive environment

exists; but when the initial *p*-cresol concentration was 400 mg/L (*ca.* 4.25 mmol/L), the absorbability of acetamiprid decreases slowly on the resin, that should due to the effect of

cooperative adsorption. For *p*-cresol onto the resin ZHP02 with changes of the acetamiprid' concentration, it shows competitive adsorption phenomenon exists too. When the initial acetamiprid' concentration was 400 mg/L (*ca.* 1.749 mmol/L), cooperative adsorption doesn't appear, maybe for the concentration is not big enough. The change of acetamiprid' concentration has greater effect on the adsorption of *p*-cresol onto ZHP02 by the stronger interaction between acetamiprid and the resin.

Selectivity index: Selectivity index often used to evaluate an adsorbent or an adsorptive process. If we define the distribution coefficient (solid-to-liquid) as:

$$D = \frac{q_e}{C_e} \tag{6}$$

Then the selectivity index of the first component has the following form:

$$S_{1/2} = \frac{D_1}{D_2} \tag{7}$$

where D_1 and D_2 represent the distribution coefficient of two solutes, respectively.

The selectivity indexes for the adsorption of acetamiprid onto the adsorbent tested are compared in Table-5, with 400 mg/L of *p*-cresol as the competitive component. It can be seen that the adsorption selectivity of acetamiprid on ZHP02 is larger than one. Simultaneously an obvious variation of selectivity indexes with temperature and original concentration of acetamiprid may be contributed to the larger difference in the adsorbent-solute interaction and solvent-solute interaction. Consequently, it is expected to apply ZHP02 for the successful separation and recovery of acetamiprid from the water containing *p*-cresol. The proposed technique has its practicability.

TABLE-5
SELECTIVITY INDEX OF ACETAMIPRID

Adsorbent	C_0 of acetamiprid (mg/L)	Temperature (K)		
		288	303	313
ZHP02	200	24.24	26.12	15.49
	250	11.11	13.11	9.38
	300	7.59	8.83	6.66
	350	5.76	6.47	5.02
	400	4.51	5.07	4.03

Conclusion

The adsorption was fitted by Langmuir and Freundlich model, with high linearity. The adsorption of acetamiprid and *p*-cresol on ZHP02 modified with proline based on NDA150 is an exothermic process. And the resin ZHP02 has better absorbability for *p*-cresol than for acetamiprid, but the adsorption selectivity of acetamiprid on ZHP02 is larger. The adsorption of acetamiprid or *p*-cresol on ZHP02 is an exothermic process by the adsorption enthalpy. Gibbs free energy, enthalpy change and entropy change have changed in binary components system, to demonstrate the existence of the cooperative effect.

A high removal efficiency of 61.18 to 85.85 % is obtained for acetamiprid and 32.77 to 49.45 % for *p*-cresol in single component system, which is higher in binary components system. In binary components system of the same initial concentration of acetamiprid and *p*-cresol, when the equilibrium concentration is higher, the cooperative adsorption exists, which is presumably due to the cooperative effect primarily arisen from the hydrogen bonding or weak acid-base interaction between acetamiprid and *p*-cresol. The competitive adsorption exists to varying degrees. The adsorption of acetamiprid onto ZHP02 had just small change in the presence of *p*-cresol, but the adsorption of *p*-cresol onto ZHP02 is weakened significantly in the presence of acetamiprid.

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