Asian Journal of Chemistry; Vol. 27, No. 1 (2015), 123-128

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.16802

Single and Binary Adsorption of Nitenpyram and *p*-Cresol onto Resin Modified with Ethyl Cellulose

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Received: 2 December 2013; *Accepted*: 12 February 2014; *Published online*: 26 December 2014; AJC-16520

The adsorption of nitenpyram and *p*-cresol in water onto the resin that was modified with ethyl cellulose based on Amberlite XAD-4, which was investigated by static adsorption experiments, at different temperatures (288, 303 and 318 K) in single component and binary components system. The adsorption capacities for nitenpyram and *p*-cresol in water and the thermodynamical study were tested. The results showed the adsorption of nitenpyram on the resin was an endothermic process by the positive adsorption enthalpy and an exothermic process of *p*-cresol by the negative adsorption enthalpy. Entropy change was giving a friendly boost to adsorption of nitenpyram. In single component system the adsorption of nitenpyram was fitted by Freundlich model better than Langmuir model, but for *p*-cresol, it was well fitted by Freundlich and Langmuir model. A high adsorption rate of nitenpyram was in range of 58.62-98.09 % and the adsorption rate of *p*-cresol was 41.61-81.61 %. Adsorption rate was higher with higher temperature for nitenpyram and lower for *p*-cresol. In binary components system the adsorption rate of nitenpyram and *p*-cresol was higher, because the hydrogen bonding interaction increased between nitenpyram and *p*-cresol in the adsorption process and the locations and interactions of π-π. The equilibrium adsorption isotherms of nitenpyram and *p*-cresol in binary components system were fitted better by Freundlich model than Langmuir model. The multilayer adsorption and cooperative adsorption appeared. At the lower equilibrium concentration, there was the competitive adsorption on the adsorption sites; at higher equilibrium concentration, the cooperative effect primarily arisen for the hydrogen bonding or the locations and interactions of π-π. The change of nitenpyram's concentration had greater effect on the adsorption of *p*-cresol onto the resin modified with ethyl cellulose. So the adsorption selectivity of nitenpyram on the resin is larger than one at higher temperature with lower concentrations.

Keywords: Adsorption resin, Nitenpyram, *p*-Cresol, Ethyl cellulose.

INTRODUCTION

Resin adsorption is widely used in water treatment[1-5]. The design ability and selectivity of resin's chemical or physical structures on practical application makes resin adsorption technology has irreplaceable characteristics. The resin was modified with ethyl cellulose based on Amberlite XAD-4[3], which was used in the water treatment polluted by pesticides in the paper. Nitenpyram is a new nicotine insecticide with high and fast effectiveness, has a persistent efficiency period and better solubility under room temperature. *p*-Cresol is a raw materials in the preparation of some pesticides. There is a serious need for the high-tech about the economic, efficient, feasible water treatment, to protect the world environment for the pollution of pesticides. The resin adsorption rule is complicated in binary components system in water and some papers were reported[6-9]. The paper focuses on the adsorption of nitenpyram and *p*-cresol in water onto the resin modified with ethyl cellulose and the adsorption behaviour and adsorption selectivity of two pollutants coexisting in water. Modified adsorption resin was adsorbent, nitenpyram and *p*-cresol was the adsorbates in the static adsorption experiments at the temperature 288, 303 and 318 K. The thermodynamical study was made. These data will provide reference for theory research and engineering design.

EXPERIMENTAL

Methanol is of G.R. grade. Nitenpyram is of A.R. grade, *p*-cresol A.R. grade; the resin is modified[3] with ethyl cellulose based on Amberlite XAD-4. (The specific surface area of the resin was 1083.92 $m^2 g^{-1}$ and the average pore radius was 3.67 nm.)

Static adsorption experiment: A bottle point isotherm procedure was used to conduct all the equilibrium studies in single component system. 0.1 g of the resin was directly weighed accurately. The adsorbents were contacted, in 250 mL stoppered conical flasks, with 100 mL of nitenpyram or *p*-cresol solution of initial concentration (C_0, mg/L) ranging

from 100 to 500 mg/L. The flasks were completely sealed and then placed in an incubator shaker at different temperatures (288, 303, 318 K) until the equilibrium was achieved.

Experiments of binary system were performed according to the above procedure. The main difference was that the initial concentrations of nitenpyram and *p*-cresol were equal to each other at the concentration of 100, 150, 200, 250, 300 mg/L. Other binary solute isotherms were also performed following the above procedure. The difference was that the initial concentrations of nitenpyram were constant at 300 mg/L and the initial concentrations of *p*-cresol were at 100, 200, 300, 400, 500 mg/L. Conversely, the initial concentrations of *p*-cresol were constant at 300 mg/L.

RESULTS AND DISCUSSION

Static adsorption in single component system

Static adsorption of nitenpyram and *p*-cresol in single component system: Equilibrium adsorption isotherms of nitenpyram and *p*-cresol onto the resin in single component system were presented in Fig. 1. The isotherm corresponding to higher temperature laid above, which showed the endothermic process, with higher adsorption amounts at higher temperature for nitenpyram, but for *p*-cresol, the exothermic process. In Fig. 1, at the same equilibrium concentration, the resin has stronger adsorbability at *p*-cresol.

A high adsorption rate of nitenpryram was in range of 58.62-98.09 %, as shown in Fig. 2 the adsorption rate of *p*-cresol was 41.61-81.61 %. Adsorption rate was higher with higher temperature for nitenpryram. Adsorption rate was lower with lower temperature for *p*-cresol. The results showed the modified resin had been optimized. Many theories, used to model the adsorption process, 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[10].

$$\text{Langmuir model: } 1/Q_e = 1/(C_e M K_L) + 1/M \quad (1)$$

$$\text{Freundlich model: } \log Q_e = \log K_f + (1/n)\log C_e \quad (2)$$

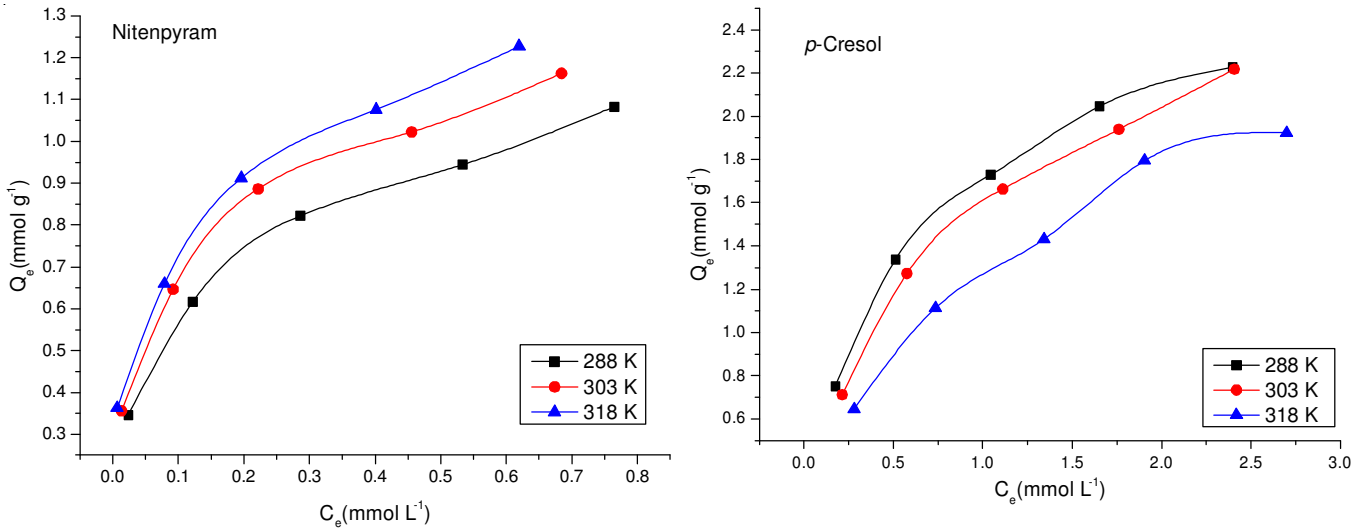

Fig. 1. Equilibrium adsorption isotherms of nitenpyram and *p*-cresol in single component system on the resin at 288-318 K

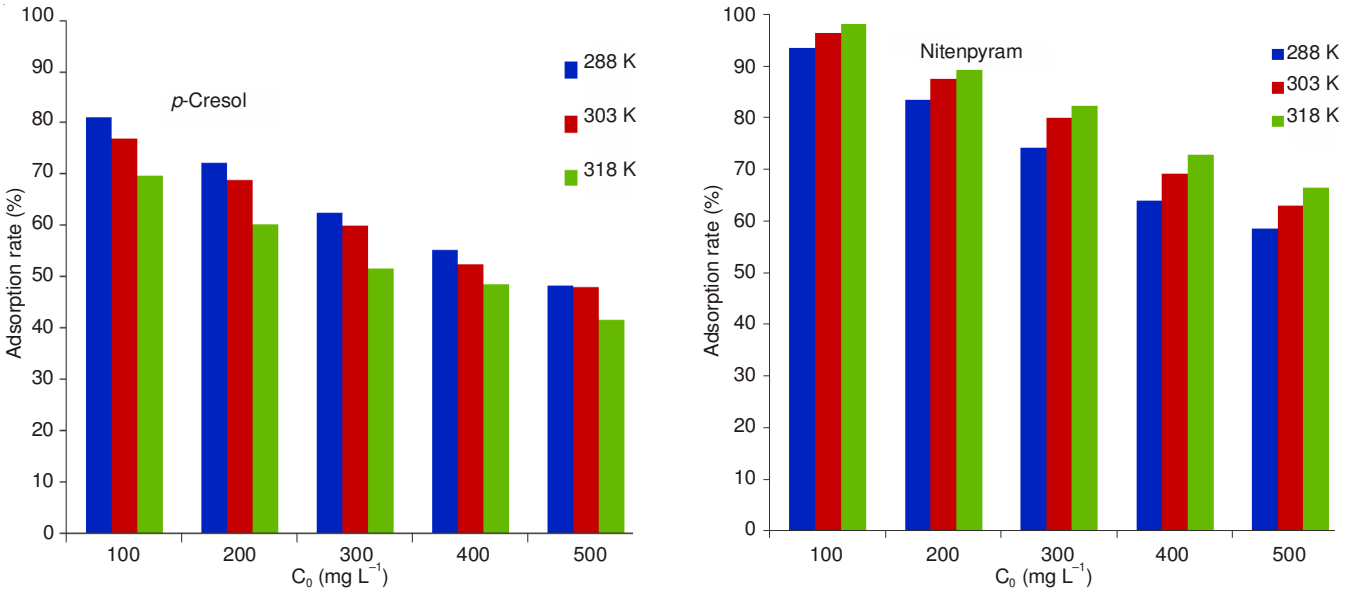

Fig. 2. Adsorption rate of nitenpyram or *p*-cresol at different temperatures and initial solute concentrations in single component system

Corresponding equations were given with computer fitting. And their constants with the correlation coefficients r are summarized in Table-1. The results showed that the adsorption data for the studied adsorption systems of nitenpyram fitted better to Freundlich model than Langmuir model. Equilibrium adsorption isotherms of *p*-cresol were fitted better to both Freundlich and Langmuir model. The adsorption mechanism was more complex.

Table-1 suggested that n increase with the higher temperature, so the resin modified with ethyl cellulose had greater affinity for nitenpyram n > 3 (but for *p*-cresol, n > 2). Nitenpyram tended to become attached by the resin. Chemisorption processes existed in processes. The values n of *p*-cresol increase with the lower temperature. K_f, M showed the adsorption capability. K_f, M of *p*-cresol were greater than that of nitenpyram, as seen Q_e in Fig. 1.

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

ΔG is calculated according to Eqn. (3), for the data onto the resin better fitted to the Freundlich model. And so the calculation of ΔG in binary components system is the same as in single component system[11].

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

where n is the Freundlich model characteristic constant, R is the gas constant (kJ mol^{-1} K^{-1}) and T is the absolute temperature (K).

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

$$\Delta G = \Delta H - T\Delta S \quad (4)$$

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

$$\ln(Q_e/C_e) = -\Delta H/RT + \ln K_0 \quad (5)$$

The estimated enthalpy of adsorption of nitenpyram was positive, indicating the adsorption process was an endothermic one. The enthalpy of *p*-cresol was negative, an exothermic process. they were low and the absolute values were in the range of 10-40 kJ mol^{-1} where physical adsorption is expected to be the dominant mechanism. It is well known that the free energy change value for a physical sorption is in the range of -20 to 0 kJ mol^{-1} and chemical sorption process is in the range[12] of -400 to -80 kJ mol^{-1} (Table-2). We further confirm the physical character of the adsorption for nitenpyram and *p*-cresol. The values of the adsorption entropy of nitenpyram were positive. The resin has powerful water absorption, with the multi-pore structure and functional groups. So at low temperature water molecules were adsorbed. Then with the different interactions changing, nitenpyram was adsorbed little by little, associated with desorption of water molecules, because the molecular size of nitenpyram is more than water molecule. That's solute-solvent measurement replacement. Then the entropy-increase effect came, gave a friendly boost. But the adsorption entropy of *p*-cresol was negative, because the molecular *p*-cresol moved in aqueous solution more freely than on the surface of the resin. The entropy of adsorption of *p*-cresol decreased.

Static adsorption in binary components system

Same initial concentration of nitenpyram and *p*-cresolin binary components system: Equilibrium adsorption isotherms of nitenpyram and *p*-cresol onto the resin in binary components system were, respectively presented in Fig. 3 (nitenpyram, *p*-cresol). The effect of the temperature cohered with it in single component system (Fig. 1).

High adsorption rate removal rate was obtained for nitenpyram studied (Fig. 4), in the range of 66.63-98.73 %, higher than it in single component system. For *p*-cresol adsorption rate was higher in the range of 53.10-80.33 %, being improved better than it in single component system. Two components coexisted in the solution, which had produced an effect on the resin adsorption. It made the adsorption rate higher and the adsorptivity of the resin enhanced.

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

Adsorbate	Temperature (K)	Langmuir				Freundlich			
		Equation	M	K_L	r	Equation	K_f	n	r
Nitenpyram	288	Y = 0.0459x + 1.0251	0.976	22.333	0.984	Y = 0.3273x + 0.0774	1.195	3.055	0.998
	303	Y = 0.0248x + 1.0017	0.998	40.391	0.977	Y = 0.3023x + 0.1227	1.326	3.308	0.998
	318	Y = 0.0125x + 1.0143	0.986	81.144	0.963	Y = 0.2741x + 0.142	1.387	3.648	0.998
p-Cresol	288	Y = 0.1643x + 0.4022	2.486	2.448	0.998	Y = 0.4178x + 0.2157	1.643	2.393	0.991
	303	Y = 0.2172x + 0.3898	2.565	1.795	0.999	Y = 0.4611 x + 0.1846	1.530	2.169	0.993
	318	Y = 0.3198x + 0.4249	2.353	1.329	0.997	Y = 0.494 x + 0.0949	1.244	2.024	0.995

TABLE-2
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF NITENPRYRAM AND *p*-CRESOL ONTO THE RESIN IN SINGLE COMPONENT SYSTEM

Adsorbate	Q_e (mmol g^{-1})	Temperature (K)	ΔH (k J mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})
Nitenpyram	1.0	288	16.497	82.68	-7.315
	1.0	303		81.95	-8.333
	1.0	318		82.21	-9.645
p-Cresol	1.0	288	-18.840	-45.52	-5.730
	1.0	303		-44.14	-5.464
	1.0	318		-42.41	-5.351

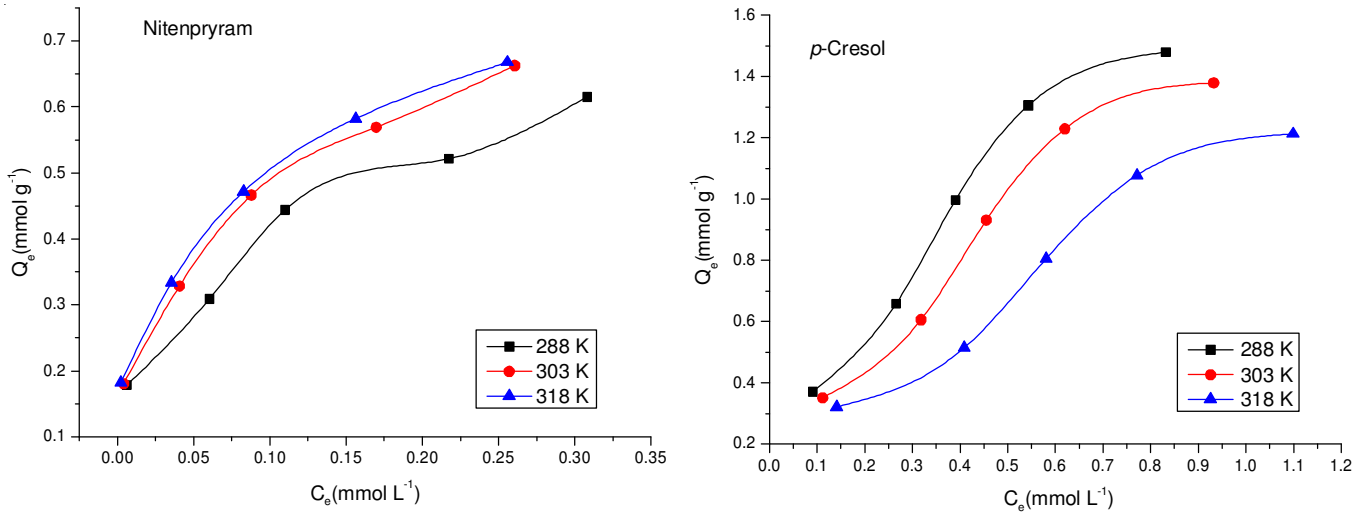

Fig. 3. Equilibrium adsorption isotherms of nitenpyram or *p*-cresol in binary components system

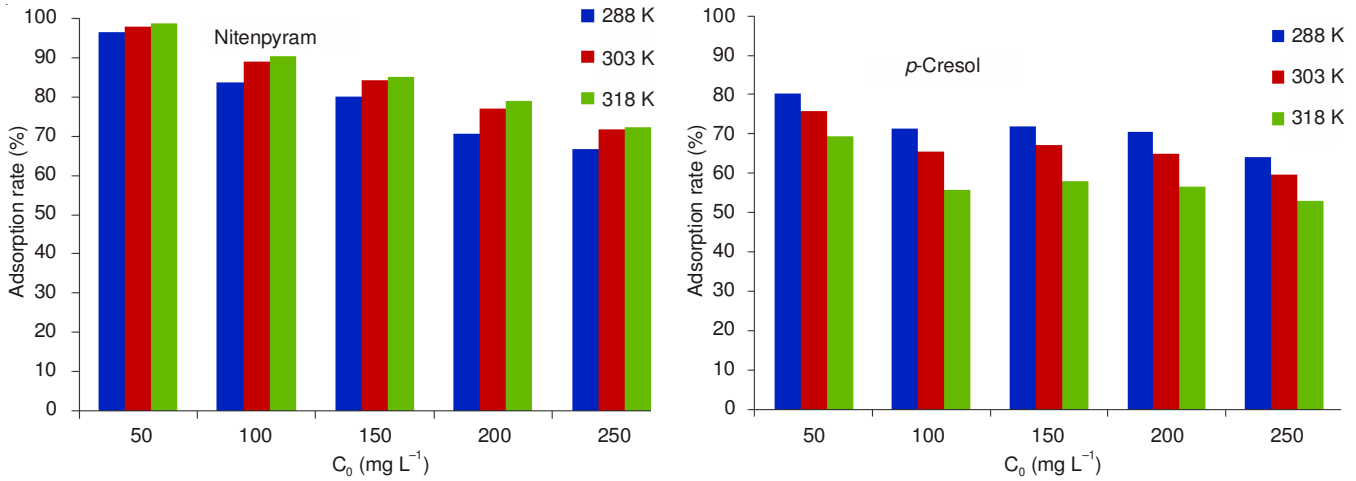

Fig. 4. Adsorption rate of nitenpyram or *p*-cresol in binary components system

Based on Fig. 5 and Table-3, the equilibrium adsorption isotherms of both nitenpyram and *p*-cresol in binary components system were fitted better by Freundlich model. So the adsorption of nitenpyram and *p*-cresol on the resin modified with ethyl cellulose was the multilayer adsorption. The specific surface area of the resin modified with ethyl cellulose was 1083.92 m^2/g and the average pore radius was 3.67 nm, which made nitenpyram and *p*-cresol arranged orderly on the surface of the resin. The hydrogen bonding interaction between nitenpyram and *p*-cresol increased in the adsorption process and the locations and interactions of π-π. So the adsorption capacity increased. With the increasing adsorption capacity, orientation state of adsorbate on the resin changed from equatorial to perpendicular,which could produce new locations and interactions of π-π to absorb more adsorbate. The multilayer adsorption and cooperative adsorption appeared. It is presented nicely with the results in Table-3.

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

Adsorbate	Temperature (K)	Langmuir				Freundlich			
		Equation	M	K_L	r	Equation	K_f	n	r
Nitenpyram	288	Y = 0.0226x + 2.0510	0.488	90.75	0.953	Y = 0.3162x – 0.0695	0.852	3.163	0.989
	303	Y = 0.0145x + 1.9321	0.518	133.25	0.958	Y = 0.3118x – 0.0092	0.979	3.207	0.995
	318	Y = 0.0084x + 1.9659	0.509	234.04	0.952	Y = 0.2786x – 0.0249	0.944	3.589	0.992
Nitenpyram	288	Y = 0.0226x + 2.0510	0.488	90.75	0.953	Y = 0.3162x – 0.0695	0.852	3.163	0.989
	303	Y = 0.0145x + 1.9321	0.518	133.25	0.958	Y = 0.3118x – 0.0092	0.979	3.207	0.995
	318	Y = 0.0084x + 1.9659	0.509	234.04	0.952	Y = 0.2786x – 0.0249	0.944	3.589	0.992
p-Cresol	288	Y = 0.2046x + 0.4976	2.010	2.432	0.985	Y = 0.6605x + 0.2478	1.769	1.514	0.988
	303	Y = 0.2665x + 0.5234	1.911	1.964	0.983	Y = 0.6768x + 0.1756	1.498	1.477	0.989
	318	Y = 0.3619x + 0.6406	1.561	1.770	0.968	Y = 0.6823x + 0.0567	1.139	1.466	0.981
Nitenpyram + *p*-Cresol	288	Y = 0.139x + 0.42630	2.346	3.070	0.982	Y = 0.567x + 0.3047	2.017	1.764	0.992
	303	Y = 0.1745x + 0.4080	2.451	2.338	0.985	Y = 0.600x + 0.2792	1.902	1.667	0.993
	318	Y = 0.2276x + 0.4474	2.235	1.966	0.977	Y = 0.6149x + 0.2012	1.589	1.626	0.990

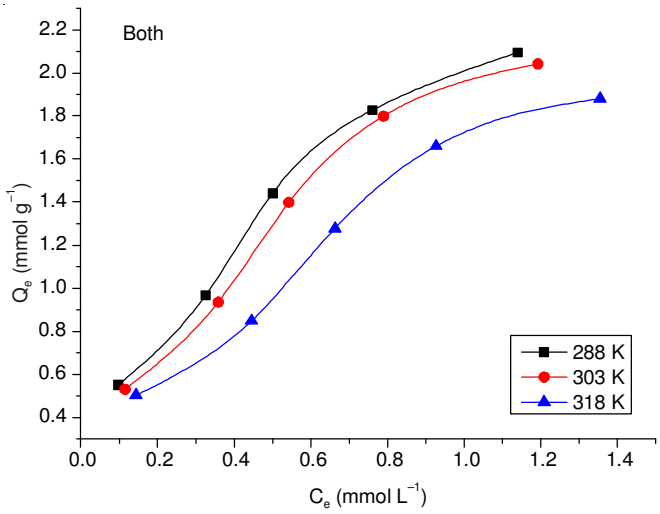

Fig. 5. Equilibrium adsorption isotherms of both nitenpyram and *p*-cresol in binary components system

In Table-4, they were the thermodynamic parameters for the adsorption of nitenpyram or *p*-cresol onto the resin in binary components system. The results were in agreement with Table-2, There had been a few change in the value. Because of the cooperative effect, the absolute value of enthalpy change became smaller. Analysis of Figs. 1 and 5, the total uptake amounts of *p*-cresol and nitenpyram were less than the pure uptake amounts in single component system (Fig. 1) onto the resin at the lower equilibrium concentration, which was the competitive adsorption on the adsorption sites. It was noteworthy that at higher equilibrium concentration (Fig. 5), the total uptake amounts in binary components systems are obviously larger than the pure uptake amounts in single component system, which is presumably due to the cooperative effect primarily arisen for the hydrogen bonding or the locations and interactions of π-π.

Simultaneous adsorption in binary components system: For further testifying the above predominant mechanism,the influence of initial concentration on the adsorption capacity was demonstrated in Fig. 6. There was some drop in the adsorption amount of nitenpyram with the increasing initial concentration of *p*-cresol, but larger distinction for *p*-cresol with the increasing initial concentration of nitenpyram, which showed competitive adsorption phenomenon existed. The change of nitenpyram' concentration had greater effect on the adsorption of *p*-cresol onto the resin modified with ethyl cellulose.

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

$$D = Q_e/C_e \quad (6)$$

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

$$S_{1/2} = D_1/D_2 \quad (7)$$

D_1 and D_2 represent the distribution coefficient of two solutes, respectively[12,13].

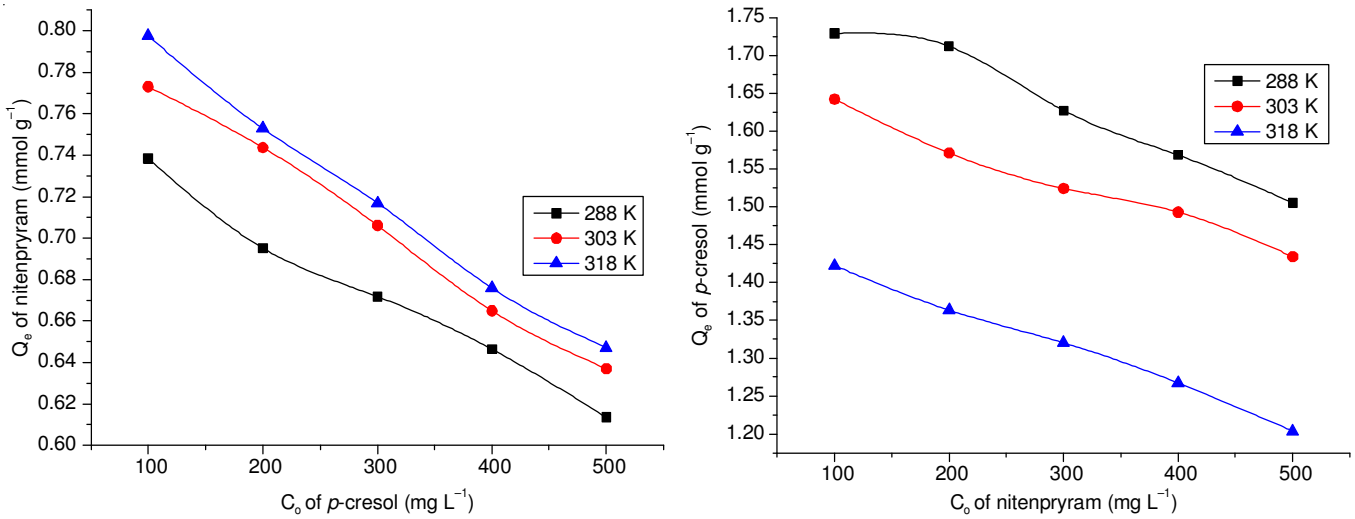

Fig. 6. Influence of initial concentration on the adsorption amount onto the resin from the binary components adsorptive environment

TABLE-4
THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF NITENPYRAM OR P-CRESOL ONTO THE RESIN IN BINARY COMPONENTS SYSTEM

Adsorbate	Q_e (mmol g^{-1})	Temperature (K)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})
Nitenpyram	1.0	288	7.859	53.58	-7.573
	1.0	303		52.60	-8.079
	1.0	318		54.55	-9.489
p-Cresol	1.0	288	-17.00	-46.44	-3.625
	1.0	303		-43.83	-3.721
	1.0	318		-41.27	-3.876
Nitenpyram + *p*-Cresol	1.0	288	-12.21	-27.73	-4.224
	1.0	303		-26.43	-4.201
	1.0	318		-24.88	-4.299

The selectivity indexes for the adsorption of nitenpryram onto the adsorbent were tested in Table-5, *p*-cresol as the competitive component. It can be seen that the adsorption selectivity of nitenpryram on the resin modified with ethyl cellulose is larger than one on higher temperature with lower concentrations, contributed to the larger difference in the adsorbent-solute interaction and solvent-solute interaction.

TABLE-5
SELECTIVITY INDEX OF NITENPRYRAM

C_0 of nitenpryram (mg/L)	C_0 of *p*-cresol (mg/L)	Temperature (K)		
		288	303	318
100	300	2.17	3.36	5.44
200	300	0.59	0.79	1.16
300	300	1.01	1.28	1.87
400	300	0.77	0.94	1.42
500	300	0.72	0.87	1.31
300	100	1.02	1.60	2.91
300	200	0.75	1.13	1.64
300	300	1.10	1.46	2.03
300	400	1.48	1.76	2.36
300	500	1.70	1.97	2.59

Conclusion

The resin was modified with ethyl cellulose based on Amberlite XAD-4, which had greater specific surface area and the average pore radius. The adsorption of nitenpryram on the resin modified with ethyl cellulose was an endothermic process by the positive adsorption enthalpy and an exothermic process of *p*-cresol with the negative adsorption enthalpy. There was solute-solvent measurement replacement in the process of nitenpryram and entropy change was giving a friendly boost to adsorption of nitenpryram. In single system the adsorption of nitenpryram was fitted by Freundlich model better than Langmuir model, with higher linearity in single system. But for *p*-cresol, it was well fitted by Freundlich and Langmuir model. The resin had better absorbability of nitenpryram than of *p*-cresol. A high adsorption rate of nitenpryram was in range of 58.62-98.09 % and the adsorption rate of *p*-cresol was 41.61-81.61 %. Adsorption rate was higher with higher temperature for nitenpryram and lower for *p*-cresol. In binary components system the adsorption rate of nitenpryram and *p*-cresol was higher, because the hydrogen bonding interaction increased between nitenpryram and *p*-cresol in the adsorption process and the locations and interactions of π-π. So the adsorption capacity increased. The equilibrium adsorption isotherms of nitenpryram and *p*-cresol in binary components system were fitted better by Freundlich model than Langmuir model. The multilayer adsorption and cooperative adsorption appeared. At the lower equilibrium concentration, there was the competitive adsorption on the adsorption sites; at higher equilibrium concentration, the cooperative effect primarily arisen. The change of nitenpryram' concentration had greater effect on the adsorption of *p*-cresol onto the resin modified with ethyl cellulose. So the adsorption selectivity of nitenpryram on the resin is larger than one at higher temperature with lower concentrations.

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