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Adsorption of Nitenpyram and Acetamiprid on Modified Resin with Proline

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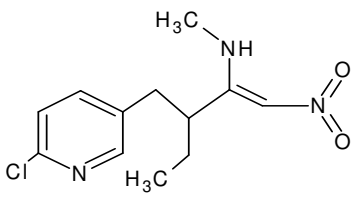
The adsorption behaviour of nitenpyram and acetamiprid in water onto the resin modified with proline based was investigated by static adsorption experiments at different temperature (288, 303 and 318 K) in single component and binary components system. The adsorption capacities and adsorption selectivity for acetamiprid in water were tested. The results showed the adsorption was fitted better by Freundlich model than Langmuir model in single system. The adsorption of nitenpyram on the resin modified with proline was an endothermic process by the positive adsorption enthalpy and an exothermic process of acetamiprid with the negative adsorption enthalpy. Entropy change was giving a friendly boost to adsorption. The resin had better absorbability for acetamiprid than for nitenpyram and the adsorption selectivity of acetamiprid was larger than one at lower temperature as well as at lower concentrations. A high removal rate of 45.56-82.66 % was obtained for nitenpyram studied and the removal rate of acetamiprid was in the range of 48.77-86.23 % in single component system. In binary components system the removal rate of acetamiprid was higher, lower for nitenpyram, because of competition in adsorption site. The equilibrium adsorption isotherms of both nitenpyram and acetamiprid in binary components system were fitted better by Langmuir model. So the adsorption of nitenpyram and acetamiprid on the resin modified with proline was on the monolayer adsorption in binary components system. But the cooperative effect existed at 318 K. In additional studies, the competitive adsorption existed. The adsorption of acetamiprid onto the resin had just smaller change in the presence of nitenpyram, but the adsorption of nitenpyram was weakened obviously in the presence of acetamiprid. The adsorption selectivity of acetamiprid on the resin is larger than one on lower temperature with lower concentrations.

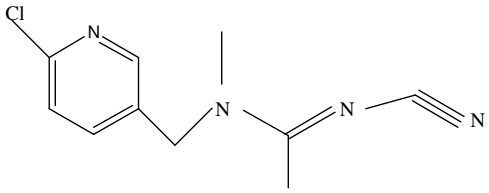
Keywords: Adsorption resin, Nitenpyram, Acetamiprid, Proline.

INTRODUCTION

Pesticides are widely used in the world. Nitenpyram and acetamiprid are new nicotine insecticide with high and fast effectiveness, destroys insects widely, has a persistent efficiency period and better solubility under room temperature[1], used in agriculture. For the natural waters, they are likely to be contaminated with nitenpyram and acetamiprid. There is a serious need for the high-tech about the economic, efficient, feasible water treatment, to protect them. Resin adsorption is widely used in wastewater treatment[2-6], which makes resin adsorption technology has irreplaceable characteristics because of the designability and selectivity of resin's chemical or physical structures on practical applications[7]. The adsorption rule is complicated in binary component system in aqueous solution and some papers were reported[8-13]. The paper focuses on the adsorption of nitenpyram and acetamiprid in aqueous solution on the resin modified with proline[14] and the adsorption behaviour and adsorption selectivity of two pollutants coexisting in water, modified adsorption resin as adsorbent, nitenpyram and acetamiprid as adsorbates through static adsorption. A thermodynamical study is made. These data will provide reference for theory research and engineering design. **Schemes I** and **II** is the structure of nitenpyram and acetamiprid.



Scheme-I: Structure of nitenpyram



Scheme-II: Structure of acetamiprid

EXPERIMENTAL

Methanol is of G.R. grade. Both acetamiprid and nitenpyram are of A.R. grade and the resin of is modified with proline based on NDA150[14].

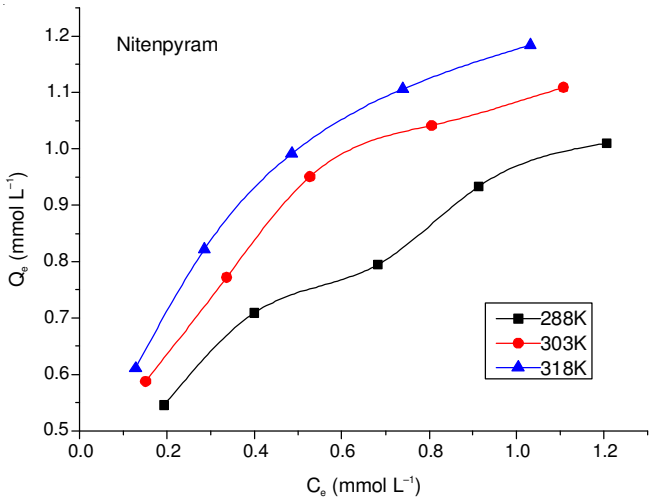
Static adsorption experiment: A bottle point isotherm procedure was used to conduct all the equilibrium studies in single component system. 0.100 g of the resin was directly weighed accurately. The adsorbents were contacted, in 250 mL stoppered conical flasks, with 100 mL of nitenpyram or acetamiprid solution of certain concentration (C_0, mg/L) ranging from 200 to 600 mg/L. The flasks were completely sealed and then placed in an incubator shaker at different temperatures (288, 303 and 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 acetamiprid were equal to each other at the concentration of 100, 150, 200, 250 and 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 400 mg/L and the initial concentrations of acetamiprid were at 200, 300, 400, 500 and 600 mg/L. Conversely, the initial concentrations of acetamiprid were constant at 400 mg/L.

RESULTS AND DISCUSSION

Static adsorption of nitenpyram and acetamiprid in single component system: Equilibrium adsorption isotherms of nitenpyram and acetamiprid 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 acetamiprid, the exothermic process. In Fig. 1, at the same equilibrium concentration, the resin has stronger adsorbability at acetamiprid.

A high removal rate of 45.56-82.66 % was obtained for nitenpyram studied, as shown in Fig. 2 and the removal rate of acetamiprid was in the range of 48.77-86.23 %. Removal rate was higher with higher temperature for nitenpyram. Contrary to nitenpyram, removal rate was lower with lower temperature for acetamiprid. The result corresponded with the equilibrium adsorption isotherms in Fig. 1.



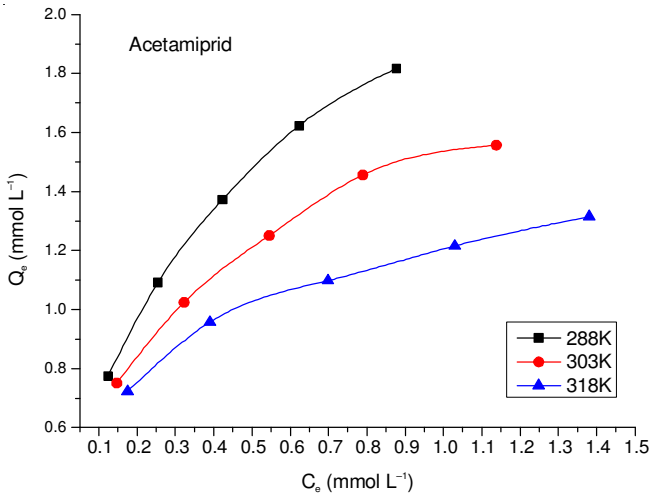


Fig. 1. Equilibrium adsorption isotherms of nitenpyram and acetamiprid in single component system on the resin at 288-318 K

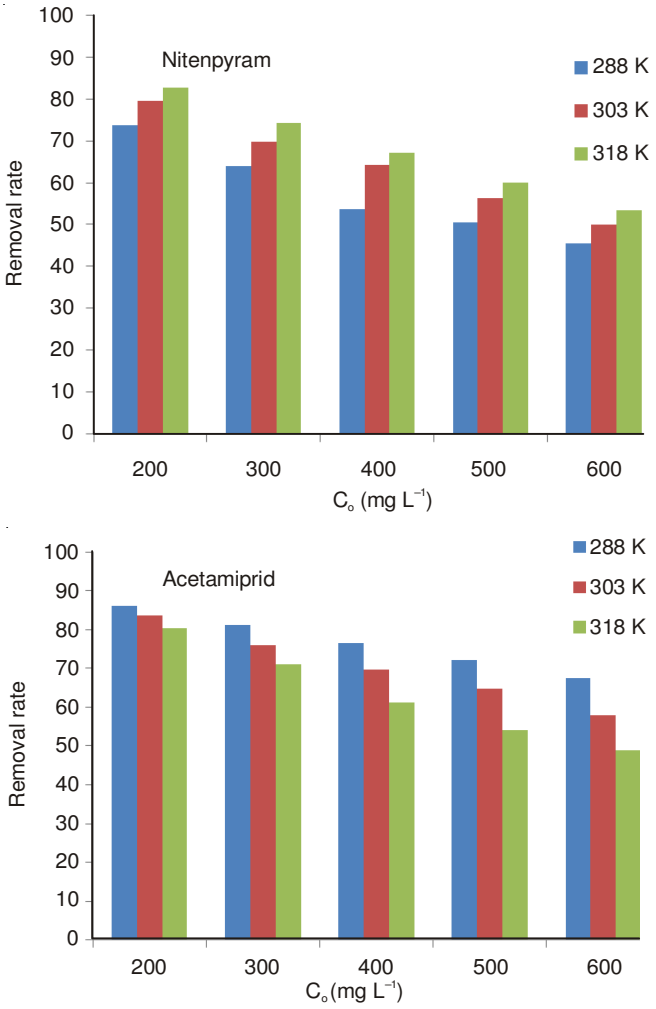


Fig. 2. Removal rate of nitenpyram or acetamiprid at different temperatures and initial solute concentrations in single component system

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[14].

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

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

Corresponding equations were given with computer fitting. And their constants along with the correlation coefficients 'r' are summarized in Table-1. The results clearly show that the adsorption data for the studied adsorption systems of nitenpyram fits better to the Freundlich and Langmuir model and to acetamiprid, too. The sorption mechanism was more complex.

As seen from the values of M, K_L, K_f, n in Table-1, the capacity of nitenpyram increases with increasing initial concentration and temperature for the interaction between basic groups of nitenpyram and acid groups on the resin modified with proline, chemisorption processes existed in processes. Conversely, M, K_f of acetamiprid decreases with the increasing temperature, physical absorption existed. And the constant n was always more than 1 in our study range, 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 nitenpyram and acetamiprid onto the resin are 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.

$$\Delta G = -n\,RT \quad (3)$$

where n is the Freundlich model characteristic constant, R is the gas constant (kJ/mol K) 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 is positive, indicating the adsorption process is an endothermic one. The enthalpy of acetamiprid is negative, an exothermic process. Both are low and in the range of 10-40 kJ/mol where physical adsorption is expected to be the dominant mechanism. 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. A chemical sorption process is in the range of -400 to -80 kJ/mol. ΔG was small, shown in Table-2, further confirming the physical character of the adsorption. And as expected they were negative in processes. The values of the adsorption entropy were positive. For the resin with the multi-pore structure and functional groups, has powerful water absorption. So in lower temperature the water molecules were adsorbed preferentially then with the different interactions changing, nitenpyram or acetamiprid was adsorbed little by little, with the more desorptions of water molecules, because the molecular size of nitenpyram or acetamiprid is higher than water molecule. That's solute-solvent measurement replacement. Then the entropy-increase effect, gave a friendly boost.

Same initial concentration of nitenpyram and acetamiprid in binary components system: Equilibrium adsorption isotherms of nitenpyram and acetamiprid onto the resin in binary components system are presented in Fig. 3. The effect of the temperature cohered with it in single component system (Fig. 1). Comparing with Fig. 1, equilibrium adsorption isotherms of nitenpyram or acetamiprid in binary components system changed irregularly. For example, the adsorptive capacity of nitenpyram at the initial concentration (250 and 300 mg L^{-1}) decreased greatly, because of the existence of acetamiprid. The coexistence of nitenpyram or acetamiprid in water caused the competition on the resin.

High removal rate was obtained for nitenpyram studied from Fig. 4, in the range of 25.91-82.24 %, lower than it in single component system. But for acetamiprid removal rate was higher in the range of 67.04-92.30 %, being improved better than it in single component system.

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

Adsorbate	Temp. (K)	Langmuir				Freundlich			
		Equation	M	K_L	r	Equation	K_f	n	r
Nitenpyram	288	Y=0.1854x+0.9027	1.108	4.869	0.983	Y=0.3329x-0.0254	0.943	3.004	0.994
	303	Y=0.1398x+0.8008	1.249	5.728	0.991	Y=0.3283x+0.046	1.112	3.046	0.991
	318	Y=0.1146x+0.7624	1.312	6.653	0.995	Y=0.322x+0.0831	1.211	3.105	0.995
Acetamiprid	288	Y=0.1052x+0.4602	2.173	4.374	0.995	Y=0.4405x+0.2952	1.961	2.270	0.998
	303	Y=0.1153x+0.5668	1.764	4.916	0.992	Y=0.3667x+0.1877	1.541	2.727	0.996
	318	Y=0.1207x+0.7097	1.413	5.880	0.994	Y=0.2853x+0.0834	1.212	3.505	0.996

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

Adsorbate	q_e (mmol/g)	Temperature (K)	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)
Nitenpyram	1	288	11.388	64.52	-7.193
	1	303		62.91	-7.673
	1	318		61.62	-8.209
Acetamiprid	1	288	-4.081	4.698	-5.435
	1	303		9.205	-6.870
	1	318		16.31	-9.267

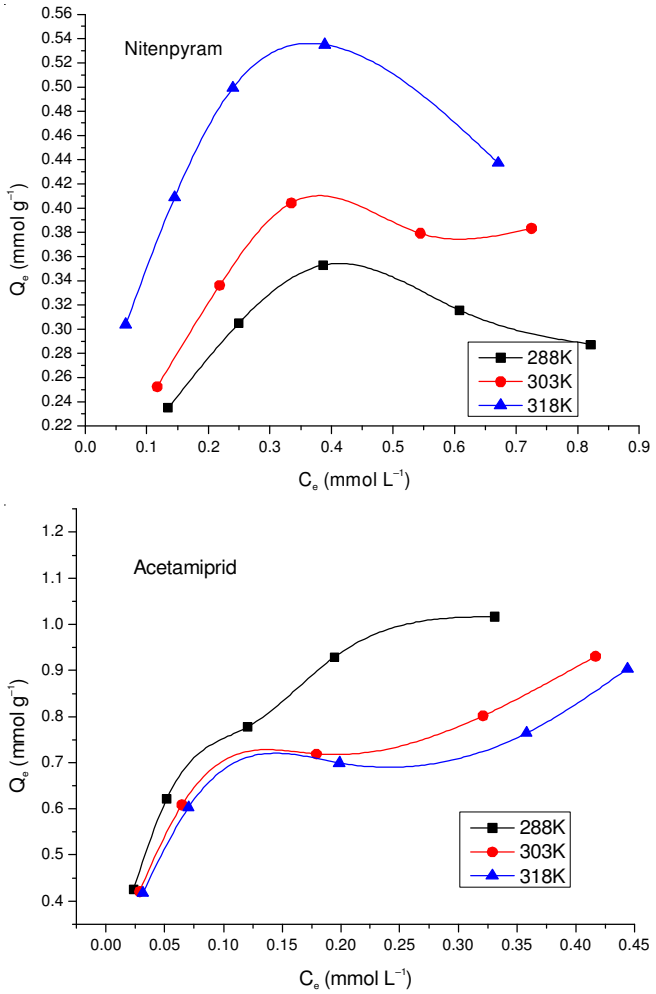


Fig. 3. Equilibrium adsorption isotherms of nitenpyram or acetamiprid in binary components system

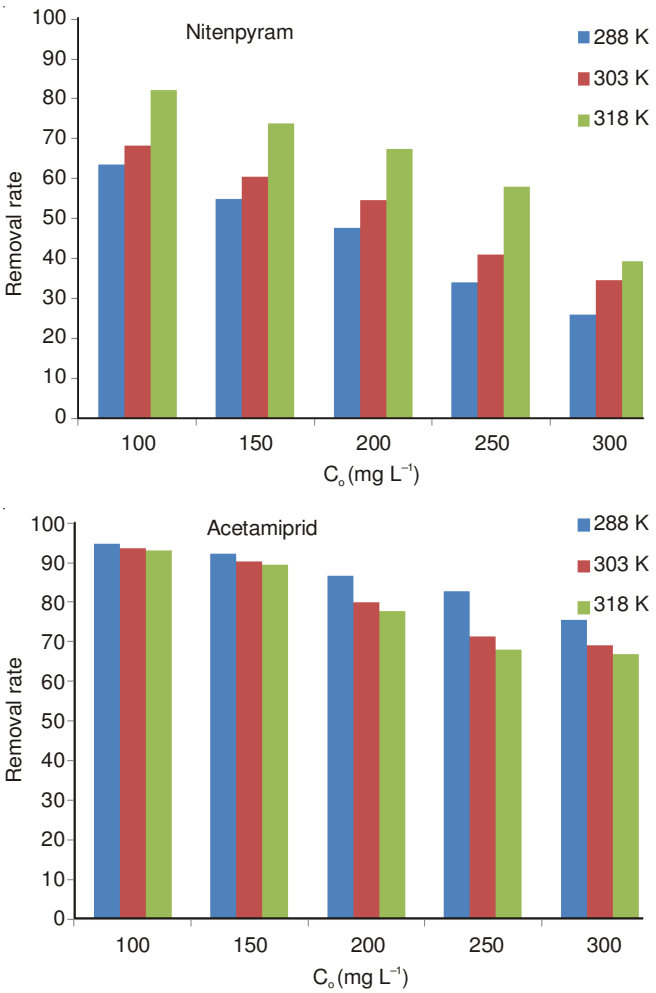


Fig. 4. Removal rate of nitenpyram and acetamiprid at different initial solute concentrations in binary components system

Based on Fig. 5 and Table-3, the equilibrium adsorption isotherms of both nitenpyram and acetamiprid in binary components system were fitted better by Langmuir model. So the adsorption of nitenpyram and acetamiprid on the resin modified with proline was on the monolayer adsorption. There was the competition on adsorption site.

From Table-4, the adsorption capacity of acetamiprid and nitenpyram in binary components system were more than the adsorption capacity in single component system (nitenpyram or acetamiprid) on the resin at the same higher equilibrium concentration at 318 K, which would be due to the cooperative effect and solute-solvent measurement replacement. When temperature was at 288 K, 313 K, the capacity in binary components system was between nitenpyram and acetamiprid in single system, because of the competition on the adsorption locus, these molecules were organized in the arrangement out of disorder, according to Table-3. In binary components system the equilibrium adsorption isotherms could not be fitted by Freundlich and Langmuir model for individual adsorbate. The competitive adsorption was existed. Cooperative adsorption was existed at 318 K.

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 acetamiprid with the increasing initial concentration of nitenpyram, but larger distinction for nitenpyram with the increasing initial concentration of acetamiprid, competitive adsorption phenomenon existed. The change of acetamiprid' concentration had greater effect on the adsorption of nitenpyram onto the resin modified with proline.

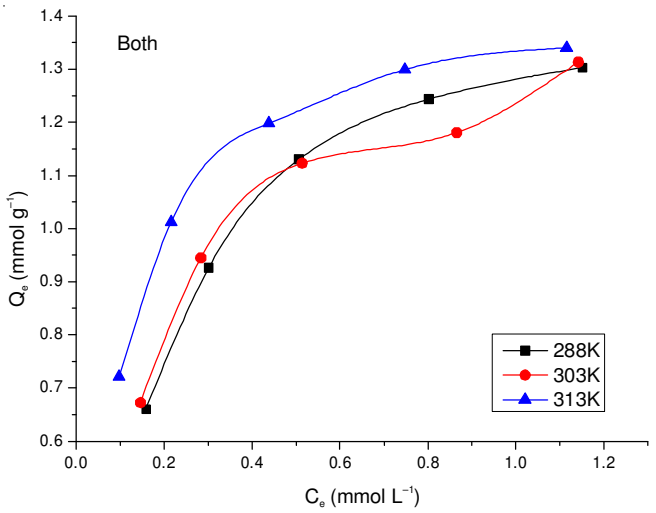


Fig. 5. Equilibrium adsorption isotherms of both nitenpyram and acetamiprid in binary components system

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

Adsorbate	Temp. (K)	Langmuir				Freundlich			
		Equation	M	K_L	r	Equation	K_f	n	r
Nitenpyram	288	Y=0.1627x+2.8567	0.350	17.558	0.764	Y=0.1156x-0.4776	0.333	8.650	0.551
	303	Y=0.1989x+2.1635	0.462	11.399	0.950	Y=0.2214x-0.3512	0.445	4.517	0.849
	318	Y=0.0932x+1.8140	0.551	19.463	0.921	Y=0.1862x-0.2478	0.565	5.371	0.849
Acetamiprid	288	Y=0.0333x+0.9361	1.068	28.111	0.996	Y=0.3266x+0.1862	1.535	3.062	0.989
	303	Y=0.0365x+1.0958	0.912	30.022	0.989	Y=0.2646x+0.0582	1.143	3.779	0.978
	318	Y=0.0392x+1.1387	0.878	29.048	0.985	Y=0.2518x+0.0264	1.063	3.971	0.968
Nitenpyram + Acetamiprid	288	Y=0.1386x+0.6291	1.590	4.539	0.999	Y=0.3427x+0.1232	1.328	2.918	0.972
	303	Y=0.1165x+0.6732	1.485	5.778	0.996	Y=0.3033x+0.1108	1.291	3.297	0.970
	318	Y=0.0683x+0.6791	1.472	9.943	0.999	Y=0.2512x+0.143	1.390	3.981	0.966

TABLE-4
CONTRASTIVE ANALYSIS OF THE ADSORPTIVE CAPACITY OF SINGLE SYSTEM AND BINARY SYSTEM AT THE SAME EQUILIBRIUM CONCENTRATION

System	Adsorbate	Langmuir model	Temp. (K)	C_e	Q_e	C_e	Q_e	C_e	Q_e
Single	Nitenpyram	Y=0.1854x+0.9027	288	0.1	0.363	0.5	0.785	1.0	0.919
		Y=0.1398x+0.8008	303	0.1	0.455	0.5	0.925	1.0	1.063
		Y=0.1146x+0.7624	318	0.1	0.524	0.5	1.008	1.0	1.140
	Acetamiprid	Y=0.1052x+0.4602	288	0.1	0.661	0.5	1.491	1.0	1.769
		Y=0.1153x+0.5668	303	0.1	0.581	0.5	1.254	1.0	1.466
		Y=0.1207x+0.7097	318	0.1	0.522	0.5	1.051	1.0	1.204
Binary	Nitenpyram + Acetamiprid	Y=0.1386x+0.6291	288	0.1	0.496	0.5	1.103	1.0	1.303
		Y=0.1165x+0.6732	303	0.1	0.544	0.5	1.104	1.0	1.266
		Y=0.0683x+0.6791	318	0.1	0.734	0.5	1.226	1.0	1.338

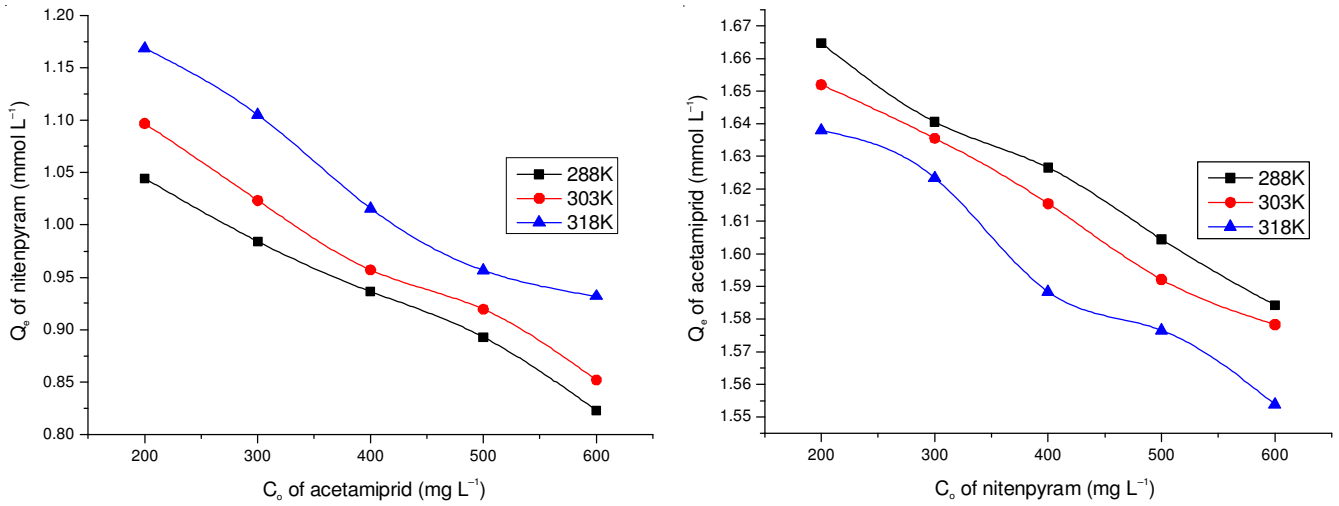


Fig. 6. Influence of initial concentration on the adsorption amount onto the resin from the binary components adsorptive environment

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].

The selectivity indexes for the adsorption of acetamiprid onto the adsorbent tested are compared in Table-5, nitenpyram as the competitive component. It can be seen that the adsorption selectivity of acetamiprid on the resin is larger than one on lower temperature with lower concentrations, contributed to the larger difference in the adsorbent-solute interaction and solvent-solute interaction. Consequently, it is expected to apply the resin for the successful separation and recovery of acetamiprid from the water containing nitenpyram. The proposed technique has its practicability.

Conclusion

The adsorption of nitenpyram on the resin modified with proline was an endothermic process by the positive adsorption enthalpy and an exothermic process of acetamiprid with the negative adsorption enthalpy. Entropy change was giving a friendly behaviour to adsorption. The adsorption was fitted by Freundlich model better than Langmuir model, with higher linearity in single system. The resin had better absorbability for acetamiprid than for nitenpyram and the adsorption selectivity of acetamiprid was larger than one at lower temperature

TABLE-5
SELECTIVITY INDEX OF ACETAMIPRID AND NITENPYRAM

C_0 of nitenpyram (mg/L)	C_0 of acetamiprid (mg/L)	Temperature (K)			C_0 of nitenpyram (mg/L)	C_0 of acetamiprid (mg/L)	Temperature (K)		
		288	303	318			288	303	318
200	400	18.781	13.074	5.456	400	200	2.403	1.974	1.155
300	400	10.776	7.277	3.890	400	300	2.083	1.712	1.106
400	400	8.941	5.838	4.056	400	400	1.494	1.277	0.944
500	400	10.094	6.596	4.501	400	500	1.282	1.108	0.823
600	400	8.392	6.173	3.760	400	600	1.132	0.948	0.645

and at lower concentrations. A high removal rate of 45.56-82.66 % was obtained for nitenpyram studied and the removal rate of acetamiprid was in the range of 48.77-86.23 % in single component system. In binary components system the removal rate of acetamiprid was higher, lower for nitenpyram, because of competition in adsorption site. The equilibrium adsorption isotherms of both nitenpyram and acetamiprid in binary components system were fitted better by Langmuir model. So the adsorption of nitenpyram and acetamiprid on the resin modified with proline was on the monolayer adsorption in binary components system. But the cooperative effect existed at 318 K. In additional studies, the competitive adsorption existed. The adsorption of acetamiprid onto the resin had just smaller change in the presence of nitenpyram, but the adsorption of nitenpyram was weakened obviously in the presence of acetamiprid. The adsorption selectivity of acetamiprid on the resin is larger than one on lower temperature with lower concentrations.

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