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Adsorption Behaviour of XDA-200 Resin Toward *p*-Nitrophenol in Aqueous Solution

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The adsorption behaviour of a colloidal solid particle of adsorption resin XDA-200 for *p*-nitrophenol was carried out using batch and column techniques. After characterization by direct photometric studies, the static and dynamic adsorption behaviour of *p*-nitrophenol onto adsorption resin XDA-200 was investigated. The adsorption was optimized with respect to pH, contact time and oscillation frequency. Maximum adsorption capacity was achieved from solution of pH 3-8 after 5.5 h agitation time. The adsorption behaviour of XDA-200 resin for *p*-nitrophenol obeyed both the Freundlich and Langmuir isotherms. The variation of the equilibrium constant 'D' with temperatures between 288 and 308 K yields values of $\Delta H = -7.12$ kJ/mol, $\Delta S = 41.72$J/(mol K), and $\Delta G_{298} = -19.55$ kJ/mol, respectively. The kinetics of adsorption follows the Brykina's equation with the rate constant $k_{298} = 1.06 \times 10^{-4}\ s^{-1}$.

Key Words: XDA-200 resin, Kinetics, Thermodynamics.

INTRODUCTION

The wide use of nitroaromatics, which was brought by synthetic intermediate in the manufacture of pharmaceuticals, pigments, dyes, plastics, pesticides and fungicidal agents, explosives and industrial solvents[1], leads to accumulation of nitrophenols. *p*-Nitrophenol (PNP) is probably the most important among the mononitrophenols in terms of the quantities used and potential environmental contamination[2]. *p*-Nitrophenol has been classified as a priority pollutant by the United States Environmental Protection Agency (EPA, 1980), which recommends restriction of *p*-nitrophenol concentrations in natural waters[3] to < 10 ng/L. Therefore, *p*-nitrophenol poses significant health and environmental risks, because it is toxic to many living organisms and it may accumulate in the food chain[4].

Adsorption by activated carbon has been widely used to treat wastewater containing phenolic compounds. However, how to readily regenerate the spent activated carbon for repeated use still remains as a great challenge. In recent years, polymeric adsorbents have been increasingly regarded as an alternative to activated carbon due to their feasible adsorption-regeneration properties and perfect mechanical intensity. Since the invention of the hyper-cross-linked polymeric adsorbent by Davankov and Tsyurupa, it has achieved wide applications in many fields such as separation and analysis science because of its unique adsorption properties, including ideal pore structure and various surface functional groups available[5].

In this study, we attempted to examine the effects of various factors on the adsorption of XDA-200 for *p*-nitrophenol such as pH, adsorbent mass, *p*-nitrophenol initial concentration, contact time, temperature, oscillation frequency, the elution conditions, *etc*. The experimental results may provide theory for the design of an effective way to treat wastewater containing phenolic compounds.

EXPERIMENTAL

The flask was shaken in a THZ-C-1 temperature constant shaking machine. The content of *p*-nitrophenol in the aqueous phase was quantitatively determined by using a Shimadzu UV-2550 UV-VISIBLE spectrophotometer at 402.5 nm. The pH measurements were performed with an Mettler toledo delta 320 pH meter.

Reagents and solutions: Adsorption resin XDA-200 was provided by Xi'an Sun Resin Technology Ltd. (activated before use). The physical properties of resin are summarized in Table-1. Buffer solution with pH 3.0-8.0 was prepared from acetic acid-sodium acetate (CH_3COOH-CH_3COONa). A stock solution of *p*-nitrophenol (Analytical grade from the chemical plant of the East China Normal University) was prepared in double-distilled water. All the other reagents were of AR grade.

TABLE-1
PHYSICAL PROPERTIES OF THE ADSORPTION RESIN XDA-200

Name	Average pore diameter	Surface area	True wet density	Moisture content, % (mass)
XDA-200	2.5 *ca.* 3.5 nm	≥ 800 m^2/g	1.05-1.15 g/mL	50-60

Adsorption experiments: Batch adsorption experiments were carried out by allowing an accurately weighed amount of XDA-200 resin to reach equilibrium with *p*-nitrophenol solutions of various initial concentrations at temperatures of 288, 298 and 308 K. Known weights of XDA-200 resin (15.0 mg) were added to 100 mL reaction bottles each containing 32 mL solution. The bottles were shaken in a temperature-controlled shaker at a constant speed of 100 rpm. Preliminary experiments showed that adsorption equilibrium was reached within 5.5 h. When adsorption equilibrium was reached, the upper layer of clear solution was analyzed for residual concentration of *p*-nitrophenol following the direct photometric method. The effect of temperature on the adsorption characteristics was investigated by determining the adsorption isotherms at 288, 298 and 308 K. Thermodynamic parameters of adsorption have been determined using classical thermodynamic equations. Brykina's method was used to determine rate of the adsorption process.

RESULTS AND DISCUSSION

Effect of pH: The test was carried out according to the above mentioned method. The effect of pH on the adsorption behaviour of resins for *p*-nitrophenol was shown in Fig. 1. The results indicated that the adsorption capacity was the highest at pH

5.49 for XDA-200 and decreased by either raising or lowering pH under the experiment conditions and the equilibrium adsorption capacity was 175.5 mg/g resin at 298 K. All the following experiments were performed at pH = 5.49 in the CH_3COOH-CH_3COONa system.

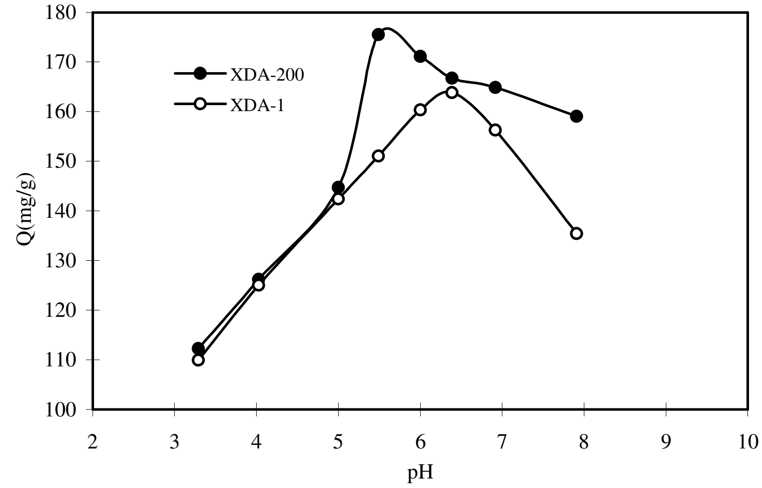

Fig.1. Influence of pH on adsorption capacity (Resin 15.0 mg, 298 K, r = 100 rpm, C_0 = 4.725 mg/32.0 mL)

Isotherm adsorption curve: An adsorption isotherm describes the relationship between the amount of adsorbate which is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. Several 2 or 3 parameter models have been published to describe experimental data of adsorption isotherms. The Langmuir and Freundlich models are the most frequently used models. The Langmuir model is obtained under the ideal assumption of a totally homogenous adsorption surface, whereas the Freundlich isotherm is suitable for a highly heterogenous surface[6].

Freundlich isotherm curve: The semi-empirical Freundlich equation was employed to describe the adsorption data for phenolic compounds[7]:

$$\lg Q = \lg K_f + \left(\frac{1}{n}\right)\lg C_e$$

where K_f is the Freundlich parameter for a heterogeneous adsorbent; n is related to the magnitude of the adsorption driving force and the site energy distribution of the adsorbent. The above isotherm parameters can be determined graphically by plotting lg Q_e against lg C_e according to the Eqn. The experimental results were shown in Table-2 and Fig. 2. The isotherms were nonlinear and could be described by Freundlich isotherm. The fact that n values were between 1 and 10 showed that the adsorption of XDA-200 for *p*-nitrophenol was beneficial adsorption.

TABLE-2
LINEARITY RELATION OF lg Q AND lg C_e

T (K)	Linearity relation of lg Q and lg C_e	R^2	n
288	y = 0.9232x + 3.3637	0.9951	1.08
298	y = 0.4467x + 2.7733	0.9999	2.24
308	y = 0.5234x + 2.8408	0.9857	1.91

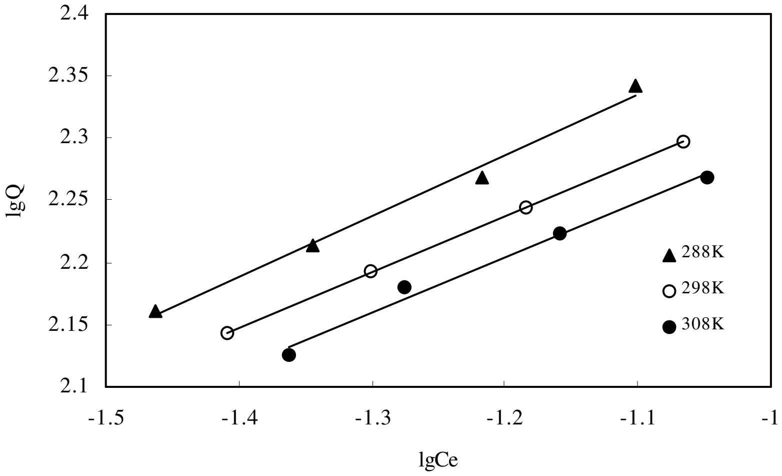

Fig. 2. Freundlich isotherm curve (C_0 = 4.725 mg/32.0 mL, pH = 5.49, r = 100 rpm, Resin: 10.0 mg *ca.* 25.0 mg)

Langmuir isotherm curve: The Langmuir model represents one of the first theoretical treatments of non-linear adsorption and has been successfully applied to a wide range of systems that exhibit limiting or maximum adsorption capacities. The model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate in the plane of the surface. The Langmuir isotherm is given by:

$$Q = Q^0 b \frac{C_e}{(1 + bC_e)}$$

where Q^0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively[8]. It is usually linearized by inversion to obtain the following form:

$$\frac{C_e}{Q} = \frac{C_e}{Q^0} + \frac{1}{(Q^0 b)}$$

It is equally used to analyze batch equilibrium data by plotting C_e/Q *versus* C_e, which yields a linear plot if the data conform to the Langmuir isotherm. The results are shown in Table-3 and Fig. 3, with the correlation coefficients R^2_{288} = 0.9833, R^2_{298} = 0.9943 and R^2_{308} = 0.9876, the Langmuir-type adsorption isotherm was suitable for equilibrium studies.

TABLE-3
LINEARITY RELATION OF C_e/Q AND C_e

T (K)	Linearity relation of C_e/Q and C_e	R^2	b
288	y = 0.0031x + 0.0001	0.9833	31.0
298	y = 0.0033x + 0.0002	0.9943	33.0
308	y = 0.0034x + 0.0002	0.9976	34.0

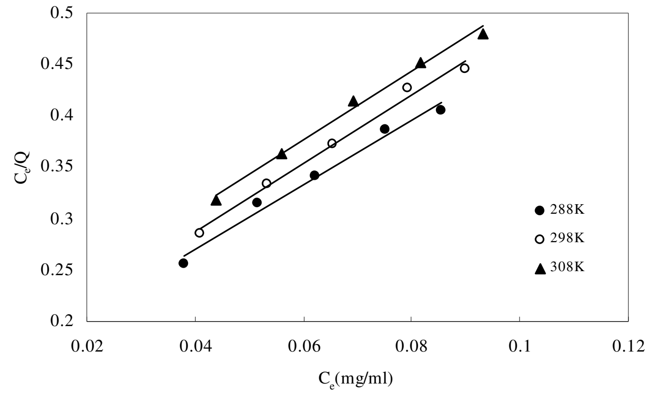

Fig. 3. Langmuir isotherm curve (Resin: 15.0 mg, pH = 5.94, r = 100 rpm, C_0: 5 × 0.675 mg/32 mL *ca.* 8 × 0.675 mg/32 mL)

Determination of adsorption rate constant at different temperature and apparent activation energy of XDA-200 for *p*-nitrophenol[9,10]: With three portions of 15.0 mg of resin weighed accurately and put into conical flasks individually, the experiment was progressed by using the above-mentioned method at 288, 298 and 308 K, according to the experimental condition (Fig. 4). 0.1 mL of clear upper layer solution was taken out, respectively at intervals to determine the concentrations of the remains. After their concentration kept constant, a series of data was obtained.

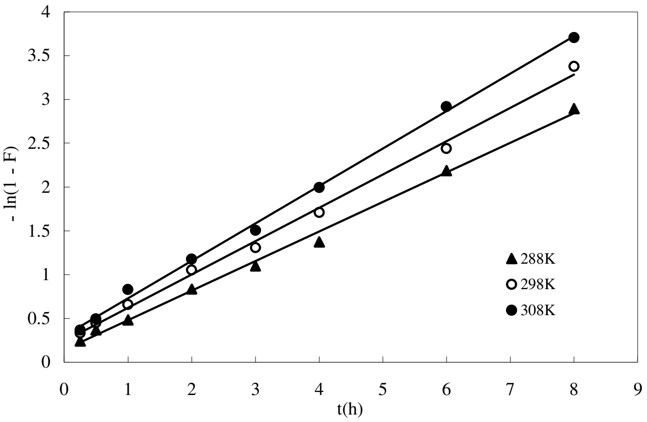

Fig. 4. Determination of adsorption rate constant (C_0 = 4.725 mg/32.0 mL, pH = 5.49, r = 100 rpm)

The kinetics of *p*-nitrophenol removal has been carried out to understand the behaviour of this adsorbent. According to Brykina's method[11], the adsorption rate constant k can be calculated from $-\ln(1-F) = kt$, where $F = Q_t/Q_\infty$. Q_t and Q_∞ are the adsorption amounts at certain time and at the equilibrium time, respectively. The equations given in previous work and plotting -ln (1-F) *versus* t (Fig. 4), yields the adsorption rate constant k (shown in Table-4).

TABLE-4
ADSORPTION RATE CONSTANTS (k) FOR THE ADSORPTION OF *p*-NITROPHENOL WITH XDA-200 RESIN AND ITS CORRELATION COEFFICIENT (R^2)

Temperature (K)	288	298	308
k ($\times 10^{-4} s^{-1}$)	0.9380	1.0600	1.1400
R^2	0.9959	0.9964	0.9944

According to Boyd's liquid film spreading equation[12], it can be known from the linear relationship between -ln (1-F) and t, that liquid film spreading is the predominant step of the adsorption process.

According to Arrhenius equation:

$$\lg k = -\frac{E_a}{2.303\,RT} + \lg A$$

where A is the temperature independent factor, E_a is the activation energy of adsorption (kJ/mol), R is the gas constant and T is the solution temperature (K). The slope of plot of lg k *versus* 1/T is used to evaluate the activation energy (Fig. 5). The magnitude of activation energy gives an idea about the type of adsorption, which is mainly physical or chemical. Low activation energies (5-40 kJ/mol) are characteristics for physio-sorption, while higher activation energies (40-800 kJ/mol) suggest chemisorption[13]. The obtained result (7.37 kJ/mol) for the adsorption of *p*-nitrophenol by XDA-200 indicates that the adsorption has a potential barrier and corresponds to a physi-sorption.

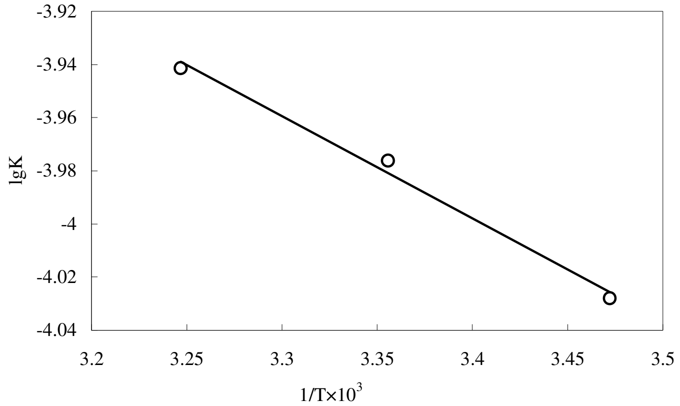

Fig. 5. Determination of apparent activation energy

Influence of adsorption temperature on distribution coefficient and the determination of thermodynamic parameters: The Gibbs free energy change ΔG, indicates the degree of the spontaneity of the adsorption process. For significant adsorption to occur, the free energy changes of adsorption, ΔG, must be negative. The Gibbs free energy change of adsorption is defined as:

$$\Delta G = -2.303\ RT\ \lg D$$
$$\Delta G = \Delta H - T\Delta S$$

After integration and rearrangements the above eqn. gives:

$$\lg D = -\frac{\Delta H}{2.303\ RT} + \frac{\Delta S}{2.303\ R}$$

ΔH and ΔS can be determined from the slope and the intercept of the linear plot of lg D *versus* 1/T.

According to the experimental condition (Fig. 6), the distribution coefficient of the resin adsorbing *p*-nitrophenol over the range of temperature from 288 to 308 K was measured. The values of the standard enthalpy and the entropy changes were determined as -7.12 kJ/mol and 41.72 kJ/(mol K) from Fig. 6 ($R^2 = 0.994$), respectively. And the Gibbs free energy change ΔG at 288, 298 and 308 K were -19.14, 19.55 and -19.97 kJ/mol, respectively. The negative value of ΔH suggested the exothermic nature of the adsorption and ΔH was less than 42 kJ/mol, which was comparable to those reported for adsorption of phenols on non-ionic polymeric resins[14]. Based on the apparent enthalpy changes of adsorption (< 42 kJ/mol), the uptake of *p*-nitrophenol on non-ionic polymeric XDA-200 resin was a type of physical adsorption[15].

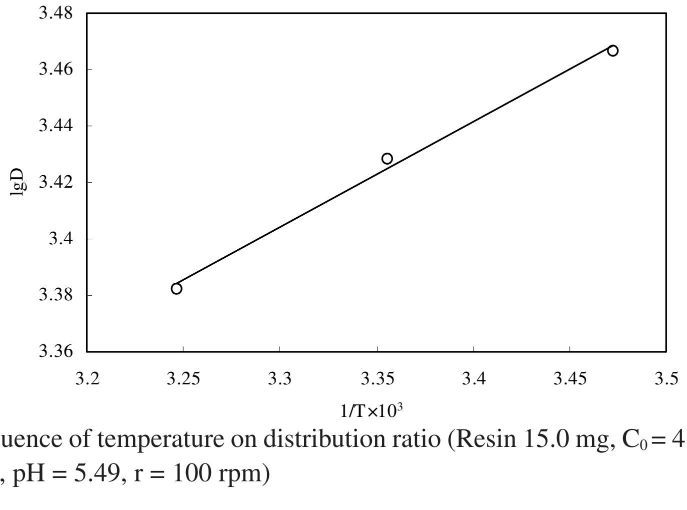

Fig. 6. Influence of temperature on distribution ratio (Resin 15.0 mg, $C_0 = 4.725$ mg/32.0 mL, pH = 5.49, r = 100 rpm)

The fact that ΔG values were negative indicated that the adsorption process led to a decrease in Gibbs free energy and was feasibility and spontaneity.

Influence of oscillation frequency of shaker on the adsorption rate: The adsorption rate curve of different oscillation frequency was studied during the range from 50-150 rpm. Under the experimental condition as shown in Fig. 7, the adsorption rate curve was obtained. The results showed that the uptake capacity of *p*-nitrophenol was independent of oscillation frequency, but with the oscillation frequency increasing, the equilibrium time notablely decreased.

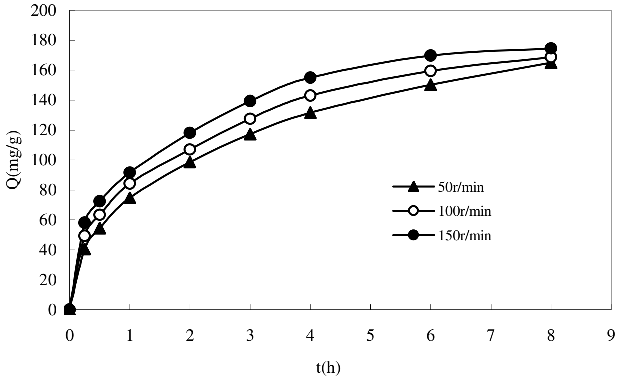

Fig. 7. Influence of oscillations frequency on the adsorption amount (Resin 15.0 mg, C_0 = 4.725 mg/32.0 mL, pH = 5.49, T = 298 K)

Dynamic leakage curve on XDA-200 resin[16]: Dynamic adsorption was conducted using a glass column (Φ6 × 180 mm) packed with the newly prepared XDA-200 resin (630.0 mg) at room temperature. After the column had been conditioned, a solution with a known concentration of 0.1476 mg/mL of *p*-nitrophenol was continuously fed into the column at a constant flow rate of 4.97 BV/h. The effluents from the column were analyzed quantitatively according to the above-mentioned method. Breakthrough data were acquired by plotting the volume of solution that was passed through the column *versus* the concentration of *p*-nitrophenol as it appeared in the effluent. When the concentration of *p*-nitrophenol emerging from the bottom of the column was equal to that entering the top of the resin bed, the experiment was terminated. Then a plot of C_e/C_0 *versus* the volume of effluent gave a typical breakthrough curve in Fig. 8.

Elution

Static elution: In order to obtain basic information on the recovery of *p*-nitrophenol, desorption behaviour of XDA-200 resin for *p*-nitrophenol was investigated based on the kind of desorption solution and the concentration in the desorption solution (Table-5). The results (Table-5) showed that the percentage of elution was different when the kind of eluent or the concentration of eluent was changed. The elution percentage was up to 99.6 % both in 100 % methanol and 100 % ethanol. But it was not advisable to use methanol for the desorption studies, due to its acute toxicity. Then, 100 % ethanol was chosen as the best elution.

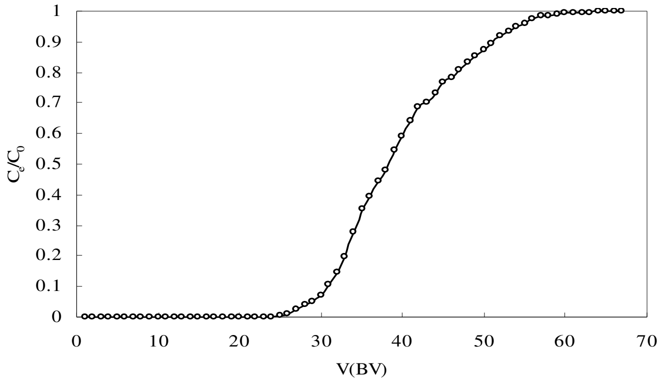

Fig. 8. Dynamic leakage curve

TABLE-5
ELUTION TEST OF *p*-NITROPHENOL

Concentration of eluent		Elution percentage (%)	Concentration of eluent		Elution percentage (%)	Concentration of eluent		Elution percentage (%)
Methanol (v/v, %)	65	93.2	Ethanol (v/v, %)	65	91.5	NaOH (mass, %)	1	86.8
	75	93.7		75	93.5		2	86.9
	85	94.9		85	94.7		3	87.2
	95	96.7		95	96.6		4	87.8
	100	99.6		100	99.6			

Dynamic elution: 100 % Ethanol was used to elute the saturated adsorption column with a flow rate of 1.99 BV/h. 10 mL eluate was intercepted at intervals for the determination of absorbency and a series of elution rates were calculated (Fig. 9). It indicated that the elution percentage reached 98.4 % with 1BV and reached 99.9 % with 2BV. Above all, by using 100 % ethanol as an eluent, the elution efficiency was well and elution rate was fast, so it was suitable for industrial application.

Conclusion

In this study, the influence of operational conditions such as pH, adsorbent mass, *p*-nitrophenol initial concentration, contact time, temperature, oscillation frequency and dynamic adsorption of *p*-nitrophenol were studied. The optimal pH for the adsorption of *p*-nitrophenol was found to be 5.49 in the CH_3COOH-CH_3COONa system. The adsorption behaviour of XDA-200 resin for *p*-nitrophenol obeys both the Freundlich isotherm and the Langmiur isotherm. The adsorption rate constant was $k_{298} = 1.06 \times 10^{-4}$ s^{-1}. The apparent adsorption activation energy of XDA-200 resin for *p*-nitrophenol was 7.37 kJ/mol. The thermodynamic adsorption parameters, enthalpy change ΔH, entropy change ΔS and free energy change ΔG_{298} of XDA-200 resin for *p*-nitrophenol were -7.12, 41.72 and -19.55 kJ/mol, respectively. Dynamic adsorption and desorption experiments had been carried out with the column packed by XDA-200 resin. *p*-Nitrophenol adsorbed on XDA-200 resin can be reductively eluted by 100 % ethanol and the elution percentage was up to 99.6 %. The results showed that XDA-200 resin revealed a good ability to reclaim and reuse *p*-nitrophenol from aqueous solutions.

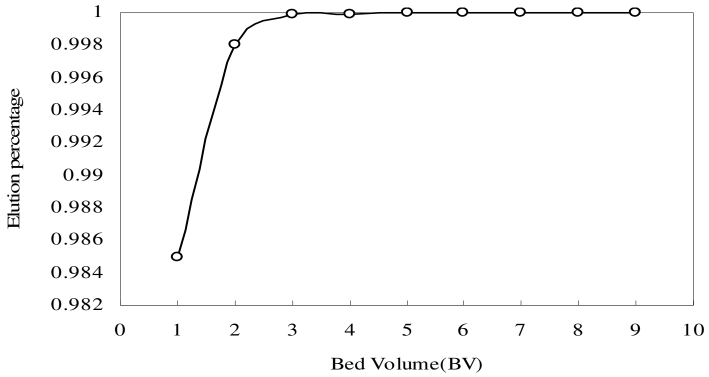

Fig. 9. Dynamic desorption curve

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