

STUDIES ON THE ADSORPTION OF PHENOLIC COMPOUNDS ON A PS-BASED RESIN MODIFIED BY NITRO FUNCTIONAL GROUPS*

Jin-nan Wang^{a,b}, Ai-min Li^{a,b**}, Sheng Zhong^{a,b}, Wei-ben Yan^c and Quan-xing Zhang^{a,b}

^a State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment,
Nanjing University, Nanjing 210093, China

^b Research Center of Organic Toxic Substance Control and Resource Reuse of Jiangsu Province, Nanjing 210038, China

^c Department of Chemical Engineering, Nanjing College of Chemical Technology, Nanjing 210048, China

Abstract A new adsorbent (JN-01) was prepared by modifying resin NDA-1800 with nitro functional groups. The adsorption capacities of resins XAD-4, NDA-1800 and JN-01 were investigated, and the results indicated that the modified resin JN-01 was much better in adsorbing phenol, *p*-nitrophenol and *p*-cresol. The adsorption capacities of the resin JN-01 were higher than those of the resins XAD-4 and NDA-1800 within a temperature range of 283–323 K, which might be attributed to the higher surface area and the partial polarity on its matrix. The new adsorbent could be widely used in wastewater treatment.

Keywords: Nitro-modified; Resin; Adsorption; Phenolic compounds.

INTRODUCTION

Phenolic compounds are controlled as one of the key pollutants because of their acute toxicity. Presently biodegradation, membrane separation, oxidation, adsorption and some other methods have been used to remove those pollutants^[1–5]. Adsorption has been proved to be one of the most attractive and effective techniques for separation and purification. Generally, resins have homogeneous surface chemistry offering the potential for limiting adsorption forces to specific mechanistic interactions, such as hydrophobic or hydrophilic interactions. Therefore, they are widely used in adsorbing organic matters mainly from wastewater^[6–13].

Recently a new resin NDA-1800 was developed by Nan Ge Environmental Protection Company Limited, but this resin has the same shortcomings as the famous resin Amberlite XAD-4: (1) the adsorption capacity of phenolic compounds is low; (2) it couldn't be easily wetted by water so as to be saturated by polar organic solvent before use. In response to these defects, a new adsorbent (JN-01) modified with nitro groups was prepared.

In this paper, static and dynamic adsorption of phenolic compounds on this new resin was conducted, and its better adsorption capacity than XAD-4 and NDA-1800 was observed in the tests. Adsorption thermodynamics and kinetics were investigated, indicating JN-01 has excellent absorption capacity to phenolic compounds.

EXPERIMENTAL

Chemicals

NDA-1800 resin was purchased from NG Co.Ltd (China). Amberlite XAD-4 resin was purchased from Rohm &

* This work was financially supported by the National Nature Science Fund (No. 50778088) and Resources Special Subject of National High Technology Research & Development Project (863 Project No. 2006AA06Z383), China.

** Corresponding author: Ai-min Li (李爱民), E-mail: liaimin@nju.edu.cn

Received September 10, 2007; Revised December 11, 2007; Accepted December 25, 2007

Haas Co. (Philadelphia, PA, USA). The phenolic compounds were dissolved in deionized water without any pH adjustment. Their physical properties are listed in Table 1.

Table 1. Properties of adsorbates

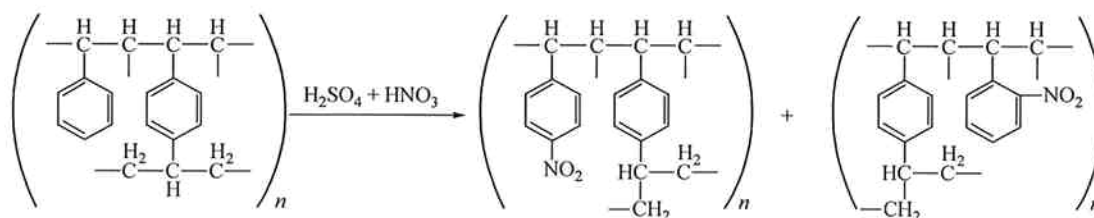
Property	Adsorbate		
	Phenol	<i>p</i> -Cresol	<i>p</i> -Nitrophenol
Dydrophobic parameter ($\lg K_{ow}^a$)	2.17	2.83	1.91
Dissociation constant (pK_a^b)	10.00	10.26	7.15
Solubility (g) ^c	9.3	2.3	1.7

^a Calculated according to Wang's handbook of Organic Pollutant Chemistry;

^b Taken from Lange's handbook of chemistry; ^c The quality of adsorbate dissolved in 100 g water

Preparation of JN-01 Adsorbent

A known amount (40 g) of NDA-1800 resin was placed in a 500 mL round-bottomed flask and swollen in 100 mL DMF for 1 h. With mechanical stirring, nitro-sulfuric acid (20 mL nitric acid (70%), 40 mL sulfuric acid (98%)) was slowly added into the flask at 303 K. The mixture was further stirred for 12 h at 350 K. The reaction process was as follows:



After being cooled, the mixture was poured slowly into water and washed to neutral point. The resin filtered was extracted by ethanol in a Soxhlet apparatus for 4 h and dried under vacuum at 333 K for 8 h.

Characterization of Polymer Beads

The specific surface area and the pore distribution of resins were measured with a Micrometrics ASAP-2010 surface area measurement instrument (Micrometrics Instrument, Norcross, USA) following the BET method. Infrared spectra of the polymeric adsorbent were obtained from a Nicolet 170 SX IR spectrometer (USA). The elemental analysis of the JN-01 polymeric adsorbent was obtained from a Perkin-Elmer 240 C Elemental Analytical Instrument (USA).

Static Adsorption Assay

Prior to their initial use, all adsorbents were extracted with acetone for 8 h and then dried for 2 h under vacuum at 333 K. Equilibrium adsorptions of phenol, *p*-cresol and *p*-nitrophenol were conducted at three different temperatures 283, 303 and 323 K. Briefly, 0.100 g of resin was introduced directly into a 250 mL conical flask, while Amberlite XAD-4 and NDA-1800 were first 'wetted' with 0.5 mL of methanol and then rinsed three times with deionized water before use. 100 mL aqueous solution of certain phenolic compound was added into each flask. The initial concentrations (c_0) of the solutions ranged from 200 mg/L to 1000 mg/L. The flasks were completely sealed and placed in a G 25 model incubator shaker (New Brunswick Scientific) at a pre-settled temperature and shaken under 120 r/min. The batch equilibrium test ran continuously over 24 h to ensure that the adsorption equilibrium had been reached and the concentrations of phenolic compounds (c_e) were determined. Thus, q_e (mmol/g), the adsorption capacity, was calculated according to Eq. (1):

$$q_e = V_1(c_0 - c_e)/WM \quad (1)$$

Where V_1 is the volume of solution (L), W is the weight of dry resin (g). M is the molecular weight of phenol.

The kinetic adsorption was performed at 303 K by analyzing the uptake of phenol at different time from an aqueous solution with initial concentration of 1000 mg/L. Each point on the resulting graph represents the data obtained from a separate bottle containing the adsorbent and the corresponding phenolic compound solution.

Dynamic Adsorption Assay

Column adsorption was conducted using a 10 cm 4.6 mm I.D. stainless-steel column packed with one of the three polymeric adsorbents and connected with a reciprocating pump (Beijing Analytical Instrument Plant) at 298 K. The 70.9 mmol/L phenolic compound solution was passed through the column at a flow rate of 1 BV/h, where BV is the total volume of resin bed. The adsorption capacities (q_c) were calculated with Eq. (2):

$$q_c = V_2 \times (c_i - c_e) / V_3 \quad (2)$$

Where V_2 is the volume of solution through column (L), c_i is the initial concentration of solution (mmol/L), c_e is the average concentration of the effluent, and V_3 is the volume of polymeric adsorbent in column (mL).

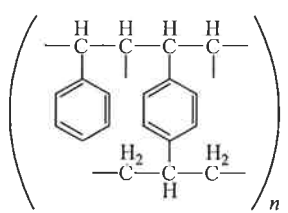
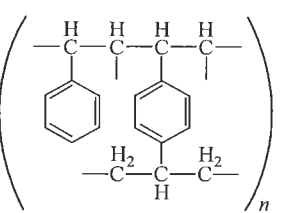
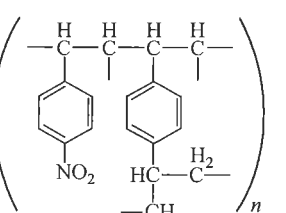
Analytical Methods

The solution concentrations were determined using a high performance liquid chromatograph (HPLC), which was connected to Waters 600 controller, Waters 600 pump and Waters 2487 Dual Absorbance UV detector at 275 nm (Waters, USA). The mobile phase was 0.1% $\text{KH}_2\text{PO}_4\text{:H}_2\text{O}$:methanol = 70:30 (V/V), and the flow rate was $1 \text{ mL} \cdot \text{min}^{-1}$.

RESULTS AND DISCUSSION**Characterization of JN-01 Polymeric Adsorbent**

Some characteristics of the three resins Amberlite XAD-4, NDA-1800 and JN-01 are listed in Table 2, and JN-01 has the biggest surface area and micropore area. IR spectra of resins before and after modification by nitro functional groups are shown in Fig. 1. The strong new bands at 1523 and 1427 cm^{-1} indicate the formation of $-\text{NO}_2$ groups on the surface of the resin JN-01 after the reaction. There is no significant change in morphology after nitro modification (Fig. 2). The elemental analysis showed that the nitrogen content of resin increased from 0 to 1.6% after the reaction (Table 3), and also indicated that the nitro groups had been anchored onto the resin NDA-1800 by the reactions.

Table 2. Typical properties of the polymeric resins

	XAD-4	1800	JN-01
Polarity	Nonpolar	Nonpolar	Polar
BET surface area (m^2/g)	880.14	870.02	920.46
Micropore area (m^2/g)	3.26	78.80	95.94
Average pore diameter (nm)	7.0	7.1	7.4
BJH desorption average pore diameter (nm)	5.8	9.7	10.9
Color	White	White	Yellow
Chemical structure			

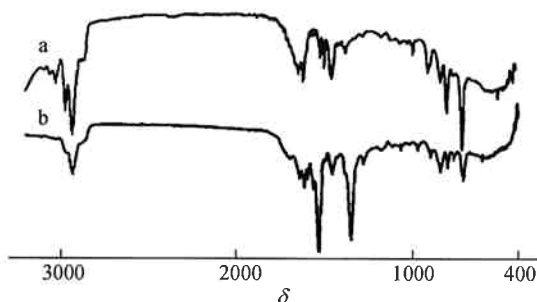


Fig. 1 IR spectra of NDA-1800 (a) and IR spectra of JN-01 (b)

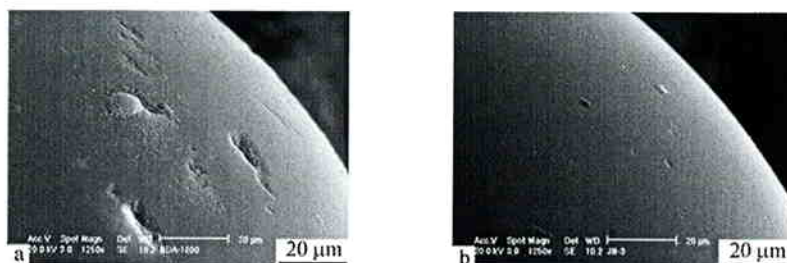


Fig. 2 Scanning electron microscopy (SEM $\times 1250$) analysis of two resins (a) NDA-1800 and (b) JN-01

Table 3. E.A Results

Adsorbent	C	H	N	S
XAD-4	89.78	9.76	0	0
NDA-1800	89.28	8.46	0	0
JN-01	87.14	7.78	1.6	0

Static Adsorption Assay

Equilibrium adsorption

The equilibrium adsorption isotherms of phenol, *p*-cresol and *p*-nitrophenol from water onto Amberlite XAD-4, NDA-1800 and JN-01 resins at 303 K are depicted in Figs. 3(a)–3(c), respectively. These all indicated that the JN-01 had excellent adsorption efficiencies. The isothermal equilibrium adsorption data for JN-01 were fitted and compared with those for XAD-4 and NDA-1800 by means of the rearranged Freundlich and Langmuir adsorption models^[14]:

$$\text{Langmuir equation} \quad 1/q_e = 1/Q_m + 1/bc_e \quad (3)$$

$$\text{Freundlich equation} \quad \ln q_e = \ln K_F + 1/n \ln c_e \quad (4)$$

Where q_e is the equilibrium adsorption capacity (mmol/g), c_e the equilibrium concentration (mmol/L), Q_m the maximum surface coverage (formation of a monolayer) of the adsorbent (mmol/g), b the adsorption energy constant (1/mmol), and K_F and n are characteristic constants. The constants evaluated by application of both isotherm equations are listed in Table 4.

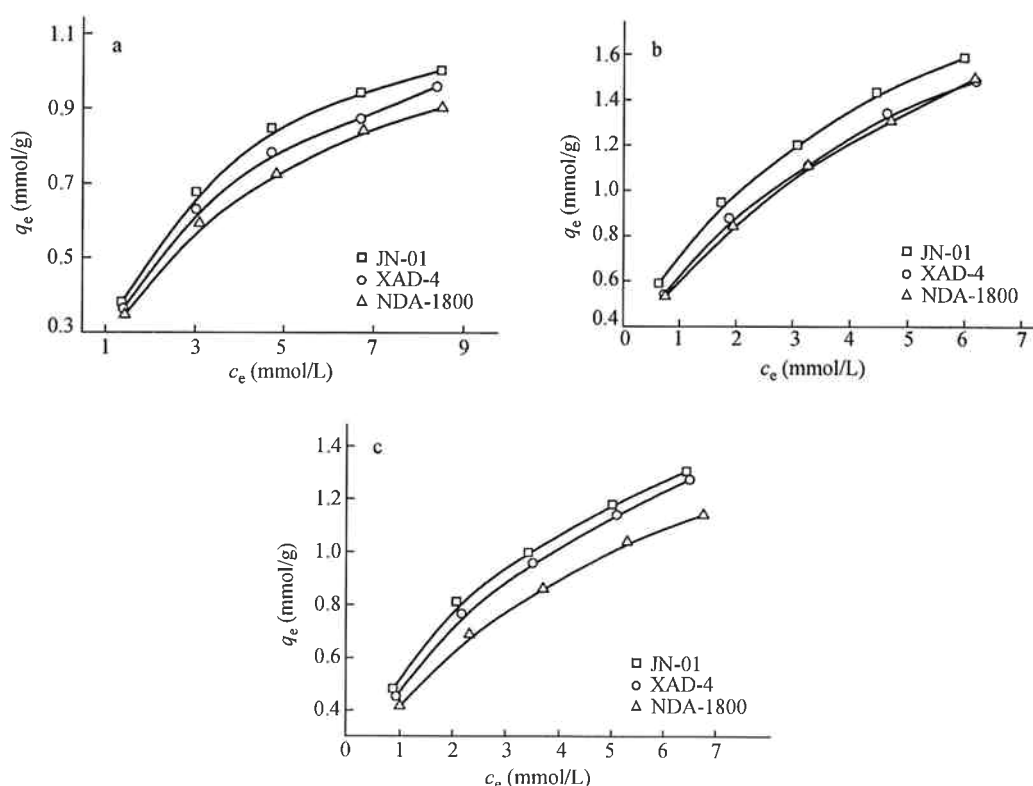


Fig. 3 The equilibrium adsorption isotherms of phenolic compounds on XAD-4, NDA-1800, JN-01
a) Phenol; b) *p*-Nitrophenol; c) *p*-Cresol

Table 4. Evaluated constants for the adsorption of phenol, *p*-cresol and *p*-nitrophenol from water onto JN-01, NDA-1800 and XAD-4 at 303 K as obtained from the Freundlich equation and Langmuir equation

Adsorbent	Adsorbate	Freundlich equation			Langmuir equation		
		K_F	n	R^2	Q_m	b	R^2
XAD-4	Phenol	0.321	1.853	0.988	1.363	0.347	0.999
	<i>p</i> -Cresol	0.619	2.168	0.999	1.603	1.097	0.983
	<i>p</i> -Nitrophenol	0.855	2.361	0.999	1.754	1.049	0.982
NDA-1800	Phenol	0.299	1.856	0.991	1.297	0.325	0.998
	<i>p</i> -Cresol	0.650	2.263	0.999	1.602	1.199	0.980
	<i>p</i> -Nitrophenol	0.823	2.322	0.999	1.743	0.996	0.990
JN-01	Phenol	0.344	2.052	0.986	1.466	0.395	0.999
	<i>p</i> -Cresol	0.715	2.333	0.999	1.665	1.410	0.981
	<i>p</i> -Nitrophenol	0.910	2.399	0.997	1.785	1.355	0.986

All equations are reliable because all the correlation factors (R) are larger than 0.99. In most cases, the specific surface area of adsorbent is a predominant factor affecting the adsorption capacity. The BET surface area of JN-01 is larger than that of NDA-1800 and XAD-4, which agrees with the Q_m of Langmuir equation. The values of K_F , a relative indicator of adsorption capacity in the Freundlich theory, indicate that the adsorption capacities of JN-01 are higher than those of XAD-4 and NDA-1800 for phenolic compounds. It is well known that the match in polarity between the adsorbent and the adsorbate could enhance the adsorption capacity. JN-01 possess polar groups after nitro modification, therefore it shows a better adsorption capacity to phenolic compounds. The exponent n is larger than 1 in all cases, indicating favorable adsorptions.

Isometric enthalpies for the adsorption of phenolic compounds

The isometric enthalpies of adsorption were calculated from the derivative Van't Hoff equation^[15]:

$$\ln(1/c_e) = \ln K_0 + (-\Delta H/RT) \quad (5)$$

where ΔH is the isosteric enthalpy of adsorption when q_e is a fixed value, R the gas constant, and c_e the equilibrium concentration of solute (mol/L) at the absolute temperature T (K). The value of c_e at different temperatures (283, 303, 323 K) was obtained from the Freundlich isotherm when q_e is equal to 0.5 mmol/g, 1.0 mmol/g and 1.5 mmol/g, respectively. The value of ΔH was calculated from the slope obtained by plotting $\ln c_e$ versus $1/T$. A summary of the calculated values for the enthalpy involved in the adsorption of the three phenolic compounds onto NDA-1800, XAD-4 and JN-01 is given in Table 5.

Table 5. Isosteric adsorption enthalpy (ΔH , kJ/mol) calculated at different adsorption capacities for NDA-1800, XAD-4 and JN-01 over the temperature range 283–323 K

Adsorbate	Adsorbent	$q_e = 0.5$ mmol/g	$q_e = 1.0$ mmol/g	$q_e = 1.5$ mmol/g
Phenol	NDA-1800	-19.8	-11.8	-8.1
	XAD-4	-20.6	-13.2	-8.9
	JN-01	-21.5	-12.4	-9.2
<i>p</i> -Cresol	NDA-1800	-21.7	-15.4	-11.3
	XAD-4	-22.4	-15.6	-11.2
	JN-01	-23.2	-16.4	-13.3
<i>p</i> -Nitrophenol	NDA-1800	-29.0	-18.8	-14.2
	XAD-4	-32.3	-19.6	-13.8
	JN-01	-34.7	-20.6	-14.7

It will be seen from Table 5 that values of the enthalpy changes (always negative) are indicative of an exothermic process, and physical adsorption predominates the adsorption process because of the magnitudes (< 40 kJ/mol). The absolute value of enthalpy changes (ΔH) presents the intensity of interaction forces between adsorbent and adsorbate, and it agrees with the equilibrium adsorption.

p-Nitrophenol shows different enthalpy change trends from its two analogues on the same resin, this indicates that the interaction force between *p*-nitrophenol and resins is stronger than phenol and *p*-cresol, which agrees with the constant K_F of Freundlich equation.

Adsorption kinetics studies

As given in Fig. 4, phenol adsorption on the three resins got equilibrium in short time, and JN-01 performed the best adsorption capacity. All the data were fitted by the first-order equation expressed as:

$$-\ln(1-F) = kt \quad (6)$$

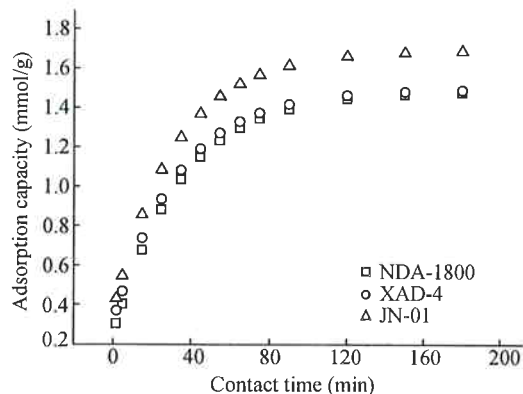


Fig. 4 Influence of contact time on phenol removal by (□) NDA-1800, (○) Amberlite XAD-4 and (Δ) JN-01

As shown in Fig. 5, the first-order equation is reliable because all the correlation factors (R) are larger than 0.99, so the adsorption process accords with the membrane diffusion model, and the aperture of JN-01 is large enough for phenol molecules to enter in rapidly.

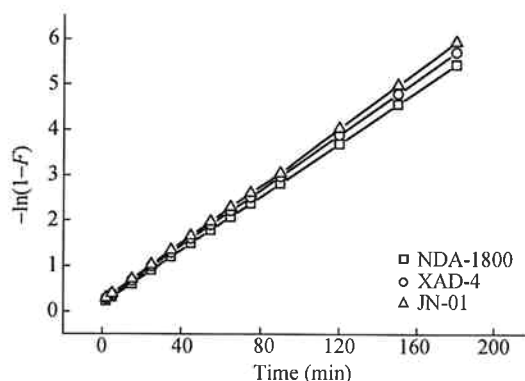


Fig. 5 Plots of $-\ln(1-F)$ versus contact time for the adsorption of *p*-nitrophenol by (□) NDA-1800, (○) Amberlite XAD-4 and (Δ) JN-01

Experimental conditions: initial *p*-nitrophenol conc. 1000 mg/L, Temp. 303 K;

The following equations describe the linear plots: for JN-01 $y = 0.0317x + 0.231$ ($R^2 = 0.999$); for XAD-4, $y = 0.0305x + 0.224$ ($R^2 = 0.998$); and for NDA-1800, $y = 0.0293x + 0.171$ ($R^2 = 0.996$)

In the frontier orbital theory^[16], the adsorption is essentially an electric charge transport process between electron donor and acceptor, the smaller disparities of the frontier orbital level (ΔE) between adsorbate and adsorbent, the stronger complexation formed. The LUMO and HOMO of phenol and adsorbents could be calculated by Chem3D Ultra and shown in Table 6 and Table 7, nitro functions made JN-01 have the lower ΔE than NDA-1800 and XAD-4, so as to be more adsorptive to phenol.

Table 6. LUMO and HOMO of phenol

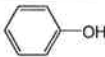
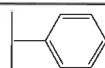
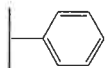
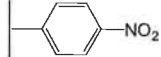
		Analogical structure	LUMO energy (eV)	HOMO energy (eV)
Adsorbate	Phenol		3.828	-12.347

Table 7. LUMO and HOMO of adsorbents

		Analogical Structure	LUMO energy (eV)	HOMO energy (eV)	Frontier orbital level with phenol ΔE (eV)
Adsorbents	XAD-4		0.533841	-9.35548	12.881
	NDA-1800		0.533841	-9.35548	12.881
	JN-01		-1.42538	-10.1455	10.921

Dynamic Column Adsorption

There are many factors affecting the column adsorption effects, such as flow velocity, temperature and I.D. of column. As shown in Fig. 6, under the same conditions, JN-01 shows the best adsorption capacity of phenol which agrees with the static adsorption tests, so it promises wide use in phenol wastewater treatment in the future.

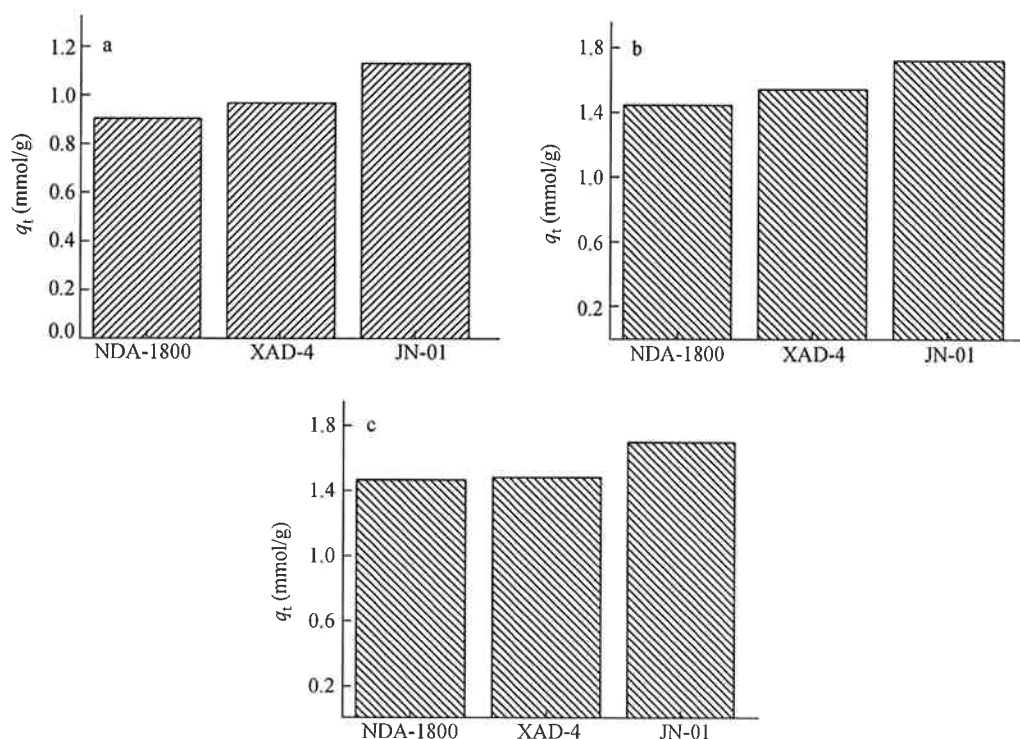


Fig. 6 Equilibrium adsorption capacities at 303 K exhibited towards (a) phenol, (b) *p*-cresol and (c) *p*-nitrophenol by NDA-1800, XAD-4 and JN-01

CONCLUSIONS

The following conclusions can be drawn from the conducted studies: (1) A new adsorbent (JN-01) was prepared from NDA-1800 modified by nitro functions. It can be used directly without a wetting process for its higher polarity and hydrophilicity. (2) All the isotherm data for the resins XAD-4, NDA-1800 and JN-01 in adsorption of phenolic, *p*-cresol and *p*-nitrophenol could be well fitted by the Langmuir and Freundlich equations, and the equilibrium adsorption capacities of phenolic compounds on JN-01 were obviously higher than those on XAD-4 and NDA-1800, such advantages were attributed to its high hydrophilicity, higher surface area and polarity due to the nitro group modification. (3) Batch kinetic studies indicated that the adsorption of phenol on the three resins could be fitted by the membrane diffusion model. Moreover, the adsorption of phenol on JN-01 approaches equilibrium rapidly, such property is also credited to high polarity and hydrophilicity. Nitro functions also result in the lower ΔE with phenol for JN-01, so it is more adsorptive to phenol. (4) Dynamic column adsorption also demonstrated the advantages of JN-01 in adsorbing phenolic compounds. For the low cost, high performance and synthetic simplicity of JN-01, it can be widely used in treatments of wastewater and resources with phenolic compounds.

REGERENCES

- 1 Ramos, A.F., Gómez, M.A., Hontoria, E. and González-López, J., J. Hazard. Mater., 2007, 142(1-2): 175
- 2 Kobayashi, F., Daidai, M., Suzuki, N. and Nakamura, Y., Int. Biodeterior. & Biodegrad., 2007, 59(3): 252
- 3 Sano, N., Yamamoto, T. and Yamamoto, D., Chem. Eng. Process., 2007, 46(6): 513
- 4 Otero, M., Zabkova, M. and Rodrigues, A.E., Water Res., 2005, 39(15): 3467
- 5 Lin, S.H. and Wan, C.S., J. Hazard. Mater., 2002, 90(2): 205

- 6 Oh, C.G., Ahn, J.H. and Ihm, S.K., *Reacti. Funct. Polym.*, 2003, 57(2-3): 103
- 7 Hosseini, S.N., Borghei, S.M., Vossoughi, M. and Taghavinia, N., *Appl. Catal., B: Environmental*, 2007, 74(1-2): 53
- 8 Kujawski, W., Warszawski, A. and Ratajczak, W., *Sep. Purif. Technol.*, 2004, 40(2): 123
- 9 Cavaco, S.A., Fernandes, S., Quina, M.M. and Ferreira, L.M., *J. Hazard. Mater.*, 2007, 144(3): 634
- 10 Vázquez, I., Rodríguez-Iglesias, J., Marañón, E., Castrillón, L. and Álvarez, M., *J. Hazard. Mater.*, 2007, 147(1-2): 395
- 11 Li, A.M., Zhang, Q.X. and Zhang, G.C., *Chemosphere*, 2002, 47(9): 981
- 12 Li, A.M., Zhang, Q.X., Chen, J.L. and Fei, Z.H., *React. Funct. Polym.*, 2001, 49(3): 225
- 13 Jiang, Z.M., Li, A.M., Cai, J.G., Wang, C., and Zhang, Q.X., *J. Environ. Sci.*, 2007, 19(2): 135
- 14 Slejko, F.L., "Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application", Marcel Dekker, New York, 1985, p.13
- 15 García-Delgado, R.A., Cotouelo-Minguez, L.M. and Rodríguez, J.J., *Sep. Sci. Technol.*, 1992, 27(7): 975
- 16 Mattson, J.S. and Mark, H.B., Jr., *J. Colloid Interface Sci.*, 1969, 31(1): 131