

# Preparation of an aminated macroreticular resin adsorbent and its adsorption of *p*-nitrophenol from water

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## Abstract

A chloromethylated styrene–divinylbenzene copolymer was post-cross-linked through Friedel–Crafts reaction to get a macroreticular resin adsorbent NA-01, and then chemically modified by dimethylamine to obtain an aminated adsorbent NA-01A. Batch adsorption runs of *p*-nitrophenol from aqueous solution onto adsorbent NA-01A were conducted to evaluate the effect of amino group on adsorption. The adsorption capacity of *p*-nitrophenol on NA-01A increased noticeably by comparison with the mother adsorbent. A linear relationship was observed between the adsorption capacity of NA-01A caused by amination and the equilibrium concentration of *p*-nitrophenol in aqueous solution, which can be reasonably elucidated by a modified isotherm equation based on the Freundlich model. The breakthrough curves on both adsorbents were experimentally determined and also predicted by the mathematic model based on the non-linear wave propagation theory and the corresponding isotherm model. The model based on the Freundlich model gave a good prediction of the breakthrough curve on NA-01, but a deviation occurred for NA-01A when  $C/C_0$  less than 0.3. However, another model based on the modified isotherm equation provided a better prediction for the breakthrough curves on NA-01A.

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**Keywords:** Macroreticular resin adsorbent; Amination; *p*-Nitrophenol; Modified isotherm model; Breakthrough curve

## 1. Introduction

Phenolic compounds are commonly encountered organic contaminants in environmental systems [1]. Adsorption by activated carbon has been widely used to treat wastewater containing phenolic compounds [2–4], however, how to readily regenerate the spent activated carbon for repeated use is 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 [5–8]. Since the invention of the hyper-cross-linked polymeric adsorbent by Davankov and Tsyurupa [9–10], 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. In order to obtain higher adsorption capacity or

better selectivity of the target pollutants, chemical modification of the resin adsorbent by introducing functional group onto the polymeric matrix was taken as a potential path, such as acetyl, *o*-carboxybenzoyl, benzoyl, and hydroxymethyl functionalities [11,12]. These functional groups introduced to the polymer matrix are able to modify the surface chemistry of the adsorbent allowing specific adsorbent–adsorbate interactions and then to improve adsorption behavior of organic compounds [13].

In the present study, a chloromethylated styrene–divinylbenzene copolymer was post-cross-linked through Friedel–Crafts reaction to obtain a macroreticular resin adsorbent NA-01, then followed with a chemical modification by dimethylamine to get an aminated adsorbent NA-01A. *p*-Nitrophenol was selected as a model phenolic compound for the study. Batch adsorption runs of *p*-nitrophenol from aqueous solution onto both adsorbents were conducted to evaluate the effect of amino group on adsorption. The breakthrough curves were also determined experimentally and predicted simultaneously by the mathematic model based on the non-linear wave propagation theory and the corresponding isotherm model.

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## 2. Experimental

### 2.1. Materials

*p*-Nitrophenol and dimethylamine in analytical grade were purchased from Shanghai Chemical Reagent Plant (Shanghai, China), and the chloromethylated styrene–divinylbenzene copolymer beads with the cross-linking density of 8% were provided kindly by Langfang Electrical Resin Co. Ltd. (Hebei Province, China).

### 2.2. Synthesis and amination of macroreticular resin adsorbent

#### 2.2.1. Synthesis of macroreticular resin adsorbent NA-01

About 40 g of the chloromethylated styrene–divinylbenzene copolymer beads was dried under vacuum at 328 K for 10 h and then swollen in 150 ml of nitrobenzene for 12 h. Two grams of zinc chloride was added gradually in the above system at 353 K under mechanical stirring. The mixture was further stirred at 383 K for 5 h and then cooled to 298 K to obtain the macroreticular resin adsorbent NA-01. The resin NA-01 was extracted with ethanol for 8 h and then dried under vacuum at 323 K for 10 h before use.

#### 2.2.2. Amination of adsorbent NA-01

Before amination about 20 g of resin NA-01 was swollen in 80 ml of 1,2-dichloroethane for 12 h. The dimethylamine solution (30%) was added gradually under an expected stirring speed at 303 K for 6 h. Afterwards, the residual dimethylamine was removed and the aminated resin adsorbent denoted NA-01A was washed with water until the density of the solution was near to 1. The adsorbent NA-01A was also followed the procedure for NA-01 before use.

#### 2.2.3. Characterization of resin adsorbents

Surface area and pore size distribution of both resins were determined using ASAP-2010 (Micromeritics Instrument Corporation, USA) and the amount of amino group on the resin matrix was measured as reported in the reference [14].

### 2.3. Batch adsorption runs of *p*-nitrophenol onto adsorbent NA-01 and NA-01A

#### 2.3.1. Adsorption isotherms

The accurately weighted NA-01 and NA-01A beads (about 0.150 g) were taken into several 250 ml sealed flasks, respectively, and a 100-ml aqueous solution containing different concentration of *p*-nitrophenol (ranging from 400 to 1400 mg/l) was introduced into each flask. The flasks were then shaken under 200 rpm at 298 K for 24 h to ensure equilibrium. The equilibrium concentration ( $C_e$ ) of *p*-nitrophenol was determined by UV-spectrophotometer (Helios Beta UV-VIS, UK) at 318 nm and the equilibrium adsorption capacity  $Q_e$  (mg/g) were calculated according to

$$Q_e = \frac{V(C_0 - C_e)}{w} \quad (1)$$

where  $V$  is the volume of solution (L);  $w$  is the weight of dry adsorbent (g);  $C_0$  is the initial concentration of *p*-nitrophenol in aqueous solution (mg/L).

#### 2.3.2. Breakthrough curves

Fix-bed adsorption runs were carried out in a glass column with inside diameter of 1.48 cm and length of 20 cm, which was packed with a water jacket to maintain an expected operation temperature. The adsorbents NA-01 and NA-01A (about 3.0 g) were filled respectively in the column and the solution containing 2000 mg/L of *p*-nitrophenol (pH 5.4) was fed to top of the column at 40 ml/h until the breakthrough curve completed. The operational parameters for fixed-bed adsorption onto both adsorbents are identical and listed as follows: empty bed velocity (EBV) = 40 ml/h; empty bed contact time (EBCT) = 7.5 min. The effluent samples were collected at intervals to determine the solute concentration by UV-spectrophotometer.

## 3. Results and discussion

### 3.1. Characterization of adsorbents

The characteristics of adsorbent NA-01 and NA-01A were listed in Table 1. The BET surface area and micropore volume of adsorbent NA-01A increased a little only by comparison with NA-01 [15]. The presence of the amino group on adsorbent NA-01A was further supported by the absorbance bands at 2772 and 2816  $\text{cm}^{-1}$  in the IR spectra (Nexus 870 FT-IR spectrometer, USA) in Fig. 1.

### 3.2. Adsorption isotherms

Adsorption isotherms of *p*-nitrophenol on NA-01 and NA-01A at 298 K were shown in Fig. 2. The adsorption isotherms were further correlated to the Freundlich equation:

$$Q_e = KC_e^{1/n} \quad (2)$$

where  $K$  is the Freundlich parameter;  $n$  is the Freundlich parameter related to the magnitude of adsorption driving force.

The data plotted according to the Freundlich isotherm are listed in Table 2. The results indicate that the Freundlich isotherm can represent the isotherm data of each adsorbent appropriately in the given concentration range.

After amination the adsorption capacity of *p*-nitrophenol on NA-01A increases noticeably by comparison with NA-01 (shown in Fig. 2). It is primarily attributed to the hydrogen-

Table 1  
Characteristics of adsorbent NA-01 and NA-01A

Property	NA-01	NA-01A
BET surface area ( $\text{m}^2/\text{g}$ )	787	810
Micropore area ( $\text{m}^2/\text{g}$ )	422	462
Micropore volume ( $\text{cm}^3/\text{g}$ )	0.19	0.21
Amino group (mmol/g)	0	1.1
Average pore diameter (nm)	3.8	4.2
Colour	Brown	Brown

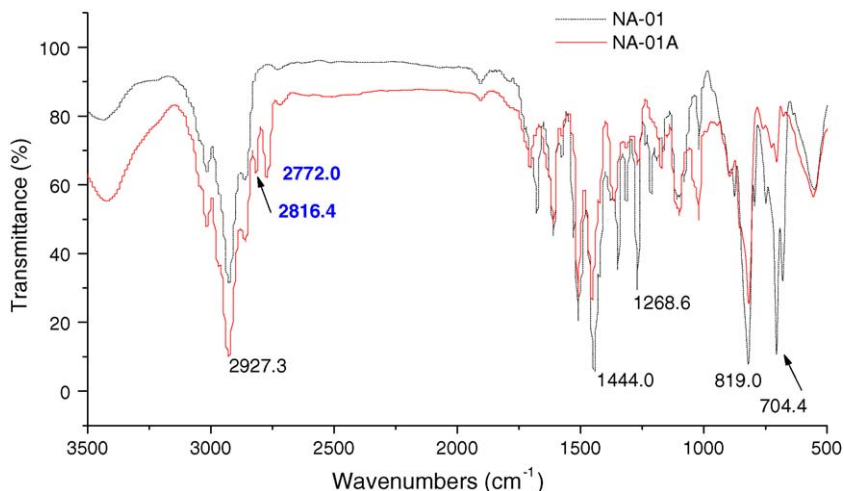
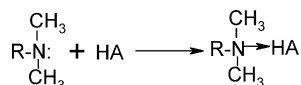


Fig. 1. IR spectra of adsorbent NA-01 and NA-01A.

bonding interaction between *p*-nitrophenol and the amino group introduced onto the polymeric matrix. The schematic representation of the specific interaction can be listed as follows [16]:



where *R* stands for the polymeric backbone and HA represents *p*-nitrophenol.

In the previous study [16], the amino group on a polymeric adsorbent was always regarded as a solid-phase extraction reagent when used for adsorption of aromatic acids from aqueous solution, just like a liquid amine compounds when used for extraction of aromatic acids from aqueous solution. There-

fore, the solid-phase extraction mechanism was always adopted to elucidate the effect of amino group on adsorption. Here we define the margin of the equilibrium adsorption capacity of both adsorbents,  $Q_A$ , as the ideal capacity caused by amino group. From the  $Q_A$  versus  $C_e$  curve presented in Fig. 3, a linear relationship between  $Q_A$  and  $C_e$  was observed with the correlation coefficient of 0.99. Note that a constant exists instead of zero in Fig. 3, which may be caused partly by the variation of micropore region due to amination of the adsorbent and needs further study. Accordingly, the isotherm equation for NA-01A can also be modified as  $Q_e = 54.3C_e^{0.29} + 0.012C_e + 25.9$ .

### 3.3. Dynamic breakthrough curves

In order to properly evaluate the fix-bed adsorption process, the breakthrough curves should be determined experimentally or by mathematic models. At present various mass-transfer models were found to predict the fixed bed dynamics [17–21], among which the mathematic model based on non-linear wave propagation theory was used widely as follows [22]:

$$t = t_{1/2} + \frac{\rho q_0}{\epsilon k_1 \alpha c_0} \int_{c_0/2}^c \frac{1}{c - g(q_0 c / c_0)} dc \quad (3)$$

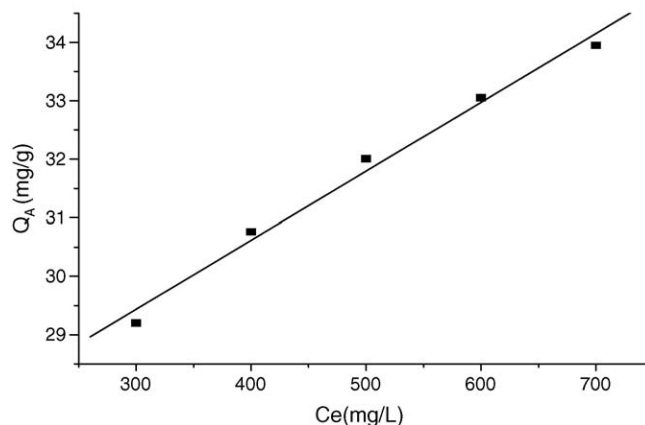


Fig. 3. Correlation of  $Q_A$  and equilibrium concentration of *p*-nitrophenol in aqueous solution ( $C_e$ ).

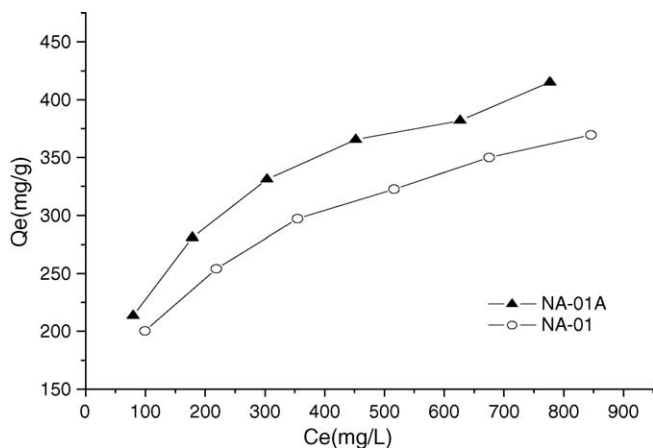


Fig. 2. Adsorption isotherms of *p*-nitrophenol on NA-01 and NA-01A at 298 K (solution pH is about 5.3–5.6 dependent upon the initial solute concentration).

Table 2  
Freundlich isotherm parameters for adsorption of *p*-nitrophenol on adsorbent NA-01 and NA-01A

Adsorbent	<i>K</i>	<i>n</i>	<i>R</i> <sup>2</sup>
NA-01	54.3	3.45	0.990
NA-01A	63.4	3.57	0.998

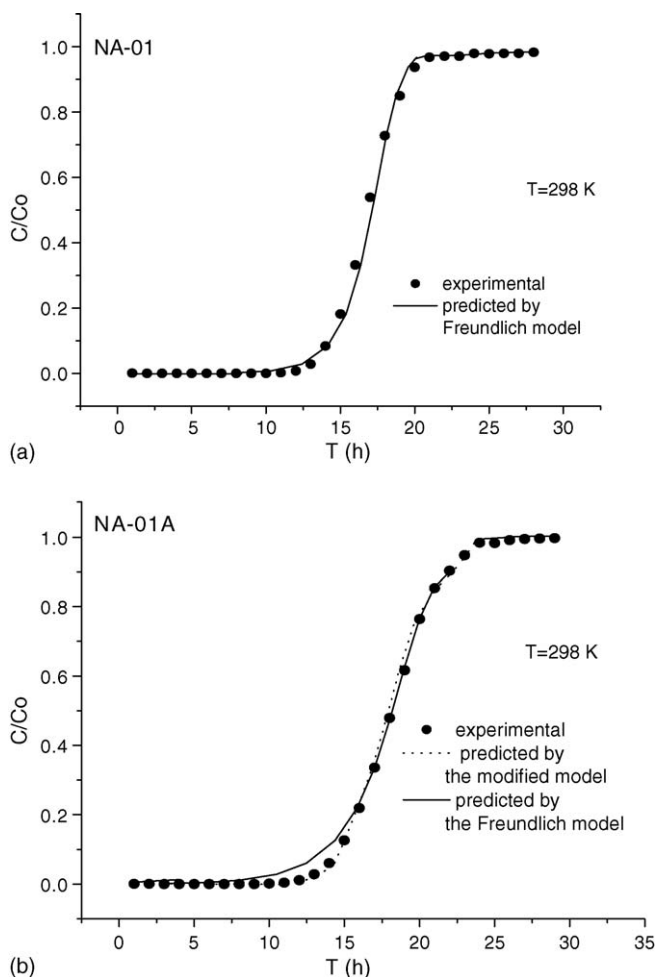


Fig. 4. Experimental and predicted breakthrough curve of *p*-nitrophenol on adsorbent NA-01 and NA-01A.

where  $t$  is the adsorption time (h);  $t_{1/2}$  is the time when the effluent adsorbate concentration reaches half of the feed concentration (h);  $K_1$  is the Langmuir model parameter ( $\text{m}^3/\text{mol}$ );  $\varepsilon$  is void fraction of bed;  $\alpha$  is mass-transfer area per unit volume of the bed ( $1/\text{m}$ );  $\rho$  is resin bed density ( $\text{kg}/\text{m}^3$ );  $g(x)$  is the inverse function of the corresponding isotherm;  $C$  is *p*-nitrophenol concentration in the mobile phase ( $\text{mg}/\text{L}$ );  $q_0$  is equilibrium concentration in the stationary phase ( $\text{mg}/\text{g}$ ).

Combining Eqs. (2) and (3) leads to:

$$t = t_{1/2} + \frac{\rho q_0}{\varepsilon k_1 \alpha c_0} \left[ \ln 2x - \frac{1}{n-1} \ln \frac{1-x^{n-1}}{1-(2)^{1-n}} \right] \quad (4)$$

where  $x$  is the normalized effluent pollutant concentration, defined as  $x = C/C_0$ .

The value of  $t_{1/2}$  and  $\rho q_0/\varepsilon k_1 \alpha c_0$  can be determined from the intercept and slope of  $[\ln 2x - (1/(n-1)) \ln(1-x^{n-1}/1-2^{1-n})]$  versus  $t$  curve.

The experimental and predicted breakthrough curves of NA-01 and NA-01A were depicted in Fig. 4(a and b). The model based on the Freundlich isotherm gave a good fit to breakthrough curve on NA-01, but a deviation was observed for NA-01A when  $C/C_0$  less than 0.3. However, when the modified isotherm equation for NA-01A,  $Q_e = 54.3C_e^{0.29} + 0.012C_e + 25.9$ , was

combined into Eq. (4) and with the help of a mathematic software LabView 7.0, a better prediction of the breakthrough curve on NA-01A was observed (in Fig. 4b), which might be an indirect evidence for solid-phase extraction when adsorption of *p*-nitrophenol onto NA-01A.

#### 4. Conclusions

Adsorption of *p*-nitrophenol from water was enhanced after amination of a polymeric adsorbent NA-01. A linear relationship was observed between the adsorption capacity due to amination and the equilibrium solute concentration in aqueous solution, which resulted in a modified isotherm developed from the Freundlich model. The breakthrough curves on adsorbent NA-01 and NA-01A were experimentally determined and also predicted by the mathematic model based on the non-linear wave propagation theory and the corresponding isotherm model. The model based on the non-linear wave propagation theory and the Freundlich model gave a good fit for the breakthrough curve on NA-01A, but a deviation occurred for NA-01 when  $C/C_0$  less than 0.3. However, another model based on the modified isotherm model seemed to provide a better fit for the breakthrough curve on NA-01A, which might be a new evidence of the solid-phase extraction mechanism as the role of amino group on adsorption of *p*-nitrophenol.

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