

EFFECT OF WEAK INTERACTIONS ON PHENOL ADSORPTION FROM AQUEOUS SOLUTIONS BY AMINATED POLYMERIC ADSORBENTS*

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Abstract Adsorption behaviors of phenol from aqueous solutions have been investigated in batch systems at 303 K and 318 K respectively, using hypercrosslinked polymeric adsorbent (CHA111), aminated hypercrosslinked polymeric adsorbents (NDA101, NDA103, NDA105) and weakly basic polymeric adsorbent (D301) with a view to studying the effect of hydrogen bonding and Van der Waals interactions between adsorbate and the adsorbent. All adsorption isotherms can be well fitted by Langmuir and Freundlich equations. Compared with D301 driven by hydrogen bonding interaction only and CHA111 driven by Van der Waals interaction only, phenol adsorption on aminated adsorbents driven by both hydrogen bonding and Van der Waals interactions were apparently different, *i.e.*, negative effect for NDA105, positive effect for NDA101 and synergistic effect for NDA103. In this synergistic action, some weak interactions would contribute more or less to the adsorption than they work individually.

Keywords: Polymeric adsorbent; Phenol; Adsorption behaviours; Negative effect; Positive effect; Synergistic effect.

INTRODUCTION

Phenol is an important starting material used in the chemical industry. Because it is toxic and readily soluble in water, the efficient removal of phenol from waste streams has become a significant environmental concern^[1–5]. In the past two decades, polymeric adsorbents have become a practical alternative to activated carbon for efficient removal of aromatic pollutants from wastewater^[6–9]. Extensive literatures are available regarding experimental and theoretical studies on phenol adsorption on synthetic adsorbents. Because the adsorption of adsorbates is usually attained by a single type of weak interactions such as Van der Waals interaction, hydrogen bonding interaction or electrostatic interaction, and the adsorption capability and selectivity is not satisfactory^[10–13]. Scientists have made much effort on the chemical modification of polymeric adsorbents and some of them have better adsorption capacities towards organic compounds. Although some mechanisms on the positive adsorption effect have been proposed^[14–17], little studies illustrated the negative, positive or synergistic effect by weak adsorption driving forces.

In this paper, in comparison with CHA111 and D301 without amino groups or micropore volume, respectively, aminated adsorbents NDA101, NDA103 and NDA105 were employed to mimic the multiple weak interactions on phenol adsorption from aqueous solutions^[18]. The present work was aimed at achieving a better qualitative and quantitative understanding on the interactions between phenol and adsorbents.

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EXPERIMENTAL

Materials

CHA111 and D301 as well as NDA101, NDA103 and NDA105^[11] (the newly aminated adsorbents by chemically modifying CHA111 with different pre-quantified dimethylamine) were supplied by Jiangsu N & G Environmental Technology Co. Ltd. (Jiangsu, China). Aqueous solutions of phenol were prepared by dissolving phenol in deionized water without further pH adjustment. Juang *et al.*^[7] have reported the surface area, cross-sectional distance, and pK_a value of phenol molecule to be 0.305 nm², 0.43 nm and 9.89, respectively.

Characterization of Polymeric Adsorbents

The specific surface area and the pore distribution of the polymeric adsorbents were determined in dry state with a Micromeritics ASAP 2010 M surface area measurement instrument (Micromeritics Instrument, Norcross, USA). The basic exchange capacity was measured by the titration method. Table 1 presents the characteristic properties of the test adsorbents.

Table 1. Characteristic properties of CHA111, NDA101, NDA103, NDA105 and D301

Property	D301	NDA105	NDA103	NDA101	CHA111
Structure	Weakly basic polystyrene	Aminated hypercrosslinked polystyrene	Aminated hypercrosslinked polystyrene	Aminated hypercrosslinked polystyrene	hypercrosslinked polystyrene
Polarity	Strong polar	Moderately polar	Moderately polar	Moderately polar	Non polar
BET surface area (m ² /g)	32	483	727	819	934
Micropore area (m ² /g)	4	261	394	463	561
Micropore volume (mL/g)	0.0005	0.118	0.179	0.29	0.253
Average pore diameter (nm)	16.6	1.5	1.3	1.2	1.2
Particle size (mm)	0.4–0.6	0.4–0.6	0.4–0.6	0.4–0.6	0.4–0.6
Tertiary amino group (mmol/g)	4.9	2.75	2.1	1.51	0
Colour	Yellow	Deep brown	Deep brown	Deep brown	Deep brown

Adsorption Isotherms

Batch adsorption runs were performed using the conventional bottle-point technique in 100 mL glass flasks at 303 K and 318 K. 0.050 g adsorbents were directly introduced into a 250 mL glass flask. Subsequently, 100 mL of an aqueous solution of phenol with an initial concentration ranging from 2 to 12 mmol/L was added into each flask. The flasks were then placed on a G 25 model incubator shaker with thermostat (New Brunswick Scientific Co. Inc.) and shaken under 150 r/min for 24 h, during which the adsorption is sufficient to attain equilibrium according to preliminary kinetics studies.

The solution concentrations were determined using a Waters HPLC (Waters, USA), which was connected to Waters 600 controller, Waters 600 pump and Waters 2487 Dual absorbance UV detector at 274 nm. Mobile phase was 0.2% KH₂PO₄ • H₂O: methanol = 30:70 (V/V) and flow rate was 1 mL/min.

RESULTS AND DISCUSSION

Equilibrium Adsorption

Adsorption isotherms for phenol on five adsorbents at (a) 303 K and (b) 318 K are shown in Fig. 1. The adsorption of aromatic compounds on polymeric adsorbents has been successfully described by Langmuir and Freundlich equations^[19–20].

$$\text{Langmuir equation} \quad Q_e = \frac{K_1 Q_m c_e}{1 + K_1 c_e} \quad (1)$$

Freundlich equation
$$Q_e = K_f c_e^{\frac{1}{n}} \quad (2)$$

where Q_e is the amount adsorbed at equilibrium (mmol/g), c_e is the equilibrium concentration in bulk fluid phase (mmol/L), Q_m is the maximum adsorption capacity (mmol/g), namely complete coverage of available adsorption sites, K_1 is the affinity constant, K_f is an indicator of adsorption capacity, and $1/n$ is related to the magnitude of the adsorption driving force and to the adsorbent site energy distribution. Generally, Freundlich isotherm is viewed as strictly empirical and the Langmuir isotherm as theoretically based, assuming the energetically homogeneous surface of adsorbents, no interaction between the adsorbed molecules, the identical mechanisms for adsorption, and a complete monolayer adsorption on the surface.

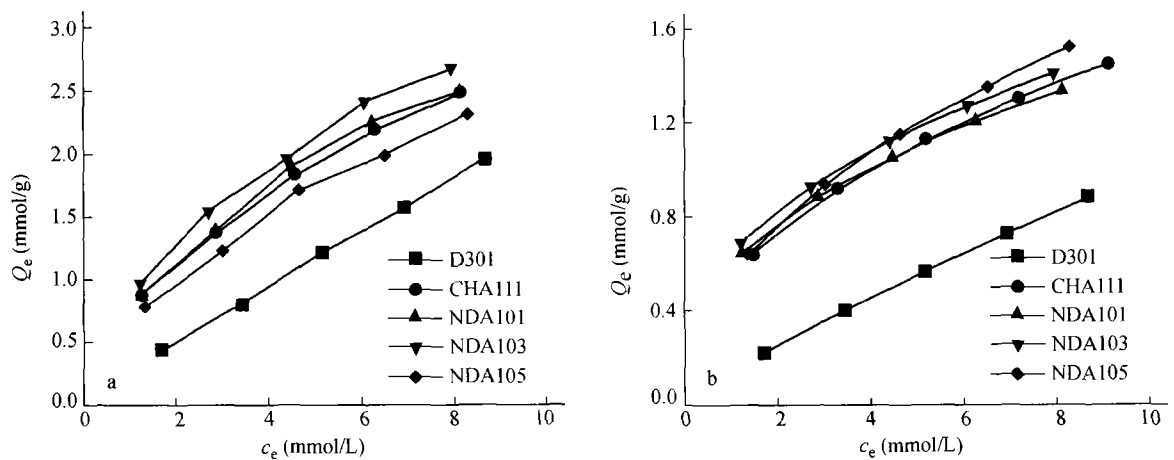


Fig. 1 Equilibrium adsorption isotherms of phenol on adsorbents CHA111, NDA101, NDA103, NDA105 and D301 at (a) 303 K and (b) 318 K

Table 2. Adsorption isotherms of phenol on CHA111, NDA101, NDA103, NDA105 and D301

Adsorbent	Temp. (K)	Langmuir isotherm			Freundlich isotherm			Q_e (mmol/g) ^a
		K_1	Q_m (mmol/g)	R^2	K_f	n	R^2	
CHA111	303	0.19	4.03	0.99	0.77	1.78	1.00	2.49
	318	0.30	1.92	0.97	0.54	2.26	0.98	1.36
NDA101	303	0.20	4.00	1.00	0.80	1.81	0.99	2.52
	318	0.45	1.65	0.97	0.59	2.57	1.00	1.33
NDA103	303	0.22	4.14	0.99	0.89	1.86	1.00	2.73
	318	0.48	1.72	0.97	0.64	2.61	0.99	1.41
NDA105	303	0.16	4.05	0.99	0.66	1.67	1.00	2.28
	318	0.28	2.11	0.98	0.56	2.10	0.99	1.49
D301	303	0.01	21.95	1.00	0.26	1.06	1.00	1.81
	318	0.03	4.00	0.98	0.14	1.17	0.98	0.82

^aCalculated by Freundlich equation when $c_e = 8.0$ mmol/L

The results of the nonlinear least-squares regression with the Langmuir and Freundlich equations are presented in Table 2. It can be seen that both Langmuir and Freundlich isotherm equations fit the adsorption data well since all the correlative factors R^2 are larger than 0.97^[20]. However, Freundlich isotherm was slightly better in this respect than Langmuir isotherm. Therefore, the parameter K_f was selected and compared in this paper as a relative indicator of the adsorption capacity. At the same residual concentration (c_e) of 8.0 mmol/L, the uptakes (Q_e) calculated by Freundlich equation at 303 K on NDA101 and NDA103 for phenol are larger by about

40%–50% as compared with D301 and larger by about 2%–10% as compared with CHA111; additionally, the adsorption capacity on NDA105 is larger by about 26% as compared with D301 but lower by about 8% as compared with CHA111. In addition, n of NDA103 is the largest, suggesting that NDA103 provides an easiest access for the phenol molecule into its pores to interact with the active sites in comparison with other four adsorbents^[9].

Adsorption of Phenol on Polymeric Adsorbents

We assume that for a certain solute and solvent the adsorption capacity is dominated by the properties of the adsorbent. The hydrophobic surface of the test polymeric adsorbents could provide Van der Waals interaction sites, while the tertiary amino groups could provide proton acceptors for hydrogen bonding interaction. Both of which could affect the adsorption capacity and attractive force of the adsorbent. According to Table 1, as D301 contains fewer Van der Waals interaction sites (BET surface area 32 m²/g and micropore volume 0.0005 ml/g), the hydrogen bonding interaction, if any, may be the only interaction between the amino groups on the matrix of D301 and the hydroxyl groups of phenol molecules. On the contrary, there is no amino group on the matrix of CHA111, we could assume that phenol adsorption on CHA111 is only driven by π - π interaction between the aromatic ring of phenol molecules and the hydrophobic matrix of CHA111. Due to the presence of both amino groups and micropore volume, the driving forces of the aminated adsorbents NDA101, NDA103 and NDA105 are expected to include not only hydrogen bonding interaction but also Van der Waals interaction.

Negative/positive Effect on Phenol Adsorption on Aminated Polymeric Adsorbents

As seen in Table 2, the adsorption capacities (K_f) of the five adsorbents could be arranged in the following order: NDA103 > NDA101 > CHA111 > NDA105 > D301. Pan *et al.*^[11] suggested that by adding little amount of pre-quantified dimethylamine, amination reaction of NDA101 occurs mainly in the macroporous region and NDA101 specially obtains some amino groups as well as enhanced micropore volume. However, amination reaction of NDA103 and NDA105 occurs in the macroporous region as well as in microporous region with increased amount of pre-quantified dimethylamine, which makes NDA103 and NDA105 to obtain some amino groups but lose some micropore volume (cf. Table 1). Accordingly, the adsorption capacity of NDA101 is obviously larger than that of CHA111 and D301. Because the augment of adsorption contribution from increasing hydrogen bonding interaction sites could counteract the loss of adsorption contribution from decreasing Van der Waals interaction sites, the adsorption capacity of NDA103 is higher than CHA111 and D301. On the contrary, the adsorption capacity of NDA105 is higher than D301 but lower than CHA111. Hence, NDA101 and NDA103 have a positive effect on phenol adsorption, while NDA105 shows a negative effect.

Synergistic Effect on Phenol Adsorption Enhancement on Aminated Polymeric Adsorbents

The above results indicate that NDA101 and NDA103 have an adsorption-enhancement effect on phenol adsorption. However, whether Van der Waals interaction and hydrogen bonding interaction occur simultaneously with the same phenol molecule (chelating effect) or whether there is any synergistic effect between them is still unclear. If the two interactions occur synergistically, the total adsorption capacity should be larger than the sum of the two interactions that occur individually.

In order to quantify the synergistic adsorption, the adsorption capacity, indicated by K_f of Freundlich equation, should be normalized to the amount of micropore volume and amino groups of adsorbents respectively. In addition, if it was assumed^[3, 21–22] that (1) the adsorption contribution of Van der Waals interaction is linearly correlated with the magnitude of micropore volume normalized by that of CHA111, and the adsorption contribution of hydrogen bonding interaction is linearly correlated with the magnitude of amino groups normalized by that of D301; (2) Van der Waals interaction and hydrogen bonding interaction act individually without any competitive or synergistic effect during the phenol adsorption on NDA101 and NDA103, the adsorption capacity of them could be decomposed by the adsorption contributions of the two interactions as the Eq. (3):

$$K_f' = K_{fH}' + K_{fh}' = V \times \alpha \quad G \times \beta \quad (3)$$

where K_f' refers to the normalized adsorption capacity of NDA101 and NDA103 for phenol without any competitive or synergistic effect, K_{fH}' and K_{fV}' present the corresponding contributions of Van der Waals and hydrogen bonding interaction, respectively, α and β indicate the corresponding contribution coefficients of Van der Waals interaction per unit micropore volume normalized by CHA111 and hydrogen bonding interaction per unit molar normalized by D301, respectively, V and G are the magnitudes of micropore volume and amino groups of NDA101 and NDA103, respectively. Due to the value of experimental adsorption capacity K_f in Tables 2 and 3 is larger than the normalized adsorption capacity K_f' in Table 3, the experimental adsorption capacity of phenol on NDA103 is larger than the sum of Van der Waals interaction and hydrogen bonding interaction that occur individually, indicating that the two weak interactions occur simultaneously and synergistically. On the contrary, the smaller value of experimental adsorption capacity K_f than the normalized adsorption capacity K_f' indicates that Van der Waals interaction and hydrogen bonding interaction do not occur synergistically but positively during phenol adsorption on NDA101. The different performances of phenol adsorption are probably due to the different structures of NDA101 and NDA103. According to Polanyi-Dubinin theory^[22] phenol adsorption on microporous adsorbents mostly takes place in the microporous region. However, Pan *et al.*^[11] suggested that amino groups of NDA101 distributes mainly in the macroporous region. Therefore, Van der Waals interaction in the microporous region and hydrogen bonding interaction in the macroporous region could not act with the same phenol molecular and the synergistic effect hardly occurs on NDA101. On the contrary, hydrogen bonding interaction from amino groups of NDA103 in the microporous region together with Van der Waals interaction provides the synergistic effect on phenol adsorption from aqueous solutions. The results are identical with the order of the Freundlich parameter n in Table 2: NDA103 > NDA101 > CHA111 > NDA105 > D301. Finally, the synergistic effect of Van der Waals and hydrogen bonding interaction on phenol adsorption of NDA101 and NDA103 might be schematically represented in Fig. 2(b)^[18].

Table 3. Synergistic effect for phenol adsorption capacities on NDA101 and NDA103

Adsorbent	Temp.(K)	K_{fH}'	K_{fV}'	K_f'	K_f
NDA101	303	0.08	0.89	0.96	0.80
	318	0.04	0.62	0.67	0.59
NDA103	303	0.11	0.55	0.66	0.89
	318	0.06	0.38	0.44	0.64

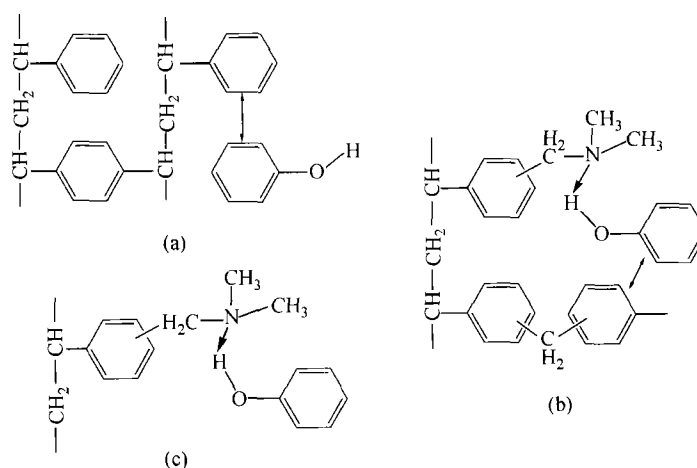


Fig. 2 Schematic presentation of the chemical structure of adsorbents and the interactions between adsorbents and phenol
a) CHA111; b) NDA103; c) D301

CONCLUSIONS

The isotherm data for phenol adsorption on hypercrosslinked polymeric adsorbent (CHA111), aminated hypercrosslinked polymeric adsorbents (NDA101, NDA103, NDA105) and weakly basic polymeric adsorbent (D301) could be fitted well by Langmuir and Freundlich equations. The adsorption driving forces on these aminated adsorbents mainly include hydrogen bonding interaction and Van der Waals interaction. In comparison with CHA111 and D301, NDA101 and NDA103 have a positive effect on phenol adsorption, but NDA105 has a negative effect. Furthermore, because the experimental adsorption capacity is much larger than the sum of Van der Waals and hydrogen bonding interactions that occur individually, the two weak interactions might occur simultaneously and synergistically on the phenol adsorption process for NDA103.

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