



Adsorption behaviors of a novel carbonyl and hydroxyl groups modified hyper-cross-linked poly(styrene-co-divinylbenzene) resin for β -naphthol from aqueous solution

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ABSTRACT

A series of novel hyper-cross-linked resins were synthesized from macroporous cross-linked chloromethylated poly(styrene-co-divinylbenzene) by adding different dosage of hydroquinone in Friedel-Crafts reaction. The results of the pore structures revealed that the prepared resins possessed micropores, mesopores and macropores, and the chloromethyl groups and the uploaded hydroquinone were partly oxidized according to the results of Fourier-transformed infrared ray spectra. Among these hydroquinone modified resins, HJ-Y06 resin held the largest adsorption capacity for β -naphthol, and its adsorption capacity was comparable with XAD-4 while much larger than X-5. The adsorption kinetics could be characterized by pseudo-second-order rate equation and intra-particle diffusion model was the rate-limiting step at the initial process. The adsorption was favorable at solution pH lower than 6.5. The adsorption isotherms could be fitted by Langmuir model and the adsorption was an endothermic process. Hydrogen bonding between formaldehyde carbonyl and quinone carbonyl groups on HJ-Y06 and phenolic hydroxyl groups of β -naphthol was the main driving force for the adsorption.

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1. Introduction

Polycyclic aromatic compounds are specifically chemical species with 2–6 fused benzene rings and they are toxic hazardous pollutants of highly potent carcinogens [1]. β -Naphthol, for instance, is a favorable raw and processed material to prepare medicines, azo dyes and synthetic rubber antioxidants. It is appreciably hydrophobic with high boiling point (396 K), melting point (558 K) and electrochemical stability, hence it can exist and be accumulated in soils or water for a long time. The main sources of β -naphthol in surface water are atmospheric deposition, runoff from contaminated soils and deposition from sewage discharges. β -Naphthol can be applied as bactericide at a very low concentration. However, its corrosive action is much higher than phenol, its existence in water will induce dermatitis, permanent pigmentation and even cancer, and it also has bad effects on blood circulation and kidney [2]. Therefore, β -naphthol has attracted increasing attentions recently in environmental field and its efficient removal from water is a very pressing problem.

Adsorption by adsorbents is proven to a universal physical approach to effectively removing organic pollutants from aquatic

environment [3–6]. Activated carbons present outstanding adsorption capability for organic pollutants due to their high specific surface area, predominant micropores and surface chemical structures [7]. Nevertheless, how to effectively regenerate the used activated carbons is a boring problem. Synthetic polymeric adsorbents, as excellent substitutes for activated carbons, have drawn many attentions in recent years because of their possible diverse surface chemical structures and feasible regeneration properties [8–11].

In the 1970s, Davankov synthesized a type of super-excellent hyper-cross-linked poly(styrene-co-divinylbenzene) (PS) using bi-functional cross-linking agents and Friedel-Crafts catalysts from linear or low cross-linked PS [12,13]. By this method, a lot of rigid methylene cross-linked bridges are formed between the polymeric chains, and hence the polymeric skeleton is consumedly reinforced. If low cross-linked chloromethylated PS is used as reacting substance, some other reagents like hydroquinone are added in the reaction, and at least two possible reactions will arise. One is Friedel-Crafts reaction of the low cross-linked chloromethylated PS itself, the other is that of the chloromethylated PS with hydroquinone. The respective extent of the two reactions will determine the structures (surface chemical structure and pore structure) and adsorption behaviors of the obtained resin. To the best of our knowledge, there is no report focusing on synthesis and adsorption behaviors of hydroquinone modified hyper-cross-linked PS resin.

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This work aimed at preparation of a series of novel hyper-cross-linked PS resins from macroporous cross-linked chloromethylated PS by adding different dosage of hydroquinone in Friedel-Crafts reaction, their pore structures, surface chemical structures and adsorption capacities for β -naphthol were compared. Thereafter HJ-Y06 was selected as a polymeric adsorbent, β -naphthol was chosen as an adsorbate, and the adsorption behaviors of HJ-Y06 for β -naphthol were investigated in comparison with XAD-4 and X-5. Its adsorption kinetics and thermodynamics were conducted and adsorption mechanism was expounded by Fourier-transformed infrared ray (FT-IR) spectrum.

2. Experimental method

2.1. Materials

Macroporous cross-linked chloromethylated PS was purchased from Langfang Chemical Co. Ltd. (Hubei province, China), its cross-linking degree was 6%, chlorine content was 17.3%, specific surface area was $28 \text{ m}^2/\text{g}$, and average pore diameter was 25.2 nm. β -Naphthol applied as the adsorbate was an analytical reagent (molecular formula: $\text{C}_{10}\text{H}_7\text{OH}$, molecular weight: 144.2). Hydroquinone, anhydrous zinc chloride, sodium chloride and anhydrous ethanol were also analytical reagents and used in this study.

2.2. Synthesis of hyper-cross-linked resins

40 g of chloromethylated PS was swollen by 120 mL of nitrobenzene for 12 h at room temperature, and different dosage of hydroquinone (0%, 2%, 6%, 10% and 15% relative to chloromethylated PS, w/w) was dissolved by nitrobenzene and also added into the reaction flask. At a moderate stirring speed, 4 g of anhydrous zinc chloride was added at 323 K. After the added zinc chloride was completely dissolved, the reaction mixture was heated to 388 K within 1 h. The hyper-cross-linked PS resins tagged as the post-cross-linked resin, HJ-Y02, HJ-Y06, HJ-Y10 and HJ-Y15 were obtained after retaining at 388 K for 8 h.

2.3. Characterization of the resins

The specific surface area was determined by N_2 adsorption–desorption isotherms at 77 K using a Micromeritics Tristar 3000 surface area and porosity analyzer. Before measuring the N_2 adsorption–desorption isotherms, the polymeric sample was outgassed for 24 h with the temperature at 373 K. The FT-IR spectrum of the resin with vibrational frequencies in the range of $500\text{--}4000 \text{ cm}^{-1}$ was collected by KBr disks on a Nicolet 510P Fourier-transformed infrared instrument.

2.4. Adsorption kinetic curves

For measurement of time resolved uptake of β -naphthol on the resin, about 1.000 g of resin and 250 mL of β -naphthol solution (about 500 mg/L) were quickly introduced into a cone-shaped flask and continuously shaken at 299 K. 0.5 mL of solution was sampled as fast as possible at different time intervals and concentration of residual β -naphthol was determined until adsorption equilibrium was reached, the adsorption capacity at contact time t was calculated as [14]:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where q_t is the adsorption capacity at contact time t (mg/g), C_0 and C_t are the initial concentration of β -naphthol and that at contact time t (mg/L), V is the volume of the solution (L), and W is the mass of the resin (g).

2.5. Adsorption isotherms

In a cone-shaped flask with a stopper, about 0.100 g of resin was accurately weighed and mixed with 50 mL of β -naphthol solution. The initial concentrations of β -naphthol were set to be about 100–700 mg/L with 100 mg/L interval. Hydrochloric acid and sodium hydroxide were applied to adjust solution pH. The flasks were then shaken in a thermostatic oscillator (its agitation speed was 150 rpm) for about 24 h at a desired temperature (288, 299, 309, 319 and 328 K, variables ± 0.2 K) until adsorption equilibrium was reached, concentration of β -naphthol of the equilibrium solution was measured by UV spectrometry at a wavelength of 273.2 nm [15,16] and the adsorption capacity onto the resin was calculated based on the differences of concentrations of β -naphthol before and after the experiment as [14]:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentration of β -naphthol (mg/L), and q_e is the equilibrium adsorption capacity of β -naphthol on the resin (mg/g).

3. Results and discussion

3.1. Characterization of the resin

As can be seen in Fig. 1(a), the specific surface area of the prepared resin decreases sharply as adding hydroquinone in Friedel-Crafts reaction. This may be from the reasons as follows. Hydroquinone and zinc chloride will form a complex, decreasing the degree of Friedel-Crafts reaction. On the other hand, Friedel-Crafts reaction between chloromethylated PS and hydroquinone will restrain that of chloromethylated PS itself, making the specific surface area decreased. As compared the specific surface area of hydroquinone modified resins including HJ-Y02, HJ-Y06, HJ-Y10 and HJ-Y15, it firstly decreases and then increases with increment of dosage of hydroquinone. At first, hydroquinone forms a complex with zinc chloride, inducing Friedel-Crafts reaction of chloromethylated PS itself insufficient. After that, the added hydroquinone can be cross-linked on the resin, and form accessional cross-linked bridge on the resin, increasing the specific surface area appreciably.

Fig. 1(b) describes N_2 adsorption–desorption isotherms of the post-cross-linked resin, HJ-Y02, HJ-Y06, HJ-Y10 and HJ-Y15 resins. All of the adsorption isotherms seem close to type-II isotherm. At the initial part of the adsorption isotherm with a relative pressure below 0.05, the N_2 adsorption capacity increases sharply with increment of the relative pressure, proving that micropores are existent. The visible hysteresis loops of the N_2 desorption isotherms indicate that these resins contain mesopores. These analyses agree with the pore diameter distribution in Fig. 1(c). In particular, the N_2 adsorption capacity of the post-cross-linked resin is much larger than the corresponding ones of HJ-Y02, HJ-Y06, HJ-Y10 and HJ-Y15 at the same relative pressure, which may be resulted from the different polarity of the resins. The apparent pictures of the resins are shown in Fig. 1(d), the color of the resin is firstly light-colored and then darkened as adding hydroquinone in the reaction.

FT-IR spectrum is a useful tool to identify presence of certain functional groups on the resin because each unique absorption peak reveals the specific chemical bond [17]. As displayed in Fig. 1(e), two strong representative peaks of the CH_2Cl groups at 1265.1 and 669.2 cm^{-1} are weakened greatly after Friedel-Crafts reaction (FT-IR spectrum of chloromethylated PS is not shown), and some new transformations arises for the hydroquinone modified resins. Firstly, a moderate C=O stretching vibration appears

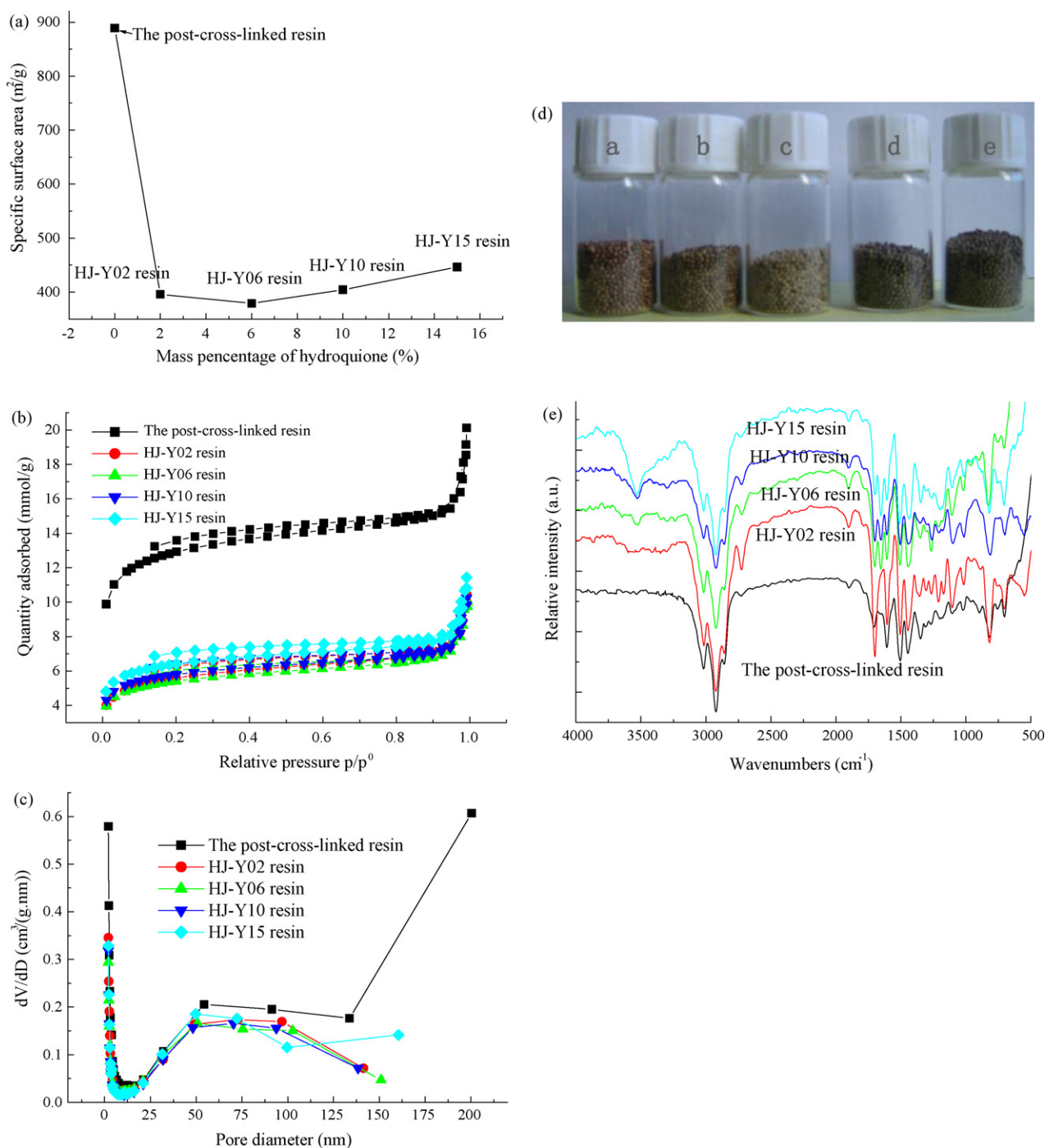


Fig. 1. Characterization of the post-cross-linked resin, HJ-Y02, HJ-Y06, HJ-Y10 and HJ-Y15: (a) specific surface area; (b) N₂ adsorption–desorption isotherms; (c) pore diameter distribution; (d) apparent pictures; (e) FT-IR spectra.

at 1701.2 cm⁻¹, and this vibration can be assigned to formaldehyde carbonyl groups due to oxidation of CH₂Cl groups [18]. Secondly, with increment of dosage of hydroquinone in Friedel-Crafts reaction, especially for HJ-Y10 and HJ-Y15, a weak absorption peak appears at 3530.5 cm⁻¹, and which is concerned with O-H stretching of hydroquinone. At last, with increasing of dosage of hydroquinone in Friedel-Crafts reaction, especially for HJ-Y06, HJ-Y10 and HJ-Y15, a moderate C=O stretching vibration appears at 1652.9 cm⁻¹, and this vibration is related to quinone carbonyl groups, implying that the uploaded hydroquinone on the resin is partly oxidized.

3.2. Comparison of adsorption capacity of β -naphthol onto different resins from aqueous solution

Adsorption capacities of β -naphthol onto hydroquinone modified resins including HJ-Y02, HJ-Y06, HJ-Y10 and HJ-Y15 are firstly compared from aqueous solution and the results are displayed in Fig. S1. The adsorption capacity of β -naphthol on HJ-Y06 is the largest among the four resins, and hence HJ-Y06 is employed as a specific polymeric adsorbent in the present study. Adsorption isotherms of β -naphthol onto HJ-Y06 are thereafter compared with the commercial resins XAD-4 and X-5. Note that XAD-4 and X-5 are

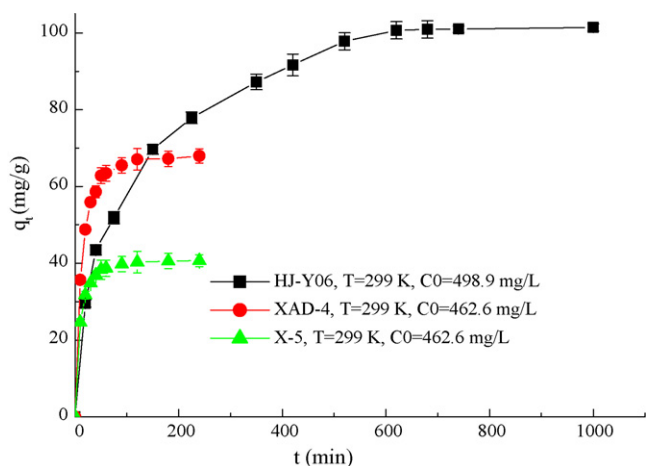


Fig. 2. Adsorption kinetic curves for the adsorption of β -naphthol onto HJ-Y06, XAD-4 and X-5 from aqueous solution (about 1.000 g of resin, 250 mL of β -naphthol solution, $T = 299$ K, 0.5 mL of solution was sampled at different time intervals).

both polystyrene resins with high hydrophobicity [19], and they are considered to be the most efficient polymeric adsorbents for removing aromatic pollutants from wastewater [20]. Fig. s2 indicates that the adsorption of β -naphthol onto HJ-Y06 is comparable with XAD-4 while much enhanced than X-5. The specific surface area of HJ-Y06 is much lower than the corresponding one of XAD-4 and comparable with that of X-5, the possible reason for the above observation may be from the chemical modification of formaldehyde carbonyl and quinone carbonyl groups on the surface of the resin.

3.3. Adsorption of different pollutants onto HJ-06 resin from aqueous solution

To reveal the feasibility for the adsorption of β -naphthol onto HJ-Y06 resin, the adsorption isotherms of four pollutants including β -naphthol, phenol, *p*-aminobenzoic acid and salicylic acid are compared from aqueous solution with the temperature at 299 K (Fig. s3). It is seen that HJ-Y06 resin possesses the largest adsorption capacity for β -naphthol at the same equilibrium concentration, and hence β -naphthol is employed as the adsorbate in this study.

3.4. Adsorption kinetic curves of β -naphthol

Fig. 2 displays the adsorption kinetic curves of β -naphthol onto HJ-Y06, XAD-4 and X-5 resin from aqueous solution. It is observed that the required time for the adsorption of β -naphthol onto HJ-Y06 from the beginning to the equilibrium is about 600 min, much longer than XAD-4 and X-5.

Generally, the pseudo-first-order rate equation is only suitable for the adsorption at the beginning process while not the whole process, and the pseudo-second-order rate equation is appropriate for the whole process, hence it is employed to fit the adsorption kinetic data, its linear form is [21]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 is the pseudo-second-order rate constant ($\text{g}/(\text{mg min})$).

Plotting of t/q_t versus t for the adsorption of β -naphthol onto HJ-Y06, XAD-4 and X-5 resin is depicted in Fig. s4 and the fitted correlative parameters are summarized in Table s1. It is noted that the pseudo-second-order rate equation can characterize the adsorption well due to $R^2 > 0.99$. In particular, the rate constant of XAD-4 and X-5 is much greater than that of HJ-Y06, accordant with the above observation that the required adsorption time for the adsorp-

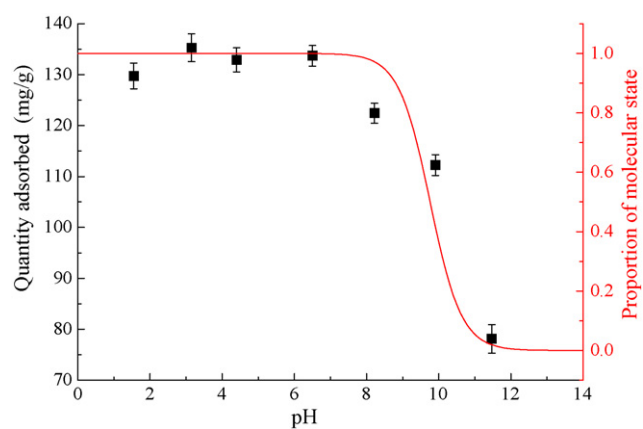


Fig. 3. Effect of solution pH on the adsorption of β -naphthol onto HJ-Y06 (about 0.100 g of resin, 50 mL of β -naphthol solution was applied and the concentration was 498.9 mg/L, 0.1 mol/L of hydrochloric acid and 0.1 mol/L of sodium hydroxide were used to adjust solution pH, the agitation speed of the thermostatic oscillator was 150 rpm, $T = 299$ K, adsorption time was 24 h).

tion onto XAD-4 and X-5 is much shorter than that onto HJ-Y06 in Fig. 2.

In general, several steps such as external mass transfer from the liquid solution to the solid particle surface, internal mass transfer in the pore of the solid particle, and adsorption on the active sites of the solid particle are necessary for the adsorbate transporting from the solution to the active sites on the resin [22], and the intra-particle diffusion is frequently the rate-limiting step. The kinetic data are further dealt with the intra-particle diffusion proposed by Weber and Morris [23]:

$$q_t = k_d t^{1/2} + C \quad (4)$$

where k_d is the intra-particle diffusion rate ($\text{mg}/(\text{g min}^{1/2})$), and C is a constant.

If plot of q_t versus $t^{1/2}$ gives a straight line and the straight line passes through the origin, and it can be deduced that the adsorption is only controlled by the intra-particle diffusion. While if plot of q_t versus $t^{1/2}$ presents a multi-linear relationship or it does not pass through the origin, two or more diffusion mechanisms will influence the adsorption [24]. Fig. s5 is plots of q_t versus $t^{1/2}$ for the adsorption of β -naphthol onto HJ-Y06, XAD-4 and X-5 from aqueous solution, and it is found that they yield a three-stage process. At the initial stage, it poses linear relationships and the straight lines pass through the origin, indicating that the intra-particle diffusion is the sole rate-limiting step. At the second stage, plots of q_t versus $t^{1/2}$ also yield linear relationships while does not pass through the origin, revealing that multi-diffusion mechanisms are involved. After that, the adsorption reaches equilibrium.

3.5. Effect of pH on the adsorption of β -naphthol onto HJ-Y06 from aqueous solution

The pH is one of the most important factors influencing the adsorption. Actually, the pH can affect the form of the functional groups on the resin, it also has an impact on the charge profile of the adsorbate, and thereby it induces different interaction between the resin and the adsorbate at different pH [25]. The effect of pH on the adsorption of β -naphthol onto HJ-Y06 resin is illustrated in Fig. 3, and the dissociation curve of β -naphthol on dependency of pH is also shown (the $\text{p}K_a$ of β -naphthol used for simulation is 9.76). The adsorption capacity of β -naphthol onto HJ-Y06 remains almost invariable at pH lower than 6.5 while it decreases rapidly at pH higher than 6.5. The pH of the original β -naphthol solution unadjusted by hydrochloric acid or sodium hydroxide is measured

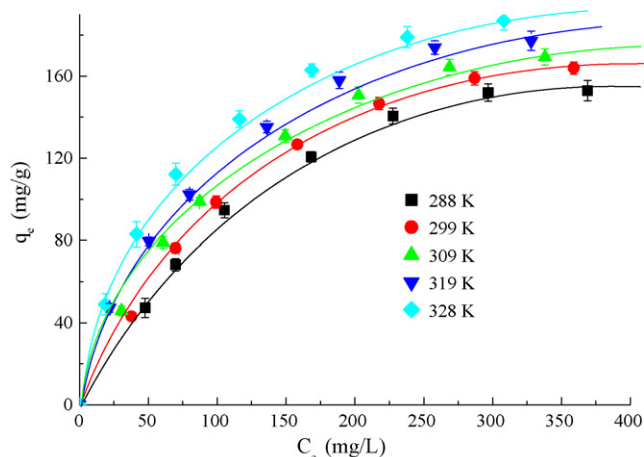


Fig. 4. Adsorption isotherms of β -naphthol adsorbed onto HJ-Y06 from aqueous solution (about 0.100 g of resin, 50 mL of β -naphthol solution was applied, the agitation speed of the thermostatic oscillator was 150 rpm, adsorption time was 24 h, $T=288, 299, 309, 319$ and 328 K, lines presented by Langmuir isotherm equation).

to be 6.5 in this study, and hence it is concluded that the molecular form of β -naphthol is suitable for the adsorption. As pH is higher than 6.5, β -naphthol will be ionized gradually, and which is not appropriate for the adsorption.

3.6. Adsorption isotherms

Fig. 4 depicts the adsorption isotherms of β -naphthol onto HJ-Y06 from aqueous solution at 288, 299, 309 and 319 and 328 K, respectively. It is obvious that the adsorption capacity of β -naphthol onto HJ-Y06 increases with increasing of the temperature, suggesting an endothermic process [26]. Langmuir and Freundlich isotherm models are adopted to describe the adsorption data [27], the corresponding parameters K_L , K_F and n , as well as the correlation coefficients R^2 are summarized in **Table s2**. All of the adsorption isotherm data can be fitted by Langmuir model since $R^2 > 0.98$. With increasing of the temperature, the K_L increases, implying the stronger adsorption driving force at a higher temperature.

3.7. Adsorption thermodynamics

As the adsorption follows a Langmuir model, the thermodynamic parameters such as adsorption enthalpy ΔH (kJ/mol), adsorption free energy ΔG (kJ/mol) and adsorption entropy ΔS (J/(mol K)) can be calculated as [28,29]:

$$\ln K_L = -\frac{\Delta H}{RT} + \ln K_0 \quad (5)$$

$$\Delta G = -RT \ln K_L \quad (6)$$

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \quad (7)$$

where R is the universal gas constant, 8.314 J/mol K, T is the absolute temperature, and K_0 is a constant. By plotting $\ln K_L$ versus $1/T$, a straight line can be gained (**Fig. s6**), and the ΔH can be figured out from the slope of the straight line.

As can be seen in **Table s3**, the positive ΔH means the adsorption is an endothermic process [26]. The positive ΔG indicates that the adsorption is an unfavorable process. The positive ΔS suggests the whole system is disordered after adsorption, and this may be from the following reasons. HJ-Y06 is hydrophilic after introducing formaldehyde carbonyl, quinone carbonyl and phenolic hydroxyl groups on its surface, it can be easily wetted by water molecules, and hence its surface is surrounded by water molecules entirely in aqueous solution, β -naphthol can also interact with

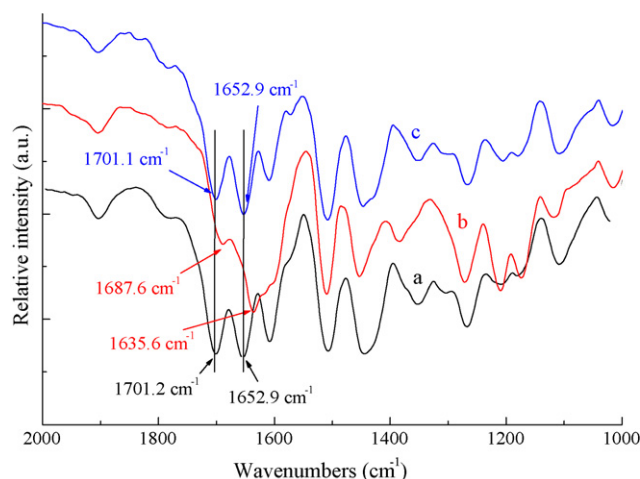


Fig. 5. FT-IR spectra of HJ-Y06: (a) before adsorption of β -naphthol; (b) after adsorption of β -naphthol; (c) after the adsorbed β -naphthol on HJ-Y06 was desorbed (all of the FT-IR experiments were performed after drying HJ-Y06 in vacuum for 8 h with the temperature at 323 K).

water molecules in aqueous solution due to its hydrophilic phenolic hydroxyl groups (**Scheme s1**). Before β -naphthol is adsorbed on the active sites of HJ-Y06 resin, it must break the bond (if existed) between β -naphthol and water molecules as well as that between HJ-Y06 and water molecules. After that, β -naphthol will take the place of water molecules and interact with HJ-Y06. This process is called "Solvent replacement" [30,31]. For the much bigger molecular size of β -naphthol than water molecule, the number of water molecules pushed out from the surface of β -naphthol and HJ-Y06 is much more than that of β -naphthol molecules adsorbed on HJ-Y06. So the solvent replacement process brings an increase of the adsorption entropy.

3.8. Adsorption mechanisms

Since the characteristic absorption peaks in FT-IR spectrum are hyper-sensitive to the changes of the chemical bond [32–34], and in this study the FT-IR spectrum is utilized to examine the shifts of the formaldehyde carbonyl and quinone carbonyl groups uploaded on HJ-Y06 resin so that the adsorption mechanism can be clarified. **Fig. 5** shows the typical FT-IR results of HJ-Y06 before adsorption of β -naphthol, after adsorption of β -naphthol, and after desorption of β -naphthol. The two main vibrational peaks of HJ-Y06 can be assigned as: 1701.2 cm^{-1} (formaldehyde carbonyl groups), 1652.9 cm^{-1} (quinone carbonyl groups). After adsorption of β -naphthol, the vibrational frequency of the formaldehyde carbonyl groups appears at 1687.6 cm^{-1} , red-shifted by 13.6 cm^{-1} . While the quinone carbonyl groups have their vibrational frequency at 1635.6 cm^{-1} , red-shifted by 16.3 cm^{-1} . Moreover, after the adsorbed β -naphthol is desorbed from on HJ-Y06, the vibrational frequencies of these two vibrational peaks come back to 1701.1 and 1652.9 cm^{-1} . Commonly, formation of hydrogen bonding leads some characteristic vibrational bands to be red-shifted [35]. We deduce that hydrogen bonding is formed between the formaldehyde carbonyl and quinone carbonyl groups on HJ-Y06 and the phenolic hydroxyl groups of β -naphthol, and hydrogen bonding is one of the main driving forces for the adsorption.

4. Conclusions

We synthesize a series of novel hyper-cross-linked resins and their surface is chemically modified by formaldehyde carbonyl, quinone carbonyl and phenolic hydroxyl groups. The adsorption

capacity of β -naphthol is the largest as the dosage of hydroquinone is 6% relative to chloromethylated PS. The pseudo-second-order rate equation characterizes the adsorption kinetic curves well and the intra-particle diffusion model plays a predominant role at the initial adsorption process. Langmuir model depicts the adsorption isotherms well and adsorption enthalpy, adsorption entropy and adsorption free energy are all positive. Hydrogen bonding between the formaldehyde carbonyl and quinone carbonyl groups on HJ-Y06 and the phenolic hydroxyl groups of β -naphthol is one of the main driving forces for the adsorption.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.04.083.

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