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Gallic acid modified hyper-cross-linked resin and its adsorption equilibria and kinetics toward salicylic acid from aqueous solution

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ABSTRACT

We synthesized a series of gallic acid modified hyper-cross-linked resins named HJ-D11, HJ-D22, HJ-D44, HJ-D55 and HJ-D66 from macroporous chloromethylated styrene–divinylbenzene copolymer (PS) by adjusting the Friedel–Crafts reaction time from 1 h to 6 h and a further chemical modification by sodium gallate. These resins held different chemical structure (different uploading amounts of gallic acid on the surface) and different pore structure (different Brunauer–Emmett–Teller (BET) surface area and pore volume), which determined their different adsorption selectivity toward salicylic acid. HJ-D55 had the largest adsorption capacity toward salicylic acid and hence was employed as a specific adsorbent for adsorption equilibria and kinetics from aqueous solution. The isotherms were correlated by four linear Langmuir and a Freundlich equations and the Langmuir-II equation was shown to be the most suitable. The enthalpy ΔH, Gibb's free energy ΔG and entropy ΔS were calculated to be negative. The kinetics was fitted by the pseudo-first-order and four linear pseudo-second-order rate equations and it was found that the pseudo-second-order rate equation-I was the best one for characterizing the kinetics.

1. Introduction

Salicylic acid (*o*-hydroxylbenzoic acid) is a typical pollutant in the industrial wastewater [1]. It is commercially synthesized from phenol by treating sodium phenolate with carbon dioxide at a high pressure (100 atm) and a high temperature (390 K) via a Kolbe–Schmitt reaction. It is also frequently employed as a intermediate to produce many medicines. Although salicylic acid is known for its super ability to ease aches and pains and reduce fevers, it is proven to be very dangerous to human being at a high concentration. It is capable of penetrating and breaking down fats and lipids, causing moderate chemical burns of the skin. It can damage the lining of pores; even have some bad effects on the liver, kidney and spleen. As a result, efficient removal and recycling of salicylic acid from aqueous solution has received a lot of attentions in recent years.

Adsorption has been known to mankind for a long time and it is shown to be one of the most efficient methods for separation or purification of organic compounds from aqueous solution [2]. Since the 1970s, hyper-cross-linked resins are recognized as one kind of efficient polymeric adsorbents for adsorptive removal of aromatic compounds from aqueous solution [3,4]. Of course, this type of resins can also be used as excellent column packing materials in high-performance liquid chromatography (HPLC), ion size-exclusion chromatography and solid-phase extraction for adsorptive removal of gases, organic contaminants and organic vapors [5,6]. The hyper-cross-linked resins owe their high adsorption potential to their unique synthesis method. In general, they are synthesized from linear styrene–divinylbenzene copolymer (PS) or low cross-linked PS by adding bi-functional cross-linking reagents such as monochloromethylether, α,α'-dichloro-*p*-xylene and 1,4-bis(chloromethyl)benzene, and Friedel–Crafts catalysts including anhydrous zinc chloride, iron (III) chloride, aluminum (III) choride and stannic (IV) chloride are employed in the synthesis procedure. They can also be prepared from macroporous low cross-linked chloromethylated PS via its self-Friedel–Crafts reaction [7]. After the corresponding reactions, the synthesized hyper-cross-linked PS networks consist in the intensive bridging of highly swollen polystyrene chains with a large number of rigid links, leading to a major shift of their pore diameter distribution (PSD) from predominate mesopores to mesopores-micropores bi-modal distribution, and hence results in a sharp increase of the Brunauer–Emmett–Teller (BET) surface area and pore volume.

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Because of these significant changes, the hyper-cross-linked resins display very large adsorption capacities toward non-polar and weakly polar aromatic compounds in aqueous solution [8,9]

As the macroporous low cross-linked chloromethylated PS was applied as the raw material to synthesize the hyper-cross-linked resins, the residual chlorine content of the synthesized hyper-cross-linked resins was quite different at a different Friedel–Crafts reaction time [10]. We believe that the different chlorine content should determine the pore structure of the obtained hyper-cross-linked resins. If a further nucleophilic substituted reaction is applied for the hyper-cross-linked resins, different surface functionality should be exhibited for the hyper-cross-linked resins. Therefore, it is feasible to adjust the pore structure of the hyper-cross-linked resins by accurately controlling the self-Friedel–Crafts reaction time firstly, and then adjust the surface functionality of the resins by a further chemical modification, which allows us to synthesize some special polymeric adsorbents with controllable adsorption selectivity toward aromatic compounds with different polarity. To the best of our knowledge, this reaction time control approach for optimizing the hyper-cross-linked resin has not been reported.

In this study, we firstly synthesized a series of hyper-cross-linked resins labeled HJ-11, HJ-22, HJ-44, HJ-55 and HJ-66 from the macroporous low cross-linked chloromethylated PS through the self-Friedel–Crafts reaction with different Friedel–Crafts reaction time from 1 h to 6 h. These hyper-cross-linked resins were then chemically modified by an esterified reaction with sodium gallate to produce the gallic acid modified hyper-cross-liked resins named HJ-D11, HJ-D22, HJ-D44, HJ-D55 and HJ-D66. Thereafter, the adsorption selectivity of these resins toward salicylic acid was confirmed by batch adsorption experiments. The most promising resin HJ-D55 was thereafter selected for the equilibria and kinetics of salicylic acid from aqueous solution in detail.

2. Experimental method

2.1. Preparation of the gallic acid modified hyper-cross-linked resins

The gallic acid modified hyper-cross-linked resins were prepared by a Friedel–Crafts reaction from the macroporous low cross-linked chloromethylated PS (purchased from Langfang Chemical Co. Ltd., Hebei province, China; Chlorine content: 4.87 mmol/g; BET surface area: 28.2 m^2/g; pore volume: 0.0036 $cm^{3/}$g; particle size: 20–40 mesh) and followed by an esterified reaction of the obtained hyper-cross-linked resins. The Friedel–Crafts reaction was usually performed by using nitrobenzene as the solvent and anhydrous zinc chloride as the catalyst in many literatures [7–9]. In this study, we applied 1,2-dichloroethane as the solvent and anhydrous iron (III) chloride as the catalyst. 25 g of macroporous low cross-linked chloromethylated PS was swollen by 120 ml of 1,2-dichloroethane overnight. At a moderate stirring speed, the temperature of the reaction mixture was risen to 323 K and 5.0 g of anhydrous iron (III) chloride was added into the reaction mixture. After the added iron (III) chloride was completely dissolved in the solution, the reaction mixture was heated refluxing and it was retained for 1 h, 2 h, 4 h, 5 h and 6 h, respectively, and then the hyper-cross-linked resins named HJ-11, HJ-22, HJ-44, HJ-55 and HJ-66 were obtained in this step. The esterified reaction of the hyper-cross-linked resins was performed according to the method in Ref. [11] and the gallic acid modified hyper-cross-linked resins named as HJ-D11, HJ-D22, HJ-D44, HJ-D55 and HJ-D66 were obtained accordingly.

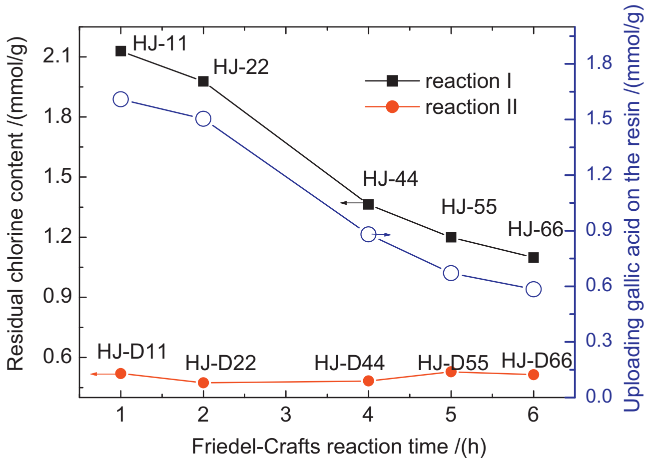

Fig. 1. The residual chlorine content of HJ-11, HJ-22, HJ-44, HJ-55, HJ-66 and HJ-D11, HJ-D22, HJ-D44, HJ-D55 and HJ-D66 as well as the uploading amounts of gallic acid on HJ-D11, HJ-D22, HJ-D44, HJ-D55 and HJ-D66.

2.2. Batch adsorption experiment

The equilibrium adsorption isotherm was performed at four different temperatures 303 K, 313 K, 323 K and 343 K, respectively. About 0.1000 g of resin was mixed with 50 ml of salicylic acid aqueous solution with different initial concentrations in a 100 ml of conical flask. The initial concentrations of salicylic acid were set to be about 200, 400, 600, 800 and 1000 mg/L, respectively. The series of flasks were then shaken in a thermostatic oscillator for about 8 h at a desired temperature to ensure the adsorption process to reach equilibrium. The equilibrium concentration of salicylic acid, C_e (mg/L), was determined and the equilibrium adsorption capacity q_e (mg/g) was calculated by conducting a mass balance on salicylic acid before and after the adsorption experiment. The adsorption kinetic curves of salicylic acid on the resin were performed by analyzing the adsorption uptakes of salicylic acid on the resin until the adsorption equilibrium was reached.

2.3. Analysis

The chorine content of the resin was measured by Volhard method according to the Ref. [12]. The BET surface area and pore volume of the resin were determined by N_2 adsorption–desorption isotherms at 77 K using a Micromeritics Tristar 3000 surface area and porosity analyzer. The FT-IR spectrum of the resin was collected by KBr disks on a Nicolet 510P Fourier transformed infrared instrument. The concentration of salicylic acid, *p*-aminobenzoic acid and aniline in aqueous solution was analyzed by UV analysis at the wavelength of 296.5 nm, 278.4 nm and 280.2 nm, respectively.

3. Results and discussion

3.1. Characterization of resins

As can be observed from Fig. 1, the residual chlorine content of the obtained hyper-cross-linked resins, HJ-11, HJ-22, HJ-44, HJ-55 and HJ-66, sharply decreases from 4.87 mmol/g to about 1.09–2.13 mmol/g after the Friedel–Crafts reaction, implying that self-Friedel–Crafts reaction occurs for the chloromethylated PS itself. Additionally, a longer Friedel–Crafts reaction time induces a lower residual chlorine content, identical to the results reported previously [10], and the obtained hyper-cross-linked resins with different residual chlorine content implies that the pore structure such as BET surface area and pore volume of the reins should be respectively different.

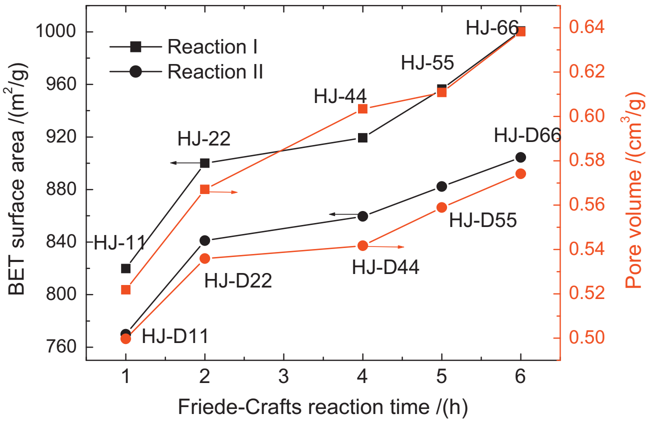

Fig. 2. BET surface area and pore volume of the hyper-cross-linked resins.

After the esterified reaction of the hyper-cross-linked resins with sodium gallate, the residual chlorine content of obtained resins further decreases and the final chlorine content of obtained resins is roughly equivalent to be 0.5 mmol/g, which suggested that the residual chlorine of the hyper-cross-linked resin was further substituted and the uploading amounts of gallic acid on the surface of the resins were different (1.61 mmol/g, 1.50 mmol/g, 0.88 mmol/g, 0.67 mmol/g and 0.58 mmol/g for HJ-D11, HJ-D22, HJ-D44, HJ-D55 and HJ-D66, respectively), manifesting a different surface chemical polarity for these gallic acid modified hyper-cross-linked resins. From the results of FT-IR spectra (see Fig S1), it can be concluded that gallic acid is uploaded on the surface of the resin successfully [13].

According to N_2 adsorption–desorption isotherms of the unmodified hyper-cross-linked resins and the gallic acid modified hyper-cross-linked resins (see Fig S2), the BET surface area and pore volume of the hyper-cross-linked resins increase with increasing of the Friedel–Crafts reaction time, which may be from the fact that the macro-pore volume might be reduced with an increasing time of the Friedel–Crafts reaction (see Fig. 2 and Fig. S3). This result confirms that our purpose of adjusting the pore structure of the resin by applying different Friedel–Crafts reaction time is feasible. In addition, the further chemical modification makes the BET surface area and pore volume decreased due to the increased polarity and a longer Friedel–Crafts reaction time induces a larger decrease for the BET surface area and pore volume.

3.2. Adsorption selectivity of the resins toward salicylic acid

From the analysis above, the synthesized gallic acid modified hyper-cross-linked resins, HJ-D11, HJ-D22, HJ-D44, HJ-D55 and HJ-D66 in this study possess a different chemical structure (different uploading amounts of gallic acid on the surface) and pore structure (different BET surface area and pore volume), and hence they should display a different adsorption selectivity toward different aromatic compounds with different polarity. As shown in Fig. 3, HJ-D55 has the largest adsorption capacity toward salicylic acid among the five resins although it does not have the highest BET surface area and pore volume or the highest uploading amount of gallic acid on the surface. The combinations of the appropriate pore structure and uploading amount of gallic acid of HJ-D55 help to bring a better adsorption of salicylic acid on HJ-D55. Hence, HJ-D55 is employed as a specific polymeric adsorbent for the adsorption equilibria and kinetics of salicylic acid from aqueous solution in the present study.

In order to testify the necessity of the chemical modification, the isotherms of salicylic acid adsorbed on the unmodified hyper-cross-linked resin, HJ-55 and the gallic acid modified hyper-cross-linked resin, HJ-D55 are compared with the temperature at 303 K and the results are displayed in Fig. 4. It is clear that the adsorption on HJ-D55 is enhanced in comparison with HJ-55. The BET surface area and pore volume of HJ-55 are higher than those of HJ-D55, and the pore diameter distribution of the two resins is similar (see Fig. S3). Hence, there is no question to believe that it is these polar gallic acid groups uploaded on the surface of HJ-D55 that improve the adsorption capacity.

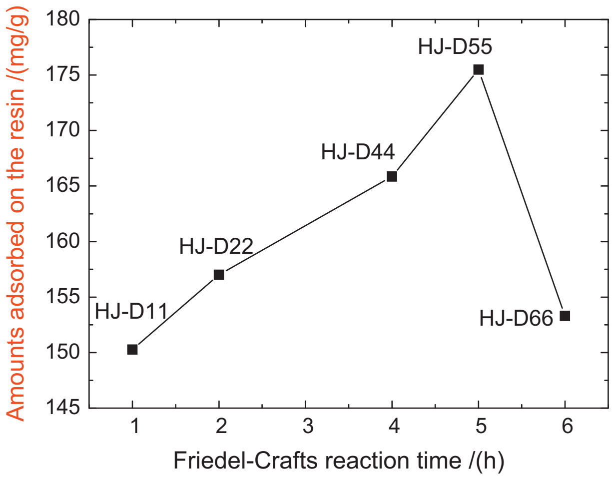

Fig. 3. Adsorption comparison of salicylic acid adsorbed on HJ-D11, HJ-D22, HJ-D44, HJ-D55 and HJ-D66.

The functional groups on a polymeric adsorbent, especially macroporous polymeric adsorbent, are important for separation and purification and these functional groups are frequently regarded as a solid-phase extraction (SPE) reagent, and a SPE mechanism is often adopted to elucidate the effect of the functional groups on the adsorption [14,15]. SPE is a typical separation process by which organic compounds that are dissolved or suspended in a liquid mixture are separated from other organic compounds in the mixture according to their physical and chemical properties. Here we define the increased adsorption capacity of salicylic acid on HJ-D55 in contrast with HJ-55 as the net adsorption capacity caused by the gallic acid groups of HJ-D55. Taking consideration of the mass increase before and after the chemical functionalization, it is interesting to see that plotting of q_a versus C_e presents a linear relationship (see Fig. S4) with a very small intercept and a very high

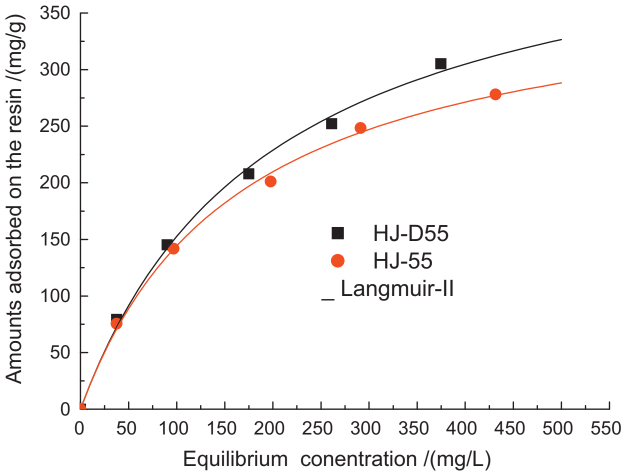

Fig. 4. Adsorption isotherm of salicylic acid on the gallic acid modified hyper-cross-linked resin HJ-D55 in comparison with the unmodified hyper-cross-linked resin HJ-55.

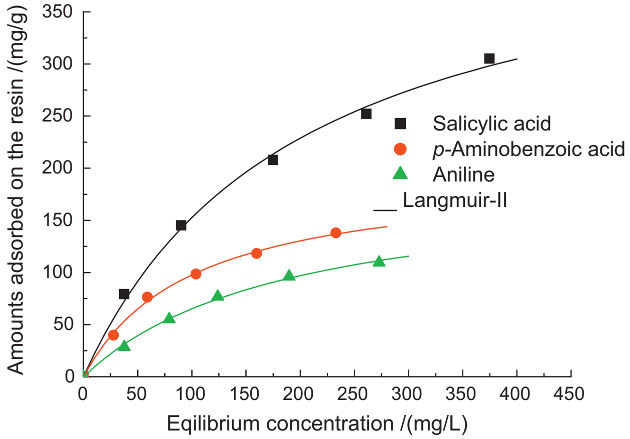

Fig. 5. Adsorption comparison of salicylic acid, *p*-aminobenzoic acid and aniline on HJ-D55.

correlation coefficient (>0.96). Hence, it can be concluded that the gallic acid groups on HJ-D55 can be looked on as SPE reagents.

Langmuir and Freundlich models are two typical adsorption models to describe the adsorption process [16,17]. Langmuir equation assumes that the adsorption occurs on a structurally homogeneous adsorbent and all the adsorption sites are energetically identical, and it can be represented as:

$$q_e = \frac{q_m K_s C_e}{1 + K_a C_e} \tag{1}$$

where q_m is the maximum adsorption capacity (mg/g) and K_L is a constant. The constants of q_m and K_a can be obtained from a linear form of Eq. (1). However, the Langmuir equation can be linearized as four different types (see Table S1). Hence, we have performed the linear fitting by the four linear Langmuir equations and the corresponding parameters K_a, q_m and the correlation coefficients are summarized in Table S2 and Fig. S5, respectively.

Certainly, Freundlich equation occurs on a heterogeneous surface and it can be expressed as:

$$q_e = K_F {C_e}^{1/n} \tag{2}$$

where K_F [(mg/g)(L/mg)$^{1/n}$] and n are the constants. The linear Freundlich equation can be obtained by taking the logarithm of both sides as:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{3}$$

The results in Table S2 and Fig. S5 indicate that values of R^2 (>0.99) obtained from the linear Langmuir-II are always the highest among these models, implying that a different axis setting in the regression can change the results of a linear fitting and the Langmuir equation-II is most suitable for the adsorption, which may be resulted from the fact that a homogeneous surface structure is formed after the esterified reaction of HJ-55 with sodium gallate.

3.3. Adsorption of different adsorbates on HJ-D55

To reveal the feasibility for the adsorption of salicylic acid on HJ-D55, the isotherms of three pollutants including salicylic acid, *p*-aminobenzoic acid and aniline are compared with the temperature at 303 K (see Fig. 5). It is clear that HJ-D55 possesses the largest adsorption capacity toward salicylic acid at the same equilibrium concentration, and hence salicylic acid is employed as the adsorbate in this study. Table S3 and Fig. S6 show the fitted results by applicability of four types of Langmuir and Freundlich equations and it can be observed that the Langmuir equation-II is the most suitable model for the adsorption.

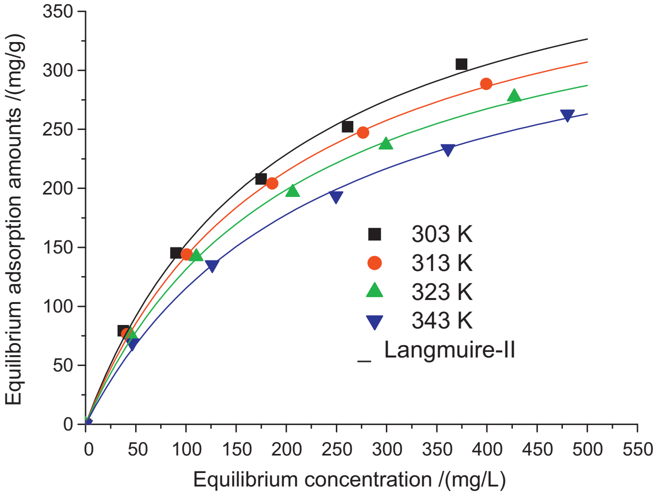

Fig. 6. Adsorption isotherms of salicylic acid on HJ-D55 from aqueous solution at 303 K, 313 K, 323 K and 343 K, respectively.

3.4. Adsorption isotherms

Fig. 6 presents the adsorption isotherms of salicylic acid on HJ-D55 from aqueous solution with four different temperatures at 303 K, 313 K, 323 K and 343 K, respectively. It is clear that low temperature and high equilibrium concentration are favorable for the adsorption [18,19], and the equilibrium adsorption capacity reaches 231.7 mg/g at an equilibrium concentration of 200 mg/L. As compared the adsorption of salicylic acid on HJ-D55 with the other commercial adsorbents such as XAD-4 and X-5, activated carbon fibers and some other functional polymers such as HJ-L02 (a bisphenol-A modified hyper-cross-linked resin [20]), HJ-Y15 (a hydroquinone-modified hyper-cross-linked resin [21]) and HJ-G02 (a β-naphthol-modified hyper-cross-linked resin [22]), the adsorption of salicylic acid on HJ-D55 is superior. This encouraging result strongly suggests that the new resin being developed is a promising replacement for many commercial polymeric adsorbents for aromatic pollutant like salicylic acid from wastewater. Four linear Langmuir and Freundlich equations are adopted to describe the adsorption and the typical parameters and correlated parameters are summarized in Table 1 and Fig. S7. It is seen that Langmuir equation-II is most suitable for the adsorption of salicylic acid on HJ-D55 because the correlation coefficients by Langmuir equation-II are the highest.

According to Tiwari et al. [23], the important parameter K_R which represents a dimensionless constant separation factor can be applied to predict whether the adsorption process is favorable or not and it can be defined as:

$$K_R = \frac{1}{1 + K_a C_0} \tag{4}$$

If the value of K_R is higher than unit and the adsorption is unfavorable, while the adsorption is linear as K_R is unit. On the other hand, if K_R is lower than unit while higher than zero, implying that the adsorption is favorable and a lower K_R means a more favorable adsorption process. Of course the adsorption is irreversible as K_R is zero. The relationship between K_R and the initial concentration of salicylic acid C_0 (mg/L) is given in Fig. S8. It can be seen that the adsorption is more favorable for the adsorption at a higher initial concentration and a lower temperature.

Table 1
Constants for the adsorption isotherms of salicylic acid on HJ-D55 from aqueous solution according to the four-type Langmuir and Freundlich equations.

T (K)	Langmuir-I		Langmuir-II			Langmuir-III		Langmuir-IV		Freundlich	
	q_m (mg/g)	K_a (L/g)	q_m (mg/g)	K_a (L/g)	ΔG (kJ/mol)	q_m (mg/g)	K_a (L/g)	q_m (mg/g)	K_a (L/g)	n	K_F
303	444.4	5.38	401.6	6.50	−17.13	420.2	6.02	426.1	5.86	1.721	10.52
313	427.4	5.08	392.2	5.75	−17.38	417.2	5.31	418.1	5.29	1.695	8.937
323	401.6	4.95	375.9	5.63	−17.87	387.0	5.34	389.9	5.27	1.744	9.001
343	378.8	4.50	349.7	5.25	−18.78	363.2	4.91	366.8	4.82	1.741	7.920

3.5. *Adsorption thermodynamics*

Adsorption enthalpy ΔH (kJ/mol), Gibb's free energy ΔG (kJ/mol) and entropy ΔS (kJ/(mol K)) are basic aspects for the adsorption process. ΔG is a fundamental criterion of adsorption spontaneity and an adsorption occur spontaneously at a given temperature if ΔG is negative. In the present study, the thermodynamic parameters of ΔG, ΔH and ΔS are calculated using the following equations as [24]:

$$\Delta G = -RT\ \ln K_a \tag{5}$$

$$\Delta G = \Delta H - T\Delta S \tag{6}$$

where R is universal gas constant (8.314 J/mol K) and T is the absolute temperature (K).

In Table 1, ΔG is calculated using K_a obtained from Langmuir equation-II (where the unit of K_a should be converted to L/mol). Then a plot of ΔG as a function of the temperature T was found to be linear (see Fig. 7), and ΔH and ΔS can be determined to be −4.168 kJ/mol and −0.0425 kJ/(mol K), respectively. The negative ΔG confirms the feasibility of the present adsorption process and the spontaneous nature of adsorption with a high preference of salicylic acid on HJ-D55. The decrease of the negative ΔG with increasing of the temperature indicates that the adsorption of salicylic acid on HJ-D55 is more favorable at higher temperature [25]. The value of ΔH is also negative, indicating that the adsorption is an exothermic process. Entropy is defined as the degree of chaos for a given system. A positive ΔS reflects an increasing randomness at the solid-liquid interface during the adsorption while a negative ΔS implies that the whole system is more ordered after the adsorption, the present negative ΔS reflects the ordered arrangement of the system after the adsorption of salicylic acid on HJ-D55.

3.6. *Adsorption kinetics*

A detailed equilibrium study of adsorbent toward an adsorbate is fundamental for evaluation of the adsorption capacity as well as the adsorption thermodynamic data. Of course, all of thermodynamic data only predict the equilibrium state, and hence it is important to determine how the adsorption rates depend on the concentrations of adsorbate in a solution and how rates are affected by the adsorption capacity or by the character of the adsorbent in terms of kinetics. Fig. 8 shows the adsorption kinetic curves of salicylic acid adsorbed on HJ-D55 with three different temperatures 303 K, 313 K and 323 K, respectively. It is clear that the adsorbed salicylic acid on HJ-D55 after 200 min (at equilibrium) decreases with increasing of the adsorption temperature from 303 K to 323 K while the required time from the beginning to the equilibrium is shortened from 300 min to 180 min. The fact that the adsorption is weakened by the temperature agrees with the equilibrium adsorption data while the adsorption is enhanced with increasing of the temperature due to the faster diffusion rate in the pore of the adsorbent HJ-D55.

Lagergren model (also named pseudo-first-order rate equation) and the pseudo-second-order rate equation are extensively employed [26,27] to the kinetic data. The Lagergren model can be arranged as:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{7}$$

where k_1 is the pseudo-first-order rate constant (min^{-1}).

Integration of Eq. (7) applying boundary conditions, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ will result in:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{8}$$

If the adsorption follows the pseudo-first-order rate equation, a plot of $\ln(q_e - q_t)$ versus t should be a straight line. On the other

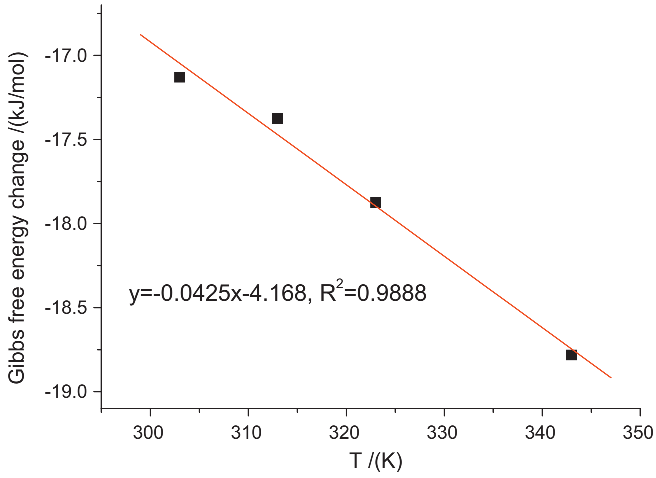

Fig. 7. Plot of Gibb's free energy change, ΔG, versus T.

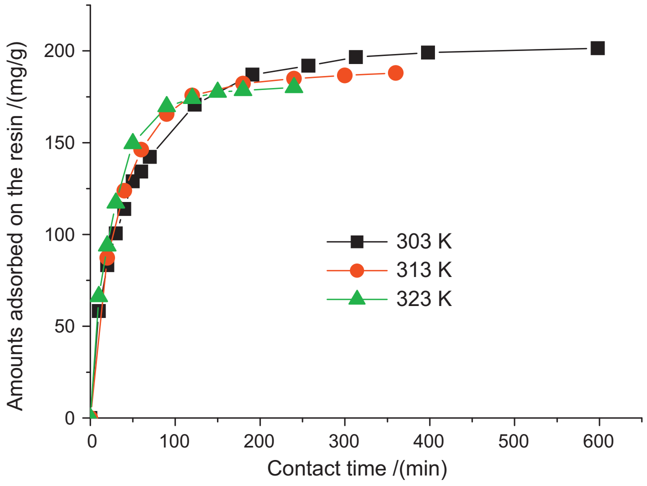

Fig. 8. Plots of the adsorbed amounts of salicylic acid on HJ-D55 as a function of the contact time t.

hand, pseudo-second-order equation proposed by Ho and McKay can be expressed as [28,29]:

$$\frac{dq}{dt} = k_2(q_e - q_t) \tag{9}$$

where k_2 is the pseudo-second-order rate constant(g/(mg min)). If integration is given for Eq. (9), the pseudo-second-order kinetic model can be linearized as four different types (see Table S4) and a simple linear regression will result in a different parameter [30].

Values of the pseudo-first-order rate constant k_1, pseudo-second-order rate constant k_2, the adsorbed amount of salicylic acid on HJ-D55 at equilibrium q_e, the initial adsorption rate h (where $h = k_2 q_e^2$) as well as the correlation coefficients R^2 are listed in Tables S5. It can be found that all of pseudo-second-order kinetic equations is more suitable for characterizing the kinetic adsorption curves than the pseudo-first-order kinetic equation and pseudo-second-order kinetic equation-I is the most appropriate one. In addition, the calculated q_e decreases with increasing of the temperature while k_2 increases, which is in accordant with the observed phenomena above.

The k_2 were found to increase from 1.477×10^{-4} to 2.778×10^{-4} g/(mg min) for an increase in the adsorption temperature of 303–323 K. When performing $\ln k_2$ as a function of $1/T$, it is seen that there is a linear relationship between $\ln k_2$ and $1/T$ with correlation coefficient of 0.9682 (Fig. S9). The rate constant is usually expressed as a function of the temperature by the relationship as:

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{10}$$

where k is the rate constant (g/(mg min)), k_0 is the temperature independent factor (g/(mg min)) and E is the adsorption activation energy (kJ/mol). Therefore, the adsorption activation energy can be determined to be 25.79 kJ/mol.

4. Conclusions

In the present study, we presented an effective method for adjusting the pore structure and surface polarity of a hyper-cross-linked resin by simply adjusting the Friedel–Crafts reaction time of the macroporous low cross-linked chloromethylated PS. The gallic acid modified hyper-cross-linked resins named HJ-D11, HJ-D22, HJ-D44, HJ-D55 and HJ-D66 were synthesized and they displayed different pore structure and different surface polarity. HJ-D55 held the largest adsorption capacity toward salicylic acid from aqueous solution and it was superior to some other commercial adsorbents.

The isotherms were fitted by four types of linear Langmuir and Freundlich equations and Langmuir-II was the most suitable equation for characterizing the adsorption. The ΔG was calculated to be −17.13 to 18.78 kJ/mol and it deceased with increasing of the temperature, the ΔH and ΔS were fitted to be −4.168 kJ/mol and −0.0425 kJ/(mol K), respectively. The adsorption kinetics were fitted by pseudo-first-order and four types of linear pseudo-second-order rate equations and the pseudo-second-order rate equation-I was the most suitable one and the adsorption activation energy was fitted to be 25.79 kJ/mol.

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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.cej.2012.03.003.

References

[1] L. Khenniche, F. Aissani, Preparation and characterization of carbons from coffee residue: adsorption of salicylic acid on the prepared carbons, J. Chem. Eng. Data 55 (2010) 728–734.

[2] D.D. Duong, Adsorption Analysis: Equilibria and Kinetics, World Scientific Publishing, Singapore, 1998.

[3] M.P. Tsyurupa, V.A. Davankov, Hypercrosslinked polymers: basic principle of preparing the new class of polymeric materials, React. Funct. Polym. 53 (2002) 193–203.

[4] M.P. Tsyurupa, V.A. Davankov, Porous structure of hypercrosslinked polystyrene: state-of-the-art mini-review, React. Funct. Polym. 66 (2006) 768–779.

[5] V. Davankov, M.P. Tsyurupa, Preparative frontal size-exclusion chromatography of mineral ions on neutral hypercrosslinked polystyrene, J. Chromatogr. A 1087 (2005) 3–12.

[6] V. Davankov, M.P. Tsyurupa, M. Ilyin, L. Pavlova, Hypercross-linked polystyrene and its potentials for liquid chromatography: a mini-review, J. Chromatogr. A 965 (2002) 65–73.

[7] A.M. Li, Q.X. Zhang, G.C. Zhang, J.L. Chen, Z.H. Fei, F.Q. Liu, Adsorption of phenolic compounds from aqueous solutions by a water-compatible hypercrosslinked polymeric adsorbent, Chemosphere 47 (2002) 981–989.

[8] C.L. He, J.H. Huang, C. Yan, J.B. Liu, L.B. Deng, K.L. Huang, Adsorption behaviors of a novel carbonyl and hydroxyl groups modified hyper-cross-linked poly(styrene-co-divinylbenzene) resin for β-naphthol from aqueous solution, J. Hazard. Mater. 180 (2010) 634–639.

[9] B.C. Pan, W.M. Zhang, B.J. Pan, H. Qiu, Q.R. Zhang, Q.X. Zhang, S.R. Zheng, Efficient removal of aromatic sulfonates from wasterwater by a recyclable polymer: 2-naphthalene sulfonate as a representative pollutant, Environ. Sci. Technol. 42 (2008) 7411–7416.

[10] J.H. Ahn, J.E. Jang, C.G. Oh, S.K. Ihm, J. Cortez, D.C. Sherrington, Rapid generation and control of microporosity, bimodal pore size distribution, and surface area in davankov-type hyper-cross-linked resins, Macromolecules 39 (2006) 627–632.

[11] C.L. He, K.L. Huang, J.H. Huang, Surface modification on a hyper-cross-linked polymeric adsorbent by multiple phenolic hydroxyl groups to be used as a specific adsorbent for adsorptive removal of p-nitroaniline from aqueous solution, J. Colloid Interface Sci. 342 (2010) 462–466.

[12] C.P. Wu, C.H. Zhou, F.X. Li, Experiments of Polymeric Chemistry, Anhui Science and Technology Press, Hefei, 1987.

[13] J.T. Wang, Q.M. Hu, B.S. Zhang, Y.M. Wang, Organic Chemistry, Nankai University Press, Tianjing, 1998.

[14] E.M. Thurman, M.S. Mills, Solid Phase Extraction Principles and Practice, John Wiley & Sons Inc., New York, 1998.

[15] G. Saini, L. Yang, M.L. Lee, A. Dadson, M.A. Vail, M.R. Linford, Anal. Chem. 80 (2008) 6253.

[16] I. Langmuir, The constitution and fundamental properties of solids and liquids, J. Am. Chem. Soc. 38 (1916) 2221–2295.

[17] H.M.F. Freundlich, Uber die adsorption in losungen, Z. Phys. Chem. 57A (1906) 385–470.

[18] B.L. He, W.Q. Huang, Ion Exchange Adsorption Resin, Shanghai Science and Technology Education Press, Shanghai, 1995.

[19] D.M. Ruthven, Principles and Adsorption and Adsorption Processes, Willey, New York, 1984.

[20] H.X. Hu, X.M. Wang, S.Y. Li, J.H. Huang, S.G. Deng, Bispheno-A modified hyper-cross-linked polystyrene resin for salicylic acid removal from aqueous solution: adsorption equilibrium kinetics and breakthrough studies, J. Colloid Interface Sci. 372 (2012) 108–112.

[21] J.H. Huang, Hydroquinone modified hyper-cross-linked resin to be used as a polymeric adsorbent for adsorption of salicylic acid from aqueous solution, J. Appl. Polym. Sci. 121 (2011) 3717–3723.

[22] J.H. Huang, G. Wang, K.L. Huang, Enhanced adsorption of salicylic acid onto a β-naphthol-modified hyper-cross-linked poly(styrene-co-divinylbenzene) resin from aqueous solution, Chem. Eng. J. 168 (2011) 715–721.

[23] R.K. Tiwari, S.K. Ghosh, D.C. Rupainwar, Y.C. Sharma, Managing aqueous-solutions rich in Mn(II): an inexpensive technique, Colloids Surf. A 70 (1993) 131–137.

[24] Y.S. Ho, C.C. Wang, Sorption equilibrium of mercury onto ground-up tree fern, J. Hazard. Mater. 156 (2008) 398–404.

[25] P.W. Atkins, Physical Chemistry, 1st ed., Oxford University Press, 1978 (7th ed. 2002).

[26] S. Lagergren, About the theory of so-called adsorption of soluble substances, *Kungliga Svenska Vetenskapsakademiens*, Handlingar Band 24 (1898) 1–39.
[27] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.
[28] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.
[29] Y.S. Ho, Review of second-order models for adsorption systems, J. Hazard. Mater. 136 (2006) 681–689.
[30] Y.S. Ho, A.E. Ofomaja, Kinetic studies of copper ion adsorption on palm kernel fibre, J. Hazard. Mater. 137 (2006) 1796–1802.