

Adsorption behavior of α -tocopheryl succinate and α -tocopheryl polyethylene glycol succinate onto weakly basic anion exchange resins

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Abstract—Polyethylene glycol (PEG) esters are important, nontoxic and biodegradable non-ionic surfactants. A key procedure in producing PEG esters is their separation from unreacted or excess acids. We propose an adsorption method using the weakly basic anion exchange resins for the separation of organic acids and PEG esters for the first time. With α -tocopheryl polyethylene glycol succinate (TPGS) and α -tocopheryl succinate (α -TS) as the examples of PEG ester and organic acid, respectively, single-component equilibrium experiments revealed the great potential of this method. Studies on the adsorption equilibrium, thermodynamics and kinetics of α -TS onto a weakly basic anion exchange resin were also carried out. This research is not only important for the production of TPGS, but also instructive for the separation of other PEG-esters from the reaction mixtures.

Keywords: PEG Esters, Organic Acids, Adsorption, Weakly Basic Anion Exchange Resin

INTRODUCTION

PEG esters are an important class of non-ionic surfactant for their lack of toxicity, biodegradability, absence of antigenicity and immunogenicity, and higher solubility in water and most organic solvents [1]. They show extensive applications as solubilizers, emulsifiers and lubricants in pharmaceuticals, cosmetics and other industries [2,3]. Esterification between organic acids and PEG is the most commonly employed method for the production of PEG esters. Due to the equal reactivity of the two terminal hydroxyl groups in PEG, two types of esters exist in PEG esters, which are with one hydroxyl group esterified mono-ester and with both of the two hydroxyl groups esterified di-ester [4-6]. Different number of hydrophobic substituents in the PEG esters results in different properties of PEG mono- and di-esters. PEG mono-ester with higher hydrophilic-lipophilic balance (HLB) number and higher water solubility than di-ester is usually more desired [4]. Sometimes, PEG diester shows superior performance. Buckingham et al. found fatty acid-PEG-fatty acid diesters were significantly more effective inhibitors of multi-drug-resistance than monoesters in vitro [7,8]. Considering the significantly different properties of mono- and di-esters, many efforts has been tried to synthesize high purity of PEG monoesters and diesters. High purity of diesters can be easily obtained with a large excess of organic acids. However, high selectivity of monoesters is always difficult. Researches by Hamid et al. revealed that the selectivity of mono-ester decreased with the increase of the conversion of the organic acid with *p*-toluene sulfonic acid as the catalyst. They also found that when solid acids were used as catalysts, although the selectivity of monoester could be as high as 95%, the conversion of

the organic acid was less than 80% after 12 hours' reaction [5]. Thus total conversion of the organic acid is almost impossible, especially when high selectivity of monoester is more concerned. Therefore, a separation process is needed to remove incompletely reacted or excess organic acids to get pure products and to recover the raw materials after the esterification.

The main difference between the organic acids and their PEG esters lies in the activated carboxyl group in the organic acids. Therefore, a basic material is expected to be favorable. Padmavathi et al. [9] reported the separation of behenic acid from the esterification products by passing the reaction mixture through alkaline silica gel with a chloroform-ether mixture as eluant. The reusable basic anion exchange resins, especially the weakly basic anion exchange resins, may be efficient for the separation of organic acids and PEG esters. First, the weakly basic anion exchange resins have large capacity for acid sorption and have been widely applied in the separation and purification of organic acids, such as lactic acid, salicylic acid, propionic acid and benzoic acid etc. [10-13]. Second, compared to the strongly basic anion exchange resins, the weakly basic anion exchange resins are easier to regenerate for the weaker interaction between the adsorbate and the adsorbent. Besides, the strongly basic anion exchange resins were effective catalysts for the hydrolysis reaction of the esters [14,15]. So the PEG esters might be hydrolyzed if a strongly basic anion exchange resin is used as the adsorbent. Thus, we propose a method for separating PEG esters and the organic acids using the weakly basic anion exchange resin as the adsorbent for the first time.

A wide variety of PEG esters with different properties can be achieved by changing the type of the organic acids and varying the polymerization degree of the PEG part. We took the separation of α -tocopheryl succinate (α -TS, Fig. 1(a)) and its PEG 1000 ester, tocopheryl polyethylene glycol 1000 succinate (TPGS, Fig. 1(b)), as an example. α -TS is a succinyl ester of α -tocopherol (α -T), which

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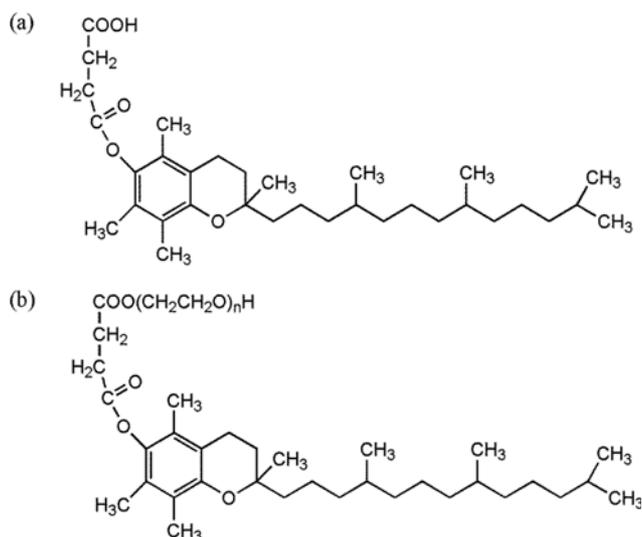


Fig. 1. Chemical structures of α -TS (a) and TPGS (b).

is more stable against heat and oxidation than α -T, but still insoluble in water. TPGS, a water-soluble derivative of natural source Vitamin E, is synthesized by the esterification of α -TS and PEG [5,16-18]. In the crude TPGS products, incompletely reacted α -TS needs to be removed to get pure TPGS [19,20]. Not only in TPGS, but the ester-bond also exists in α -TS. When 0.5 g DowexTM MonoSphereTM 550A UPW resin - a strongly basic anion exchange resin was used to adsorb 10 mL ethanol solution of α -TS at the initial concentrations of 10, 50 and 90 mg/mL at 293 K for 12 hours; 0.9%, 1.1% and 0.8% of α -TS was hydrolyzed to α -T, respectively. This result confirmed that the ester compound was not stable with the strongly basic anion exchange resin as the adsorbent. So the strongly basic anion exchange resin was unsuitable for the separation of α -TS and TPGS. In view of the low hydrolysis rate of the strongly basic anion exchange resin, the weakly basic anion exchange resin with weaker basicity might show good affinity to α -TS and do not affect the stability of α -TS simultaneously.

For efficient separation, the adsorbent must have high selectivity and large adsorption capacity for the adsorbate. Single-component adsorption experiments of α -TS and TPGS onto four weakly basic anion exchange resins were carried out to investigate the potential of this method. The adsorption equilibrium, thermodynamics

and kinetics were investigated, and the influence of the physical properties of the resins on the adsorption capacity was studied. As expected, the results showed that the proposed adsorption method using the weakly basic anion exchange resin as adsorbent was very efficient for the separation of organic acids and their PEG esters.

MATERIALS AND METHODS

1. Materials and Instruments

1-1. Materials

Alpha-TS standard was obtained from Sigma-Aldrich (St. Louis, USA). Commercial α -TS (purity greater than 98%) was received from Zhejiang Worldbest Pharmaceuticals Science Technic Development Co., Ltd. (Lanxi, China) and used without further purification. Anhydrous alcohol (AR) and acetic acid (AR) were from Shanghai Reagent Company (Shanghai, China). HPLC grade acetonitrile, isopropanol and methanol were from Tedia Company Inc. (OH, USA). The weakly basic anion exchangers D301, D315 and HZD-9 were obtained from Shanghai Huazhen Science & Technology Co., Ltd. (Shanghai, China), and another weakly basic anion exchanger D301r was supplied by the Chemical Plant of Nankai University (Tianjin, China). The physical properties of the four resins are summarized in Table 1. All of the resins were pretreated in a column by washing with 1.0 M HCl, deionized water and 1.0 M NaOH in turn and finally washed thoroughly with deionized water to pH around 7.0 before use. The anion exchangers were in free base form after pretreatment. Following pretreatment, the samples were dried under vacuum and stored in sealed containers.

1-2. Instruments

Concentrations of α -TS and TPGS were measured by Waters HPLC system (Milford, MA, USA), equipped with a 1525 binary HPLC pump, a Waters 717 plus auto-injector and a Waters 2487 dual absorbance UV detector at a wavelength of 284 nm. A Sunfire C₁₈ column (4.6 mm i.d.×250 mm, 5 μ m, Waters Co., Milford, MA, USA) for α -TS and a Develosil[®] Rpaqueous C₃₀ column (4.6 mm i.d.×250 mm, 5 μ m, Nomura, Japan) for TPGS were the stationary phases. The column temperature was maintained at 308 K and the mobile phases were methanol/acetic acid (100/0.5, v/v) for α -TS, acetonitrile/isopropanol (65/35, v/v) for TPGS at 1 mL/min. The adsorption experiments were carried out in a Julabo SW22 thermostatic shaker (Seelbach, German) at a certain speed and temperature (± 0.1 K).

Table 1. Physical properties of basic polymeric adsorbents used in this study

| Typical properties | Trade name | | | |
|-------------------------------------|----------------|----------------|----------------|-----------------|
| | HZD-9 | D315 | D301 | D301r |
| Matrix | Polyacrylic | Polyacrylic | Polystyrene | Polystyrene |
| Functional groups | Tertiary amine | Tertiary amine | Tertiary amine | Secondary amine |
| Ionic form | Free base | Free base | Free base | Free base |
| Particle size (mm) | 0.60-0.90 | 0.60-0.90 | 0.60-0.90 | 0.60-0.90 |
| Water content (%) | 0.63 | 0.46 | 0.52 | 0.56 |
| Apparent density (g/mL) | 1.07 | 1.10 | 1.05 | 1.04 |
| Porosity | 0.68 | 0.51 | 0.55 | 0.59 |
| Saturation capacity of HCl (mmol/g) | 4.44 | 5.62 | 4.15 | 4.06 |

2. Single-component Adsorption Experiments

Single-component adsorption experiments of α -TS onto four weakly basic anion exchange resins were performed by adding known amounts of dry adsorbents (0.5 g for HZD-9, 1.5 g for D315, 1.0 g for D301, 0.5 g for D301r) to a set of 50 mL conical flasks filled with 10 mL α -TS solutions having various initial concentrations (5-90 mg/mL). To reduce the effect of the analysis error (within $\pm 3\%$) to the experimental results, different amounts of resins were added to make sure the ratios (C_e/C_0) of the liquid-phase concentrations of α -TS at equilibrium (C_e) and at the beginning (C_0) were between 0.10 and 0.90. The flasks were placed in a thermostatic shaker (Julabo SW22, German) and agitated at 200 rpm at 293 K for 24 h to allow attainment of equilibrium to determine the equilibrium isotherms. Upon equilibrium, shaking was stopped and samples were taken from each flask and analyzed by HPLC.

TPGS used in this study was synthesized and purified in our laboratory as described before [21]. Single-component adsorption experiments of TPGS onto these anion exchange resins were completed by adding known amounts of dry adsorbents (0.5 g for HZD-9, D301 and D301r, 1.0 g for D315) to a set of 50 mL conical flasks filled with 20 mL TPGS solutions at the concentration of 31 mg/mL. The flasks were placed in a thermostatic shaker (Julabo SW22, German) and agitated at 200 rpm at 293 K. Samples were taken and analyzed after agitation for 2, 4, 6, 8 and 10 h, respectively.

The amount adsorbed at equilibrium, q_e was calculated as:

$$q_e = \frac{V(C_0 - C_e)}{M} \quad (1)$$

where V is the volume of solution, M is the mass of the resin, and C_0 and C_e are the liquid-phase concentrations of solutes at initial and equilibrium time, respectively. The adsorbed amounts of TPGS at time t , q_t , were calculated by analogy from Eq. (1).

3. Equilibrium Experiments of α -TS onto HZD-9

Adsorption of α -TS onto HZD-9 at different temperatures (273, 283 and 293 K) was done by adding 0.5 g of HZD-9 to a set of 50 mL conical flasks filled with 10 mL α -TS solutions having various initial concentrations (5-110 mg/mL). The flasks were placed in a thermostatic shaker (Julabo SW22, German) and agitated with 200 rpm at different temperatures for 24 h to allow attainment of equilibrium to determine the equilibrium isotherms. Upon equilibrium, shaking was stopped and samples were taken from each flask and analyzed by HPLC. The amount adsorbed at equilibrium, q_e was calculated by Eq. (1).

4. Kinetic Experiments

For the kinetic studies, 50 ml of α -TS solution at the desired initial concentrations was added into a 250 ml conical flask containing 2.5 g of the dried resin beads. The flask was capped and agitated at constant temperature of 273 K at 200 rpm in the shaker for 24 h. Preliminary experiments showed that increasing the rotation speed from 100 to 400 rpm resulted in slight increase in the initial adsorption rate of α -TS onto the resin. This meant that the external film mass transfer was not the rate-limiting step in this adsorption process and 200 rpm was fast enough to eliminate the resistance to external film mass transfer. At determined time intervals, fixed-volume samples of 100 μ L were withdrawn and analyzed by HPLC. The total solution volume reduction due to sampling was less than

3% for all experiments, so the adsorption rates were measured under essentially constant liquid volume.

To evaluate the influence of temperature on the α -TS uptake, kinetic experiments at other two temperatures (283 and 293 K) were done as well. The adsorbed amounts of α -TS at time t , q_t , were calculated by analogy from Eq. (1).

MODELING

Adsorption isotherms are used to describe adsorption equilibria at given temperatures. The isotherms obtained under different temperatures can also provide basic data for thermodynamic study. We tested three isotherm models: Langmuir [22], Freundlich [23-26], and Dubinin-Radushkevich [27,28] shown in Eqs. (2), (3), and (4), respectively:

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

$$q_e = q_m e^{-\beta \varepsilon^2} \quad (4)$$

The linear forms of these models are Eqs. (5), (6), and (7), respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}} C_e \quad (5)$$

$$\log q_e = \log K_F + 1/n \log C_e \quad (6)$$

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (7)$$

where C_e and q_e are the adsorbate equilibrium concentrations in the liquid and the adsorbate equilibrium amount in solid phases, respectively; q_{max} is the maximum adsorption capacity according to Langmuir monolayer adsorption; K_L is the Langmuir constant related to the rate of adsorption; K_F and n are Freundlich constants related to adsorption capacity and the adsorbent surface heterogeneity ($1/n=0$ -irreversible; $0 < 1/n < 1$ -favorable; $1/n > 1$ -unfavorable); q_m is the D-R monolayer capacity; β is a constant related to adsorption energy, and ε is the Polanyi potential which is related to the equilibrium concentration as shown in Eq. (8):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

where R is the gas constant (8.314 J/mol K) and T is the absolute temperature; The constant β gives the mean free energy, E , of adsorption per molar of adsorbate when they are transferred to the surface of the solid from infinity in the solution and can be computed using Eq. (9):

$$E = \frac{1}{\sqrt{2\beta}} \quad (9)$$

The thermodynamic parameters that must be considered to determine the adsorption process are changes in enthalpy (ΔH^0), entropy (ΔS^0), and free energy (ΔG^0) due to transfer unit mole of solute from solution onto the solid-liquid interface. The thermodynamic parameters, ΔH^0 , ΔS^0 , and ΔG^0 can be computed using equations as follows [29]:

$$\Delta G^0 = -RT \ln K_L \quad (10)$$

$$\ln K_L = -\frac{\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (11)$$

where K_L is the Langmuir isotherm constant; R is the gas constant (8.314 J/mol K) and T is the absolute temperature.

ΔG^0 at different temperatures can be obtained by Eq. (10). According to Eq. (11), the values of ΔH^0 and ΔS^0 can be calculated from the slope and intercept of the plot of $\ln K_L$ vs. $1/T$. The negative value of ΔH^0 indicates the exothermic process and the positive value indicates the endothermic process. Negative ΔG^0 indicates the spontaneity of the adsorption process, and a higher negative value reflects a more energetically favorable adsorption. A positive ΔS^0 value reflects the increase of random and a negative ΔS^0 value represents the decrease of random at the solid-liquid interface.

Three kinetic models were used to study this adsorption process: the pseudo-first-order equation (Eq. (12)) of Lagergren [30, 31], the pseudo-second-order rate equation (Eq. (13)) [32], and the intraparticle diffusion equation (Eq. (14)) [33,34]:

$$\frac{dq_t}{dt} = k_{s1}(q_e - q_t) \quad (12)$$

$$\frac{dq_t}{dt} = k_{s2}(q_e - q_t)^2 \quad (13)$$

$$q_t = f(t^{1/2}) \quad (14)$$

where q_e and q_t are the amount of α -TS adsorbed per unit weight of adsorbent at equilibrium and at any time t , respectively; k_{s1} is the rate constant of pseudo-first-order adsorption; k_{s2} is the rate constant of pseudo-second-order adsorption. Integrating these and applying initial condition $q_t=0$ when $t=0$, Eqs. (12), (13) may be rearranged for linearized data plotting shown as Eqs. (15), (16), the initial rate of the intraparticle diffusion is shown as Eq. (17):

$$\log(q_e - q_t) = \log q_e - \frac{k_{s1}}{2.303} t \quad (15)$$

$$\frac{t}{q_t} = \frac{1}{k_{s2} q_e^2} + \frac{1}{q_e} t \quad (16)$$

$$q_t = k_{int} t^{1/2} \quad (17)$$

where k_{int} is the intraparticle diffusion rate constant. The parameters for the three kinetic models can be calculated from the slopes and intercepts of these linearized equations.

We used the root mean square error (RMSE), mean absolute error (MAE) and determination coefficient (R^2) statistics to evaluate the accuracy of the isotherm and kinetic models. The RMSE and MAE are defined as follows:

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (Y_{i\text{observed}} - Y_{i\text{predicted}})^2} \quad (18)$$

$$MAE = \frac{1}{N} \sum_{i=1}^N |Y_{i\text{observed}} - Y_{i\text{predicted}}| \quad (19)$$

in which N is the number of the data set, Y_i is the adsorbate equilibrium amount in solid phases q_e or the adsorption amount of α -

TS at time t q_t .

RESULTS AND DISCUSSION

1. Single-component Adsorption Isotherms

Two polyacrylic resins, D315 and HZD-9, with different porosity and two polystyrene resins, D301 and D301r, having different functional groups were chosen to explore the effect of the resin matrix, functional group and porosity of the anion exchange resins to the adsorption of α -TS. The physical properties of the four weakly basic anion exchange resins are shown in Table 1. For D315 and HZD-9, the matrix and the functional group were the same. The porosity of HZD-9 was higher (0.68 for HZD-9, 0.51 for D315), and higher saturation capacity of HCl was possessed by D315, mean-

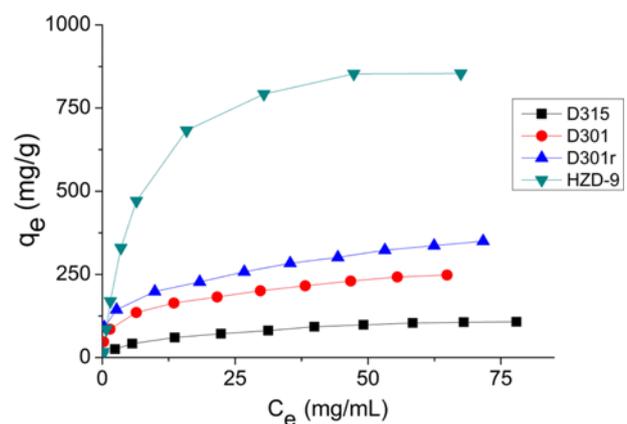


Fig. 2. Adsorption isotherms of α -TS onto four weakly basic anion exchange resins at 293 K.

Table 2. Values of isotherm parameters for α -TS adsorption on the four weakly basic anion exchangers at 293 K

| Isotherm model | Parameters | | | |
|--|------------|--------|--------|--------|
| | HZD-9 | D315 | D301 | D301r |
| Langmuir | | | | |
| K_L (mL/mg) | 0.149 | 0.075 | 0.183 | 0.140 |
| q_{max} (mg/g) | 952.38 | 124.87 | 258.29 | 365.31 |
| R^2 | 0.9991 | 0.9919 | 0.9858 | 0.9808 |
| MAE (mg/g) | 9.70 | 3.25 | 16.08 | 25.63 |
| RMSE (mg/g) | 10.86 | 4.06 | 19.54 | 32.39 |
| Freundlich | | | | |
| K_F (mL/g) | 140.28 | 19.34 | 74.32 | 112.56 |
| n | 2.02 | 2.42 | 3.39 | 3.86 |
| R^2 | 0.9216 | 0.9868 | 0.9972 | 0.9959 |
| MAE (mg/g) | 94.51 | 3.50 | 2.82 | 5.32 |
| RMSE (mg/g) | 123.59 | 4.18 | 3.50 | 6.50 |
| Dubinin-Radushkevich | | | | |
| q_m (mg/g) | 625.78 | 86.12 | 185.86 | 263.33 |
| β (mol ² /kJ ²) | 0.515 | 1.84 | 0.094 | 0.115 |
| E (kJ/mol) | 0.99 | 0.52 | 2.31 | 2.09 |
| R^2 | 0.8367 | 0.7684 | 0.7153 | 0.6431 |
| MAE (mg/g) | 140.50 | 15.96 | 35.85 | 48.68 |
| RMSE (mg/g) | 157.53 | 17.45 | 42.96 | 58.24 |

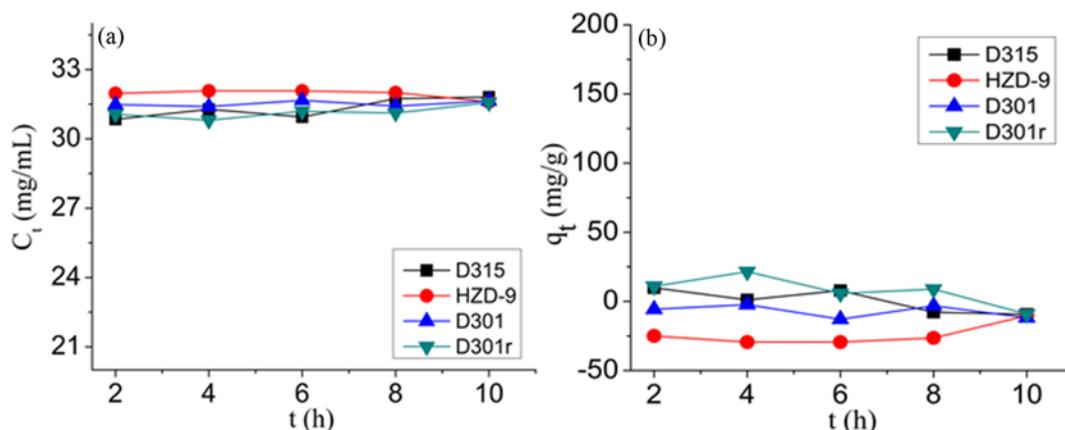


Fig. 3. Adsorption of TPGS onto four weakly basic anion exchange resins with the initial concentration of 31 mg/mL at 293 K. (a) Plot of C_t vs. t ; (b) Plot of q_t vs. t .

ing that there were more basic adsorption sites on D315. D301 and D301r had close water content, apparent density and porosity, while D301r had the stronger basic secondary amine as the functional group and showed higher saturation capacity of HCl.

The adsorption isotherms of α -TS onto the four resins are shown in Fig. 2 and the calculated parameters are listed in Table 2. No α -T was detected after 24 hours with the four weakly basic anion exchange resins as the adsorbents. The amounts of α -TS adsorbed onto the four resins increased as D315 < D301 < D301r < HZD-9, which was consistent with the increasing order of the porosity of the resins. For the polystyrene resins D301 and D301r, D301r with stronger basicity and higher porosity showed higher adsorption capacity for α -TS. Although there were more basic adsorption sites on D315, the D301 resin having the same functional group with D315 but different polystyrene matrix and higher porosity showed higher adsorption capacity. For the polyacrylic resins D315 and HZD-9, although D315 possessed more basic adsorption sites, HZD-9 with higher porosity exhibited higher adsorption capacity. Among the four weakly basic anion exchange resins, HZD-9 having the highest porosity showed the highest adsorption capacity. Thus the basicity of the functional group, the type of the matrix and the porosity might all affect the adsorption of α -TS. Among them, porosity showed the greatest impact. The reason might be that the resin with higher porosity might have more large-sized and effective adsorption sites available for the large-sized α -TS molecule.

The Langmuir isotherm having the smallest RMSE, MAE and the highest R^2 best described the isotherms of α -TS adsorbed on D315 and HZD-9 (Table 2). HZD-9 showed much higher adsorption capacity for α -TS than D315 with q_{max} as high as 953.29 mg/g at 293 K. The Langmuir isotherms revealed the monolayer adsorption mode for α -TS adsorbed onto D315 and HZD-9. The Freundlich isotherm with the smallest RMSE, MAE and the highest R^2 best depicted the isotherms on D301 and D301r. D301r had higher adsorption capacity with higher K_F and n values. For D301 and D301r, $1/n < 1$ reflected the favorable adsorption of α -TS onto D301 and D301r.

To explore the adsorption selectivity of the weakly basic anion exchange resin, single-component adsorption experiments of TPGS onto the four resins were carried out. The liquid-phase concentra-

tions of TPGS at time t , C_t , and the corresponding adsorbed amounts of TPGS, q_t , are depicted in Fig. 3(a) and Fig. 3(b), respectively. No α -T and α -TS were detected implying the stability of the ester-bonds with the four weakly basic anion exchange resins as the adsorbents. The C_t could be considered constant during 10 h with the relative standard deviation (RSD) of the five C_t 's < 1.5%. The values of C_t were close to the initial concentration of TPGS and the calculated q_t were between ± 30 mg/g, which can be attributed to the assay variation. These results revealed that TPGS was almost not adsorbed onto the four weakly basic anion exchange resins.

According to the single-component adsorption experiments, α -TS was strongly adsorbed onto the investigated four weakly basic anion exchange resins, due to the carboxyl group in it, while TPGS was almost not adsorbed. Thus the weakly basic anion exchange resins exhibited excellent selectivity for the adsorption of α -TS against TPGS, and might be successfully applied to the separation of α -TS and TPGS. Coupled with the consideration of the adsorption capacity of the four resins, the anion exchange resin HZD-9 was selected for the following equilibrium, thermodynamic and kinetic studies.

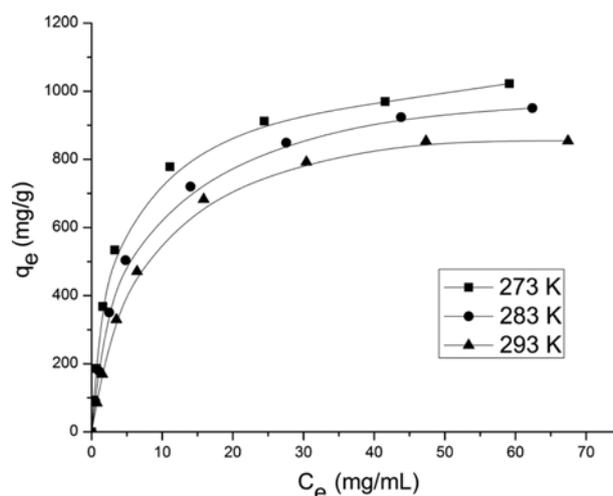


Fig. 4. Adsorption isotherms of α -TS onto HZD-9. Conditions: 0.6 to 0.9 mm particle size, 0.5 g/10 mL dose, 273, 283 and 293 K temperature.

Table 3. Values of isotherm parameters for α -TS adsorption on the weakly basic anion exchanger HZD-9

| Isotherm model | Parameters | | |
|---|------------|---------|--------|
| | 273 K | 283 K | 293 K |
| Langmuir | | | |
| K_L (mL/mg) | 0.283 | 0.191 | 0.149 |
| q_{max} (mg/g) | 1068.38 | 1027.75 | 953.29 |
| R^2 | 0.9993 | 0.9996 | 0.9991 |
| MAE (mg/g) | 19.06 | 12.16 | 9.70 |
| RMSE (mg/g) | 21.75 | 14.78 | 10.86 |
| Freundlich | | | |
| K_F (mL/g) | 226.99 | 177.83 | 140.28 |
| n | 2.33 | 2.15 | 2.02 |
| R^2 | 0.9077 | 0.9215 | 0.9216 |
| MAE (mg/g) | 112.32 | 95.04 | 94.51 |
| RMSE (mg/g) | 141.42 | 123.16 | 123.59 |
| Dubinin-Radushkevich | | | |
| q_m (mg/g) | 743.23 | 685.40 | 625.78 |
| β (mol ² /J ²) | 0.232 | 0.354 | 0.515 |
| E (J/mol) | 1.47 | 1.19 | 0.99 |
| R^2 | 0.8723 | 0.8564 | 0.8367 |
| MAE (mg/g) | 146.80 | 145.00 | 140.50 |
| RMSE (mg/g) | 169.04 | 167.18 | 157.53 |

2. Equilibrium Study of α -TS Adsorbed onto HZD-9

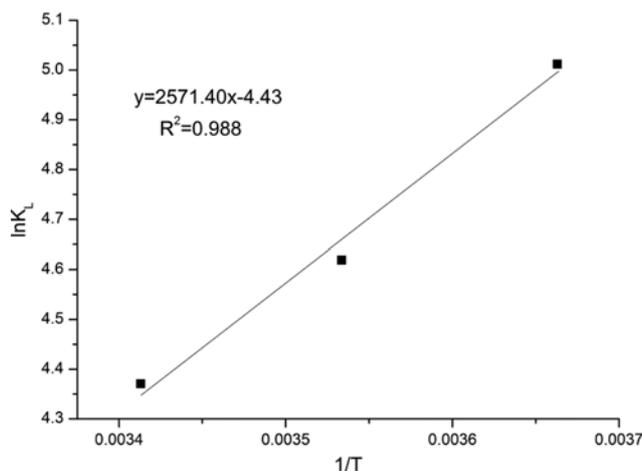
The adsorption isotherms of α -TS onto HZD-9 at three temperatures are shown in Fig. 4, the calculated parameters are listed in Table 3. The adsorption amount of α -TS exhibited steep increase at low concentrations and the trend became weaker as the equilibrium concentration increased. Clearly in Fig. 4 the adsorption capacity decreased as the temperature increased. The Langmuir isotherm showed the best fit to the adsorption data compared with other isotherm equations with the highest R^2 and smallest RMSE and MAE (Table 3). This fact indicated the monolayer coverage of α -TS onto the HZD-9 resin. According to the Langmuir equation, the monolayer saturation capacities of α -TS onto HZD-9 at 273, 283 and 293 K were 1068.38, 1027.75, and 953.29 mg/g, respectively. They decreased when the temperature increased.

The Freundlich isotherm did not fit the experimental data very well with R^2 lower than the Langmuir isotherm but higher than the Dubinin-Radushkevich isotherm. The Freundlich constant, K_F , which is related to the adsorption capacity, also showed that the adsorption capacity decreased with temperature increased. The $1/n$ values for the system studied were less than unity and reflected the favorable adsorption of α -TS onto HZD-9 indicating a strong interaction between the α -TS and HZD-9 resin.

The Dubinin-Radushkevich equation represented the poorest fit to the experimental data (Table 3). The calculated monolayer capacities, q_m , were much lower than the experimental data.

3. Thermodynamic Study of α -TS Adsorbed onto HZD-9

The plot of $\ln K_L$ vs. $1/T$ is shown in Fig. 5, the calculated ΔH^0 , ΔS^0 and ΔG^0 are listed in Table 4. Negative ΔG^0 values were obtained revealing the spontaneous nature of this adsorption process. With temperature increased, the ΔG^0 values varied slightly but still de-

**Fig. 5. Plot of $\ln K_L$ vs. $1/T$.****Table 4. Thermodynamic parameters for adsorption of α -TS on HZD-9**

| ΔH^0 (kJ/mol) | ΔS^0 (kJ/mol K) | ΔG^0 (kJ/mol) | | |
|--------------------------|----------------------------|-----------------------|--------|--------|
| | | 273 K | 283 K | 293 K |
| -21.38 | -0.037 | -11.38 | -10.87 | -10.65 |

creased, indicating that higher temperature was unfavorable for the adsorption process.

The negative ΔH^0 value demonstrated the exothermic nature of the adsorption process. The calculated results were in agreement with the experimental data that the adsorption amount decreased as temperature increased.

The ΔS^0 value was quite small, suggesting that the entropy of α -TS was almost constant before and after the adsorption. Thus, the adsorption of α -TS onto the anion exchange resin under employed conditions was considered as an enthalpy driven process.

4. Adsorption Kinetic Study of α -TS Adsorbed onto HZD-9

The study of adsorption kinetics is significant as it provides valuable insights into the adsorption pathway and describes the solute uptake rate. It is important to be able to predict the rate at which the adsorbate is removed from solutions in order to design appropriate adsorption treatment processes. In this paper, the effects of the initial concentrations and the adsorption temperatures to the adsorption rates of α -TS onto HZD-9 were investigated.

4-1. The Effect of the Initial Concentration

Fig. 6 shows the curves of q_t over the contact time t for the adsorption of α -TS onto HZD-9 under five different initial concentrations at 273 K. It was apparent that both q_t and the adsorption rates (the slope of q_t vs. t) increased as the initial concentration of α -TS increased. The adsorption showed rapid uptake in the early period with all the different initial concentrations. After 3 hours' contact, 83.6%, 61.5%, 61.7%, 67.4%, and 67.3% of α -TS with respect to q_t at 24 h were already adsorbed onto HZD-9 corresponding to the initial concentrations of 10.012, 30.024, 50.006, 70.054 and 90.032 mg/mL, respectively. After 6 hours' contact, the adsorption rate decreased significantly. When the contact time extended to 12 h, 98.1%, 92.1%, 93.8%, 94.0% and 94.0% of α -TS with respect to q_t at 24 h

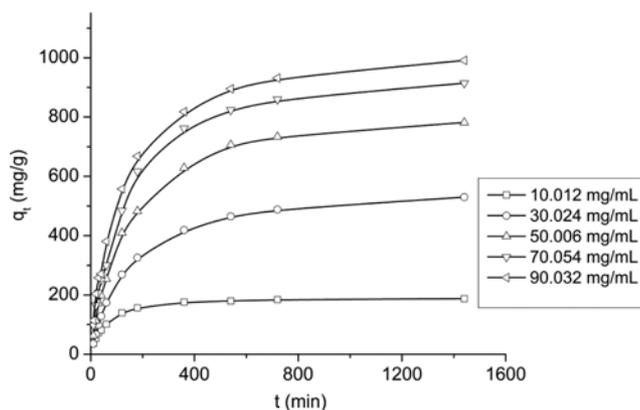


Fig. 6. Effect of agitation time on α -TS adsorbed onto HZD-9 at various initial concentrations (10-90 mg/mL) at 273 K.

were adsorbed corresponding to the above initial concentrations, respectively. Obviously the adsorption rates after 12 h were very slow, meaning the adsorption equilibrium was near. Although the adsorption rate for α -TS with the initial concentration of 10.012 mg/mL was lower, the experimental results showed that 12 h was long enough for it to reach the adsorption equilibrium, which could be attributed to the lower adsorption amount at this initial concentration. For the higher initial concentrations from 30.024 to 90.032 mg/mL, the equilibrium time was alike under the joint action of the adsorption rate and the adsorption amount. Considering the low adsorption rate after 12 h and the possible evaporation of the solvent-alcohol, 24 h was decided as the equilibrium time for the adsorption of α -TS with the above initial concentrations at 273 K.

The experimental data were fitted to the linearized forms of the kinetic models. Table 5 presents the parameters of the kinetic models fitted to the experimental data. The pseudo-first-order model did not show good fit with R^2 between 0.958 and 0.989 for the whole range of contact time. The plots were almost linear in the initial one hour shown in Fig. 7, which means that the adsorption pro-

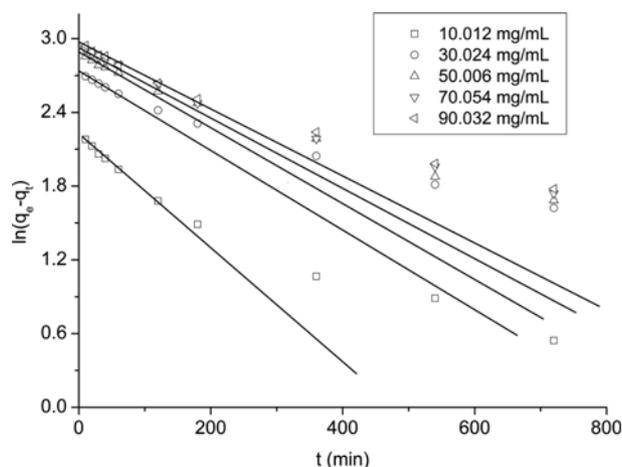


Fig. 7. Pseudo-first-order adsorption kinetics of α -TS adsorbed onto HZD-9 at various initial concentrations at 273 K.

cess may be a multiple pseudo-first-order kinetics that was also represented in some adsorption systems such as β -lactoglobulin and hemoglobin adsorption by silica [35] and bisphenol A adsorption by kaolinite [36]. We could see from Fig. 7 that the adsorption in the beginning hours was more rapid than the following hours.

However, the pseudo-second-order model provided good agreement with the experimental data with R^2 larger than 0.999, and with RMSE and MAE smaller than other models. The $q_{e,cal}$ value estimated by the pseudo-second-order model was close to the experimental $q_{e,exp}$. So the pseudo-second-order equation best described the adsorption rate of α -TS onto HZD-9 (Fig. 8).

From the plot of the linearized form of the intraparticle diffusion model shown in Fig. 9, the plots are not linear over the whole range of contact time, implying that more than one process affected the α -TS adsorption process. The mass-transport processes during the adsorption involve bulk transport in the liquid phase, diffusion across the liquid film surrounding the adsorbent particles, and diffusion into micropores and macropores in the adsorbent

Table 5. Kinetic constants of pseudo-first-order, pseudo-second-order, and intra-particle diffusion models for the adsorption of α -TS onto HZD-9

| C_0 (mg/ mL) | $q_{e,exp}$ (mg/g) | Pseudo-first-order equation | | | | | Pseudo-second-order equation | | | | Intraparticle diffusion | | |
|----------------------|-----------------------|-----------------------------|-----------------------|--------|------------------------|---------------------------|------------------------------|---------|------------------------|--|-------------------------|------------------------|---------------|
| | | k_{s1} (1/min) | $q_{e,cal}$ (mg/g) | R^2 | RMSE/ MAE (mg/g) | k_{s2} (g/mg min) | $q_{e,cal}$ (mg/g) | R^2 | RMSE/ MAE (mg/g) | k_p (mg/g min ^{1/2}) | R^2 | RMSE/ MAE (mg/g) | |
| 273 K | 10.012 | 187.47 | 5.30×10^{-3} | 118.58 | 0.9587 | 34.63/28.64 | 1.07×10^{-4} | 194.55 | 0.9998 | 6.64/5.55 | 12.357 | 0.9846 | 102.76/56.96 |
| | 30.024 | 529.87 | 3.46×10^{-3} | 448.75 | 0.9835 | 49.28/39.44 | 1.19×10^{-5} | 581.40 | 0.9998 | 41.64/36.64 | 22.677 | 0.9377 | 115.14/70.28 |
| | 50.006 | 781.90 | 3.85×10^{-3} | 665.27 | 0.9897 | 69.46/57.74 | 9.01×10^{-6} | 854.70 | 0.9996 | 53.26/46.75 | 34.420 | 0.9567 | 172.26/92.87 |
| | 70.054 | 914.47 | 3.87×10^{-3} | 744.73 | 0.9817 | 96.83/81.88 | 9.03×10^{-6} | 987.17 | 0.9992 | 53.72/46.84 | 42.758 | 0.9692 | 237.77/128.76 |
| | 90.032 | 991.42 | 3.69×10^{-3} | 779.83 | 0.9825 | 132.65/113.44 | 9.62×10^{-6} | 1058.20 | 0.9995 | 48.75/43.85 | 49.124 | 0.9816 | 293.08/155.86 |
| 283 K | 10.064 | 181.25 | 1.64×10^{-3} | 97.95 | 0.9580 | 89.60/84.21 | 2.31×10^{-4} | 186.22 | 1.0000 | 3.55/3.34 | 14.755 | 0.6453 | 144.15/90.13 |
| | 50.032 | 720.66 | 7.74×10^{-3} | 592.93 | 0.9874 | 64.70/50.53 | 2.35×10^{-5} | 763.36 | 0.9992 | 34.63/25.54 | 44.799 | 0.9902 | 346.25/185.82 |
| | 90.070 | 909.56 | 7.33×10^{-3} | 651.63 | 0.9867 | 115.23/92.50 | 2.23×10^{-5} | 949.67 | 0.9992 | 46.65/41.85 | 60.793 | 0.9832 | 507.54/280.25 |
| 293 K | 10.032 | 172.72 | 1.17×10^{-2} | 79.43 | 0.9635 | 43.82/32.21 | 4.28×10^{-4} | 175.75 | 0.9999 | 4.10/2.62 | 20.557 | 0.4518 | 246.86/159.28 |
| | 49.988 | 671.87 | 1.16×10^{-2} | 475.34 | 0.9950 | 92.69/68.60 | 5.81×10^{-5} | 689.66 | 0.9996 | 21.07/17.38 | 52.256 | 0.8331 | 492.69/296.41 |
| | 90.060 | 850.69 | 1.29×10^{-2} | 537.03 | 0.9596 | 113.47/86.75 | 5.45×10^{-5} | 869.56 | 0.9996 | 43.80/37.14 | 70.050 | 0.8841 | 687.47/407.83 |

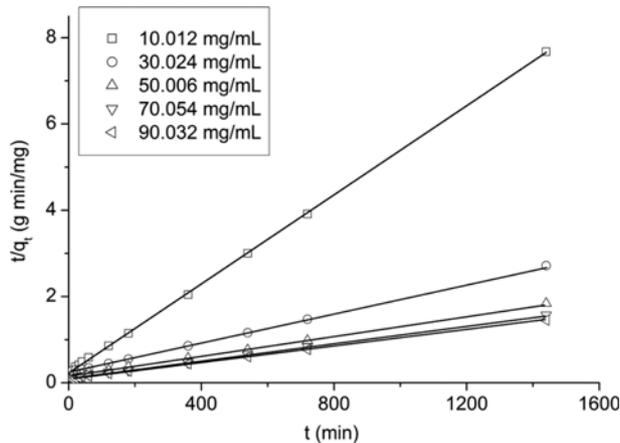


Fig. 8. Pseudo-second-order adsorption kinetics of α -TS adsorbed onto HZD-9 at various initial concentrations at 273 K.

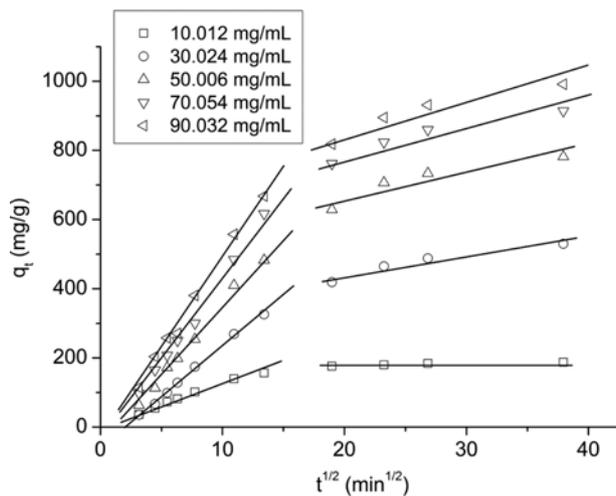


Fig. 9. Intraparticle diffusion plots of α -TS adsorbed onto HZD-9 at various initial concentrations at 273 K.

particles. The intraparticle diffusion may be controlled by the pore diffusion or surface diffusion, or the combination of them. The overall adsorption process may be controlled by one step, like film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or the combination of more than one step [37]. If the intraparticle diffusion is the only rate-controlling step, the plot passes through the origin; if more than one process controls the adsorption, multi-linear plots are obtained, the adsorption is controlled by the process having lower slope.

As shown in Fig. 9, the plot passes almost through the origin, indicating that intraparticle diffusion was the only rate-controlling step during the initial 180 min. The linearized correlation parameters for the data of the initial 180 min are shown in Table 5, and the adsorption rate (k_{int}) increased with the concentration increased as shown in the table. Then the second linear portion starts from 360 min to 720 min, with a lower slope representing a slower mass transfer. This can be explained in two ways: on one hand, after 3 hours' contact, 83.6%, 61.5%, 61.7%, 67.4%, 67.3% of α -TS with respect to the equilibrium adsorption amounts had been adsorbed

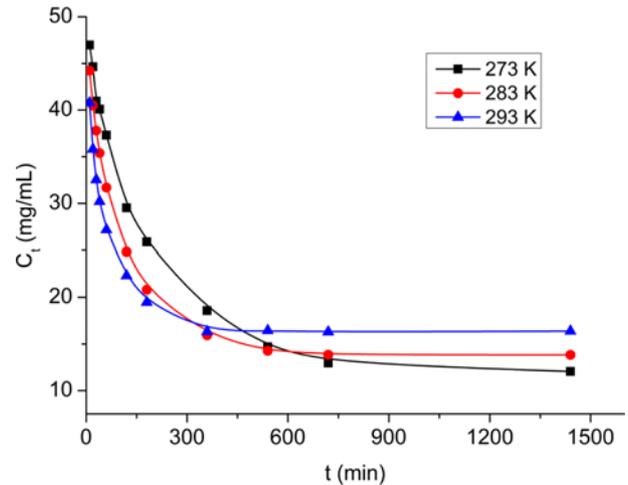


Fig. 10. Experimental concentration decay curves of α -TS adsorbed onto HZD-9 at different temperatures. Conditions: 0.6 to 0.9 mm, 273, 283 and 293 K temperature, $C_0=50.0$ mg/mL, and 200 rpm.

onto the resin leaving less available sites on the resin surface, so the adsorption rate fell; on the other hand, the adsorbed molecules of α -TS added extra steric hindrance in the channels, inhibiting the adsorption of the following molecules.

4-2. The Effect of Temperature

Fig. 10 illustrates the experimental data for the temperature dependence of α -TS adsorbed onto HZD-9 with the initial concentration of 50.0 mg/mL for an example, similar regularity applies to other initial concentrations (10.0 and 90.0 mg/mL). The liquid-phase concentration of α -TS, C_t , decreased faster at higher temperature, but the equilibrium concentration at higher temperature was higher, meaning that the adsorption rate quickened but the adsorption capacity decreased when the temperature increased. So the equilibrium time shortened with the increase of temperature. For α -TS with the initial concentration of 50.0 mg/mL, the equilibrium amount decreased from 778.15 mg/g to 719.92 mg/g and 682.69 mg/g, and the adsorption equilibrium time decreased from 24 h to 12 h and 9 h when the temperature increased from 273 K to 283 K and 293 K, respectively.

The kinetic simulation results at different temperatures are also listed in Table 5. The pseudo-second-order equation with R^2 larger than 0.999, and with RMSE and MAE smaller than the other models best described the adsorption behavior of α -TS at all the three temperatures. The $q_{e,cal}$ values estimated by the pseudo-second-order model were close to the experimental $q_{e,exp}$. Taking the initial concentration of 50.0 mg/mL as an example, the adsorption rate k_{s2} increased from 9.01×10^{-6} to 2.35×10^{-5} and 5.81×10^{-5} g/mg min when the temperature increased from 273 K to 283 K and 293 K, respectively. Although the temperature affected the adsorption rate and the equilibrium amount, the pseudo-second-order equation fitted best with the kinetic data at the three temperatures, meaning that there was no change in the type of kinetics with temperature changed.

CONCLUSIONS

The results of present investigation showed that α -TS was strongly

adsorbed onto the weakly basic anion exchange resins, while TPGS was almost not adsorbed, due to the carboxyl group existing in α -TS. The weakly basic anion exchange resins exhibited excellent selectivity for the adsorption of α -TS against TPGS, and might be successfully applied to the separation of α -TS and TPGS. The basic strength of the functional group, the type of the matrix and the porosity of the resin all influenced the adsorption of α -TS. Among all the factors, the porosity showed the greatest impact. The resin HZD-9 with the highest porosity showed the highest adsorption capacity for α -TS, q_{max} was as high as 953.29 mg/g at 293 K.

Equilibrium, thermodynamic and kinetic studies were conducted for the adsorption of α -TS onto HZD-9. The Langmuir isotherm described the experimental data very well. The adsorption capacity decreased with the increase of temperature; the monolayer saturation capacities of α -TS onto HZD-9 at 273, 283 and 293 K were 1068.38, 1027.75, and 953.29 mg/g, respectively. The thermodynamic study confirmed the spontaneous adsorption process with negative ΔG^0 . The negative values of ΔH^0 revealed the exothermic property of the process. The value of ΔS^0 was quite small, implying that the entropy of α -TS was almost constant before and after the adsorption. So this adsorption was an enthalpy driven process. The kinetics of α -TS adsorbed onto HZD-9 was studied, and the pseudo-second-order equation provided the best correlation of the experimental data. The mass transfer rate increased with the increment of the initial concentrations and the adsorption temperatures.

These studies provided the basic data for the separation of α -TS and TPGS. The acid and ester structures contribute to a large proportion of compounds, and there are numerous kinds of resins having specific properties that can be applied to the separation and purification. Thus this adsorption method using the weakly basic anion exchange resins is not only important for the production of TPGS, but also instructive for the separation of other PEG-esters from reaction mixtures.

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NOMENCLATURE

| | |
|-------------|--|
| C_0 | : initial liquid-phase concentration [mg/mL] |
| C_e | : equilibrium liquid-phase concentration [mg/mL] |
| E | : Dubinin-Radushkevich isotherm constant [J/mol] |
| k_{int} | : intraparticle diffusion rate constant [mg/g min ^{1/2}] |
| k_{s1} | : pseudo-first-order adsorption rate constant [1/min] |
| k_{s2} | : pseudo-second-order adsorption rate constant [g/mg min] |
| K_F | : Freundlich isotherm constant [mL/g] |
| K_L | : Langmuir constant [mL/mg] |
| M | : mass of the resin [g] |
| n | : Freundlich isotherm constant |
| q_e | : equilibrium solid-phase concentration [mg/g] |
| $q_{e,cal}$ | : calculated equilibrium solid phase concentration [mg/g] |

| | |
|---------------|--|
| $q_{e,exp}$ | : experimental equilibrium solid phase concentration [mg/g] |
| q_{max} | : Langmuir constant [mL/mg] |
| q_t | : solid-phase concentration at time t [mg/g] |
| R | : gas constant [J/mol K] |
| t | : time [min] |
| T | : temperature [K] |
| V | : volume of the solute [mL] |
| β | : Dubinin-Radushkevich isotherm constant [mol ² /J ²] |
| ε | : Dubinin-Radushkevich isotherm constant [J/mol] |
| ΔG^0 | : free energy change [kJ/mol] |
| ΔH^0 | : enthalpy change [kJ/mol] |
| ΔS^0 | : entropy change [kJ/mol K] |

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