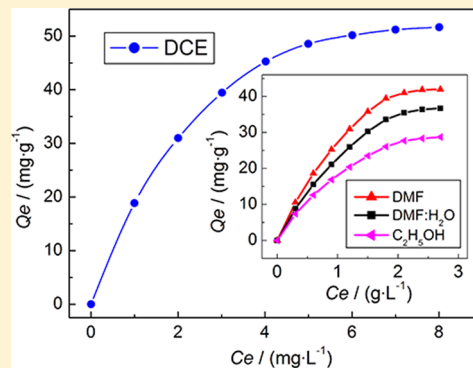


Adsorption Properties of Polyvinyl-Alcohol-Grafted Particles Toward Genistein Driven by Hydrogen-Bond Interaction

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ABSTRACT: The adsorption properties of polyvinyl alcohol (PVA)-grafted silica gel particles PVA/SiO₂ toward genistein are researched in this paper. The effects of the main factors on the adsorption properties are investigated, the adsorption mechanism is explored in depth, and the adsorption thermodynamics is researched. The experimental results show that the conventional hydrogen bond is formed between the hydroxyl groups with high density on the surfaces of PVA/SiO₂ and the phenolic hydroxyl groups in genistein, while π -type hydrogen bond is formed between the hydroxyl groups of PVA/SiO₂ and the conjugated aromatic rings. It is the two types of hydrogen bond that make the functional composite particles PVA/SiO₂ produce very strong physical adsorption toward genistein. The competitive adsorption of the solvent can have severe negative impact on the adsorption capacity of genistein. Increasing temperature will weaken the hydrogen-bond interaction between PVA/SiO₂ particles and genistein. The existence of electrolytes in the protic solvent will affect the adsorption negatively. The adsorption process of PVA/SiO₂ particles toward genistein is exothermic and driven by enthalpy. The adsorption isotherm data matches the Langmuir model.



1. INTRODUCTION

The hydrogen-bonding interaction is an important secondary bond force that exists in all sorts of states such as gas, liquid, crystal, and so on. It influences the properties and structures of many matters, and it has wide applications such as molecular self-assembly, molecular recognition, the extraction of pharmacological active substance, the separation of biological macromolecules, the protection of environment, and so on.^{1–5} Solid adsorbents driven by hydrogen-bond interaction are prepared through molecular design, which are of great scientific significance and practical applications to extract, separate, and enrich bioactivator from plant tissue.^{6–8}

Flavonoids are a broad class of natural substance that exist extensively in certain plants and berries and have various biological activities. Modern pharmacological studies indicate that they have multiple functions of free-radical scavenging, antioxidation, antitumor, sterilization, and so on.^{9–12} Flavonoids are natural organic compounds with 2-phenyl chromone structure. Multiphenolic hydroxyl groups as well as alcoholic hydroxyl groups are also contained in their molecules. Therefore, the flavonoid molecule can be used as not only a hydrogen-bond donor but also a hydrogen-bond receptor. The host–guest system between flavonoid molecule and other substances can be constructed by the hydrogen-bonding interaction. On the basis of these characteristics, some researchers have synthesized multifarious adsorbents through the polymerization of conventional monomers such as vinyl pyridine, acrylic acid, methacrylate, vinyl acetate, and so on.^{8,13–15} However, there is a lack of further theoretical analysis in the literature.

Genistein is a typical flavonoid compound. Its pharmacological activities have attracted much attention in the medical field. Therefore, effective extraction and separation of genistein from plants becomes an important research project. Various methods or technologies, such as solvent extraction, subcritical water extraction, chromatography separation, and adsorption,^{16–19} have been used to extract genistein from certain plants. Among them, adsorption has received more and more attention in recent years because this method is easy to handle and highly effective. Besides, adsorbents can be regenerated after simple treatment.

In our previous study, the preparation process of PVA/SiO₂ was studied, and the product and intermediates were fully characterized.²⁰ This study uses composite particles PVA/SiO₂ as solid adsorbent to explore the adsorption ability of PVA/SiO₂ for genistein by virtue of the hydrogen-bonding interaction. The influences of main factors on the adsorption process of genistein are studied, and the adsorption thermodynamics is explored in depth. Similar studies had not been previously reported in the literature. The research result shows that the composite particles PVA/SiO₂ not only can produce high adsorption capacity for genistein but also have excellent mechanical properties and fine thermal and chemical stability. Therefore, they are high-performance solid adsorbents and have potential application prospect in extraction and separation of genistein.

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2. EXPERIMENTAL SECTION

2.1. Materials and Instruments. Silica (120–160 mesh, $\sim 125\ \mu\text{m}$ in diameter, Ocean Chemical, Qingdao City, China) is of reagent grade. γ -Aminopropyltrimethoxysilane (AMPS, Qufu Wanda Chemical, Shandong Province, China) is of analytical grade. Vinyl acetate (VAc, Guangfu Chemical Reagent, Tianjin City, China) is of analytical grade and is purified by vacuum distillation before use. Ammonium persulfate (APS, Fushu Chemical Engineering, Shanghai, China) is of analytical grade. Genistein (Sinopharm Chemical Reagent) is of analytical grade. Other chemicals are of analytical grade and purchased from Chinese companies.

The instruments used in this study are as follows: Perkin-Elmer 1700 infrared spectrometer (FTIR, Perkin-Elmer Company, USA), THZ-92C vapor-bathing constant temperature vibrator (Shanghai Boxun Industry & Commerce, Shanghai, China), and UV-2602 UV/vis spectrophotometer (Unico Instrument, Shanghai, China).

2.2. Preparation and Characterization of Functional Grafted Particles PVA/SiO₂. **2.2.1. Preparation and Characterization of Grafted Particles PVAc/SiO₂.** The grafted particles PVAc/SiO₂ with a high grafting degree (32 g/100 g) are prepared according to the procedures described in ref 20. The main procedures are as follows. First, silica gel particles are treated by using aqueous solution of methane sulfonic acid as activation reagent. Second, activated silica gel particles are surface-modified with coupling agent γ -aminopropyltrimethoxysilane (AMPS), and we obtain the modified particles AMPS-SiO₂ to which primary amine groups are chemically attached. Lastly, the surface-initiated graft-polymerization of VAc is carried out in a solution polymerization system. The procedures are as follows: AMPS-SiO₂ particles and monomer VAc are added to the mixed solvent of dimethyl sulfoxide and water (V/V 36:64), then graft polymerization is performed by using ammonium persulfate (1.1 wt % of monomer) as initiator under a N₂ atmosphere at 30 °C for 12 h. The PVAc/SiO₂ particles are extracted in methanol in a Soxhlet extractor to remove the polymer attaching physically to the particles and dried under vacuum.

The FTIR spectrum of the grafted particles PVAc/SiO₂ is measured with the KBr pellet method to confirm their structures, and their morphology is observed with SEM. The grafting degree of PVAc is determined by TGA under an air atmosphere.

2.2.2. Preparation and Characterization of Functional Grafted Particles PVA/SiO₂. One gram of the grafted particles PVAc/SiO₂ are added to 100 g of sodium hydroxide methanol solution with the concentration of 4% (wt %). The alcoholysis reaction is taken place at a constant temperature of 35 °C with stirring for 12 h. Finally, the adsorbent PVA/SiO₂ is obtained.

The FTIR spectrum of the functional grafted particles PVA/SiO₂ is measured with the KBr pellet method to confirm their structures. On the basis of grafting degrees data of PVAc/SiO₂, the alcoholysis degree of PVAc/SiO₂ is determined by acid–base titration. Calculation results show that the alcoholysis degree of PVAc/SiO₂ achieves 90%; that is, the adsorbent PVA/SiO₂ used in this study has a grafting degree of 0.147 g·g^{−1}.

2.3. Examination of Adsorption Property of PVA/SiO₂ for Genistein. **2.3.1. Measurement of Adsorption Isotherm with Static Method.** 20 mL of the prepared N,N-dimethylformamide (DMF) solution of genistein with different

initial concentrations C_0 (concentration range from 0.3 to 2.7 g·L^{−1}) is placed in several conical flasks, respectively. 0.05 g of particles PVA/SiO₂ weighed accurately is added to these solutions, respectively. These mixtures are oscillated in a thermostatic oscillator for 3 h. (Please note that the adsorption kinetics experiment is performed in advance, and the equilibrium time is determined as 3 h.) After the adsorption reached equilibrium, the concentration (C_e) of supernatant is determined by a UV/vis spectrophotometer ($\lambda_{\text{max}} = 339\ \text{nm}$). The equilibrium adsorption amount (Q_e) is calculated according to eq 1.

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

where C_0 (g·L^{−1}) is the concentration of the initial solution, C_e (g·L^{−1}) is the equilibrium concentration, V (mL) is the volume of the adsorbate solution, m (g) is the weight of the adsorbent PVA/SiO₂ particles, and Q_e (mg·g^{−1}) is the adsorption amount at equilibrium.

2.3.2. Examination of the Main Factors Affecting Adsorption Property of PVA/SiO₂. To further research the adsorption property and mechanism of PVA/SiO₂ for genistein, we examined the effects of three main factors on adsorption property. (1) By varying the type of solvents (1,2-dichloroethane (DCE), DMF, ethanol, and mixed solvent DMF and water), the impact of solvent type is discussed. (2) By altering the temperature of shaker, the influence of temperature on the adsorption property of PVA/SiO₂ is examined. (3) By changing the amount of KCl in ethanol, the effect of salinity on adsorption capacity is investigated.

3. RESULTS AND DISCUSSION

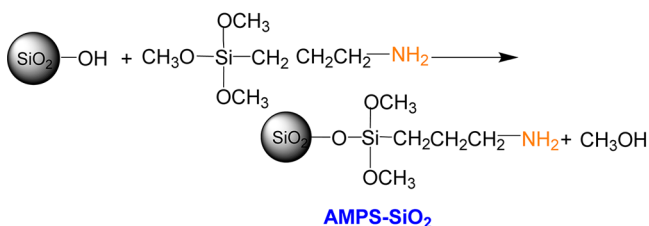
3.1. Preparation Process and Structural Characterization of PVA/SiO₂. Silica gel particles are first surface-modified with coupling reagent AMPS to introduce amino groups onto the surfaces of silica gel particles, preparing modified particles AMPS-SiO₂. Subsequently, a redox surface-initiated system is constituted between primary amine group on the AMPS-SiO₂ and the ammonium persulfate in the solution, resulting in the generation of free radicals on the silica gel particles. So the surface-initiated free radical graft-polymerization of VAc on the silica gel particles will be developed, obtaining the grafted particles PVAc/SiO₂. Finally, the alcoholysis reaction of the grafted PVAc is conducted in sodium hydroxide methanol solution, forming the adsorbent PVA/SiO₂ with high-density hydroxyl. The entire chemical process to prepare PVA/SiO₂ is expressed in Scheme 1.

To confirm the grafting of PVAc onto the silica gel particles and the transforming of PVAc into PVA via alcoholysis reaction, we present the infrared spectra of four particles, SiO₂, AMPS-SiO₂, PVAc/SiO₂, and PVA/SiO₂, in Figure 1. At the same time, for the convenience of comparison, the spectra of the linear polymers, PVAc and PVA, are also given in Figure 1.

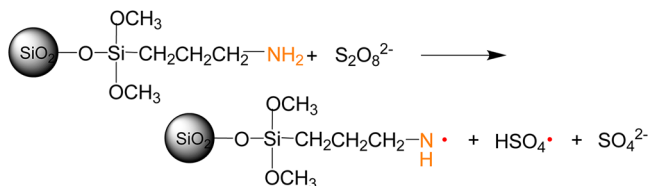
In the spectrum of PVAc/SiO₂ particles, the stretching vibration absorption of the carbonyl group C=O appears at 1738 cm^{−1}, and the new peak at 1373 cm^{−1} is ascribed to the in-plane bending vibration absorption of −CH₃ groups. The above spectrum changes sufficiently to show that PVAc has been grafted onto the silica gel particles. In the spectrum of PVA/SiO₂ particles, the absorption peak at 1738 cm^{−1} almost completely disappeared. In addition, the characteristic absorption peaks of the polyhydroxy group and C–O appear

Scheme 1. Schematic Illustration of Preparation Process of Functional Particles PVA/SiO₂

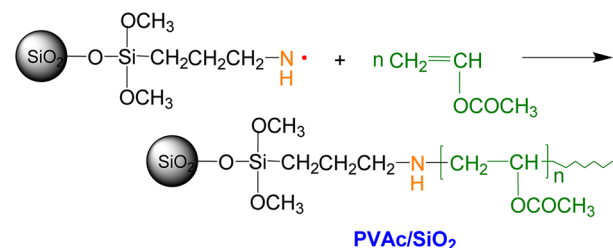
(1) Surface modification of silica gel particles with coupling agent AMPS



(2) Production of free radicals on surfaces of modified particles



(3) Surface-initiated graft-polymerization of vinyl acetate



(4) Alcoholysis reaction of poly vinyl acetate

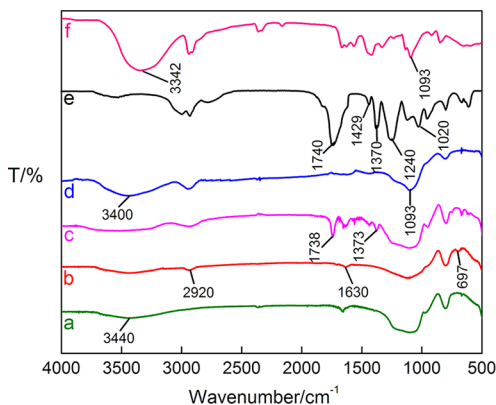
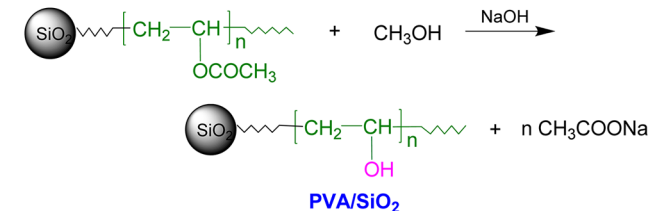


Figure 1. FTIR spectra.

at 3378 and 1093 cm⁻¹, respectively. These show that the alcoholysis reaction of PVAc occurs and PVA/SiO₂ has been formed.

In the infrared spectrum of PVAc, the strongest absorption peak appears at 1740 cm⁻¹, which is the result of the stretching vibration of the carbonyl group C=O. The characteristic peaks

that appear at 1240 and 1024 cm⁻¹ are the stretching vibration absorption of —C(=O)—O— and —O—CH— on —C(=O)—O—CH—, respectively. The above three absorption peaks indicate the existence of ester. As a result of —CH₃ connecting directly to C=O, the bending vibration absorption of —CH₃ groups at 1370 cm⁻¹ is stronger than that of —CH₂— groups at 1429 cm⁻¹. This phenomenon fully demonstrates that the acetate is obtained. In the spectrum of PVA (PVA is the alcoholysis product of PVAc), the stretching vibration absorption peaks of —O—H and C—O appear at 3342 and 1093 cm⁻¹, respectively. These changes indicate that the alcoholysis reaction is highly efficient and PVA is prepared.

The above infrared spectrum shown in Figure 1 manifests macromolecule chain PVA, which contains a huge number of isolated hydroxyl groups, and has been grafted onto the surface of silica gel particles. Therefore, polyphenol–alcohol complexation between PVA/SiO₂ and genistein tends to be formed by hydrogen-bond interaction.

3.2. Adsorption Isotherm and Adsorption Mechanism of Genistein. The adsorption isotherms of PVAc/SiO₂ and PVA/SiO₂ for genistein are shown in Figure 2.

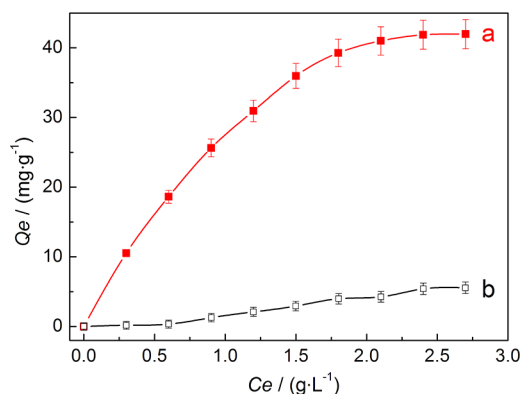
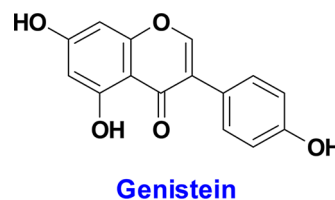


Figure 2. Adsorption isotherms of two kinds of particles toward genistein at 20 °C in DMF. Particle: (a) PVA/SiO₂ and (b) PVAc/SiO₂.

It is seen that the grafted particles PVAc/SiO₂ hardly have adsorption ability for genistein, whereas the adsorbent PVA/SiO₂ possesses strong adsorption ability and high affinity for genistein. The equilibrium adsorption amount of genistein increases rapidly with the increase in equilibrium concentration. When the equilibrium concentration of genistein reaches a certain value, the equilibrium adsorption amounts nearly no longer change; namely, the adsorption reaches saturation and the saturated adsorption amount is 42 mg·g⁻¹. The high-affinity attributes to the hydrogen-bond interaction and the interaction mechanism will be discussed below.

The chemical structure of genistein is shown in Scheme 2.

Scheme 2. Chemical Structure of Genistein Molecule



It can be clearly seen that genistein is a flavonoid containing a ketone carbonyl and multiple phenolic hydroxyl groups. A conventional hydrogen bond is formed between the hydroxyl groups with high density on the surfaces of PVA/SiO₂ and the phenolic hydroxyl groups in genistein, while π -type hydrogen bond is formed between the hydroxyl groups of PVA/SiO₂ and the conjugated aromatic rings in genistein. As a result of combined action of two types of hydrogen bond, PVA/SiO₂ possesses very strong physical adsorption for genistein. Obviously, PVA/SiO₂ has potential application value in the extraction and separation of flavonoids.

3.3. Effects of the Main Factors on Adsorption Property of PVA/SiO₂.

3.3.1. Effect of Solvent. The adsorption isotherms in four different solvents (DCE, DMF, ethanol, and mixed solvent of DMF and water (V/V 8:2) are shown in Figure 3. $E_T(25)$ (polarity parameter at 25 °C) of various solvents is displayed in Table 1. ($E_T(25)$ of mixed solvent is calculated according to the percentage of pure components.)

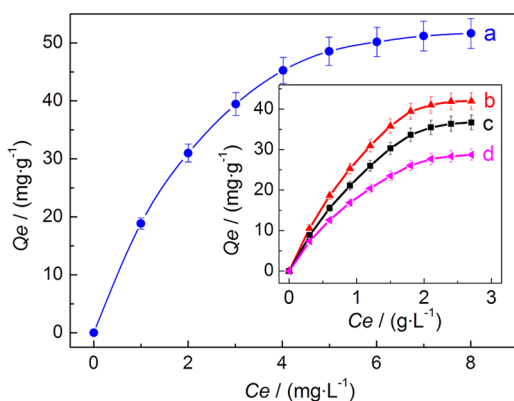


Figure 3. Adsorption isotherms of PVA/SiO₂ particles toward genistein in different solvents at 20 °C solvent: (a) DCE, (b) DMF, (c) DMF:H₂O, (d) C₂H₅OH.

Table 1. Polarity Parameter of Various Solvents

substance	DCE	DMF	DMF+H ₂ O	C ₂ H ₅ OH
$E_T(25)/(\text{kcal/mol})$	41.9	43.8	47.7	51.9

As we can see clearly from Figure 3, solvent type has a great influence on the adsorption amount of PVA/SiO₂ for genistein. The adsorption capacities order is DCE > DMF > mixed solvent > ethanol. The regularity is mainly caused by competitive adsorption of the solvent, which is a common phenomenon in the solid–liquid adsorption system.^{21–23} The property of four different solvents used in this study is quite different. DCE can be treated as a weak polarity organic solvent or nonpolar solvent, whereas DMF is a polar aprotic solvent and ethanol and water are polar protic solvents.

In DCE, there is little interaction between solvent DCE and PVA/SiO₂ particles besides van der Waals force, so the solvent molecule would not compete with genistein, resulting in high adsorption capacity. In ethanol, on one hand, the hydrogen bonding can be formed between the hydroxyl groups on the surfaces of PVA/SiO₂ and ethanol molecules, which occupy part of adsorption sites and create strong competitive adsorption of the solvent. On the other hand, ethanol molecules can produce strong solvation. The combination of two actions produces negative effects on adsorption process of

PVA/SiO₂ to genistein, leading to lower adsorption capability. In DMF, the dipole–dipole interaction between the hydroxyl groups on the surfaces of PVA/SiO₂ and DMF molecules causes the decrease in adsorption ability (relative to solvent DCE). While in mixed solvent, adsorption capacity would further reduce because of very strong competition of water molecules.

3.3.2. Effect of Temperature. The adsorption isotherms of PVA/SiO₂ toward genistein at different temperatures are shown in Figure 4. It can be found that the adsorption amount of PVA/SiO₂ toward genistein decreases with the increase in temperature.

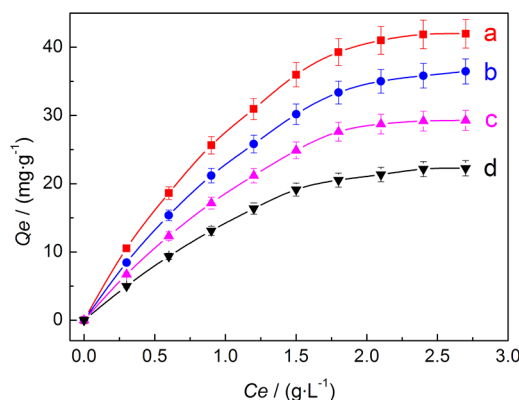


Figure 4. Adsorption isotherms of PVA/SiO₂ particles toward genistein at different temperatures in DMF. Temperature (°C): (a) 20, (b) 30, (c) 40, and (d) 50.

The reason for this is that the hydrogen-bonding interaction is highly sensitive to temperature and becomes weak with increased temperature or even ruptures^{24–26} or melts.²⁶ The hydrogen bond does not belong to the chemical bond or the van der Waals force. It is a weak interaction situated between the chemical bond and the van der Waals force. However, the hydrogen-bonding interaction between genistein and macromolecule PVA is strong because there is a large number of hydroxyl groups on PVA/SiO₂. Therefore, the hydrogen-bonding interaction leads to a strong adsorption action of PVA/SiO₂ toward genistein, and the adsorption capacity decreases with an increase in temperature. From the curves in Figure 4, we can also see that the adsorption isotherm is a typical monomolecular layer adsorption of Langmuir-type.

3.3.3. Effect of Salinity. Adsorption isotherms of PVA/SiO₂ to genistein in KCl-ethanol solutions with different salinities are shown in Figure 5.

It shows that the adsorption amount of genistein declines with the increase in concentration of KCl. The reason lies in these interactions between electrolyte ions and solute molecules. In recent years, the scientific findings show that the cationic– π interaction is an important secondary bond force and generally exists in various host–guest chemical system and biological systems.^{27,28} In particular, in biological systems, the cationic– π interaction is a very important force responsible for maintaining protein–nucleic acid complex stability.²⁹ Because of electrolyte KCl being ionized in KCl-ethanol solution, it can be speculated that the cationic– π interaction will form between cationic K⁺ in solution and the conjugated aromatic rings in genistein. The higher the concentration of KCl is, the lower the adsorption amount of

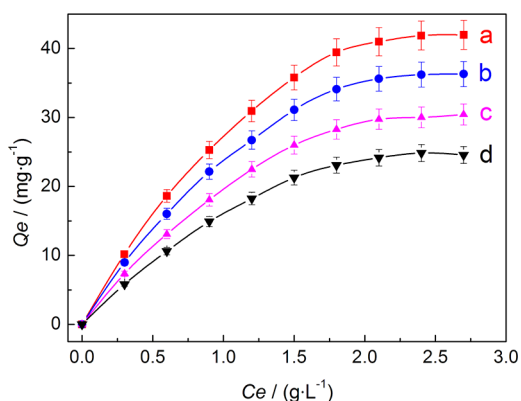


Figure 5. Adsorption isotherms of PVA/SiO₂ toward genistein in KCl-ethanol solutions with different salinities at 20 °C $c(\text{KCl})/(\text{g}\cdot\text{L}^{-1})$: (a) 0, (b) 0.1, (c) 0.2, and (d) 0.3.

genistein is. From this perspective, salinity has a great influence on the adsorption amount of PVA/SiO₂ for genistein.

3.4. Adsorption Thermodynamics. The adsorption data of Figure 4 at different temperatures are analyzed according to Langmuir isotherm equation. The linear form of Langmuir equation can be expressed as eq 2

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (2)$$

where Q_m ($\text{mg}\cdot\text{g}^{-1}$) is the saturated adsorption amount and b is the Langmuir constant. The straight lines of C_e/Q_e versus C_e are presented in Figure 6. As we can see clearly from Figure 6, it is

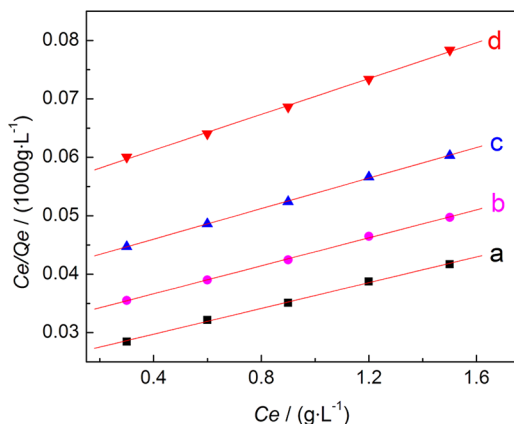


Figure 6. Linearized Langmuir isotherms at different temperatures. (a) 20 °C, $r = 0.9992$. (b) 30 °C, $r = 0.9998$. (c) 40 °C, $r = 0.9996$. (d) 50 °C, $r = 0.9992$.

a fine linear relationship of C_e/Q_e versus C_e (correlation coefficients are greater than 0.99). This indicates that the adsorption of PVA/SiO₂ toward genistein fits perfectly to Langmuir model monolayer adsorption.

Strictly speaking, when the adsorption behavior of the solute in solid–liquid system is investigated, the solvent adsorption cannot be ignored. A relation between the Langmuir adsorption constant b and the adsorption equilibrium constant K of the solute is represented as eq 3.^{30,31}

$$b = (K - 1) \times M/\rho \quad (3)$$

where M and ρ are the molecular weight and density of solvent DMF, respectively. The Langmuir adsorption constants b at

different temperatures are calculated based on the intercept and slope of the straight lines in Figure 6. Then, the adsorption equilibrium constants K at different temperatures can be obtained according to eq 3.

Equation 4, known as the van't Hoff equation, indicates the relationship between the adsorption equilibrium constant K and temperature T .³⁰ Plotting of $\ln K$ versus $1/T$ is a straight line and is shown in Figure 7.

$$\ln K = -\frac{\Delta H}{R} \times \frac{1}{T} + C \quad (4)$$

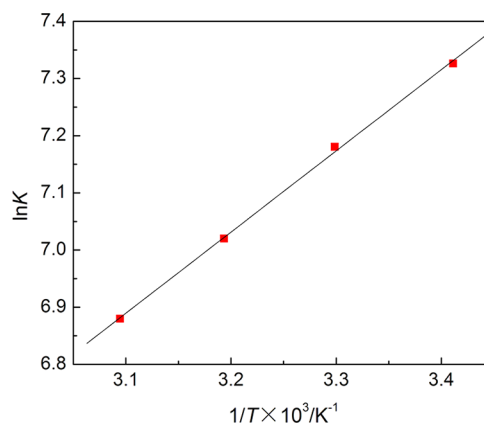


Figure 7. Relationship curve between $\ln K$ and $1/T$.

The adsorption enthalpy change ΔH can be obtained by the slope of the straight line in Figure 7. The following eqs 5 and 6 are two important thermodynamics relations, and the change of entropy ΔS and Gibbs free energy ΔG of the adsorption process at different temperatures can be calculated through them. These calculated values of ΔH , ΔS , and ΔG are listed in Table 2.

$$\Delta G = -RT \ln K \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

Table 2. Adsorption Thermodynamics Data of PVA/SiO₂ toward Genistein

T/K	K	$-\Delta G/(\text{kJ}\cdot\text{mol}^{-1})$	$-\Delta H/(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta S/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$
293.15	1520	17.86	11.81	20.64
303.15	1313	18.10	11.81	20.75
313.15	1119	18.28	11.81	20.67
323.15	972.6	18.48	11.81	20.67

It can be seen from Table 2 that Gibbs free energy ΔG is less than zero, so the adsorption course is determined as a spontaneous process. The experimental fact that the adsorption amount of genistein decreases with the increase in temperature indicates that the adsorption of PVA/SiO₂ toward genistein is an exothermic process. The value of ΔH is $-11.81 \text{ kJ}\cdot\text{mol}^{-1}$, and this also confirms that the adsorption process is exothermic. The entropy change ΔS is greater than zero, which caused by the desorption of solvents (result in the increase in entropy) has an advantage over the adsorption of solutes (result in the reduction of entropy). The relation $|\Delta H| > |T\Delta S|$ which can be obtained from the data in Table 2, indicates that the adsorption process is driven by enthalpy.

4. CONCLUSIONS

In this study, macromolecular PVAc is grafted onto micro-meter-sized silica gel to prepare PVAc/SiO₂. Then, the adsorption material PVA/SiO₂ is successfully obtained through the alcoholysis reaction of PVAc. PVA/SiO₂ has very strong physical adsorption ability for genistein by hydrogen-bonding interactions, and the adsorption amount could reach up to 51 mg·g⁻¹ (in DCE). The adsorption ability of PVA/SiO₂ for genistein is largely influenced by solvent type, temperature, and salinity. The competitive adsorption of the solvent negatively affects the adsorption capacity of genistein. The lower the temperature is, the higher the adsorption amount is. The adsorption amount decreases with the increase in salinity of solution. Also, the adsorption process is exothermic and driven by enthalpy.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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