Korean J. Chem. Eng., 34(7), 1889-1895 (2017)
DOI: 10.1007/s11814-017-0131-0
pISSN: 0256-1115
eISSN: 1975-7220

REVIEW PAPER

Preparation of cationic functional polymer poly(Acryloxyethyltrimethyl ammonium chloride)/SiO_2 and its adsorption characteristics for heparin

Jiying Men†, Jianfeng Guo, Weihong Zhou, Nanyan Dong, Xilun Pang, and Baojiao Gao

Department of Chemical Engineering, North University of China, Taiyuan 030051, P. R. China
(*Received 2 December 2015 • accepted 14 May 2017*)

Abstract−Ion-exchange is a widely used purification technology in the heparin manufacturing process. To improve the rate and efficiency, the cationic monomer Acryloxyethyltrimethyl ammonium chloride (DAC) was grafted on silica gel particles by using a surface-initiated graft-polymerization technique, and a novel adsorption polymer of PDAC/SiO_2 was prepared. The adsorption experiments of PDAC/SiO_2 for heparin show that there are strong electrostatic interactions between heparin with a high density of negative charges and PDAC/SiO_2 that exists in many quaternary ammonium cations. Comparing the adsorption kinetics of PDAC/SiO_2 with D201 anionic strong alkali exchange resin, PDAC/SiO_2 shows higher adsorption capacity and faster adsorption rate. The pH and temperature of solutions have a great influence on the adsorption amount, and there is a maximum adsorption capacity of 121 mg/g when pH=7 at 25 °C. The adsorption of PDAC/SiO_2 for heparin is an exothermic process and driven by entropy.

Keywords: Heparin, Cationic Monomer, Electrostatic Interaction, DAC, Adsorption

INTRODUCTION

Heparin is composed of disaccharide repeating units consisting of 1→4 linked residues of uronic acid and D-glucosamine with a high density of negative charge, linear long chain, highly sulfated natural polysaccharides name glycosaminoglycans (GAGs) [1]. Heparin can be extracted from a variety of tissues such as liver, lung, and intestine. But nowadays, the usual source for commercial heparin is porcine intestinal mucosa [2]. Heparin has a wide range of important biological activities, especially favorable anticoagulant effect [3], which is widely used for surgical treatment, resistance of vein thrombosis, pulmonary and systemic embolism syndrome [4]. In addition, heparin can also inhibit cancer cell growth [5], has anti-inflammatory effect [6], is antiviral [7] and delays onset of alzheimer's disease symptoms [8]. In terms of worldwide production, most of the crude, partially-purified, heparin is produced mainly in China. China is one of the main exporters of heparin, but for a long time, it was limited to producing crude, partially-purified heparin [9]. Then, much effort was applied to separate and purify heparin, including gel filtration chromatography, affinity chromatography, enzymatic degradation and ion-exchange chromatography, which could provide resulting high-pure heparin possessing high specific activities and low side effects [10-13].

Ion-exchange is one of commonly used purification technologies in the heparin manufacturing process. The performance of the ion-exchange resin is the key factor to determine heparin yield.

In the present work, a new cationic function polymer PDAC/SiO_2 is designed and prepared; in its structure poly(Acryloxyethyltrimethyl ammonium chloride) (PDAC) macromolecules are grafted on silica gel particles by using a surface-initiated graft-polymerization technique, and the adsorption properties of PDAC/SiO_2 for heparin are mainly investigated and compared with traditional type D201 Anionic alkali exchange resins. The results of adsorbing experiments indicate that particles PDAC/SiO_2 have strong adsorption ability for heparin. Functional particles PDAC/SiO_2 toward heparin possess higher adsorption capacity and faster adsorption rate than D201 resin owing to the strong electrostatic interactions between the grafted PDAC macromolecules and heparin molecules. Function polymer PDAC/SiO_2 will act as solid adsorbent of heparin with the excellent mechanical strength and thermal stability of silica gel particles, and it will be valuable for purifying heparin.

EXPERIMENTS

1. Materials

Silica (120-160 mesh) was purchased from Ocean Chemical Limited Company (Qingdao City, China). Heparin (150 μ/mg) was purchased from Francois Biological Technology Co., Ltd. D201 big hole strong alkaline styrene anion exchange resins was obtained from An Hui Wandong Chemical Co., Ltd. (Province Anhui, China). γ-Aminopropyltrimethoxysilane (AMPS) was of analytical grade as purchased from YingchengDebangChemical New Material Co., Ltd. (Province Hubei, China). Acryloxyethyltrimethyl ammonium chloride (DAC) was of analytical grade from Guang Chuang Jing Import and Export Co., Ltd. (Shanghai, China).

2. Preparation and Characterization of Functional Polymer PDAC/SiO_2

Silica gel particles were first surface-modified with coupling agent APMS, and amino groups were chemically introduced onto the surfaces of silica gel particles, forming the modified particles AMPS-SiO_2 [14]. 1.2 g of AMPS-SiO_2, 10 mL of monomer DAC, and 100

†To whom correspondence should be addressed.
E-mail: menjiying@126.com

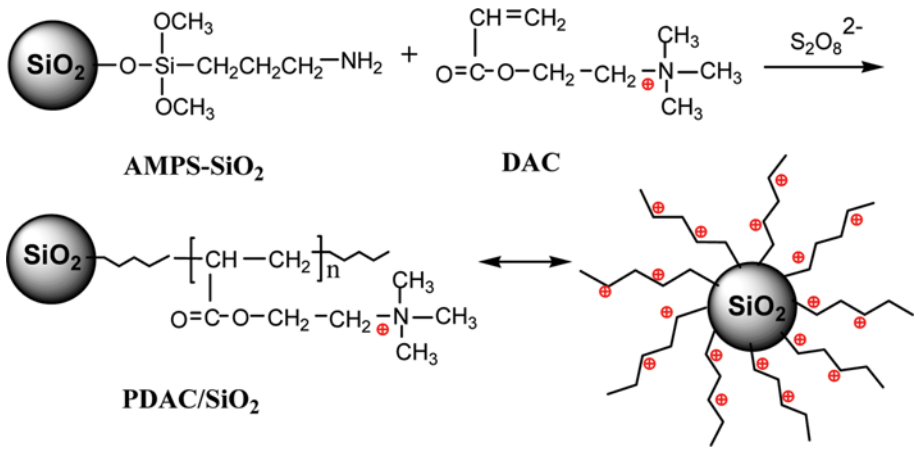

Fig. 1. Preparation process of the functional particles PDAC/SiO_2.

mL of distilled water were added into a four-necked flask equipped with a reflux condenser, a thermometer, a mechanical agitator and an N_2 inlet. The content was stirred and heated to 35 °C, and N_2 was bubbled for 30 min to exclude air. Then 0.1132 g of initiator ammonium persulfate was added, and the grafted polymerization reaction was performed for 10 h under N_2 atmosphere. The functional particles PDAC/SiO_2 were collected by filtration, and were extracted with distilled water in a Soxhlet for 20 h to remove a few of the PDAC copolymers attached physically to the particles, and finally dried under vacuum to constant weight.

The IR spectrum of particles SiO_2 and PDAC/SiO_2 was determined with 1700 infrared spectrometer (FTIR, Perkin-Elmer Company, U.S.A.) to characterize the chemical structure. The morphology of particles SiO_2 and PDAC/SiO_2 was examined with SU-1500 scanning electronic microscope (SEM, Hitachi Company, Japan). The grafting degree (GD, g/100 g) of PDAC on the grafted particles PDAC/SiO_2 was determined by TGA1 thermal gravimetric analysis (TGA, Mettler Toledo, Switzerland) under air atmosphere and a heating rate of 20 °C/min. The zeta potential of SiO_2 and PDAC/SiO_2 was determined by Zetasizer Nano-Zeta potential analyzer (Instrument Company, UK) at different pH conditions, obtaining zeta potential curve.

3. Examining the Adsorption Properties of Functional Particles PDAC/SiO_2 for Heparin

The adsorption kinetics experiments were first conducted, and adsorption equilibrium time was determined to be about 4 h. Based on the above experiments, the isothermal adsorption property of PDAC/SiO_2 particles for heparin was investigated.

Twenty (20) mL of aqueous solutions of heparin in a concentration range of 0.4-2.0 mg/mL were, respectively, placed into numerous conical flasks with a plug, and about 0.05 g of functional particles PDAC/SiO_2 weighted accurately were added into these solutions. These mixtures were shaken on a THZ-92C constant temperature shaker equipped with gas bath (Boxun Medical Treatment Equipment Factory, Shanghai, China) at 25 °C for 4 h, and the adsorptions process were allowed to reach equilibrium. After standing for 10 min, 0.3 mL of supernatants was drawn into 3 mL 90% (v/v) sulfuric acid solution containing 0.025 M borax, and the solution was shaken fully, then placed into water bath of 90 °C for 10 min under stirring. The solution was cooled to room temperature and placed for 30 min at room temperature. Heparin concentrations were determined with UV spectrophotometry at 298 nm, the equilibrium adsorption amounts were calculated, and the adsorption isotherms were plotted.

To explore the adsorption mechanism and adsorption performance of PDAC/SiO_2 for heparin, pH value and temperature were examined and adsorption thermodynamics was investigated. Also, the adsorption dynamics of functional particles PDAC/SiO_2 and D201 anionic alkali exchange resins for heparin were compared under the optimum temperature and pH.

RESULTS AND DISCUSSION

1. Preparation Process of Functional Particles PDAC/SiO_2

The preparation process of functional particles PDAC/SiO_2 is schematically illustrated in Fig. 1. There is a mass of amino groups (primary amine groups) on the modified particles APMS-SiO_2. A redox initiation system is constituted with amino group and ammonium persulfate in the solution, and abundant primary free radicals are generated on the surfaces of AMPS-SiO_2 particles. Free radicals make monomers DAC graft-polymerize on the surface of

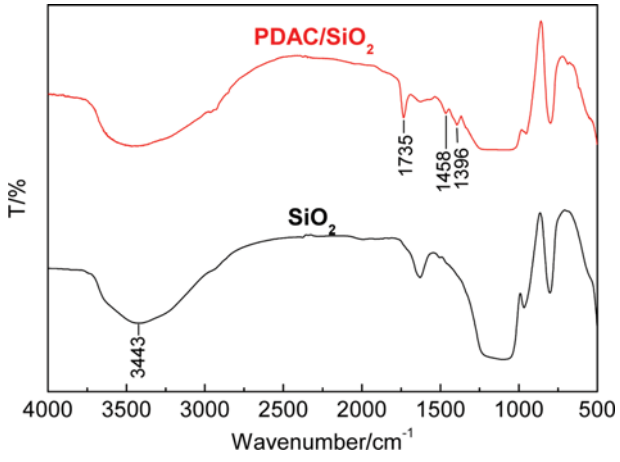

Fig. 2. FTIR spectra of SiO_2 and PDAC/SiO_2 particles.

AMPS-SiO_2, forming functional particles PDAC/SiO_2. Fig. 1 shows that there are abundant structures of chain units of DAC on the PDAC/SiO_2 particle, and a mass of positive charges exist on functional particles.

2. Characterization of Functional Particles PDAC/SiO_2

2-1. Infrared Spectra

Fig. 2 presents the infrared spectra of two kinds of particles, silica gel particles SiO_2 and functional particles PDAC/SiO_2. Several new obvious absorption bands have appeared in the spectrum of PDAC/SiO_2 as compared to the spectrum of SiO_2. The band at 1,735 cm^{-1} represents the stretching vibration absorption of the carbonyl group C=O of the ester group; the band at 1,458 cm^{-1} is attributed to the bending vibration absorption of methylene of $-CH_2N^+(CH_3)_3$, while the band at 1,396 cm^{-1} corresponds to the bending vibration adsorption of C-H bond of methyl group located in the main chain of PDAC. The above results show that cationic monomer DAC was successfully grafted on particles SiO_2, and functional particles PDAC/SiO_2 were prepared.

2-2. SEM Image

The SEM images of particles SiO_2 and functional particles PDAC/SiO_2 are given in Fig. 3(a) and (b). It can be seen from Fig. 3(a) that before the grafting of PDAC, the surfaces of particles SiO_2 are rough and scraggy. After the grafted polymerization, the surfaces of PDAC/SiO_2 become smooth and sleek, and this is caused by coating and filling up action of the grafted PDAC macromolecules.

2-3. Thermal Gravimetric Analysis

The TGA curves for grafted particle PDAC/SiO_2 and modified particle AMPS/SiO_2 are shown in Fig. 4. The curves are analyzed by the general method of discussing the thermogravimetric line, which is about the weight loss of functional macromolecules grafted onto the surfaces of inorganic particles [15,16].

From Fig. 4, modified particles AMPS-SiO_2 and grafted particles PDAC/SiO_2 begin to decompose at around 155 °C. Below 155 °C, the weight loss of particles AMPS-SiO_2 and particles PDAC/SiO_2 is less than 2%, which is mostly due to the evaporation of absorbed water. The modified particle AMPS/SiO_2 decomposes completely at about 740 °C, which corresponds to 9.16% weight loss rate. The

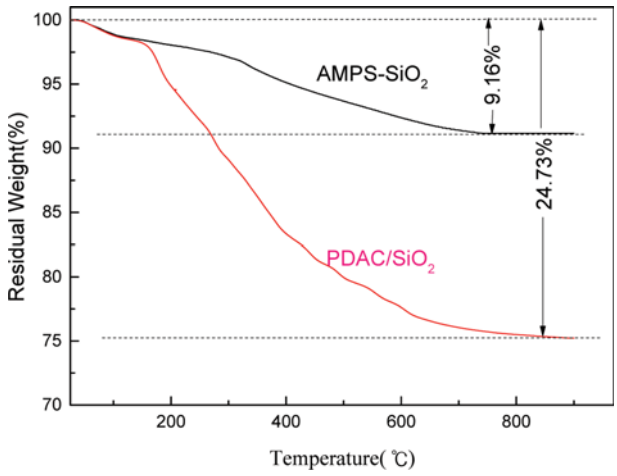

Fig. 4. TGA curves of AMPS-SiO_2 particles and PDAC/SiO_2 particles.

weight loss rate of grafted particles PDAC/SiO_2 is about 24.73%, which is decomposed totally at about 810 °C. Thus it is concluded that 15.57% of PDAC is grafted on the silica particle surface.

2-4. Zeta Potentials of Particles

To explore the adsorption mechanism of PDAC/SiO_2 for heparin, the zeta potential curves of particles SiO_2 and PDAC/SiO_2 are presented in Fig. 5.

In Fig. 5, the zeta potential of SiO_2 is negative in a wider pH range, but cationic monomer DAC is grafted on the SiO_2, the zeta potential of particles PDAC/SiO_2 is transformed into positive in a wider pH range, and further its value is large. This implies the surfaces of particles PDAC/SiO_2 possess high density of positive charges.

3. Isothermal Adsorption Behavior and Mechanism of PDAC/SiO_2 for Heparin

3-1. Adsorption Isotherms and Adsorption Mechanism

The adsorption isotherms of particles SiO_2 and PDAC/SiO_2 for heparin in aqueous solution are shown in Fig. 6. Ce and Qe are the equilibrium concentration of heparin in the supernatant and

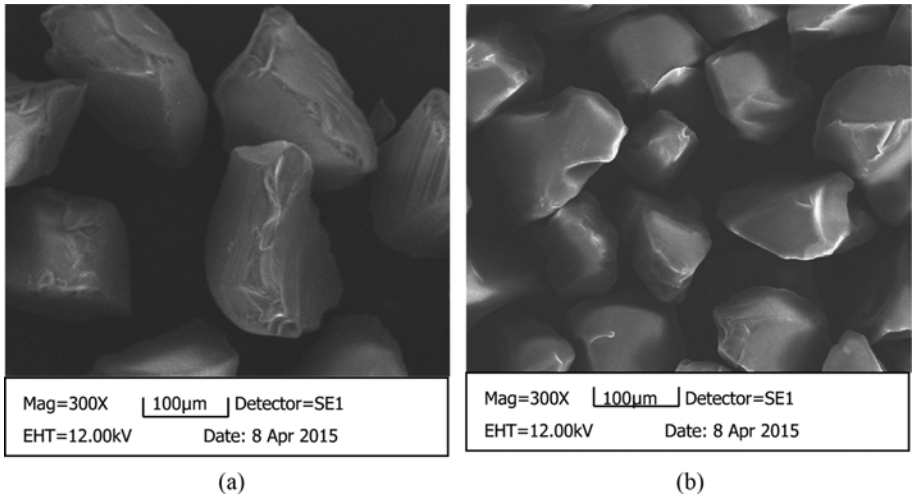

Fig. 3. SEM photographs of SiO_2 and PDAC/SiO_2.

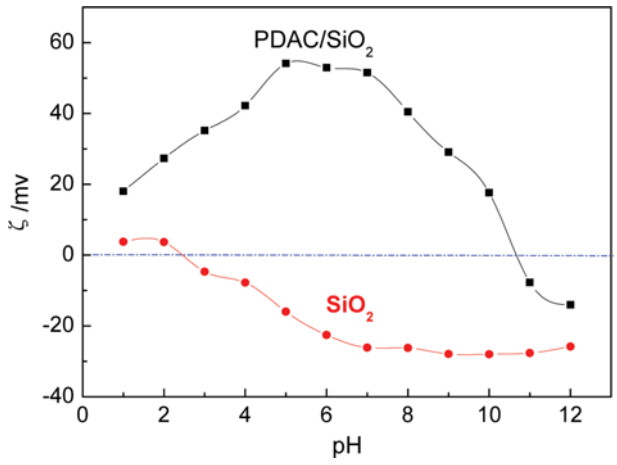

Fig. 5. Zeta potential curves of PDAC/SiO_2 particles and SiO_2.

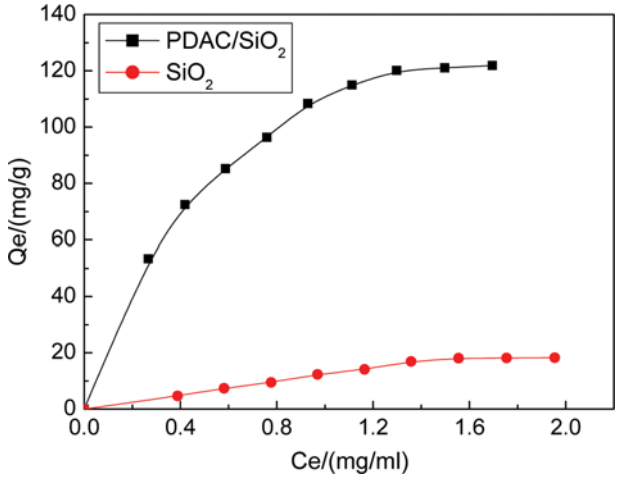

Fig. 6. Adsorption isotherms of particles PDAC/SiO_2 and SiO_2 for heparin T=25 °C pH=7.0.

the equilibrium adsorption quantity of heparin, respectively, in the adsorption isotherms of Fig. 6 and following Fig. 8, Fig. 9 and Fig. 10.

Fig. 6 shows that the adsorption ability of SiO_2 particles for heparin is very weak, only 18 mg/g, indicating a very weak interaction between the host-guest species. However, the functional particle PDAC/SiO_2 exhibits very strong adsorption ability for heparin, and the saturated adsorption amount reaches 121 mg/g, showing a very strong interaction between the host-guest species, and the interaction comes from electrostatic one. Heparin is a polyanionic glycosamino glycans (GAGs) composed of repeating disaccharide units consisting of uronic acid, either d-glucuronic acid (GIcA) or l-iduronic acid (IdoA), both of which can be modified with 2-O-sulfo groups, and the d-glucosamine (GIcN) that may be either N-acetylated (GlcNAc) or N-sulfated (GlcNS), or more rarely unsubstituted (GlcNH), and can be substituted with 3- and/or 6-O-sulfo groups [17,18]. On the surface of heparin, there are a large number of sulfonic acid groups and carboxylic acid groups that are electronegative, see Fig. 7 [19]. In neutral and alkaline aqueous solutions, sulfonic acid and carboxylic acid groups will be ionized, resulting in a large number of negative charges on the heparin. At

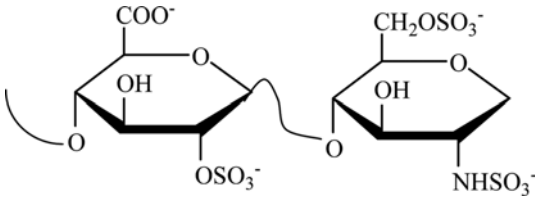

Fig. 7. Major Disaccharide Sequence of heparin.

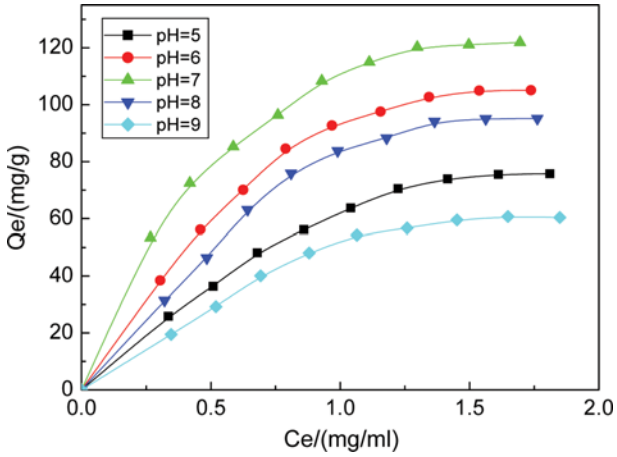

Fig. 8. Adsorption isotherms of PDAC/SiO_2 for heparin at different pH values T=25 °C.

the same time, there are positive charges with a high density on the surface of the functional particles PDAC/SiO_2 (Fig. 5). So it is obvious that strong electrostatic interaction will be produced between host-guest species in neutral aqueous solutions, leading to very strong adsorption action of particles PDAC/SiO_2 for heparin and producing high saturated adsorption amount. Whereas, there are negative charges on the surface of SiO_2 (see Fig. 5), which have an electrostatic repulsion to sulfonic acid and carboxylic acid groups on the heparin.

3-2. Effect of pH Value of Medium on Adsorption Capacity and Adsorption Mechanism

In different pH values of medium, the adsorption isotherms of the functional particles PDAC/SiO_2 for heparin are shown in Fig. 8.

Fig. 8 displays clearly that as pH<7, the adsorption capacity of PDAC/SiO_2 for heparin increases with the increase of pH value. At pH=7, the adsorption capacity reaches a maximum, 121 mg/g. Whereas, over pH 7, the adsorption capacity tends to decline with increasing pH value. This is explained as follows. Sulfonic acid groups are strong anion electrolytes, which are easily ionized to carry negative charges. The degree of ionization of carboxylic acid groups increases with the increase of pH value, making the amount of negative charges increase. And at pH=7, the zeta potential of particles PDAC/SiO_2 is larger positive, and then zeta potential falls sharply with the increase of pH value (see Fig. 5). Therefore, at pH=7, strong electrostatic interactions will be produced between quaternary ammonium cations of particles PDAC/SiO_2 and $-SO_3^-$ and $-COO^-$ of heparin, resulting in maximal adsorption capacity.

3-3. Effect of Temperature Value on Adsorption Capacity

At different temperatures, the adsorption isotherms of PDAC/

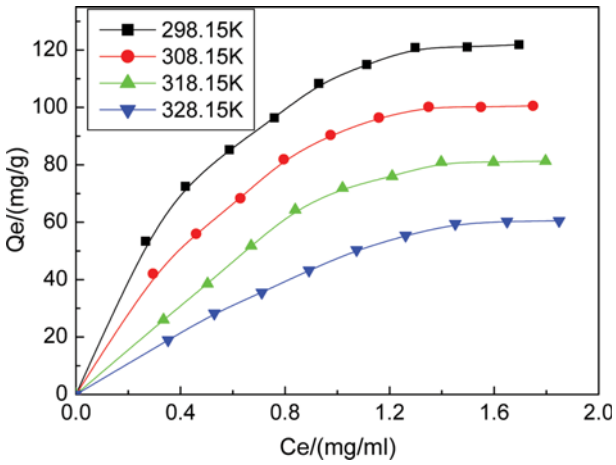

Fig. 9. Adsorption isotherm of PDAC/SiO_2 for heparin at different temperatures pH=7.0.

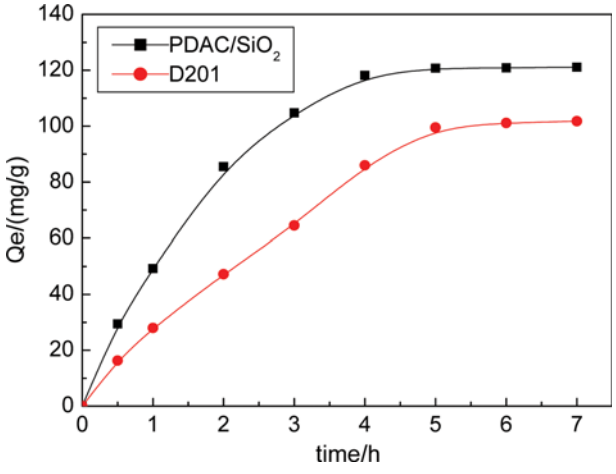

Fig. 10. Adsorption kinetic curve of PDAC/SiO_2 and D201 anionic strong alkali exchange resin for heparin.

SiO_2 for heparin are presented in Fig. 9. In Fig. 9 the adsorption capacity decreases with the increase of temperature. This is because the heparin adsorption caused by electrostatic interaction is a classic physical adsorption process that is an exothermic process on the thermodynamics [20]. So the adsorption capacity of the heparin decreases with the rise of temperature.

4. Adsorption Kinetic Curves of Functional Particles PDAC/SiO_2 and Anionic Strong Alkali Exchange Resin

Fig. 10 shows the adsorption kinetic curves of the functional particles PDAC/SiO_2 and D201 anionic strong alkali exchange resin towards heparin.

In Fig. 10, the adsorption of particles PDAC/SiO_2 for heparin can reach equilibrium in 4 h, whereas D201 anionic strong alkali exchange resin gets to equilibrium in 5 h, displaying a faster adsorption rate of PDAC/SiO_2 for heparin. This is mainly because there is a mass of quaternary ammonium cations, which are dispersed on the surfaces of functional particles PDAC/SiO_2. At the same time, the adsorption amount of the functional particles PDAC/SiO_2 for heparin is much more than D201. The saturated adsorption amount of PDAC/SiO_2 for heparin is also higher than D201; the former is 121 mg/g and the latter is 101 mg/g. These show the functional particles PDAC/SiO_2 for heparin have higher adsorption capacity and faster adsorption rate.

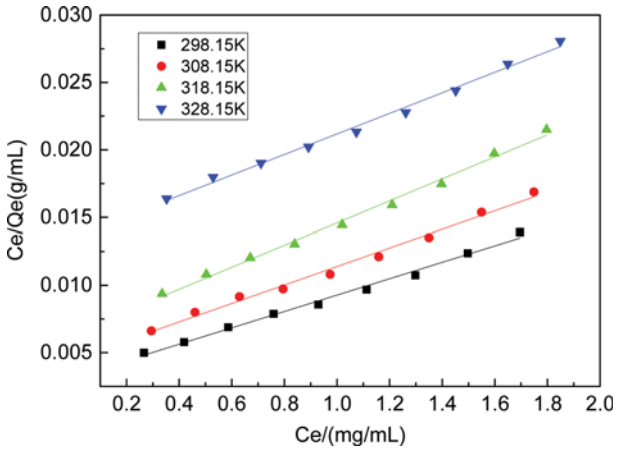

Fig. 11. Linearized Langmuir isotherms at different temperatures.

5. Adsorption Thermodynamics

The adsorption data of Fig. 9 at different temperatures were analyzed according to Langmuir isotherm equation. The straight line form of Langmuir equation is presented in Eq. (1),

$$\frac{Ce}{Qe}=\frac{1}{bQ_m}+\frac{Ce}{Q_m} \tag{1}$$

where Ce (mg/mL) is the equilibrium concentration of heparin; Qe (mg/g) is the equilibrium adsorption amount of heparin; Q_m (mg/g) is the saturated adsorption amount of heparin; b is Langmuir constant. According to Eq. (1), the data in Fig. 8 are treated, and the straight lines of Ce/Qe versus Ce are obtained and they are presented in Fig. 11.

Fig. 11 shows that the linear dependences of four straight lines are all fine (correlation coefficients are greater than 0.99). This indicates that the adsorption of PDAC/SiO_2 for heparin fits perfectly to Langmuir model monolayer adsorption. The Langmuir constant b at different temperatures can be gained by the slopes and intercepts of the four lines, respectively.

Properly speaking, solvent adsorption should be also considered in the solid-liquid adsorption system when the adsorption behavior of the solute in the system is considered. Here, a relationship between the Langmuir adsorption constant b and the adsorption equilibrium constant K is shown in Eq. (2) [21,22].

$$b=(K-1)\times M/\rho \tag{2}$$

where M and ρ are the molecular weight and density of the solvent water, respectively. The adsorption equilibrium constants K at different temperatures can be obtained according to Eq. (2).

Eq. (3) gives the van't Hoff equation, which indicates the relationship between the adsorption equilibrium constant K and the temperature T [23], in which ΔH is the adsorption enthalpy change.

$$\ln K=-\frac{\Delta H}{R}\times\frac{1}{T}+C \tag{3}$$

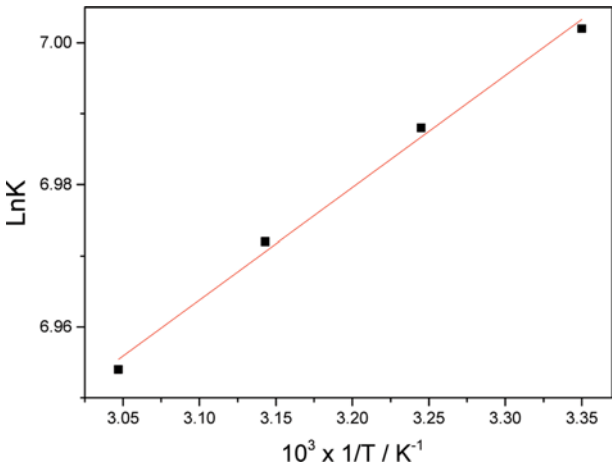

Fig. 12. Relationship curve between Ln K and 1/T.

Table 1. Adsorption Thermodynamics Data of PDAC/SiO_2 for heparin

T/K	$-\Delta G/(kJ\cdot mol^{-1})$	$-\Delta H/(kJ\cdot mol^{-1})$	$\Delta S/(J\cdot K^{-1}\cdot mol^{-1})$
298.15	17.357	1.314	53.807
308.15	17.903	1.314	53.834
318.15	18.442	1.314	53.835
328.15	18.972	1.314	53.811

For the adsorption system of PDAC/SiO_2 for heparin, the straight line of ln K versus 1/T is plotted and presented in Fig. 12. The adsorption enthalpy change ΔH is obtained from the slope of the straight line in Fig. 12, and it is equal to −1.314 kJ/mol.

Eq. (4) and Eq. (5), as the two important thermodynamics relations, can be used to calculate the change of entropy S and Gibbs free energy ΔG of adsorption process at different temperature. The calculated data of ΔH, ΔG and ΔS are listed in Table 1.

$$\Delta G = -RT \ln K \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

Table 1 clearly shows that the value of ΔG is below zero, illustrating the adsorption process of PDAC/SiO_2 for heparin is spontaneous. The value of ΔH is −1.314 kJ/mol, and this also confirms that the adsorption process is exothermic. Indeed, the experimental results just as Fig. 8 show that the adsorption amount of PDAC/SiO_2 for heparin decreases with the increase of temperature, demonstrating also the adsorption process is exothermic. The entropy change ΔS is greater than zero, which is caused by desorption of solvents (resulting in the increase in entropy) and has an advantage over the adsorption of solutes (result in the reduction of entropy) [24]. From the data in Table 1, the relation $|\Delta H| < |T\Delta S|$ can be obtained, indicating that the adsorption process is driven by entropy.

CONCLUSIONS

The functional particles PDAC/SiO_2 were successfully prepared by using surface-initiated graft-polymerization, cationic monomer DAC is grafted on the surface of silica gel particles. The functional particles PDAC/SiO_2 have strong adsorption ability for heparin by electrostatic interaction, and adsorption capacity gets up to 121 mg/g. With increasing temperature, electrostatic interaction will weaken and adsorption capacity is reduced. Also, the adsorption process is exothermic and driven by entropy. The functional particles PDAC/SiO_2 possess faster adsorption rate and higher adsorption capacity than D201 anionic strong alkali exchange resin. From the obtained results, it can be anticipated that the adsorption of particles PDAC/SiO_2 for heparin is a promising formulation techniques for the purification of heparin to improve the production of heparin.

ACKNOWLEDGEMENT

We are grateful of the financial support of this research project by Shanxi Province Youth Science and Technology Foundation (2014021015-1),Science and Technology Development Plan (Industry) of Shanxi Province (20130321017-03) and the Fund of North of University (20140403).

REFERENCES

1. J. Hirsh and R. Raschke, *Chest*., **126**, 188S (2004).
2. B. Cosmi and G. Palareti, *Thrombosis Res*., **29**, 388 (2012).
3. S. Wittfooth, R. Tertti, M. Lepäntalo, P. Porela, Q. P. Qin, J. Tynjälä, O. Inkinen, J. Perttilä, K. E. J. Airaksinen and K. Pettersson, *Clinica Chimica Acta*, **412**, 376 (2011).
4. K. N. Sask, W. G. McClung, L. R. Berry, A. K. C. Chan and J. L. Brash, *Acta Biomater*., **7**, 2029 (2011).
5. A. Durdureanu-Angheluta, C. M. Uritu, A. Coroaba, B. Minea, F. Doroftei, M. Calin, S. S. Maier, M. Pinteala, M. Simionescu and B. C. Simionescu, *J. Biomed. Nanotechnol*., **10**, 131 (2014).
6. R. M. Nelson, A. Venot, M. P. Bevilacqua, R. J. Linhardt and I. Stamenkovic, *Annu. Rev. Cell. Dev. Biol*., **11**, 601 (1995).
7. C. C. Rider, D. R. Coombe, H. A. Harrop, E. F. Hounsell, C. Bauer, J. Feeney, B. Mulloy, N. Mahmood, A. Hay and C. R. Parish, *Biochemistry*, **33**, 6974 (1994).
8. H. Cui, A. C. Hung, C. Freeman, C. Narkowicz, G. A. Jacobson and D. H. Small, *J. Neurochem*., **123**, 447 (2012).
9. R. Sasisekharan and Z. Shriver, *Thromb Haemost*., **102**, 854 (2009).
10. J. Banga and C. K. M. Tripathi, *New Biotechnology*, **26**, 99 (2009).
11. H. C. Zang, J. F. Wang, L. Li, H. Zhang, W. Jiang and F. S. Wang, *Spectrochim Acta A: MolBiomol Spectrosc*., **109**, 8 (2013).
12. C. Cai, K. Edgar, J. Liu and R. J. Linhardt, *Carbohydr. Res*., **372**, 30 (2013).
13. G. Schmer, US Patent, No. 4122250 (1978).
14. Y. B. Li, T. Chen, B. J. Gao and Z. W. Qiao, *Korean J. Chem. Eng*., **31**, 896 (2014).
15. E. Tang, G. X. Cheng and X. L. Ma, *Powder Technol*., **161**, 209 (2006).
16. V. G. Ngo, C. Bressy, C. Leroux and A. Margaillan, *Polymer*., **50**, 3095 (2009).
17. B. Yang, K. Solakyildirim, Y. Chang and R. J. Linhardt, *Anal. Bioanal. Chem*., **399**, 541 (2011).
18. R. Flengsrud, M. L. Larsen and O. R. Ødegaard, *Thrombosis Res*., **126**, e409 (2010).

19. N. S. Gunay and J. L. Robert, *J. Chromatogr. A*., **1014**, 225 (2003).
20. B. J. Gao, Y. C. Gao and Y. B. Li, *Chem. Eng. J*., **158**, 542 (2010).
21. A. R. Cestari, E. F. S. Vieira and C. R. S. Mattos, *J. Chem. Thermodyn*., **38**, 1092 (2006).
22. F. S. C. Anjos, E. F. S. Vieira and A. R. Cestari, *J. Colloid Interface Sci*., **253**, 243 (2002).
23. A. R. Cestari, E. F. S. Vieira and C. R. S. Mattos, *J. Chem. Thermodyn*., **38**, 1092 (2006).
24. Y. Y. Zhang, B. J. Gao and Z. Q. Xu, *J. Phys. Chem. B*., **117**, 5730 (2013).