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# Polystyrene nanofibers as an effective sorbent for the adsorption of clonazepam: kinetic and thermodynamic studies

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Polystyrene (PS) electrospun nanofibers were prepared *via* electrospinning for the adsorption of clonazepam from aqueous solution. The adsorption conditions such as adsorption time, solution pH and the amount of adsorbent were optimized. The adsorption kinetics and thermodynamic properties of clonazepam on PS nanofibers were studied under optimized conditions. The pseudo-second-order kinetic model can fit well the adsorption process of clonazepam on polystyrene nanofibers, indicating that the diffusion process in the fiber is the rate-limiting step of the adsorption process. The adsorption equilibrium data are in accordance with the Freundlich isotherm model, and the maximum adsorption capacity is 3.2 mg $g^{-1}$. Thermodynamic studies revealed that the adsorption process is endothermic and spontaneous in nature. It was suggested that PS electrospun nanofibers have good potential for the separation and purification of clonazepam from a water-soluble matrix as a novel effective adsorbent material.



## 1. Introduction

Benzodiazepines (BZDs) are a kind of psychoactive substance that produce sedative, hypnotic, anxiolytic, and anticonvulsant activities by enhancing the effect of gamma-aminobutyric acid (γ-GABA) on GABA receptors.[1] Clonazepam is a classic BZD used to treat epileptic seizures, insomnia, and anxiety disorders. However, due to its low price and easy availability, clonazepam has become a more commonly abused drug, whether in medical or recreational settings.[2] Moreover, criminals have illegally added it to beverages for recreational use to lure young people into drug addiction. Clonazepam alone or in combination with other psychoactive substances may have adverse health effects, such as cognitive and motor disorders, increased anxiety, and sleep disorders. Long-term use of clonazepam may lead to physical dependence and tolerance.[2] There is, therefore, a need to develop an effective analysis method for guiding the rational use of clonazepam, treating poisoned patients, or assisting the criminal investigation of crimes.

The matrix of biological samples, such as blood or urine, is complex, and the target substances are often in trace amounts. Thus, an efficient pretreatment method is required to separate and purify them from the matrix before instrumental analysis. The importance of sample pretreatment is reflected in its significant influence on the sensitivity, accuracy, and precision of the qualitative or quantitative analysis.[3] It is the key factor that determines the reliability of the analysis results and even determines the feasibility of subsequent analyses. Among various sample pretreatment methods, solid-phase extraction (SPE) is the most used technique. The concept of SPE is based on the distribution of analytes between liquid and solid adsorbents. SPE enriches the analyte from the solution by adsorbing the target compound on the solid adsorbent. The core of solid-phase extraction technology is the adsorption medium.[4,5] The proper selection of adsorbents can improve the selectivity, adsorption capacity, and efficiency of the SPE program. The most common classical adsorbents in the SPE process include chemically bonded silica gel with different functional groups, organic polymer adsorbents, and carbon-based materials.[6,7] In recent years, nanofibers have gradually become a new SPE adsorption material.[8–12] The high specific surface area of nanofibers can provide a large number of active sites, which allows for efficient separation, extraction, and enrichment. Polystyrene nanofibers have been widely used in food detection and the enrichment of environmental pollutants[13–15] because of their excellent adsorption capacity.

In this paper, PS nanofibers were prepared by electrospinning, and the adsorption behavior of the PS nanofibers to clonazepam was studied, including its kinetic and thermodynamic properties. Clonazepam was selected as the representative BZD drug in this work. The results of this study will be used to evaluate the feasibility of the efficient extraction and separation of BZDs from biological samples by using PS electrospun nanofibers as an adsorption medium for SPE. It was suggested

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that PS electrospun nanofibers had good potential for the separation and purification of BZDs from the water-soluble matrix as a novel effective sorbent material.

## 2. Material and methods

### 2.1. Materials

The standard of clonazepam (purity 100%) was provided by National Institutes for Food and Drug Control (Beijing, China). Methanol (HPLC-grade) was purchased from Fisher Scientific (Fair Lawn, NJ, USA). PS raw material (MW 230000) was acquired from Shijiazhuang Chemical Fiber Co., Ltd, China. And *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), hydrochloric acid, and sodium hydroxide were analytical-grade from Sinopharm Chemical Reagent Co.,Ltd, China.

### 2.2. Spinning of PS nanofibers

PS nanofibers were prepared by SS-2535 electrospinning apparatus (Beijing Ucalery, China) at 25 °C and 35% humidit. The 15wt% PS solution was prepared by stirring 1.5 g of PS raw material with 10 mL THF–DMF at room temperature for 4 h. The spinning solution was put into the syringe, and the spinneret is connected to the positive pole of the power supply. The aluminum foil is used as the fiber collection screen, which is connected to the negative electrode. The distance between the needle and the collecting screen is 300 mm, the voltage of the spray needle and the collecting screen were set to +16 kV and −7 kV respectively, the spinning speed is 0.08 mm $min^{-1}$, and the electrospinning time is 8–12 h. The prepared PS nanofibers are washed sequentially with methanol, water, and methanol, and dried at 40 °C. PS nanofibers were characterized by scanning electron microscope (SEM, Hitachi S-4800 I, Tokyo, Japan). A surface area and porosity analyzer (ASAP 2460, Micromeritics Instrument Corporation, USA) was used to determine the Brunauer–Emmett–Teller (BET) of the PS nanofibers.

### 2.3. Instrument and analytical conditions ions

Waters ACQuity UPLC® H-Class ultra high performance liquid chromatography systems (Waters, Milford, MA, USA) were used for the determination of clonazepam. The LC separation of the compounds was performed on an ODS column (150 mm × 4.6 mm, 5 μm) at 40 °C, with a mobile phase of methanol and water (70 : 30, v/v) at a flow rate of 0.5 mL $min^{-1}$. The injection volume was 10 μL. The compound was detected by PDA at 254 nm.

### 2.4. Adsorption experiments

The adsorption test was carried out to quantify the properties of the PS nanofibers. In this experimental study conducted under batch conditions, the effects of different parameters, such as time, pH, initial concentration of adsorbate, and amount of adsorbent in the adsorption of clonazepam, were examined.

**2.4.1 Effect of sample solution pH.** First, 20 mL aliquots of clonazepam aqueous solution with a concentration of 20 mg $L^{-1}$ were added to five 50 mL Erlenmeyer flasks. The pH of each solution was adjusted to 3, 5, 7, 9, and 11, respectively. Then, 20 mg of PS nanofibers was added to each Erlenmeyer flask and oscillated at 120 rpm at 25 °C until the adsorption equilibrium was reached. Afterward, 0.1 mL was sampled, and the concentration of clonazepam was determined. The adsorption capacity was calculated, and the effect of pH on the adsorption of clonazepam was investigated.

**2.4.2 Effect of amount of adsorbent.** To eight 50 mL Erlenmeyer flasks, 20 mL aliquots of clonazepam aqueous solution with a concentration of 20 mg $L^{-1}$ were added and adjusted to the appropriate pH value. Then, 2.4, 5.2, 8.9, 9.2, 20, 31, 45, and 54 mg of PS nanofibers were added to each flask, respectively, and oscillated at a rate of 120 rpm at 25 °C until the adsorption equilibrium was reached. Afterward, 0.1 mL was sampled, and the concentration of clonazepam was determined. The adsorption capacity was calculated, and the influence of the amount of adsorbent on the adsorption efficiency of clonazepam was investigated.

**2.4.3 Effect of the adsorption time and initial concentration on the adsorption of clonazepam.** First, 20 mL aliquots of clonazepam aqueous solution with initial concentrations of 4, 8, 12, 16, and 20 mg $L^{-1}$ were prepared in separate Erlenmeyer flasks. After adjusting to the appropriate pH value, 20 mg of PS nanofibers was added to each flask, and the oscillation rate was 120 rpm at 25 °C. At 0, 5, 10, 20, 30, 40, 50, 60, 90, and 120 min, 0.1 mL was sampled to measure the concentration of clonazepam and calculate the adsorption capacity at different times to determine the effect of adsorption time and initial concentration on the adsorption ability of clonazepam. Vegetable oil, fruit, and tea samples were purchased from local supermarkets of Shijiazhuang. For fruit, the edible part of sample was uniformly crushed using a proofer and placed in a closed container, then it was stored in a refrigerator at 4 °C away from light. The tea sample was ground in a mortar and placed in a clean self-sealing bag until use. Blank samples were used for validation studies and matrix-matched standard calibrations. Samples for recovery studies were spiked with a known amount of fortification standard and left for 10 min before the extraction.

### 2.5. Determining the kinetics of adsorption

First, 20 mL aliquots of clonazepam aqueous solution with initial concentrations of 4, 8, 12, 16, and 20 mg $L^{-1}$ were prepared separately and adjusted to the suitable pH value. Then, 20 mg of PS nanofibers were added to each solution and oscillated at 120 rpm at 25 °C until the adsorption equilibrium was achieved, and the adsorption capacity was calculated. Pseudo-first-order and pseudo-second-order kinetic models were used to fit the kinetic adsorption process.

The expressions of the pseudo-first-order kinetic eqn (1) and the pseudo-second-order kinetic eqn (2) are as follows:[16–18]

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \quad (1)$$

$$t/q_t = t/q_e + 1/k_2 q_e^2 \quad (2)$$

where $q_t$ and $q_e$ (mg $g^{-1}$) are the clonazepam uptake at time $t$ and at equilibrium, respectively; $q_t$ and $q_e$ were respectively determined using eqn (3) and (4). $k_1$ ($min^{-1}$) and $k_2$ (g

$mg^{-1}$ $min^{-1}$) are the equilibrium rate constants of pseudo-first-order and pseudo-second-order equations, respectively.

$$q_e = V \times (C_0 - C_e)/m \quad (3)$$

$$q_t = V \times (C_0 - C_t)/m \quad (4)$$

where $C_0$ is the initial concentration of clonazepam in solution (mg $L^{-1}$), $C_e$ is the equilibrium concentration (mg $L^{-1}$), $C_t$ is the concentration at time $t$ (mg $L^{-1}$), $m$ is the mass of adsorbent (g), and $V$ is the volume of solution (L).

### 2.6. Determining the isotherms of the adsorption of clonazepam

Five 20 mL clonazepam aqueous solutions with initial concentrations of 2, 4, 6, 8, and 10 mg $L^{-1}$ were prepared simultaneously and adjusted to the suitable pH value. Then, 20 mg of PS nanofibers was added and oscillated at 120 rpm at 10 °C and 25 °C until adsorption equilibrium was reached. The samples were determined by high-performance liquid chromatography, and the adsorption capacity was calculated. The data obtained from thermodynamic adsorption experiments were fitted by the Langmuir and Freundlich isothermal adsorption models. Freundlich and Langmuir isotherm model is shown as eqn (5) and (6):[16,19]

$$\ln q_e = \ln K_F + 1/n \times \ln C_e \quad (5)$$

$$C_e/q_e = C_e/q_{max} + 1/b \times q_{max} \quad (6)$$

where $q_e$ is the adsorption capacity of clonazepam per unit mass of PS nanofibers (mg $g^{-1}$), $q_{max}$ is the maximum monolayer adsorption capacity (mg $g^{-1}$), $b$ is the Langmuir constant related to binding energy (L $mg^{-1}$), and $K_F$ and $n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

### 2.7. Determining the thermodynamics of adsorption

The enthalpy ($\Delta H$), entropy ($\Delta S$), and Gibbs free energy change ($\Delta G$) of the thermodynamic parameters were calculated using eqn (7)–(9):[20]

$$\log(1/C_e) = \log k_0 + (-\Delta H/2.303RT) \quad (7)$$

$$\Delta G = -nRT \quad (8)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (9)$$

where $R$ is the universal gas constant (8.314 J $mol^{-1}$ $K^{-1}$), $T$ is the absolute solution temperature (K), and $k_0$ is a constant.

## 3. Results and discussion

### 3.1. Characterization of the PS nanofibers

A scanning electron microscope (SEM, Hitachi S-4800 I, Tokyo, Japan) was used to characterize the PS nanofibers. Fig. 1 shows the diameter of the fibers was about 400 nm, and the fibers showed uniform thickness and a smooth surface. The Brunauer–Emmett–Teller surface area of PS nanofibers was 2.65 $m^2$ $g^{-1}$, the pore diameter was 7.93 nm, and the pore volume was 0.0053 $cm^3$ $g^{-1}$.

### 3.2. Adsorption study

**3.2.1 Effect of pH.** The effect of pH on the adsorption efficiency of clonazepam by PS nanofibers at a pH range of 3.0–11.0 was explored. To adjust the pH, 1 mol $L^{-1}$ of hydrochloric acid solution or sodium hydroxide solution was used. It was found that clonazepam is unstable under alkaline conditions. When sodium hydroxide solution was added to adjust the pH to 9–11, the clonazepam aqueous solution changed from colorless and transparent to yellow instantly, which indicated that clonazepam had degraded to smaller compounds. When the solutions were adjusted to pH 3–5, the concentration of clonazepam decreased by about 30% and reached 53% after 8 h. Some impurity peaks also appeared on the chromatogram, which indicated that clonazepam had degraded under acidic conditions. Therefore, the final experiment was carried out under neutral conditions.

**3.2.2 Effect of initial concentration of clonazepam on its removal by PS nanofibers at various time intervals.** The effect of adsorption time on the adsorption capacity at different initial solution concentrations is shown in Fig. 2. It can be seen that the adsorption capacity of clonazepam increased with the adsorption time until equilibrium was reached between the adsorbent and clonazepam solution. In the first 20 minutes, the adsorption capacity of the PS nanofibers for clonazepam increased rapidly, and then gradually slowed down to reach an adsorption equilibrium after 60 min. This may be because, in the early stages of adsorption, the surface of the adsorbent

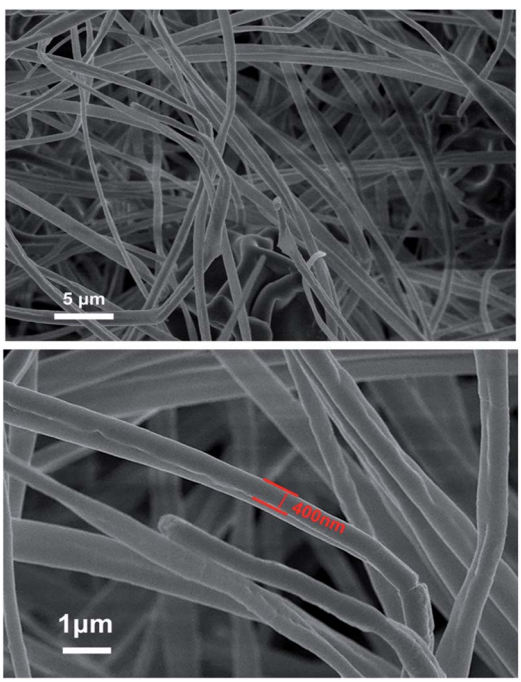


Fig. 1 Typical SEM images of electrospun PS nanofibers.

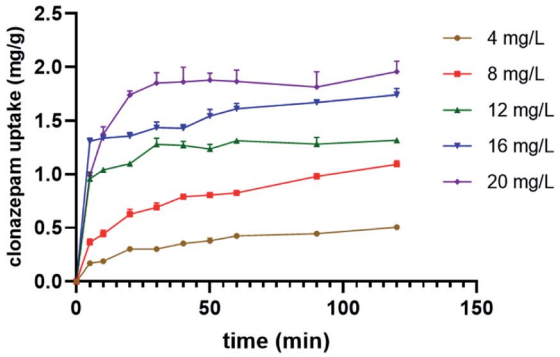


Fig. 2 Time and concentration to the adsorption of clonazepam.

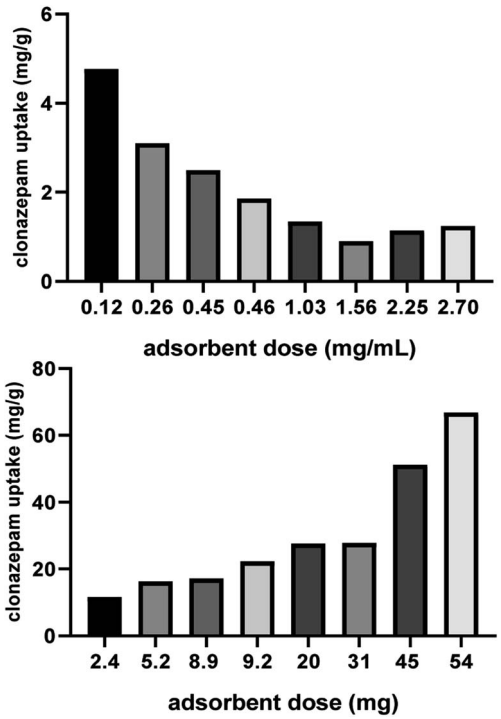


Fig. 3 Effect of adsorbent dosage on clonazepam adsorption on PS nanofibers ($T$ = 293 K, contact time = 60 min, $C$ = 15 mg $L^{-1}$).

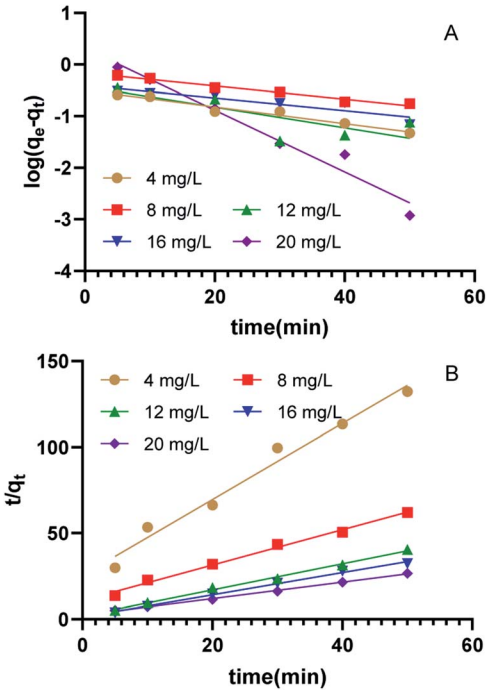


Fig. 4 The linearized plots of pseudo-first order kinetics (A), and pseudo-second order kinetics(B) model for clonazepam adsorption on PS nanofibers.

provides a large number of adsorption sites, and the difference in the concentration of clonazepam between the two phases produces a large mass transfer motive force, which causes the rapid complexation of clonazepam during the adsorption process. As the reaction progresses, clonazepam diffuses into the adsorbent until the adsorption equilibrium is reached. The equilibrium adsorption capacity of clonazepam increased from 0.42 to 1.88 mg $g^{-1}$ as the initial concentration of clonazepam solution increased from 4 to 20 mg $L^{-1}$. As the initial concentration of clonazepam increased, the adsorption capacity of PS nanofibers to clonazepam also increased, which may be due to increased contact between clonazepam and the adsorbent.

**3.2.3 Effect of adsorbent dosage.** It can be seen from Fig. 3 that as the adsorbent dosage increased, the adsorption capacity per unit mass of clonazepam gradually decreased. This might be because while the total amount of clonazepam in the solution remained unchanged, the number of active sites involved in the adsorption process increases with increasing adsorbent dosage, resulting in a decreasing trend in the adsorption capacity of clonazepam per unit mass of adsorbent. However, as the adsorbent dosage increased, the absolute amount of clonazepam adsorbed also increased. To balance the relationship between the two aspects, the adsorbent mass of 20 mg (1 mg $L^{-1}$) was chosen for the following experiment.

### 3.3. Studying the kinetics of the adsorption process

Adsorption kinetics were utilized to elucidate the controlling mechanism of the adsorption process (*e.g.*, surface adsorption, chemical adsorption, *etc.*) or the permeation mechanism.[21] The study of adsorption kinetics is very useful for predicting the adsorption rate and designing the process model. The adsorption kinetic curves of clonazepam are shown in Fig. 4, and the adsorption kinetic parameters of clonazepam are shown in Table 1. The suitability of the model can be judged by the determination coefficient ($R^2$) of the fitting equation. Compared with the $R^2$ obtained from the two models listed in Table 1, it was found that the adsorption of clonazepam by PS nanofibers was more consistent with the pseudo-second-order kinetic equation. It can be seen from Table 1 that there was good agreement between the theoretical and experimental values of $q_e$. The results show that the rate control step of the adsorption process is the diffusion process in the membrane.[22]

Table 1 Kinetic parameters for adsorption of clonazepam by PS nanofibers

| | | Pseudo-first-order model | | | Pseudo-second-order model | | |
|---|---|---|---|---|---|---|---|
| $C_0$ (mg L$^{-1}$) | $Q_{experiment}$ (mg g$^{-1}$) | $q_e$ (mg g$^{-1}$) | $k_1$ (h$^{-1}$) | $R^2$ | $q_e$ (mg g$^{-1}$) | $k_2$ (g mg$^{-1}$ h$^{-1}$) | $R^2$ |
| 4 | 0.43 | 0.32 | 0.037 | 0.9637 | 0.45 | 2.50 | 0.9786 |
| 8 | 0.98 | 0.69 | 0.028 | 0.9758 | 0.97 | 1.01 | 0.9920 |
| 12 | 1.31 | 0.38 | 0.046 | 0.6321 | 1.32 | 0.76 | 0.9957 |
| 16 | 1.61 | 0.40 | 0.028 | 0.8058 | 1.55 | 0.60 | 0.9952 |
| 20 | 1.88 | 2.06 | 0.136 | 0.9657 | 2.09 | 0.60 | 0.9981 |

### 3.4. The isotherm model of adsorption

The adsorption isotherm was to define the amount of adsorption to the target per unit mass of adsorbent. The Langmuir model assumes homogeneous adsorption, which is used to describe homogeneous monolayer adsorption, and the Freundlich model was used to describe heterogeneous multilayer adsorption. The adsorption isotherms of clonazepam removal by PS nanofibers at 283 K are shown in Table 2 and Fig. 5. The higher determination coefficient ($R^2$) value indicated that the Freundlich model fits the isotherm data better than the Langmuir model. This showed that the adsorption process of clonazepam by PS was multi-layer adsorption, which consists of both surface physical adsorption and internal chemical adsorption. It can be seen that $n$ was greater than 1, indicating that the adsorption process occurred easily.

### 3.5. Effect of temperature on adsorption and thermodynamic parameters

The adsorption behavior of clonazepam on PS nanofibers was studied in the temperature range of 283 to 298 K, from which the thermodynamic parameters such as changes in enthalpy ($\Delta H$, kJ mol$^{-1}$), entropy ($\Delta S$, kJ mol$^{-1}$ K$^{-1}$), and free energy ($\Delta G$, kJ mol$^{-1}$) could be obtained.

A plot of $\log(1/C_e)$ *vs.* $1/T$ was created and linearly fitted. According to the slope of the straight line, the change of isometric adsorption enthalpy at a certain adsorption level could be calculated, with its magnitude directly reflecting the nature of the adsorption force.

From Fig. 6 and Table 3, it can be seen that $\Delta H$ is positive, indicating that the adsorption process of clonazepam by the PS nanofiber adsorbent was endothermic. $\Delta G$ was negative and decreased with increasing temperature, meaning that the adsorption process was spontaneous. Generally speaking, the free energy of physical adsorption is less than that of chemical adsorption, the former in the range of −20–0 kJ mol$^{-1}$ and the latter in the range of −400 to −80 kJ mol$^{-1}$.[20,23] The value of $\Delta G$ in Table 3 shows that the adsorption of clonazepam by PS nanofibers is physical adsorption. $\Delta S$ was greater than 0, which showed that the adsorption process led to an increase in entropy.

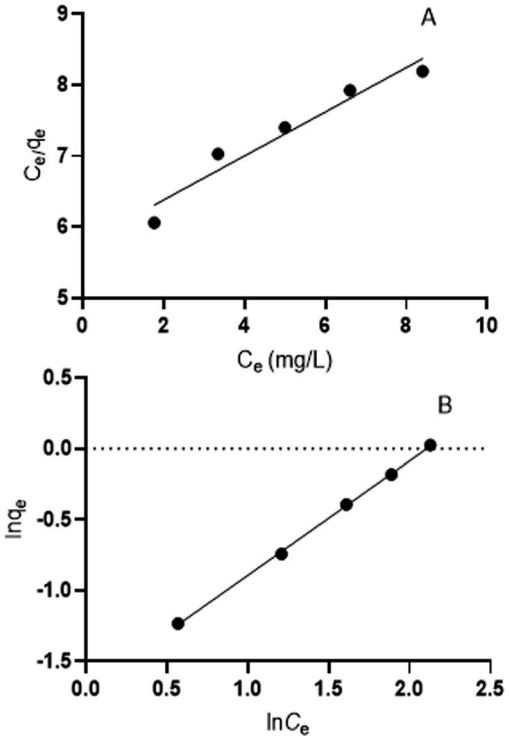


Fig. 5 The Langmuir isotherm model of clonazepam (A), and Freundlich isotherm model of clonazepam adsorption (B).

### 3.6. Comparison to other reported adsorbents

Commercial SPE cartridges[24–26] have been used to extract clonazepam from water or biological samples, and good extraction recoveries have been obtained. However, no adsorption experiment has been done by using commercial SPE cartridges, most

Table 2 Isotherm parameters for the adsorption of clonazepam by PS nanofibers ($T$ = 283.15 K)

| | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| $T$ (K) | $Q_{max}$ (mg g$^{-1}$) | $b$ (L mg$^{-1}$) | $R^2$ | $K_F$ [(mg g$^{-1}$)(L mg$^{-1}$)] | $n$ | $R^2$ |
| 283.15K | 3.225 | 0.054 | 0.9406 | 0.1827 | 1.238 | 0.9995 |

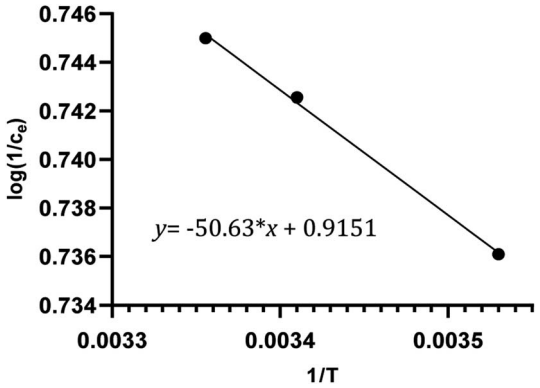


Fig. 6 Plot of $\log(1/C_e)$ *versus* $1/T$ for the estimation of thermodynamic parameters.

Table 3 Thermodynamic parameters for adsorption of clonazepam by PS nanofibers

| T (K) | $\Delta H$ (kJ mol$^{-1}$) | $\Delta G$ (kJ mol$^{-1}$) | $\Delta S$ (J mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|
| 283.15 | | −2.91 | 19.6 |
| 293.15 | 2.64 | −3.02 | 19.3 |
| 298.15 | | −3.07 | 19.2 |

of the commercial SPE adsorbents are carbon-based materials with the particle size of the packing is generally micron level, the specific surface area of the material is small, and the adsorption efficiency is generally not high. Three literature[27–29] on the adsorption of clonazepam by molecularly imprinted materials were found. The adsorption material is nanometer, and the adsorption capacity is shown in Table 4. It can be seen that the adsorption effect of materials used in this work is the best.

### 3.7. Adsorption mechanism

Physical adsorption is characterized by low adsorption heat, fast adsorption rate, non-selective, reversible and generally multi-layer adsorption. When the absolute value of adsorption free energy ($\Delta G$) was greater than 40 kJ mol$^{-1}$, chemical adsorption played an important role; otherwise, physical adsorption is the main process.[30,31] In this paper, the value of $\Delta G$ were about −3 kJ mol$^{-1}$, indicating that the adsorption of clonazepam by

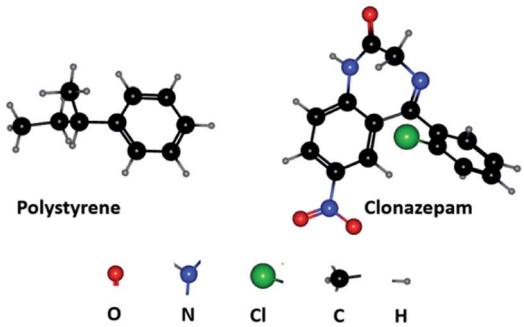


Fig. 7 Structure of polystyrene and clonazepam.

PS nanofibers may be physical adsorption. The changes of $\Delta G$ value (−2.91 to −3.07) with various temperature level is very small (Table 3), which further confirms the physical adsorption characteristics of the adsorption process. The adsorption of clonazepam by PS is multi-layer adsorption and accords with the characteristics of physical adsorption. In addition, we did the adsorption elution experiment by loading clonazepam standard (1 mL) at the concentration of 10 μg mL$^{-1}$ to 60 mg PS nanofibers, clonazepam was completely eluted by 200 μL methanol, showing that the adsorption–desorption process is reversible. The experimental results support that the adsorption of clonazepam by PS is physical adsorption. Based on the results presented in this paper, we conclude the conclusion that van der Waals forces control the adsorption.

Based on the principle that similar substances are easy to adsorb each other, in general, non-polar adsorbents are suitable for the adsorption of non-polar substances in polar solutions. PS, also known as aromatic adsorbent, is a typical non-polar adsorbent. Fig. 7 shows clonazepam is rich in benzene ring and aromatic ring. The two compounds share the similar structures. This may be the adsorption mechanism for PS adsorbing clonazepam.

Besides, the π–π interaction may also occur when the benzene ring structure of PS and clonazepam interacts with each other. π–π interaction is a general term for the interaction between aromatic molecules with planar structure or aromatic functional groups in organic compounds. The π–π interaction is a kind of non-bonding interaction. PS system is the most common and representative polymer aromatic system. Clonazepam is rich in benzene ring and aromatic

Table 4 Comparison of adsorption capacity by adsorbents in this work and other literature[a]

| Methods | Adsorbents | Adsorption capacity | Reference |
|---|---|---|---|
| MIP-SPE | Poly(AGE/IDA-*co*-DMAA) | 0.18 mg g$^{-1}$ | 27 |
| MHSPE | CTAB modified $Fe_3O_4/SiO_2$ nanocomposites | 0.8 mg g$^{-1}$ | 28 |
| MIPs-MSB | gf-$Fe_3O_4$ NPs | 0.27 mg g$^{-1}$ | 29 |
| PS-NF-based SPE | PS NFs | 3.2 mg g$^{-1}$ | This work |

[a] MIP-SPE: molecularly imprinted polymer solid-phase extraction; MHSPE: mixed hemimicelles-based solid-phase extraction; MIPs-MSB: molecularly imprinted polymers-magnetic stir bar; PS-NFs-based SPE: polystyrene nanofibers-based solid-phase extraction; AGE: allyl glycidyl ether; IDA: iminodiacetic acid; DMAA: *N*,*N*-dimethylacrylamide; CTAB: cationic surfactant cetyltrimethylammonium bromide; gf-$Fe_3O_4$ NPs: graft-functional $Fe_3O_4$ nanoparticles.

ring, and there may be π–π interaction between the two substances.

## 4. Conclusion

In this paper, the study aimed to determine the detailed adsorption characteristics of novel adsorbents, the adsorption kinetics and thermodynamic properties of clonazepam on PS electrospun nanofibers were studied for the first time, and the feasibility of PS nanofibers for pretreatment of clonazepam and other BZDs was explored. PS nanofibers adsorbed clonazepam quickly in the initial 20 min, and reached the adsorption equilibrium around 60 min. The theoretical adsorption capacity reached 3.2 mg $g^{-1}$, showing that PS nanofiber is a good adsorbent for clonazepam. The adsorption capacity of clonazepam increased with the increase of adsorbent concentration, and the adsorption of clonazepam by PS nanofibers was more in line with the second-order kinetic model and Freundlich isotherm model. The adsorption processes were found to be naturally feasible, spontaneous, and endothermic based on the thermodynamic parameters. The results showed that PS nanofibers were an efficient adsorbent for the extraction of clonazepam from aqueous solutions and had good potential for separating and purifying BZDs from water-soluble matrices.

## Author contributions

Jing An: data curation, formal analysis, methodology, writing – original draft, funding acquisition. Xin Wang: formal analysis, methodology, writing – original draft. Ying Li: data curation. Weijun Kang and Kaoqi Lian: conceptualization, funding acquisition, project administration, resources, Writing – review & editing. All authors read and approved the final manuscript.

## Conflicts of interest

The authors declare no conflict of interest.

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