Study on a new treatment method for classic pollutant diclofenac from the pharmaceutical factory

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Abstract. As a classic component of non-steroidal anti-inflammatory drug (NSAID), diclofenac has the anti-inflammatory, analgesic and antipyretic effects. As a result, the medical wastewater discharged from some diclofenac pharmaceutical factories may contain a certain amount of diclofenac. This pollutant is toxic and harmful to livestock, and if the livestock have digested diclofenac, it will affect their cellular metabolism process, cellular components and protein catalysis, which may even cause mass deaths under severe situation. An effective treatment method for this pollutant is to adopt composite aerogel adsorption. This paper briefly introduces the modification plan of cellulose and the process of using cellulose to adsorb diclofenac sodium (DCF), compares the adsorption effects before and after modification, and proposes a new direction to treat this kind of pollutant based on the comparison results. In this paper, by using cotton fiber as the material and polyvinylamine as the modifier, the hydrothermal synthesis method is employed to prepare the rGO/cellulose composite aerogel material, and the characterization analysis of its structure and performance is also conducted. The characterization results of SEM, EDS, XRD. FTIR etc. show that the composite aerogel material prepared in our experiment has maintained the crystal structure of cellulose, which has obvious 3D porous structure, and its specific surface area reaches 354.7m²/g. In addition, the material surface contains abundant amino, hydroxyl, C=N and other functional groups. Secondly, with diclofenac sodium as the targeted pollutant, this paper investigates the performance and mechanism of using rGO/cellulose composite aerogel to adsorb diclofenac sodium. The experimental results show that the rGO/cellulose composite aerogel presents outstanding performance in adsorption of DCF, which is significantly superior to the performance of cellulose aerogel material. When the rGO/cellulose composite aerogel and the cellulose aerogel are used to adsorb DCF, their maximum adsorption capacities are 242.94mg/g and 47.82mg/g, respectively. In addition, the process of using composite aerogel to adsorb DCF satisfies the Langmuir isothermal adsorption model and the pseudo-second-order kinetic model, which indicates that this adsorption is chemical adsorption mainly consisting of monolayer adsorption. The thermomechanical analysis shows that the adsorption of DCF using composite aerogel is spontaneous exothermic reaction. In the meantime, the composite aerogel has wider pH adaptability, and it presents great adsorption efficiency of DCF within the pH range of 4-10.
1. Introduction

Diclofenac is a non-steroidal anti-inflammatory drug (NSAID), which has the anti-inflammatory, analgesic and antipyretic effects. This drug provides the anti-inflammatory, analgesic and antipyretic effects by inhibiting the synthesis of prostaglandin. Its effect is 2~2.5 times stronger than that of indomethacin and 26~50 times stronger than that of acetylsalicylic acid. Diclofenac has the characteristics of strong effect, mild adverse reaction, small dose and small individual difference.

The plasma protein binding rate of this drug is 99.7%, and its half-life period is 1~2 hours. If the drug is administered according to the recommended dosage and interval, there will be no drug accumulation. After liver metabolism of this drug, the metabolite of approximately 60% therapeutic dose will be excreted from kidney, and the excretion of drug unchanged is less than 1%. The rest of dosage is excreted to intestine with bile in the form of metabolite, which will then be removed from the feces. [1] Diclofenac is a classic non-steroidal anti-inflammatory drug (NSAID), which is usually used in the treatment of various mild to moderate acute and chronic orthopedic pains, such as osteoarthritis, RA (rheumatoid arthritis) and AS (ankylosing spondylitis). Diclofenac has become a relatively common pollutant in modern society, which widely exists in rivers, lakes and other environmental water, especially in the medical wastewater discharged by some pharmaceutical factories manufacturing such drug. In addition to the medical wastewater, the diclofenac may also come from human feces after taking this drug. It’s worth noting that it is difficult to completely mineralize and degrade diclofenac using the common water treatment method, as a result of which, diclofenac has accumulated in the effluent from some receiving water bodies and sewage treatment plants. Many aquatic organisms have similar drug target molecules in human body, so the exposure of diclofenac is toxic to organisms. Even though diclofenac is not concentrated in water, its concentration is generally at the ng/L level, however, due to its lipophlicity, it tends to have biological accumulation in water environment. Therefore, even a low concentration of diclofenac in the environment could be toxic to aquatic organisms. [2] As a popular method to treat pollutants in water body, the adsorption method has not been considered in the diclofenac treatment scheme at present, but it is a reasonable option nonetheless. The cellulose base material has great chemical modification ability and high hydrophilic, which also contains abundant hydroxyls, and the natural polymeric absorbent can be prepared by introducing the functional groups with certain adsorption capacity using modified hydroxyls. The properties described above make the modification of cellulose material possible, and its adsorption ability can also be improved. Based on that, with diclofenac sodium as the targeted pollutant and modified cellulose base material as the adsorbent, this paper investigates the adsorption process and evaluates the effects. It’s worth noting that there are many methods to treat the accumulation of diclofenac sodium pollutant, and the common methods include the photocatalytic degradation method, UV-activated persulfate degradation method and adsorption method.

The photocatalytic degradation method [3] is an effective method with great removal effects. However, take the most common case of using TiO2 for photocatalytic degradation of diclofenac sodium for example, because the nano-particles have small sizes, it is difficult to recycle after water treatment, which may cause waste of resources and increase the treatment cost; the UV-activated persulfate degradation method [4] has the best treatment effects, which is proved to be an effective and relatively environmental friendly process by practice. However, it’s worth noting that different pH of solution has strong impact on the degradation of diclofenac sodium using this process, and the humic acid in the solution can inhibit the reaction. Furthermore, with the increase of humic acid dosage, the inhibition of reaction will become more obvious. Restriction from the above conditions indicates that this treatment process has high requirement of experimental conditions, so this scheme is not considered. In addition, in recent years, the method of using oxidized activated carbon to adsorb diclofenac sodium has become a mainstream method. Different from the common activated carbon, although the oxidized activated carbon has smaller surface area, however, after oxidization, its removal rate of diclofenac sodium is 6 times higher than that of commercial unmodified activated carbon. The significant increase in the removal volume of diclofenac sodium could be caused by the acidic surface functional groups. In order to evaluate the effects of these acidic functional groups on improvement of the adsorption capacity, after oxidization using different oxidizing agents, the Boehm titration [5] is employed to measure the
concentration of acidic functional groups. In recent years, the cellulose base adsorption material has become the focus of researchers. With the scientific and technological progress and the social development, increasingly more pollutants are generated in the daily work and life of people, which gives more important meaning to the research on cellulose material mentioned above. In their paper published in 2004, Wang Chunhua et al. [6] elaborated on the research value and development trend of cellulose base adsorption material; according to their experimental results, Yuan [7] found that after adding CNC to the composite material, the thermal stability, mechanical strength, hardness, rigidity and flexibility of material were all significantly improved. The nanocrystalline cellulose also presents application potential in the fields of optical material, template material and smart material. It is a nano cellulose material, the ingredient is cellulose, and it becomes nano material through physical and chemical reactions. The nano cellulose has the characteristics of big specific surface area, high Young’s modulus, great adsorption performance and high reaction activity, which has inherent optical, rheological and mechanical properties. CNC has broad applications in different fields both in China and abroad [8]. The above properties not only apply to the nano reinforced material, but also apply to medicine, packing material, paper, food additive, paint, floor material and construction material.

As a classic component of non-steroidal anti-inflammatory drug (NSAID), diclofenac has the anti-inflammatory, analgesic and antipyretic effects. As a result, the medical wastewater discharged from some diclofenac pharmaceutical factories may contain a certain amount of diclofenac. This pollutant is toxic and harmful to livestock, and if the livestock have digested diclofenac, it will affect their cellular metabolism process, cellular components and protein catalysis, which may even cause mass deaths under severe situation. An effective treatment method for this pollutant is to adopt composite aerogel adsorption. This paper briefly introduces the modification plan of cellulose and the process of using cellulose to adsorb diclofenac sodium (DCF), compares the adsorption effects before and after modification, and proposes a new direction to treat this kind of pollutant based on the comparison results.

In this paper, by using cotton fiber as the material and polyvinylamine as the modifier, the hydrothermal synthesis method is employed to prepare the rGO/cellulose composite aerogel material, and the characterization analysis of its structure and performance is also conducted.

2. Materials and method

2.1. Preparation

Preparation of CNC by acid hydrolyzation: 3.0 g absorbent cotton and 26 mL concentrated sulfuric acid (64 wt%) had reaction for 90 min in three-necked flask, and the reaction conditions were 500 rpm and 45℃. After the reaction, 300 mL deionized water was added to terminate the reaction. Then, centrifugation was conducted under the conditions of 8000 rpm and 10 min until there was no precipitate (pH=1), and the centrifugated CNC solution was dialyzed until the solution was neutral. The dialyzed CNC was extracted and placed into the sample vial, and then, it was stored in the refrigerator under 4℃ for future use.

Hydroformylation of CNC: 0.09g prepared CNC was added to the water, and the constant volume of 125 mL was achieved. Preparation of acetate buffer: 5.1 g sodium acetate was added to 20 mL acetic acid, and after achieving the constant volume of 250 mL, 25 mL was extracted. 1.3 g sodium periodate and 25 mL buffer salt solution were added with 50 mL mixture of distilled water and CNC. It was stirred for 48 h away from light, and the temperature was maintained at 45℃. After the reaction, 20 mL glycol was added to terminate the reaction, and then, it was stirred for 10 min. Next, it was placed in the dialysis tube to have dialysis for 2-3 days.

CNC grafting with PVAm: After dialysis, 110 mL sample solution was taken, and it was added with 5 g formic acid and 2.5 g PVAm. The 80 g/L NaOH solution prepared in advance was used to adjust the pH to 4.5-5. It was stirred for 6h under 45℃. Then, homogenizer was used to conduct cell disruption for 1h.

Preparation of rGO/cellulose composite aerogel by hydrothermal method: 2mg/mL graphene oxide solution was prepared, and put into the ultrasonic machine for 2h. 0.36g prepared CNC-PVAm sample
was weighed, and 20 mL graphene oxide solution was added. After magnetic stirring for 30 min, it was put into the ultrasonic machine for 30 min. Then, 0.6 mL glacial acetic acid, 4.2 mL genipin with concentration of 1% and 0.27 g sodium ascorbate were added, and it was stirred for 2 h. After stirring, the solution was put into the reactor to have reaction for 12 h under 90°C. The supernatant was removed by centrifugation, and the precipitate was extracted and put into a plastic beaker for freeze drying.

Characterization:

FTIR: The ATR module of Fourier infrared spectrometer (ESCALAB250X Nicolet iS50, ThermoFisher Scientific, U.S.) was used to conduct NDT (nondestructive testing) of adsorbing material and analyze the structure of surface material.

X-ray diffraction (XRD): The XRD characterization was carried out using X-ray diffractometer (MiniFlex600, Rigaku, Japan), which was used to characterize various adsorbing materials prepared in this experiment. Analysis conditions: Cu-Kα X-ray source, voltage of 40 kV, current of 40 mA, scanning scope of 5°-90°, scanning step of 0.04°, and scanning speed of 1°min⁻¹.

BET specific surface area:

SEM (scanning electron microscope): The scanning electron microscope (230, FEI, U.S.) was used to observe surface appearance of various adsorbing materials in this experiment.

High-performance liquid chromatography (HPLC): The C18 chromatographic column (4.6mm×250mm) HPLC (Agilent 1260 Infinity SHIMADZU LC-20AT, Polytech Instrument Ltd.) was used to measure the concentration of target pollutant diclofenac sodium in the experiment.

Study on the adsorption performance:

5 mL DCF sample was put into each of three conical flasks with cover, and 45 mL ultrapure water was added to each flask; then, the CNC-PVAm/rGO, CNC-PVAm and CNC samples were added to the three conical flasks successively, and each sample was 10 mg; next, the flasks were placed in the intelligent thermostatic oscillator to have adsorption reaction for 12 h under the conditions of 25°C and 150 rpm, and then the syringe was used to take the sample. HPLC was used to measure corresponding peak area, and the concentration of DCF solution after adsorption was measured according to marking. Then, the equilibrium adsorption capacity and adsorption efficiency were calculated based on Formulas 1.1 and 1.2, respectively.

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

\[
\eta = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (2)
\]

In order to investigate the effects of solution pH on adsorption, the DCF sample was taken for multiple times, and 10% hydrochloric acid and sodium hydroxide solution was used to adjust its pH to 4-11. These samples were used to conduct adsorption experiment. Before and after adsorption, the sample was taken to conduct chromatographic detection, so as to obtain the concentration information of pollutant. The adsorption isotherm experiment was also conducted. The DCF solution with certain concentration gradient was extracted, and it was adjusted to optimal pH and placed into 15 150 mL conical flasks; then, the 10 mg optimal sample was added to each flask, and oscillating adsorption was conducted for 12 h under the conditions of 25°C, 35°C, 45°C and 150 rpm, respectively. The solutions before and after adsorption were filtered using filter head, injected into the chromatographic bottle and
marked. The HPLCs before and after adsorption were measured, and the adsorption capacity was calculated. This experiment aimed to determine the optimal temperature of adsorption experiment and the DCF concentration when achieving maximal adsorption capacity, so that this temperature and concentration could be adopted in all following experiments. The theoretical basis of experiment is as follows: the Langmuir isothermal adsorption model. The Langmuir adsorption isotherm can demonstrate the effect of initial adsorption concentration on the adsorption progress in the characterization experiment. Its equation is as follows:

\[ \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (3) \]

where:
- \( C_e \) is the equilibrium concentration of pollutant DCF in solution (mg L\(^{-1}\));
- \( q_e \) is the equilibrium absorption capacity of unit mass adsorbent (mg g\(^{-1}\));
- \( K_L \) is the Langmuir adsorption constant (L mg\(^{-1}\));
- \( q_m \) is the maximum absorption capacity (mg g\(^{-1}\));
- \( R_L \) is the separation constant, and the expression is:
\[ R_L = \frac{1}{1 + K_L C_0} \quad (4) \]
- \( C_0 \) is the initial concentration of DCF (mg L\(^{-1}\)).

It represents the difficulty of forward adsorption reaction of DCF. When \( R_L = 0 \), it is the easiest for adsorption to occur, and this process is almost irreversible; when \( 0 < R_L < 1 \), it is relatively easy for adsorption to occur; when \( R_L = 1 \), the adsorption isotherm is a straight line; when \( R_L > 1 \), it indicates that the forward trend of adsorption is small, and the adsorption reaction almost does not occur.

With \( C_e/q_e \) as the ordinate, the slope and intercept of fitting straight line can be obtained; with the adsorption equilibrium concentration \( C_e \) as abscissa, \( K_L \) and \( q_m \) can be obtained; the Freundlich isothermal adsorption model is:

\[ \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5) \]

where:
- \( K_f \) represents the constant related to adsorption capacity (mg g\(^{-1}\)(L mg\(^{-1}\))\(^{1/n}\));
- \( n \) represents the constant related to adsorption strength.

In the kinetics experiment of adsorption material, 12.5 mL diclofenac sodium mother solution was added to 112.5 mL water, 10 mg graphene oxide adsorption material was added into the solution, then it was placed into the table concentrator, and the conditions of 150 rpm and 25°C were set. In the following 10h, sampling was conducted according to the sampling rules, chromatographic detection was conducted, and the curve of how adsorption concentration changed with time was obtained. The sampling rules are as follows: conduct sampling every 2 min, and take 15 samples each time; conduct sampling every 5 min, and take 18 samples each time; conduct sampling every 10 min, and take 6 samples each time; conduct sampling every 20 min, and take 6 samples each time; conduct sampling every 30 min, and take 4 samples each time; conduct sampling every 60 min, and take 3 samples each time. The theoretical basis of experiment is the Lagergren quasi first-order kinetics model [10].

\[ \ln(q_e - q_t) = \ln q_{eq} - k_1 t \quad (6) \]
t——adsorption time (min);
q_e——equilibrium absorption capacity (mg g\(^{-1}\));
q_t——absorption capacity when the adsorption time is t (mg g\(^{-1}\));
q_{e,c}——equilibrium absorption capacity obtained by calculation (mg g\(^{-1}\));
K_1——quasi first-order adsorption rate constant (min\(^{-1}\))

\[ t = \frac{1}{k_1 q_e} \ln(q_e - q_t), \]  

Lagergren quasi second-order kinetics model \[ 11 \]

\[ t = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \]  

\( t \) was plotted according to \( t/q_e \), based on which the slope and intercept of fitting straight line can be obtained, and then, the values of \( K_1 \) and \( q_{e,c} \) could be calculated;

In the thermodynamic experiment, after freeze drying, 10mg CNC-PVAm adsorbent solution with the concentration of 11% and 10mg CNC adsorbent solution not grafted with PVAm with the concentration of 11% were used to adsorb DCF with initial concentration of 50mg/L for 12h under 25℃.

The contrast test aims to determine the change of entropy during the adsorption process. The theoretical basis of experiment is as follows: investigate the thermodynamic parameter Gibbs free energy \( \Delta G \), enthalpy \( \Delta H \) and entropy \( \Delta S \), and discuss the effects of temperature during the complete adsorption process.

\[ \Delta G = \Delta H - T \Delta S \]  

\[ \Delta G = -RT \ln K_c \]  

\[ K_c = \frac{q_e}{C_e} \]  

\( \Delta G \)—Gibbs free energy (KJ mol\(^{-1}\));
\( \Delta H \)—enthalpy (KJ mol\(^{-1}\));
\( \Delta S \)—entropy (J mol\(^{-1}\) K\(^{-1}\))
Van't Hoff equation \[ 12 \]:

\[ \ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  

With \( 1/T \) as abscissa and \( \ln K_c \) as ordinate, \( \Delta S \) and \( \Delta H \) can be obtained based on the slope and intercept of fitting straight line.

3. Results and discussion

3.1. Results of characterization experiment

3.1.1. FTIR: CNC-PVAm/rGO structural characterization. Based on the infrared spectroscopic analysis, the specific functional groups of material can be observed more accurately. The infrared spectrograms of CNC-PVAm/rGO and CNC-PVAm are shown in Figure 1.
Figure 1. Infrared spectrograms of CNC-PVAm/rGO and CNC-PVAm.

According to Figure 1, the characteristic peak of rGO appears in the infrared spectrograms of cross-linked product, so it can be regarded as being successfully cross-linked with CNC-PVAm.

3.1.2. XRD: characterization of material crystallinity. The XRD spectrum intuitively presents related information of material crystallinity. Multiple adsorption materials and raw materials were used in the experiment, and their XRD spectrum are shown in Figure 2.

Figure 2. XRD spectra of multiple adsorption materials.

According to the analysis in Figure 2, by comparing the XRD spectra of common cotton and CNC, it can be seen that the peak intensity of cellulose material after acidolysis is much higher, which indicates that its crystallinity has been significantly improved; by comparing the XRD spectra of CNC-PVAm/rGO and CNC-PVAm materials, we can see that the peak intensity of CNC-PVAm/rGO is lower than that of CNC-PVAm, which means the crystallinity of this material has decreased, and it indicates that chemical modification has damaged partial crystalline region and further proves that the chemical modification of this experiment is successful.

3.1.3. BET specific surface area test and analysis. The N₂ absorption and desorption isotherms of CNC-PVAm/rGO are presented in Figure 3. According to the isotherms, the specific surface area of CNC-PVAm/rGO calculated by the Brunauer-Emmett-Teller (BET) method is 354.6879m³/g, which indicates
the existence of porous structure within CNC-PVAm/rGO, and this has important impact on the adsorption performance of material.

3.1.4. SEM (scanning electron microscope) test and analysis. SEM can be used to observe the surface structure and appearance of material more meticulously. In this experiment, the SEM spectra of multiple adsorption materials are as shown in Figure 4.

According to Figure 4 (right), the CNC material grafted with PVAm presents porous structure, and it has big specific surface area, which can facilitate the adsorption process. Further, as shown in Figure 3-5 (left), it is clear that the CNC-PVAm/rGO material added with graphene oxide using hydrothermal method has formed a 3D porous structure, and compared with the 2D structure of CNC-PVAm, CNC-PVAm/rGO has a bigger internal area, which can have more contact with the adsorption material, so it has better adsorption performance than CNC-PVAm.

3.2. Results of adsorption experiment

3.2.1. Influence of pH on adsorption. When investigating the influence of solution pH on adsorption effects, the experimental temperature was controlled at 25oC to have reaction for 45min. The results are as shown in Figure 5. According to Figure 3-5, when the pH is smaller than 7, with the increase of initial solution pH, the equilibrium DCF adsorption capacity of nano-cellulose adsorption material also increases accordingly, and the DCF adsorption capacity of nano-cellulose adsorption material reaches the highest value when the pH is 7. When the pH is higher than 7, the equilibrium DCF adsorption
capacity of nano-cellulose adsorption material gradually declines with the increase of pH; when pH=11, the equilibrium DCF adsorption capacity of nano-cellulose adsorption material shows significant decline.

**Figure 5.** Influence of pH on the equilibrium DCF adsorption capacity of nano-cellulose adsorption material.

3.2.2. Adsorption isotherm. The Langmuir isotherm model is adopted in the adsorption isotherm experiment. This model assumes that adsorption is a homogeneous-phase single-layer process, which means that all adsorption sites on the adsorbent surface have equal acting force on adsorbate (DCF). The images of adsorption isotherm experiment are provided in Figure 6 and Figure 7; related parameters are listed in Table 1.

**Figure 6.** Linear fitting curves of $C_e/q_e$ and $C_e$. 

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Figure 7. Adsorption isotherm.

Table 1. Parameters of adsorption isotherm experiment.

| Material  | Temperature | Langmuir adsorption isotherm | Freundlich adsorption isotherm |
|-----------|-------------|------------------------------|---------------------------------|
|           |             | q_e  | K_L  | R^2  | 1/n | K_f  | R^2  |
| CNC-PVAm/rGO | 25°C       | 588.24 | 0.35 | 0.99 | 0.60 | 144.10 | 0.97 |
| CNC-PVAm/rGO | 35°C       | 589.33 | 0.22 | 0.99 | 0.64 | 106.27 | 0.95 |
| CNC-PVAm/rGO | 45°C       | 598.80 | 0.13 | 0.99 | 0.66 | 73.94  | 0.96 |

Based on comprehensive analysis of the adsorption isotherm and the experimental parameters of adsorption isotherm, it can be seen that both q_max and KL grow with the increase of temperature, and the main reason is the exothermicity during adsorption process. The fitting coefficient of Langmuir model R^2>0.99, and it can be concluded that the DCF adsorption process by nano-cellulose adsorption material satisfies the Langmuir adsorption isotherm model.

3.2.3. Adsorption kinetics. When studying the adsorption kinetics of DCF using nano-cellulose adsorption material, the curves of how the DCF adsorption capacities of CNC-PVAm/rGO and CNC-PVAm change with time are obtained first, as shown in Figure 8. According to the diagram, the CNC-PVAm/rGO material has higher adsorption capacity than CNC-PVAm, and it can reach adsorption equilibrium within short time.

Figure 8. Curves of how the DCF adsorption capacities of CNC-PVAm/rGO and CNC-PVAm change with time.
The adsorption rate of quasi first-order kinetics model is generally decided by the diffusion step; the assumed adsorption rate of quasi second-order kinetics model is generally decided by the interaction between adsorbent and adsorbate. For this experiment, the parameters of both quasi first-order kinetics model and quasi second-order kinetics model are listed in Table 2; the quasi first-order kinetics curve and quasi second-order kinetics curve are as shown in Figure 9 and Figure 10.

Figure 9. Quasi first-order kinetics curve of using nano-cellulose adsorption material to adsorb DCF.

Figure 10. Quasi second-order kinetics curve of using nano-cellulose adsorption material to adsorb DCF.
Table 2. Kinetics parameters of using nano-cellulose adsorption material to adsorb DCF.

|                     | Quasi first-order kinetics | Quasi second-order kinetics |
|---------------------|-----------------------------|----------------------------|
| K1 (min⁻¹)         | qe1 (mg g⁻¹)               | R²                         |
| CNC-PVAm/rGO       | -0.02005                   | 2.32526                    |
|                     | 0.995                      | 0.0037                     |
|                     | 0.9776                     | 0.99733                    |

According to the quasi first-order kinetics parameters in the table, it is not difficult to see that the qe1 obtained by calculation is significantly different from the qe obtained in experiment, the fit coefficient R² is also smaller, and the CNC-PVAm/rGO obtained by experiment presents poor fitting degree of the DCF adsorption data and quasi first-order kinetics. For the quasi second-order kinetics parameters, the experimental data and linear fitting curve show high fitting degree according to analysis, and in the table, the quasi second-order kinetics fitting coefficient R² is 0.997, which is higher than the quasi first-order kinetics fitting coefficient. It is not difficult to draw the conclusion that the quasi second-order kinetics equation is more applicable to the adsorption process of this experiment.

Figure 11 shows the curve of particle internal diffusion reaction equation, and related parameters are listed in Table 3. The Weber-Morris internal diffusion rate control model was adopted in the experiment.

Figure 11. Curve of particle internal diffusion reaction equation.

Table 3. Parameters of particle internal diffusion reaction.

| C₀      | K₁   | K₂   | K₃   | C₁   | C₂   | C₃   | R₁²   | R₂²   | R₃²   |
|---------|------|------|------|------|------|------|-------|-------|-------|
| (mg/L)  | (mg/g min⁻¹) |      |      |      |      |      |       |       |       |
| 50      | 34.48| 21.21| 6.23 | -24.83| 40.03| 152.63| 0.99  | 0.98  | 0.91  |

During the liquid-solid adsorption process, the solute transfer mainly includes the external mass transfer (film diffusion) or particle internal diffusion [13], both of which may occur simultaneously under some situation. According to Figure 11, the linear fitting curve of qₜ to t½ is a polyline, which consists of three approximate straight lines. This indicates that the DCF adsorption process of nano-cellulose adsorption material is a staged process. Based on analysis by combining the data in Table 3,
3.2.4. Adsorption thermodynamics. The adsorption thermodynamics experiment is still required. In order to further understand the driving force and adsorption degree during the process of using nano-cellulose adsorption material to adsorb DCF, three different thermodynamic parameters are calculated in this section: standard Gibbs free energy $\Delta G$, standard entropy change $\Delta S$ and standard enthalpy change $\Delta H$. The linear fitting results are provided in Figure 12, and the adsorption thermodynamic parameters are recorded in Table 4.

![Figure 12. Fitting curve of adsorption thermodynamics experiment.](image)

**Table 4. Adsorption thermodynamic parameters.**

| Initial concentration of DCF | $\Delta G$ (KJ mol$^{-1}$) | $\Delta S$ (J mol$^{-1}$ K$^{-1}$) | $\Delta H$ (KJ mol$^{-1}$) |
|-----------------------------|--------------------------|----------------------------------|---------------------------|
| 25°C                        | -4068.6 -3964.5 -3794.6  | -13.6255                         | -8141.32                  |

According to the adsorption thermodynamic parameters, the process of using nano-cellulose adsorption material to adsorb DCF is an exothermic process, and $\Delta S$ is negative, which indicates the randomness of solid-liquid interphase has declined. Generally speaking, the size of $\Delta H$ can be used as the basis to determine the reaction type [14]. If $\Delta H$ is 2.1-20.9 kJ/mol, the reaction process mainly consists of physical adsorption; if $\Delta H$ is 20.9-418.4kJ/mol, the reaction process is mainly chemical adsorption. In this experiment, the value of $\Delta H$ indicates that the process of using nano-cellulose adsorption material to adsorb DCF is a chemical adsorption process.
3.2.5. **CNC-PVAm/rGO before and after adsorption.** According to the analysis of Figure 3-13, it is not difficult to see that the XRD spectral patterns before and after using the CNC-PVAm/rGO material to adsorb the pollutant are basically consistent, i.e., the peaks and trends of two curves do not present significant difference. This indicates that the adsorption process does not have remarkable effects on the CNC-PVAm/rGO material, and there is no obvious damage to its structure. This means that this process can be regarded as a nondestructive process. [15]

![Figure 13](image-url)  
*Figure 13. XRD spectra before and after using CNC-PVAm/rGO to adsorb pollutant.*

According to Figure 14, after using CNC-PVAm/rGO for adsorption, the characteristic peak of DCF shows at 1665cm\(^{-1}\) of spectrum. Based on the characteristic peak table of infrared spectrogram, this position is within the double-bond stretching vibration region (1690~1500 cm\(^{-1}\)), and this region mainly includes the stretching vibration of \(\text{C}=\text{C}, \text{C}=\text{N}, \text{N}=\text{N}, \text{N}=\text{O}\) and other bonds and the skeletal vibration of benzene ring (\(\sigma\text{C}=\text{C}\)) [16], which indicates that the compound contains DCF after adsorption. This further proves that the adsorption process of this experiment was successful.

![Figure 14](image-url)  
*Figure 14. Infrared spectrogram before and after using CNC-PVAm/rGO to adsorb pollutant.*
4. Conclusion
In the experiment, acid hydrolysis of cellulose powder was adopted to prepare the nano-cellulose aerogel, and further detection and characterization analysis of its physicochemical properties were conducted. Finally, the nano-cellulose aerogel was used to successfully adsorb the target pollutant DCF in the experiment [17], and the above process was monitored utilizing multiple liquid-phase concentration analysis and kinetic analysis. The experimental results using HPLC show that before and after the pollutant was treated with multiple adsorption materials, its concentration showed change in different degrees. According to the XDR spectra of different adsorption materials, it can be seen that the spectral patterns do not present significant difference before and after adsorption, which indicates there is no obvious change in the structure of adsorption material. According to analysis of spectra, it can also be found that the crystallinity of cellulose material after acid hydrolysis is significantly improved. After chemical modification, the XDR spectrum of adsorption material added with graphene oxide using hydrothermal method has lower peak intensity, which indicates that chemical modification has destructed partial crystalline region of material, and it further proves that the chemical modification is successful. The FT-IR infrared spectrometer was used to analyze the infrared spectrogram. According to the spectrogram, the characteristic group of target pollutant was detected in the material after adsorption, and it can be concluded that CNC-PVAm/rGO had successfully adsorbed DCF. Based on the BET specific surface area test and analysis, the specific surface area of the material prepared in our experiment reached 354.6879m²/g, which indicates that there is porous structure within the material [18]. The SEM images show that the nano-cellulose grafted with PVAm is a material with porous structure and big specific surface area, and after adding graphene oxide using hydrothermal method, this material presented obvious 3D porous structure [19]. Therefore, the introduction of PVAm can improve the adsorption performance of material, while the addition of rGO can further enhance the adsorption capacity of material.

As for the adsorption kinetics experiment, the optimal pH for CNC-PVAm/rGO to adsorb DCF was 6-7, and under this pH, the adsorption capacity reached the highest value. The results of adsorption isotherm experiment show that the DCF adsorption process by nano-cellulose aerogel satisfies the Langmuir adsorption isotherm model, and its fitting parameter is R²=0.965. The experimental results of kinetics investigation show that the fitting coefficient between the DCF adsorption process using nano-cellulose aerogel and quasi second-order kinetics fitting curve is big, which is R²=0.9973, and the fitting degree is high. The fitting curve of particle internal diffusion shows that the DCF adsorption process of nano-cellulose aerogel can be divided into three stages, and the slopes of three approximate straight lines of this curve present gradual decline, which indicates the experimental rate gradually decreases and reaches equilibrium. The experimental results of adsorption thermodynamics show that the adsorption enthalpy is -8141.32KJ mol⁻¹, which indicates that the process of using nano-cellulose aerogel to adsorb DCF is an exothermic process, and forward reaction can be facilitated by lowering the temperature. |ΔH| is within the range of 20.9-418.4kJ mol⁻¹, which means that the adsorption reaction is a chemical process.

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