Research Article

Molecular Sieving Film Prepared by Vacuum Filtration for the Efficient Removal of Tetracycline Antibiotics from Pharmaceutical Wastewater

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The pharmaceutical wastewater (PW) produced during the production of antibiotics has a huge impact on the ecological environment. The efficient removal of residual antibiotics from PW has become a great challenge. Here, a ZIF-8/GO composite film, a new material, was prepared by loading ZIF-8/GO nanosheets onto the surface of a polyethyleneimine- (PEI-) modified nylon microporous support. This new material can effectively remove tetracycline (TC) from PW with a removal rate of 99%. In addition, the layer of ZIF-8/GO nanosheets on the surface of the carrier had certain defect sites. This feature not only made the film have a relatively high flux (502 L·m⁻²·h⁻¹·bar⁻¹) but also overcame the disadvantages of the traditional membrane separation technology, such as the high operation pressure required by the easy plugging of micropores. More importantly, the above-mentioned advantages enable the novel material to be applied on a larger scale. A probable adsorption mechanism was investigated and suggested.

1. Introduction

Antibiotics have a unique position in medicine because they act selectively on pathogenic bacteria without affecting human cells and tissues [1, 2]. Tetracycline (TC) is one of the most important antibiotics, and it is widely used in veterinary treatment and as a growth promoter in animals [3–5]. The annual production and consumption of TC can reach thousands of tons worldwide. The TC used in the agricultural industry is excreted through faeces and urine as unmodified parent compounds, with only a small portion being metabolized [5–7]. In recent years, residual TC, including that discharged from pharmaceutical factories and agricultural runoff, has been frequently detected in surface water, groundwater, and even drinking water [8, 9]. Special attention needs to be paid to TC residues in the environment. Although the residual TC concentration is relatively low, it can still induce antibiotic resistance genes when exposed to the environment for a long time [10, 11]. Contamination with TC residues poses a potential threat to human health, and thus, it is important to develop efficient and economical treatment technologies to remove these compounds [9].

At present, numerous methods are being used to remove TC, including the following: biological treatment, advanced oxidation technology, membrane processes, and adsorption. All of the above methods have been applied to different degrees in the corresponding fields, but they have all exposed many shortcomings [12–16]. Thus far, a large number of different adsorbents have been used to remove TC, such as smectite clay [17], ion-exchange resin [18], zeolites [19], and activated carbon [20]. However, the demand for developing new materials to remove the above pollutants is still increasing [5]. At present, some studies have reported 2D nanocomposites, such as GO nanosheets, MOFs, and zeolites, and these materials have become research hotspots in recent years due to their unique properties [21, 22].
GO can also be used as an adsorbent due to its special surface structure and functional groups [23]. In addition, the TC molecule consists of four aromatic rings, and each aromatic ring has different functional groups, including phenol, ethanol, ketone, and amino groups [5]. It can be easily adsorbed on GO by π-π stacking and/or hydrogen bonds [24]. ZIF-8, an important subclass of MOFs, can adsorb some dyes and antibiotics in aqueous solution [25]. These two materials are compounded into ZIF-8/GO nanosheets to provide an opportunity for application in water treatment.

The abovementioned nanomaterials can not only be used as an adsorbent but also be fabricated on a porous carrier to prepare a film. These films have been widely used in sensors, low-k dielectrics, and separation films [21]. Our research team has performed much research on ZIF-L composite films. In our study, a ZIF-L film was prepared by loading ZIF-L nanoflakes on the surface of a PEI-modified nylon microporous membrane. This material could effectively remove TC from PW [26]. However, the ZIF-L layer was corroded by pharmaceutical wastewater after multiple cycles, which greatly affected the stability and service life of the composite film. Therefore, we have been attempting to replace ZIF-L with other composite materials.

To effectively remove the residual TC from PW, we successfully prepared a ZIF-8/GO film by vacuum filtration in this work. The TC adsorption rate for PW by this film was as high as 99.1%. The adsorption characteristics and mechanisms of this material for TC were investigated by batch adsorption tests, and this film could maintain a high flux after 60 cycles. Due to the addition of GO, ZIF-8/GO has better corrosion resistance than ZIF-L, which makes the composite film prepared by ZIF-8/GO have a better stability and wider application space.

2. Materials and Methods

2.1. Materials. PW was collected from the sewage treatment system of a local pharmaceutical company (Qiyan Pharmaceutical Co., Ltd. in Ningxia, China). The main components of PW are listed in Table 1. Tetracycline hydrochloride (AR, 98%), polyethyleneimine (PEI, average Mn = 2,500), NaOH (AR, 98%), HCl (AR, 36%), nylon microporous membrane (the membrane material diameter is 50 mm, and the aperture is approximately 220 nm), 2-methylimidazole (AR, 98%), Zn(NO$_3$)$_2$·6H$_2$O (AR, 99%), methanol (AR, 98%), and graphene oxide (GO) were all purchased from the Tianjin Guangfu Technology Development Co., Ltd. in Tianjin, China.

2.2. Synthesis of ZIF-8/GO Nanosheets. GO aqueous solution (5 mg·mL$^{-1}$) was diluted to 1 mg·mL$^{-1}$ by methanol and sonicated for 5 h. The final solvent for GO was a water-methanol mixture (1:4, v/v). Zn(NO$_3$)$_2$·6H$_2$O (1.098 g) was fully dissolved in 36 mL methanol and recorded as solution A. 2-Methylimidazole (2.433 g) was fully dissolved in 60 mL methanol and recorded as solution B. Solution B was quickly added to solution A and fully mixed. Immediately, approximately 24 mL GO in water and the methanol solution mentioned above were mixed. After stirring for 5 h, the product was centrifuged at 10000 rpm for 3 min and washed 3 times by using methanol under the same conditions. The product was dried at 80°C for 12 h.

2.3. Synthesis of the ZIF-8/GO Film. The nylon microporous membrane was immersed in PEI solution (1.0 wt.%) and then dried at 60°C for 30 minutes. The membrane modified by PEI was used as a carrier. Different quality ZIF-8/GO nanosheet powders (10~50 mg) were dispersed in deionized water (35 mL) by ultrasound. Finally, ZIF-8/GO nanosheets were loaded onto the PEI-modified carrier by vacuum filtration. ZIF-8/GO nanosheets can coordinate with the amine groups of PEI molecules [19]. In this way, the composite film has a certain stability.

2.4. Material Characterization. The X-ray diffraction (XRD) pattern was obtained from a powder diffractometer (Rigaku D/MAX 2200). Scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI Tecnai G20) characterization techniques were used to obtain the particle size and morphology information of the materials. The particle size distributions of the nanosheet samples were tested by Malvern Mastersizer 3000. The morphology of the sample was obtained by atomic force microscopy (AFM) tests (Dimension FastScan, Bruker). Fourier transform infrared spectroscopy (Bruker Tensor 27 FT-IR) and X-ray photoelectron spectroscopy (Kratos Ultra DLD XPS) characterization techniques were used to study the adsorption mechanisms of materials. Zeta potential measurements (90Plus Zeta, Brookhaven) were performed after thorough sonication of ZIF-8 dispersed in deionized water with different pH values.

2.5. Adsorption Test of ZIF-8/GO Nanosheet Powder. There are a large number of solid suspended particles in the PW, which will greatly influence the research on the mechanism of TC adsorption. Therefore, the adsorption properties and mechanism of ZIF-8/GO nanosheets were studied by using TC solution. TC solution (50 mL) was added to the conical bottle. After that, the pH of the solution was adjusted by adding an appropriate amount of NaOH or HCl.

| Parameters                  | Values          |
|----------------------------|-----------------|
| pH                         | 5               |
| Protein                    | 0.88 mg·L$^{-1}$|
| Oxalate                    | 4.5 mg·ml$^{-1}$|
| Amino nitrogen             | 1.35 mg·L$^{-1}$|
| Reducing sugar             | 1.6 mg·L$^{-1}$  |
| Total sugar                | 3.2 mg·L$^{-1}$  |
| Tetracycline hydrochloride | 380 mg·L$^{-1}$  |
| Pigment                    | Uncertain       |
| Inorganic ion              | Uncertain       |
| Microorganism              | Uncertain       |

Table 1: Main components of PW.
solution (0.1 mol·L\(^{-1}\)). Then, 50 mg of the ZIF-8/GO nanosheets was added to the solution. Under dark the condition, the mixture was stirred (120 rpm) for a certain amount of time. The concentration of TC solution was measured by using HPLC and calculated by using the following formula:

\[
q_e = \frac{(C_0 - C_e) \times V}{M}
\]

where \(q_e\) (mg·g\(^{-1}\)) refers to the adsorption capacity in the 2D ZIF-8/GO nanosheets at equilibrium, \(C_0\) (mg·L\(^{-1}\)) refers to the initial solution concentration, \(C_e\) (mg·L\(^{-1}\)) refers to the equilibrium solution concentration, \(V\) (L) refers to the volume of the solution, and \(M\) (g) refers to the mass of the adsorbent.

2.5.1. Adsorption Isotherms of ZIF-8/GO Nanosheets

Langmuir isotherm:

\[
q_e = \frac{q_{\text{max}} K_L C_e}{(1 + K_L C_e)}
\]

Freundlich isotherm:

\[
q_e = k_l C_e^{1/n}
\]

The linear forms:

\[
\frac{1}{q_e} = \frac{1}{(q_{\text{max}} K_L)} \times \frac{1}{C_e} + \frac{1}{q_{\text{max}}}
\]

\[
\text{lg}(q_e) = \text{lg}(k_l) + \frac{1}{n} \times \text{lg}(C_e)
\]

2.5.2. Adsorption Kinetics of ZIF-8/GO Nanosheets

The pseudo-first-order model is as follows:

\[
\ln(q_e - q_i) = \ln(q_i) - k_1 t
\]

The pseudo-second-order model is as follows:

\[
\frac{t}{q_e} = \frac{1}{k_2 q_{\text{max}}} + \frac{t}{q_{\text{max}}}
\]

where \(k_1\) (min\(^{-1}\)) and \(k_2\) (mg·g\(^{-1}\)·min\(^{-1}\)) represent the first-order rate and second-order rate constants, respectively; \(q_e\) represents the equilibrium adsorption capacity; and \(q_{\text{max}}\) (mg·g\(^{-1}\)) represents the adsorption capacity at time \(t\) (min).

2.5.3. Adsorption Thermodynamics of ZIF-8/GO Nanosheets

The thermodynamic equilibrium constant \(K\) for the adsorption was calculated from the intercept determined by plotting \(\ln(q_e/C_e)\) vs. \(q_e\) using the method of Khan and Singh [27]. The standard free energy change \(\Delta G\) was calculated using the following equation:

\[
\Delta G = -RT \ln K,
\]

where \(\Delta G\) represents the Gibbs energy change, \(R\) represents the molar gas constant, \(T\) represents the absolute temperature, and \(K\) represents the same as indicated above [27].

The enthalpy change \(\Delta H\) and entropy change \(\Delta S\) were calculated according to the following equation [24]:

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

2.6. Adsorption Test of the ZIF-8/GO Film

TC solution was used to preliminarily understand the TC adsorption performance and mechanism of the ZIF-8/GO film. Through vacuum extraction, TC solution (50 ml, 400 mg·L\(^{-1}\)) was repeatedly passed through the ZIF-8/GO layer on the surface of the carrier. After that, the concentration of the filtrate was tested.

3. Results and Discussion

3.1. Characterization of ZIF-8/GO Nanosheets and ZIF-8/GO Film

The ZIF-8 particles were found to be crystals with a regular morphology, and the average size was 50 nm (Figure 1(a)). The GO sheets were flexible flakes (Figure 1(b)). In this study, ZIF-8 nanoparticles could be grown on both sides of the GO nanosheets to form a sandwich layer structure (Figure 1(c)). Comparison of the XRD pattern between the ZIF-8/GO composite and GO indicated that the prepared composite powder had good crystallinity, suggesting that this material was successfully synthesized (Figure 1(d)). This result was consistent with that of a previous report [21].

As shown in Figures 2(b) and 2(d), GO has a flexible flake morphology. Figure 2(c) shows a typical TEM image of the synthesized ZIF-8/GO nanosheets, in which all nanosheets have a sandwich-like structural morphology. The particle size distribution characterization results showed that the diameter of ZIF-8/GO particles was mainly concentrated at approximately 200 nm. The nylon carrier has a pore size of approximately 220 nm. During the preparation of the ZIF-8/GO film, because the particle size of the ZIF-8/GO nanosheets was larger than the pore diameter of the carrier, the nanosheets were loaded on the surface of the carrier rather than through its channel.

In an effort to assess the thickness and large-area uniformity of GO and 2D ZIF-8/GO hybrid nanosheets, AFM imaging was performed at multiple locations across the sample. The AFM topographic images in Figures 3(a)–3(c) show overlapping flexible flakes and that the apparent thickness was approximately 2 nm, which was similar to the characterization results of SEM and TEM images. Figures 3(d)–3(f) show AFM images of 2D ZIF-8/GO hybrid nanosheets, and all of the AFM images clearly exhibited that the 2D ZIF-8/GO hybrid nanosheet was a rigid flake structure with an average thickness of 100 nm.

The photographs and SEM images of the nylon microporous filter modified with or without PEI showed the
same porous structural morphology, suggesting that PEI modification did not change the pore structure of the nylon microporous filter (Figure 4). This means that it will not be an influencing factor in subsequent experiments.

Equal amounts of three different samples were dispersed in deionized water by ultrasound. After resting for 30 minutes, the ZIF-8 floated on the surface of the solution due to its hydrophobicity (Figure 5). The ZIF-8/GO nanosheets obtained by combining ZIF-8 with GO had the characteristic of hydrophilicity, which was very favourable for the preparation of the ZIF-8/GO film by vacuum filtration. The preparation method of the ZIF-8/GO film used in this experiment is shown in Figure 6.

Comparing the XRD patterns of several different materials, it was found that the ZIF-8/GO film had good crystallinity, indicating that the film had been successfully prepared (Figure 7(a)). Different quality ZIF-8/GO powders (10–50 mg) were dispersed in deionized water (10 ml), and the colour of the solution gradually increased with the increase of the solution concentration (Figure 7(b)). Figures 7(c) and 7(d) show that the prepared ZIF-8/GO film had very good flexibility. The equipment used in the preparation process is shown in Figure 7(e).

3.2. Adsorption Performance of ZIF-8/GO Nanosheets

3.2.1. Effects of pH and Adsorption Time. The initial pH and concentration of TC solution were 4.0 and 400 mg·L\(^{-1}\), respectively. Then, the pH of the TC solution (50 ml) was adjusted to different pH values of 3.0, 5.0, 7.0, and 9.0, respectively. The TC adsorption on ZIF-8/GO nanosheets was studied in detail (Figure 8(a)). The adsorption kinetics, isotherm, and thermodynamics were studied in batch experiments (Tables 2–4; Figure 9). The adsorption process was fitted to the pseudo-second-order kinetic (Table 2) and Langmuir (Table 3) models. The above results indicated that the adsorption of TC on ZIF-8/GO nanosheets was chemisorption. The adsorption rate of ZIF-8/GO nanosheets sharply decreased in acidic conditions, which might be caused by the factors discussed below.

TC could have different charges on different sites depending on the solution pH [28]. TC is an amphoteric molecule with multiple ionizable functional groups, such as tricarbonylamide (C1, C2, and C3), phenolic diketone (C10, C11, and C12), and dimethylamine (C4) groups (Figure 10(a)) [29]. When \( pK_a < 3.3 \), TC exists as a cation due to the protonation of the dimethyl ammonium group. When \( 3.3 > pK_a > 7.7 \), TC exists as a zwitterion due to the loss of a proton from the phenolic diketone moiety [28]. When \( pK_a > 7.7 \), a monovalent anion or divalent anion from the loss of protons from the tricarbonyl system and phenolic diketone moiety will prevail [30]. When \( pK_a = 9.5 \), the dimethylamino group (C4) will be further deprotonated, which promotes the binding of N on the dimethylamino group in the TC molecule to the zinc ion in ZIF-8/GO nanosheets (Figures 10(a) and 11).

Meanwhile, ZIF-8 particles have certain basicity, and their structures are relatively stable in weak acid, neutral,
In a strongly acidic solution, the ZIF-8 particles attached on the GO surface are dissolved, which makes the adsorption rate decrease. On the basis of understanding its adsorption properties, the ZIF-8/GO nanosheet material was used in the treatment of PW. The initial concentration of TC solution was 400 mg·L\(^{-1}\) (pH \(\leq 4.0\)), and the initial concentration of PW was 400 mg·L\(^{-1}\) (pH = 5.0). To further investigate the effect of pH on the adsorption capacity in practical applications, the initial pH values of the above two solutions were adjusted to different values (5.0 and 7.0). The adsorption capacity of ZIF-8/GO nanosheets was tested by the method described in Section 2.3. The results indicated that the adsorption rates in both solutions were improved at a pH of 7.0. Under the same pH conditions, the TC adsorption rate in the solution was better than that in PW (Figure 8(b)). The reason for this phenomenon is that certain amounts of impurities are contained in the PW, and these impurities compete with the adsorbate and/or the adsorbent during the adsorption process, which directly affects the TC adsorption rate on the ZIF-8/GO nanosheets. The above problems could be solved by loading the ZIF-8/GO nanosheets on the surface of the carrier modified by PEI to form a composite film. On the one hand, the ZIF-8/GO nanosheet layer supported on the surface of the carrier could effectively intercept impurities in the PW. On the other hand, the selective adsorption performance of nanosheets could effectively remove residual TC from PW.

3.2.2. Effects of Temperature and Solution Concentration. At different temperatures, ZIF-8/GO powder (50 mg) was added to TC solutions (50 ml) with different concentrations. At the same concentration of the solution, the TC removal rate increases with the increase of temperature (Figure 8(c)). At the same time, when the temperature remains constant, the removal rate decreases with the increase of the solution concentration. The results show that temperature and solution concentration have a direct impact on the adsorption rate of ZIF-8/GO nanosheets.

In conclusion, many objective factors will directly influence the TC adsorption rate and seriously affect the application of ZIF-8/GO nanosheets on a large scale.
Therefore, the preparation of the composite film as described in Section 2.2 was a good way to avoid the effects of objective factors on the adsorption rate. The study on the adsorption properties of the ZIF-8/GO film will be elaborated in the following discussion.

3.3. Adsorption Test of the ZIF-8/GO Film. To better describe the adsorption mechanism of the ZIF-8/GO film for TC, the adsorption performance of this film was tested by using TC solution. Before the adsorption experiment, the pH of the TC solution should be adjusted to 5.0. Similarly, to better understand the role of ZIF-8/GO nanosheets in the composite film, it is necessary to test the adsorption properties of the carrier before and after PEI modification. The TC solution was repeatedly filtered through the carrier before and after PEI modification (Figure 8(d)). It was found that the carrier had no selective adsorption capacity for TC.
Stirring $\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ for 5 hours leads to GO nanosheets, which form flexible flakes. The combination of ZIF-8 and GO results in rigid flakes. Vacuum filtration produces ZIF-8/GO nanosheets, forming a ZIF-8/GO film.

**Figure 5:** Photograph of different solutions.

**Figure 6:** The detailed preparation process of the composite film.

**Figure 7:** (a) XRD spectra of different materials. (b) Photograph of ZIF-8/GO solution of different concentrations. (c) Outward flexibility and (d) inward flexibility of the ZIF-8/GO film. (e) Photograph of the equipment used in the preparation process.
Figure 8: (a) Adsorption capacity of ZIF-8/GO powder in TC aqueous solution. (b) Adsorption rate of ZIF-8/GO powder in TC aqueous solution. (c) Adsorption rate of TC in aqueous solution by ZIF-8/GO powder at different temperatures. (d) Adsorption rate of TC on the composite film. (e) Adsorption rate of TC by different materials. (f) Adsorption rate of TC in aqueous solution by the composite film with different cycles.
Table 2: Adsorption kinetic parameters of ZIF-8/GO powder.

| $C_0$ (mg·L$^{-1}$) | Pseudo-first-order |  | Pseudo-second-order |
|---------------------|--------------------|------------------|---------------------|
|                     | $K_1$ (min$^{-1}$) | $R^2$          | $q_e$ (mg·g$^{-1}$) | $K_2 \times 10^{-4}$ (g·mg$^{-1}$·min$^{-1}$) | $R^2$   |
| 400                 | 0.0027             | 0.8368          | 384.61              | 1.56                      | 0.9999 |

Table 3: Adsorption isotherm parameters of ZIF-8/GO powder.

| $T$ (K) | $q_{max}$ (mg·g$^{-1}$) | $K_1$ (L·mg$^{-1}$) | $R^2$ | $k_f$ | $N$ | $R^2$ |
|---------|--------------------------|----------------------|-------|-------|-----|-------|
| 298     | 556                      | 0.219               | 0.9438 | 122.49 | 2.79 | 0.9088 |
| 308     | 694                      | 0.105               | 0.9795 | 104.33 | 2.29 | 0.8325 |
| 318     | 714                      | 0.192               | 0.9438 | 112.82 | 1.88 | 0.7241 |

Table 4: Calculated thermodynamic parameters.

| $T$ (K) | $K$          | $\Delta G$ (kJ·mol$^{-1}$) | $\Delta S$ (J·mol$^{-1}$·K$^{-1}$) | $\Delta H$ (kJ·mol$^{-1}$) |
|---------|-------------|-----------------------------|-----------------------------------|---------------------------|
| 298     | 223.16      | −13.40                      | −83.02                            | −37.81                    |
| 308     | 100.28      | −12.18                      |                                   |                          |
| 318     | 86.07       | −11.41                      |                                   |                          |

Figure 9: Adsorption isotherm diagram.

Figure 10: (a) Schematic diagram of the TC molecular structure. (b) Zeta potential distribution of ZIF-8 in aqueous solution with different pH values.
Therefore, the subsequent adsorption test of the composite film will not be disturbed by the carrier.

By using the above adsorption test method, TC aqueous solution was repeatedly passed through the composite films with different ZIF-8/GO nanosheet loading amounts (10~50 mg). The results are shown in Figure 8(d), and an increase in the loading amount of the ZIF-8/GO nanosheets led to an increase in the thickness of the ZIF-8/GO layer on the surface of the carrier, which could increase the TC removal rate on the film. Under the same ZIF-8/GO nanosheet
loading amount, the removal rate of TC increases with the increase of cycle times. The relevant adsorption parameters are listed in Table 5.

Based on the above research, the adsorption capacity of the ZIF-8/GO film was studied in detail. Cyclic adsorption experiments were carried out on a ZIF-8/GO film prepared by loading 50 mg of ZIF-8/GO nanosheets onto the carrier surface. The adsorption capacity parameters of this film are shown in Table 6. For different concentrations of TC solution, the adsorption rate of the ZIF-8/GO film increases with the increase of cycle times (Figure 8(f)). At the same cycle times, the TC adsorption rate decreases with the increase of the solution concentration. In the process of the adsorption test, the adsorption parameters of this material (single cycle time and flux) were largely controlled by the concentration of TC solution. During the cyclic adsorption test, the ZIF-8/GO film maintained high flux with a high removal rate, indicating that the removal of TC was mainly due to the adsorption function from ZIF-8/GO nanosheets supported on the surface of the carrier. With the increase of the solution concentration, the flux of the ZIF-8/GO film decreased sharply while maintaining a high adsorption rate, indicating that the pore size screening function of the ZIF-8/GO nanosheet layer was the dominant function at this time.

PW (50 ml) was treated by using ZIF-8/GO nanosheet powder (50 mg) and the ZIF-8/GO film prepared using 50 mg ZIF-8/GO nanosheets, respectively. Comparison of the adsorption capacities of the ZIF-8/GO nanosheets and ZIF-8/GO film indicated that the ZIF-8/GO film had better results. The ZIF-8/GO film exhibited a higher removal rate (99% vs. 47%) compared with ZIF-8/GO nanosheets for TC removal in PW (Figure 8(e) and Table 7).

In summary, the ZIF-8/GO film was very good in avoiding the influence of objective factors on the adsorption test. At the same time, the composite film showed good performance in removing TC from PW. Thus, the application of this material on a larger scale is highly desirable.

3.4. Adsorption Mechanism of the ZIF-8/GO Film. FT-IR analysis was further carried out to verify the adsorption mechanism of TC on ZIF-8/GO nanosheets. The peak at 1589 cm\(^{-1}\) was attributed to the \(-\text{NH}_2\) group, while the peak at 3438 cm\(^{-1}\) was attributed to the \(\text{C} = \text{C}\) group. After the adsorption test, the above two peaks were enhanced, indicating that TC could be adsorbed on ZIF-8 in ZIF-8/GO nanosheets (Figure 12(a)). Before and after adsorption, the changes in the functional groups of GO were also confirmed by FT-IR spectroscopy. The intensities of the FT-IR peaks corresponding to the oxygen functionalities, such as the vibration peak of \(-\text{OH}\) groups at 3438 cm\(^{-1}\), decreased dramatically, and these observations confirmed that the \(-\text{OH}\) groups on GO combined with \(-\text{COOR}\) groups on TC to form hydrogen bonds so that the TC was adsorbed on GO.
The peak at 3365 cm$^{-1}$ was attributed to the -NH$_2$ group, while the peak at 1665 cm$^{-1}$ was attributed to the C=C group from the diketone system. The above two groups were derived from TC molecules and enhanced after the adsorption test, indicating that TC could be well adsorbed by the ZIF-8/GO nanosheets (Figure 12(c)). In this study, the adsorption process was fitted to pseudo-second-order kinetic models (Table 2), which proved that the adsorption process of TC by the ZIF-8/GO nanosheets was dominated by chemisorption. In addition, the -COOR groups in fresh ZIF-8/GO nanosheets were indicated by a shoulder observed on the main peak at 288.4 eV (Figure 13(a)). After the adsorption, the peak intensity of -COOR groups decreased sharply, while that of GO groups increased, which proved the characterization results of FT-IR analysis. The XPS spectrum showed that there were no changes in the binding energy of zinc species before and after adsorption (Figures 13(c) and 13(f)).

The adsorption mechanism is shown in Figure 11. The adsorption process of the ZIF-8/GO film is a process of synergistic action with various mechanisms, including the selective adsorption of TC on ZIF-8/GO nanosheets loaded on the carrier (Figures 12 and 13), the retention, and the pore size screening of the ZIF-8/GO film. The defects on the surface of the ZIF-8/GO film (Figures 14(a2)–14(e2)) and the interlamellar spacing in the cross section (Figures 14(a3)–14(e3)) provide a convenient path for the flow of the solution, while the high efficiency of the selective adsorption of ZIF-8/GO nanosheets of the ZIF-8/GO film can guarantee the removal rate of TC. With high flux, the film also has...
a good removal rate, which proves that the removal of TC by the ZIF-8/GO film mainly depends on the adsorption of ZIF-8/GO nanosheets loaded on the carrier rather than traditional aperture screening. Compared with adsorption, the retention and pore size screening only play a small part in the removal of TC. The adsorption mechanism of the ZIF-8/GO film mainly has three aspects: (1) Zn$^{11+}$ in ZIF-8 attached on the surface of GO sheets can form a coordination bond with N in the dimethylamino group in the TC molecule; (2) the -COOR groups on the edges of the GO sheets can form hydrogen bonds with -OH groups in the TC molecule; and (3) ZIF-8 attached on the surface of GO sheets plays a major role in the adsorption of TC by ZIF-8/GO nanosheets (Figure 11).

4. Conclusions

In this study, a ZIF-8/GO film was prepared by loading ZIF-8/GO nanosheets on the surface of a porous membrane carrier. Then, a ZIF-8/GO layer with high adsorption, stability, and flux was formed on the surface of the carrier. As a result, comparison of the TC removal rates for the PW
between the ZIF-8/GO nanosheets and ZIF-8/GO film indicates that the prepared ZIF-8/GO film had better performance (99% vs. 47%). The adsorption of residual TC by the ZIF-8/GO film is a combined action, including high efficiency selective adsorption, retention, and pore size screening of the film, but adsorption plays a major role in this process. These advantages enable the novel material to be applied on a larger scale.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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