

Article

Modified Activated Carbon Fiber Felt for the Electrosorption of Norfloxacin in Aqueous Solution

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Abstract: As an antibiotic, Norfloxacin (NOR) is widely found in the water environment and presents considerable harm to human beings. At present, the preparation of removal materials is complicated, and the removal efficiency is not high. The adsorption effect of modified activated carbon fiber felt (MACFF) electrosorption and its influencing factors on NOR were studied. Activated carbon fiber felt (ACFF) was modified with 20% nitric acid, and the ACFFs were characterized by SEM, TEM, and FTIR both before and after modification. The optimal working conditions for electrosorption with an MACFF electrode were as follows: the voltage was 1.0 V, the pH was 6, and the plate spacing was 10 mm. The maximum adsorption capacity of the MACFF for NOR was 128.55 mg/g. Model fitting showed that pseudo-second-order kinetic model and Langmuir model were more suitable for explaining this adsorption process. In addition, this study found that, with 20% nitric acid as the regeneration liquid and under the reverse charging method, the regeneration rate of the MACFF electrode was maintained at approximately 96% and the regeneration was good, therefore, this technology can not only save operation costs but also has good development prospects in sewage treatment.

Keywords: nitric acid modification 1; activated carbon fiber felt 2; electrosorption 3; norfloxacin 4

1. Introduction

In recent years, antibiotics have been widely used in human diseases and animal husbandry to treat or prevent microbial infection [1]. As a fluoroquinolone antibiotic, norfloxacin (NOR) has broad-spectrum antibacterial effects and is widely used in clinical treatment and aquaculture [2]. However, in the human body or in animals, approximately 30%–90% of the dose is nondegradable and largely excreted in the form of active compounds [3]. The impact of antibiotic residues in the environment, especially in the aqueous environment, is gradually attracting attention [3]. According to reports, the highest concentration of NOR detected in the Antarctic ocean is approximately 800 ng/L [4], while in China, the maximum concentration of NOR detected in coastal waters can reach 1990 ng/L [5]. Because of the poor stability and biodegradability of the quinolone ring, most NOR in the aqueous environment could not be effectively removed by conventional microbiological methods [6]. Without effective degradation and removal, the environment will become polluted, and serious ecological problems will be caused [7]. At present, the main methods used to remove antibiotics include adsorption [8], biosorption [9], the Fenton method [10], the electrochemical oxidation method [11] and the advanced oxidation processes (AOPs) [12]. Among these methods, adsorption has low cost, high

efficiency, environmental protection characteristics, easy operation, and good application prospects [13]. The electrosorption degradation method is characterized by simplicity, easy handling, safety, low energy consumption, and no secondary pollution; thus, it has the potential to be a beneficial technology for environmental purification [14]. In addition, electrosorption can effectively remove some biorefractory organic pollutants under low energy consumption and is a promising water purification method [15].

Electrosorption technology involves the formation of a double layer at the interface between the electrode and the solution when a voltage is applied, and then under the action of the voltage, the charged ions in the solution are carried to the electrode with opposite charge and adsorbed by the electrode to achieve water purification [16,17]. The electrode material is a critical factor in the electrosorption technology. Generally, electrode materials are required to have the advantages of strong mechanical stability, a low manufacturing cost and strong adsorption capacity [15]. At present, graphite, carbon nanotubes, and activated carbon (AC) are mainly used as electrode materials [18]. Among them, AC can be considered a high-capacity adsorbent [19], as it has a well-developed surface area, high adsorption capacity [20], and stable chemical properties [21]. However, there are some disadvantages in the application of AC, such as low porosity, low molding performance, and low adsorption and regeneration efficiency. Compared with AC, activated carbon fiber felt (ACFF) made of activated carbon fiber has a higher adsorption capacity, abundant surface micropores, a defined shape [22], and high adsorption/desorption rates [23]. It is an ideal adsorbent for water purification. ACFF is often applied as a gas adsorbent and has achieved good adsorption effects [24].

However, there are few studies on the application of ACFF in wastewater treatment. Chemical treatment of a carbon fiber surface with acids can strongly affect the surface chemistry, by changing the surface functional groups and porous structure and thus, the adsorption capacity [25]. In this study, modified activated carbon fiber felt (MACFF) is used for the adsorption of NOR in wastewater, and the results provide a reference for future research. Zhu et al. treated the ACFF with nitric acid for use as an electrode to improve its conductivity [26]; Wang et al. used nitric acid-modified AC to desalinate aqueous solutions, and the results showed that MACFF can greatly improve the desalination effect [27].

Based on a review of the reported AC adsorption technology, the use of ACFF as the electrode for the removal of NOR has not been investigated. The present study aims to assess the applicability of MACFF for the adsorptive removal of NOR from aqueous solution and to investigate the effects of operating parameters on the adsorption process. The parameters studied include the voltage, plate spacing, initial concentration, and initial solution pH. A kinetic model and isotherm model of electrosorption were established, and the electric adsorption isotherm model was studied. The effect of the electrode on the removal of antibiotics and the regeneration of the MACFF electrode were analyzed.

2. Materials and Methods

2.1. Test Materials

ACFF (Jiangsu Nantong Shuangan Active Carbon Felt Filter Material Co., Ltd.), NOR (analytically pure, State Pharmaceutical Group Chemical Reagent Co., Ltd.), nitric acid (analytically pure), 20% (w/V) nitric acid, hydrochloric acid, sodium hydroxide, etc.

2.2. Modification and Characterization of ACFF

To obtain MACFF, ACFF was uniformly cut into a rectangle of 10 cm × 20 cm, rinsed with deionized water, immersed in 1000 mL of deionized water for 2 h, and then repeatedly washed with deionized water for 40 min. The washed ACFF was placed in a container containing 20% (w/V) nitric acid in a beaker [28], shaken in a constant temperature oscillator for 2 h, and then washed with deionized water to make the conductivity of the washing solution less than 10 μ S/cm. Then, the material was put in a constant-temperature drying oven at 130 °C for drying for 10 h, removed, and put into a desiccator until it was used. A total of seven replicates of MACFF were produced.

SEM analysis: The micromorphology of ACFF and MACFF samples was observed by a Quanta 200 field emission scanning electron microscope from Fei Company by using an accelerating voltage of 3000 V, working current of 10 μ A, and working distance of 2.0–2.5 mm.

The microstructures of the materials were characterized by field emission transmission electron microscopy (Tecnai G2 F 20). The specific surface areas and pore sizes of the materials were analyzed by a BET (Brunauer-Emmett-Teller) surface area and pore size analyzer (ASAP 2020).

The surface functional groups of ACFF before and after modification were analyzed by Fourier transform infrared (FT-IR, Thermo, Nicolet, USA). ACFF (MACFF) and spectrally pure potassium bromide were mixed at a ratio of 1:100 (the same amount of ACFF and MACFF), and the infrared spectrum was determined by the pressing method.

2.3. Preparation of Electrosorption Device

The electric adsorption device was composed of a DC power supply (PWS2000 series, Xi'an Antai Testing Equipment Co., Ltd.), a latex tube, a peristaltic pump (tt-30c micro, Wuxi Tianli Fluid Technology Co., Ltd.), a liquid storage tank, and an adsorption electrode (MACFF and a stainless-steel tube were used). When pollutants with a negative charge were treated, the stainless-steel tube was connected to the negative electrode. Otherwise, the stainless-steel tube was connected to the positive electrode. During desorption and regeneration, the stainless-steel tube was connected with the positive electrode. In the process of NOR treatment, NOR mainly exists in the form of ions, and there are three forms (cations, amphoteric molecules, and anions) under different pH values. See Figure 1 for the experimental device.

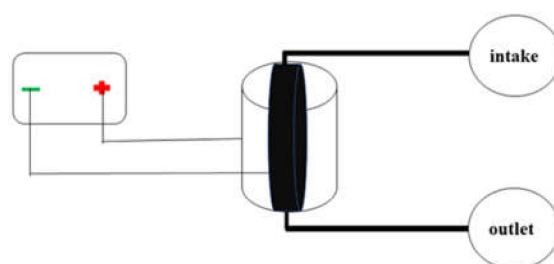


Figure 1. Diagram of the electrosorption device.

2.4. Electric Adsorption Test

The single-factor experimental method was used in the electrosorption test, and SPSS (19th edition) was used for statistical analysis via the multiple comparison method. The effects of pH (2–10), initial concentration of NOR (20–300 mg/L), voltage (0.6–1.2 V), and plate spacing (5–20 mm) on the adsorption of NOR by MACFF were studied.

Effect of solution pH: the pH of the solution was adjusted by adding either hydrochloric acid or dilute sodium hydroxide, and pH measurements were made using a pH meter. The adsorption performance of MACFF on target pollutants at pH values of 2, 4, 6, 8, and 10 was studied under a voltage of 0.6 V, plate spacing of 15 mm, and target concentration of 300 mg/L.

The influence of the initial concentration of the target pollutant (20–300 mg/L) on the electrosorption performance of MACFF was studied under a voltage of 0.6 V, plate spacing of 15 mm and pH of 6.

The influence of voltages of 0.6, 0.8, 1.0, and 1.2 V on the electrosorption performance of MACFF was studied under the condition that the spacing of plates was 15 mm, pH was 6 and the initial concentration of the target pollutant was 20 mg/L.

The influence of plate spacings of 5, 10, 15, and 20 mm on MACFF electrosorption performance was studied under a voltage of 0.6 V, pH of 6, and initial concentration of the target pollutant of 20 mg/L.

The above experiments were performed in parallel three times.

2.5. Determination of NOR in Sewage

An appropriate amount of NOR was dissolved in NaOH to make a standard solution. The NOR standard solution was placed in a 1 cm cuvette, 0.1 mol/L NaOH was used as a reference, and the absorbance was measured at a wavelength of 72.5 nm by using a TU-1901 double-beam UV–Vis spectrophotometer (Beijing Ordinary General Analysis Instrument Co., Ltd., Beijing, China).

2.6. Adsorption Kinetics Test and Adsorption Isotherms

Adsorption kinetics test: NOR solution with a concentration of 300 mg/L and a pH of 6 was used in the experiment, and a 0.6 V voltage and 15 mm plate spacing were applied. Supernatant was taken at 1, 4, 8, 12, 16, and 20 h. The concentration of NOR in the solution was determined after filtering the sample (0.45 µm microporous filter).

Adsorption isotherms: NOR solution with a concentration of 300 mg/L and pH value of 6 was prepared. Adsorption was conducted at 298 K, 0.6 V, and a plate spacing of 15 mm. After 24 h, the supernatant was filtered (0.45 µm microporous filter), and the concentration of NOR in the solution was determined.

2.7. MACFF Regeneration Test

Different regenerators (20% nitric acid, 20% hydrochloric acid, and distilled water) were used to backwash MACFF. After six adsorption–regeneration cycles, the regeneration rate was calculated. In addition, the electrosorption reactor was backwashed, and 20% nitric acid was used as the regeneration agent. The regeneration efficiency of different electrodes (AC, ACFF, and MACFF) was compared. Each electrode underwent five adsorption–regeneration cycles. The regeneration rate was calculated using Equation (1) as follows:

$$\text{Regeneration rate(\%)} = \frac{\text{readsorption capacity}}{\text{initial adsorption capacity}} \times 100. \quad (1)$$

3. Results and Discussion

3.1. Structural Characterization of Activated Carbon Fiber Felt

3.1.1. SEM Analysis

By comparing Figure 2a–c for ACFF (before modification) and Figure 2d–f for MACFF (after modification), it can be seen that the carbon felt is composed of a large number of long fibers arranged in a crisscross fashion, forming highly developed and disordered voids and exhibiting many grooves, veins, and fine spots on the surface. However, modification of ACFF makes the longitudinal grooves deeper and more regular and the fiber arrangement more compact, which is suitable for the trapping and adsorption of pollutants into pores [29]. The SEM images of MACFF confirmed the rough surface [30]. This change in structure improves the specific surface area of ACFF and its electric adsorption effect, provides more adsorption sites, and increases the adsorption space [31], and the modified material is more effective than the unmodified material when used as an electric adsorption electrode. Moreover, such modification can make desorption easier and more thorough.

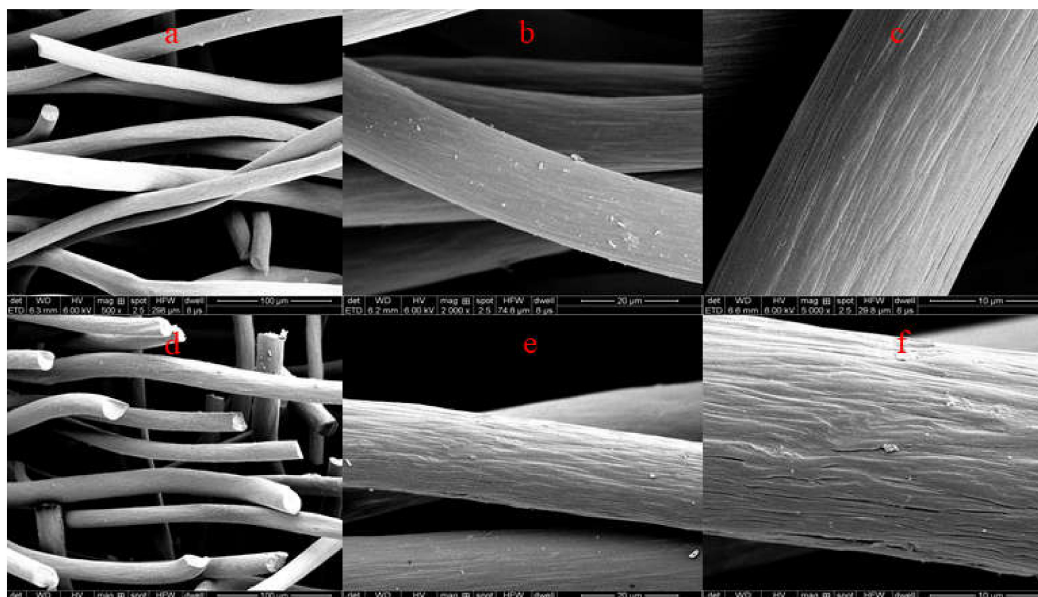


Figure 2. SEM images of activated carbon fiber felt (ACFF) (a–c) and modified activated carbon fiber felt (MACFF) (d–f).

3.1.2. Analysis of Specific Surface Area and Pore Structure

Table 1 shows the specific surface area, average pore diameter, and micropore volume of ACFF before and after modification. In accordance with the values presented in Table 1, the specific surface area of MACFF was increased by 30.9%, the average pore diameter was increased by 3.4%, and the micropore volume was increased by 36.4%, as also reflected in the SEM images in Figure 2. After the acid oxidation treatment, some originally closed micropores might have been opened and removed ash and other impurities from some pores. Moreover, the activation process at high temperature could open some new pores and add to the pore volume of some original pores, thus further increasing the specific surface area of the ACFF (before modification).

Table 1. BET(Brunauer-Emmett-Teller) results for ACFF and MACFF.

Type	Specific Surface Area	Average Pore Size	Micropore Volume
	(m ² /g)	(nm)	(cm ³ /g)
ACFF	1035.21	2.04	0.22
MACFF	1355.09	2.11	0.3

3.1.3. FTIR Analysis

The FTIR spectra of the surface functional groups of ACFF (before modification) and MACFF (after modification) were obtained. The results are shown in Figure 3. The absorption peaks of ACFF were at 1385, 1650, and 3460 cm^{−1}. The absorption peak at 1700–1800 cm^{−1} corresponds to carbonyl groups (C=O or COOH) or C=O in ester groups [32], and the absorption peak of CO₂ occurs at 2300 cm^{−1} [33]; the peak intensity of MACFF changes at 1385, 1650, and 3460 cm^{−1}. The results show that the amount of sp³ hybridized carbon and the number of defects on the surface of the carbon felt increased [34], but the positions of the absorption peaks at 1385, 1650, and 3460 cm^{−1} did not change obviously, which indicated that the active functional groups of the carbon felt were not destroyed after modification. In addition, the vibration peaks of oxygen-containing functional groups (1650 and 3460 cm^{−1}) were significantly enhanced after the modification of ACFF, which indicated that under oxidation by nitric acid, the content of oxygen-containing acid groups (carboxyl, hydroxyl, and carbonyl) on the surface

of ACFF significantly increased; these groups are all effective adsorption sites, and the adsorption capacity of the adsorbent for NOR had been greatly improved [35].

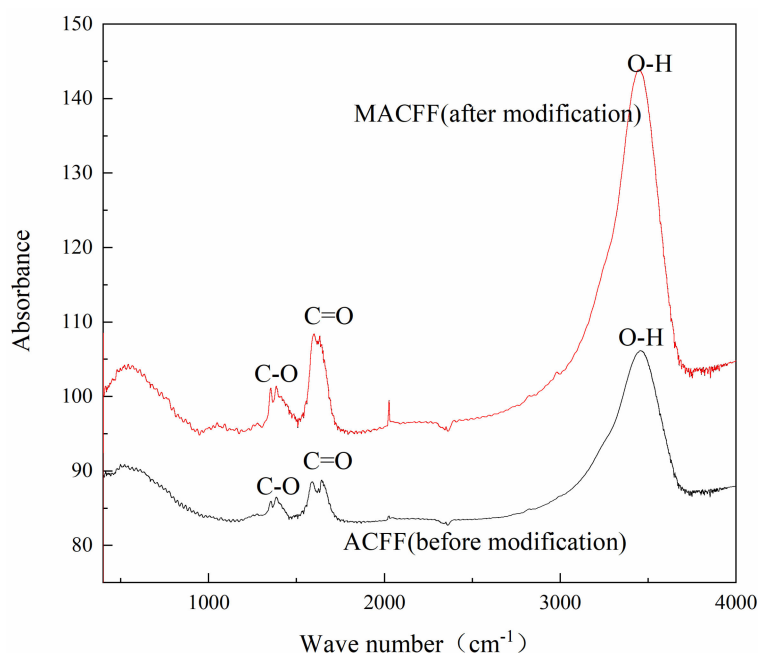


Figure 3. FTIR spectra of active carbon fiber felt.

3.2. Factors Affecting the Adsorption of NOR in Aqueous Solution by MACFF

3.2.1. Effect of pH

The pH of the solution is one of the most important variables in the adsorption process. Figure 4a shows the influence of the pH value of the solution on the adsorption performance of NOR on MACFF. It can be seen from Figure 4 that when the pH value changes from 2 to 6, the adsorption capacity increases from 0.02 to 5.68 mg/g, while when the pH value increases from weakly acidic (6) to weakly basic (10), the adsorption capacity of NOR decreases. According to the physicochemical properties of NOR, NOR has two proton-binding sites (carboxyl and piperaziny groups) with pKa values of 6.31 and 8.68, respectively. At $\text{pH} \leq 6.31$, the main form of NOR is the cationic form, NOR^+ . When the pH of the solution is between 6.31 and 8.68, NOR is mainly in the form of $\text{NOR}^\pm$, a neutral molecule. At $\text{pH} \geq 8.6$, NOR exists in the form of NOR^- [36]. As the pH decreases, the NOR^+ in the solution increases, and the electrostatic force in the adsorption process is weakened. The adsorption capacity is also weakened. Electrostatic force is one of the main mechanisms for MACFF adsorption of NOR [27]. When the pH value of the solution is less than 2.0, the amino groups on the surface of MACFF will be protonated, and NOR will have a positive charge; these properties will generate an electrostatic repulsion force, which prevents their mutual contact, resulting in almost no NOR molecules adsorbed on MACFF. In addition, almost no adsorption of NOR occurs at $\text{pH} < 2.0$, mainly due to the stronger competitive adsorption of hydrogen ions [37]. With the increase in pH value, the electrostatic repulsion gradually weakens, and the difficulty of the acidic surface groups of the adsorbent and the exchange with NOR ions also increases. The NOR molecules gradually diffuse and adsorb on the MACFF surface through interaction forces (electrostatic attraction, hydrogen bond, and amino interaction). It should be considered that the ease of deprotonation of acidic surface groups of the adsorbent and, hence, of ionic exchange with NOR will increase as the pH of the adsorbent solution increases [38]. In addition, it can be seen from the structural formula of NOR that hydrogen bonding plays a certain role in the adsorption process; functional groups such as carboxyl group are ionized at high pH, reducing the formation of hydrogen bonds. Therefore, for the adsorption process studied here, the pH value of

the solution should be kept in weakly acidic to neutral conditions to obtain a better adsorption effect. In conclusion, the optimal pH value of this study is 6, which further shows that hydrogen bonding plays a major role in the adsorption process.

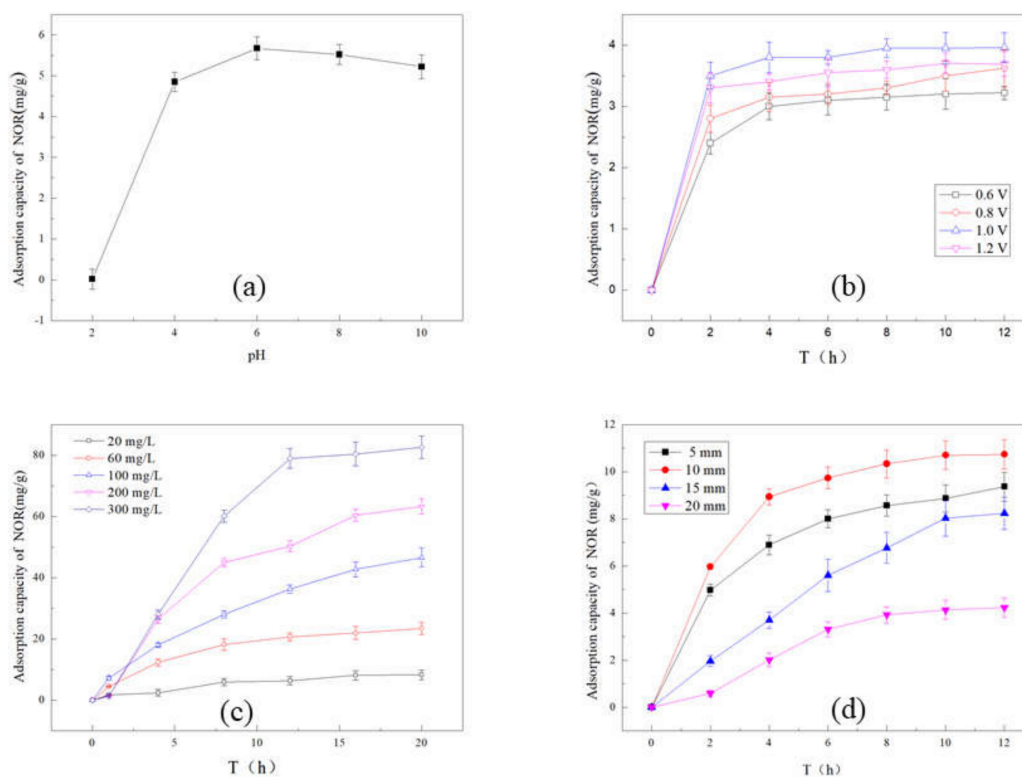


Figure 4. Effects of solution pH (a), voltage (b), initial solution concentration (c), and plate spacing (d) on norfloxacin (NOR) adsorption capacity on MACFF.

3.2.2. Effect of Voltage

The effect of voltage on the electrosorption of NOR in water by MACFF is shown in Figure 4b. It can be seen from the figure that the adsorption rates differ slightly among different voltages in the first two hours because the static adsorption of NOR by MACFF plays a leading role in the initial stage. After adsorption equilibrium, the adsorption capacity increased slightly with increasing voltage. This result occurred because with increasing voltage, the electric field force due to the charge on the surface of the adsorbent increases, and the charged NOR moves directionally under the action of the electric field force. Therefore, an increase in the voltage will lead to an increase in the adsorption of NOR on MACFF, but the influence of a change in the voltage on the adsorption of NOR on the MACFF is limited. The adsorption capacity of NOR did not increase with increasing voltage. When the voltage was 1.2 V, the water surface fluctuated and there were bubbles, which may have affected the adsorption process so that the adsorption capacity did not increase. When the voltage was 0.6 V, the adsorption amount did not change significantly, indicating that adsorption equilibrium had already been reached. Although the adsorption capacity of NOR was the highest when the voltage was 1.0 V, 0.6 V was selected as the working voltage in subsequent experiments.

3.2.3. Effect of Initial Concentration

The effect of the initial concentration of NOR (20–300 mg/L) on its electrosorption on MACFF is shown in Figure 4c. The effectiveness of the adsorption of MACFF for NOR increased with an increase in the mass of the initial concentration of NOR. When the initial concentration was 20, 60, 100, 200, and 300 mg/L, the adsorption capacity was 10.2, 18.9, 53.1, 59.8, and 87.3 mg/g, respectively. During the

whole adsorption process, the diffusion of NOR molecules plays an important role. According to Fick's law, the concentration gradient determines the driving force of the process. The higher the relative mass concentration of the adsorbent NOR in the liquid phase is, the greater the mass transfer impetus, which is more conducive to the realization of the mass transfer of NOR molecules from solution to the surface of MACFF. The diffusion driving force of the NOR molecules in aqueous environment increases with the initial concentration. Therefore, a relatively high initial adsorbent concentration is beneficial to the improvement of the adsorbent adsorption effect [39]. In practical applications, the content of NOR in the liquid phase is relatively low. For this study, the best initial concentration was 300 mg/L.

3.2.4. Effect of Plate Spacing

Figure 4d shows the influence of plate spacing on the adsorption of NOR (300 mg/L). The adsorption effect of NOR is the best when the plate spacing is 10 mm. This result may be due to a more open or porous structure resulting from the MACFF backbone. In general, the ratio of electrodes to capacitance is quite high [40]. Activated carbon electrodes can interact with ions through polarity groups and can achieve physical adsorption and electrosorption through the mutual attraction between the electrode surface and the ions [41]. When the plate spacing is 10 mm, the distance between the electrodes can generate high electrostatic attraction and the most suitable electric field force. The smaller the distance between plates is, the larger the electric field force will be. However, if the distance between plates is too small, even though the adsorption force of the electric adsorption device becomes stronger, the boundary between positive and negative ions will not be obvious, and the water area will be very small, so the ion content in the effluent will decrease less. In addition, too small a distance between plates can cause short circuiting in the electrode and increase the electric energy consumption. The larger the distance between plates is, the smaller the electric field force will be; furthermore, the resistance in water will increase with increasing distance between the plates, and the longer the distance of from the ions to the plates will be. If the plates are too far apart, the electrode surfaces may not be able to adsorb ions because they exert little force on ions that are farther away. In summary, 10 mm is the best plate spacing.

3.2.5. Comparative Study of Different Adsorption Electrodes

The maximum adsorption capacity of different adsorption electrodes for NOR (300 mg/L) under the optimal conditions is shown in Figure 5. The maximum adsorption capacities of AC, ACFF, and MACFF as adsorption electrodes are 65.6, 72.6, and 89.0 mg/g, respectively. The maximum adsorption capacity of ACFF and MACFF was significantly higher than that of AC; therefore, ACFF is more suitable for use as an electrosorption materials. Compared with AC, the adsorption capacity of MACFF increased by 35.67%. Compared with AC, the ACFF micropores had a small and uniform pore size, simple structure, large contact area with NOR, and uniform contact and adsorption, enabling full use of ACFF. Compared with ACFF, the adsorption capacity of MACFF increased by 22.59%. This increase occurred because of the chemical modification of the surface of ACFF with nitric acid. The surface modification of ACFF by nitric acid increased the surface activity of hydrophilic groups, increased the specific surface area and the number of micropores of ACFF, and thus improved its electrosorption performance, which is also consistent with the conclusions of Figure 2 and Table 1.

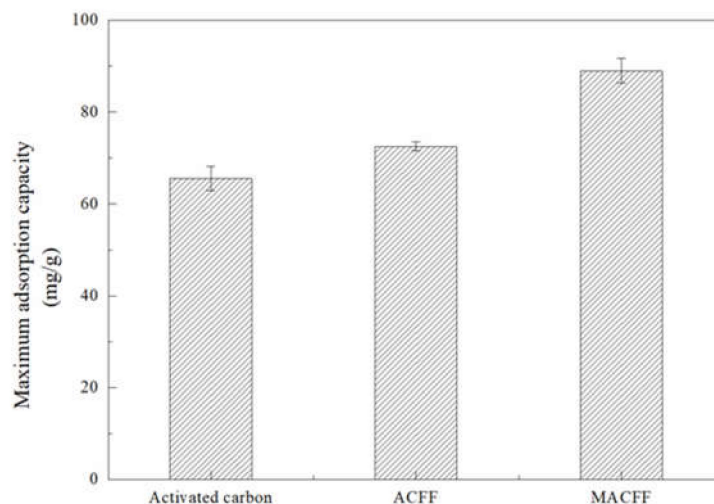


Figure 5. Maximum adsorption for NOR of different adsorption electrodes.

3.3. Adsorption Model and Mechanism Study

3.3.1. Adsorption Kinetics

To study the mechanism of the adsorption/desorption process, a kinetic adsorption experiment of 300 mg/L NOR was carried out at 25 °C. The adsorption capacity was determined after 1, 4, 8, 12, 16, and 20 h. The adsorption kinetic models were fitted under the above conditions by using the following equations:

Pseudo-first-order kinetic model equation:

$$q_t = q_e[1 - \exp(-k_1 t)] \quad (2)$$

Pseudo-second-order kinetic model equation:

$$q_t = \frac{q_e^2 k_2 t}{(1 + q_e k_2 t)} \quad (3)$$

where q_t (mg/g) is the adsorption capacity at different times; t (min) is the adsorption time; q_e (mg/g) is the equilibrium adsorption capacity; k_1 (min^{-1}) is the rate constant of the pseudo-first-order kinetic model; and k_2 ($\text{g}/(\text{mg} \cdot \text{min})$) is the rate constant of the pseudo-second-order kinetic model.

It can be seen from Figure 6 that the pseudo-first-order kinetic model is very similar to the pseudo-second-order kinetic model. The results indicate that the initial adsorption rate is the fastest but decreases with elevation of the time. The initial high speed may be due to an enhancement in the transport driving force emerging from a higher ratio of molecules to reactive vacant adsorbent sites [29]. According to the fitting parameters in Table 2, the pseudo-second-order kinetic model ($R^2 = 0.9540$) and the pseudo-first-order kinetic model ($R^2 = 0.9425$) can be used to model MACFF adsorption, the adsorption capacity under the fitting of the pseudo-second-order kinetic model is 146.24 mg/g, and the adsorption capacity under the fitting of the pseudo-first-order kinetic model is 98.39 mg/g. Under the optimal conditions, the maximum adsorption capacity of MACFF for NOR is 128.55 mg/g, which is closer to the adsorption capacity of the pseudo-second-order kinetic model fitting. The adsorption of NOR on MACFF may be a complex chemical adsorption process [42,43].

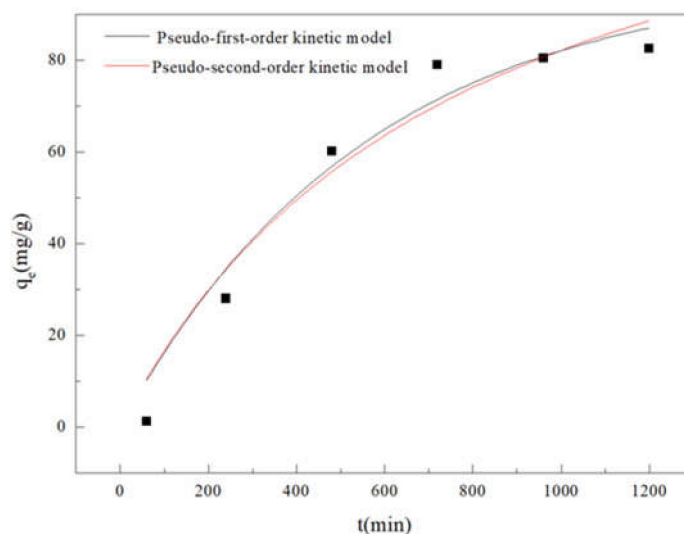


Figure 6. Adsorption kinetic diagrams of MACFF on NOR.

Table 2. Adsorption kinetic parameters of MACFF.

Model Name	Model Related Parameters
pseudo-first-order	$k_1 = 1.79 \times 10^{-3}(\text{min}^{-1})$, $q_e = 98.39(\text{mg/g})$, $R^2 = 0.9425$
pseudo-second-order	$k_2 = 8.75 \times 10^{-6}(\text{g}/(\text{mg} \cdot \text{min}))$, $q_e = 146.24(\text{mg/g})$, $R^2 = 0.9540$

3.3.2. Adsorption Isotherms

The electroadsorption performance of MACFF for NOR was studied at a temperature of 298 K, pH = 6, pollutant concentration of 0.3 g/L, and electrode spacing of 10 mm, and the Langmuir and Freundlich adsorption isotherm models were used to fit the results. The adsorption capacity of MACFF was calculated by the Langmuir and Freundlich model equations as follows:

Langmuir model equation:

$$q_e = \frac{bq_m c_e}{1 + bc_e} \quad (4)$$

Freundlich model Equation (4):

$$q_e = k_f c_e^{1/n} \quad (5)$$

where q_e (mg/g) is the equilibrium adsorption capacity of NOR; c_e (mg/L) is the concentration of NOR in aqueous solution at adsorption equilibrium; q_m is the maximum adsorption capacity; b is the Langmuir constant; k_f and n are the Freundlich constants.

It can be seen from Figure 7 and Table 3 that the experimental data of NOR removal by MACFF are fitted to Langmuir model and do not fit the Freundlich model as well. Most studies have demonstrated the applicability of the Langmuir isotherm on the premise of monolayer coverage on the adsorbent surface and constant adsorption energy [44], while the Freundlich model represents adsorption on heterogeneous surfaces. At ambient pH, the interactions in complex mixtures of amphoteric and anionic ions play a significant role, and such interactions may include complex and nonspecific interactions (such as electrostatic repulsion) [2]. The pH value of the solution in this study was 6, at this pH, the surface of MACFF is negatively charged, the target pollutant itself is a cation, and there is electrostatic attraction. If a negative voltage is applied to the MACFF, the amount of charge on the surface of the MACFF is increased, and under the effect of the electric field, the adsorption capacity will be significantly increased. This phenomenon shows that the adsorption capacity of MACFF electrode can be increased and the adsorption effect of MACFF for NOR can be enhanced by applying an external voltage.

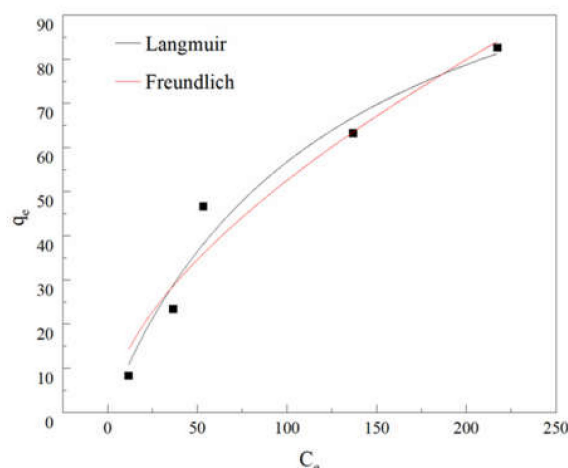


Figure 7. Adsorption isotherm fitting diagram.

Table 3. Related parameters of adsorption isotherm models of MACFF.

Langmuir Model			Freundlich Model		
R ²	b	q _m	R ²	n	k _f
0.9656	0.00791	128.5515	0.9495	0.6045	3.2484

Compared with related value in the literature (Table 4), the adsorption capacity of MACFF for NOR is higher than that of most materials. The production of most of the mentioned materials requires high-temperature pyrolysis, which not only consumes heat energy and time but also causes certain harm to the environment. However, using MACFF as the electrode to remove NOR offers several advantages over these methods, such as ease of operation, low cost, fast response times, and no harmful byproducts [36,45].

Table 4. Adsorption capacity of NOR on different materials.

Absorbent	T(K)	Sorption	Reference
		Capacity (mg/g)	
Aminated Polystyrene Resin	288	117.6	[36]
Carboxylated Carbon Nanotube	288	87	[36]
Molecular Sieves	298	102.9	[44]
Activated Carbon	298	112.48	[46]
Graphitized Carbon Nanotubes	298	57.55	[46]
Carboxylated Carbon Nanotubes	298	54.44	[46]
Hydroxylated Carbon Nanotubes	298	76.34	[46]
Granular Activated Carbon	298	112.86	[47]
Modified Activated Carbon Fiber Felt	298	128.55	This work

3.3.3. Adsorption Mechanism

Prediction of the rate-limiting step is an important factor that needs attention in the adsorption processes [48,49]. For solid–liquid adsorption processes, the solute transfer process is usually described by either external mass transfer (boundary layer diffusion), intraparticle diffusion, or both [49]. Figure 8 and Table 5 present the fitting results of the intraparticle diffusion model in the adsorption process of MACFF for NOR. The adsorption capacity of MACFF on NOR at different times was calculated by the following equation:

$$q_t = K_{id}t^{1/2} + C \quad (8)$$

where q_t (mg/g) is the adsorption capacity at different times, K_{id} (mg/g · min^{1/2}) is the diffusion rate constant in the particle, and C is the model constant.

According to Figure 8 and Table 5, the adsorption process is divided into three stages. The slope of the first stage is the highest and the adsorption rate is the highest. At this stage, the initial concentration of NOR is high, the dynamics are sufficient, and NOR diffuses rapidly to the outer surface of MACFF. This stage is mainly controlled by surface diffusion and the adsorption rate is very fast. In the second stage, the adsorption sites on the outer surface are close to saturation, the pollutant concentration is gradually reduced, and the adsorption resistance in the particles increases, resulting in slope reduction. This stage is controlled by internal diffusion of the particle. The fitting curve of the internal diffusion particles does not pass through the origin, as shown in Figure 8. This indicates that the internal diffusion of particles is not the only factor affecting adsorption; there are other mechanisms at work [48,50]. The third stage is the final adsorption equilibrium stage; and in this stage, the slope is the smallest or even approaches zero, the adsorption sites are saturated, and the power basically disappears, at which time adsorption and desorption reach dynamic equilibrium.

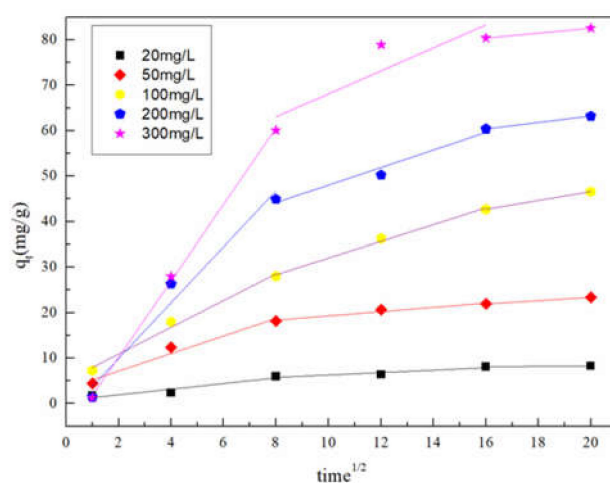


Figure 8. Intraparticle diffusion model for NOR adsorption on MACFF.

Table 5. Intraparticle diffusion model for NOR adsorption on MACFF.

Initial Concentration of NOR (mg/L)	$K_{id,1}$ (mg/g·min ^{1/2})	C_1	R^2	$K_{id,2}$ (mg/g·min ^{1/2})	C_2	R^2
20	0.6233	0.6538	0.8356	0.2671	3.6028	0.7687
50	1.9294	3.2786	0.9435	0.4702	14.5789	0.9368
100	2.9396	5.0107	0.9787	1.8369	13.618	0.9891
200	6.1399	−2.3663	0.9449	1.9294	28.7292	0.9378
300	8.3863	−6.5492	0.9983	2.5349	42.7352	0.6052

During treatment, wastewater will be subjected to the force of the electric field when flowing between the cathode and anode electrodes. The ions or charged particles of NOR in the aqueous solution will migrate to the oppositely charged electrodes and will be adsorbed by the electrodes and stored on the surface of the electrode material. The two-electron layer on the electrode surface will gradually condense and be enriched with a large number of ions or charged particles until it reaches saturation. The surface sites or free valences at the edges of the MACFF play a major role in the adsorption process and are very reactive to any suitable foreign atoms present. As a result of acid treatment (Figure 3), multiple oxygen-containing groups (carbonyl groups, weak acid carboxyl groups, strong acid carboxyl groups, phenolic hydroxyl groups) will be formed on the surface of the ACFF [26]. The NOR molecule possesses one benzene ring and two aromatic heterocyclic groups. The fluorine group on the benzene ring has a strong electron withdrawing ability, causing the aromatic ring to be electron-depleted and, hence, serves as an effective π -electron acceptor. During the adsorption process, the carboxyl group and hydroxyl group on the adsorbent become electron acceptors and

electron donors, respectively [36,51]. Initially, the adsorption was mainly controlled by surface and pore diffusion. Surface diffusion occurred first, followed by pore diffusion, as confirmed by Figure 8. The pH has a great influence on the adsorption process, including the surface charge of the adsorbent, the ionization degree of the substance in the solution, the dissociation of functional groups in the active part of the adsorbent, and the chemical properties of the solute [44]. At low pH values, the protonation of functional groups on the surface of the adsorbent is prone to occur, thereby limiting the approach of positively charged cations to the surface of the adsorbent and causing a high positive charge density due to protons on the surface, as well as high electrostatic repulsion, resulting in lower adsorption. Relevant studies have shown that as the concentration of hydrogen ions in the solution decreases, functional groups on the surface of MACFF will deprotonate, resulting in the increase of negative charge density on the surface of MACFF, which can promote the combination of NOR^+ [44]. Other mechanisms that contribute to NOR adsorption process include π - π EDA interactions and the additive effect of multiple H-bonds [52–55], but these mechanisms are very complex. Clearly, further study is required to evaluate the importance of different adsorption interactions.

3.4. Backwash Regeneration of the Electrosorption Reactor

The recycling and reuse of the sorbent for subsequent removal of NOR from the aqueous solution contributes to the economic viability of the sorption process. The desorption medium used for regeneration of the adsorbent should not damage the sorbent [56]. As shown in Figure 9, ACFF maintains a high regeneration rate in different regenerants. Through six adsorption–regeneration cycles, the regeneration rates of 20% nitric acid, 20% hydrochloric acid, and distilled water were approximately 96%, 89%, and 71%, respectively. The regeneration effect is the best in 20% nitric acid, making the regeneration and reutilization of this sorbent promising [44]. Because 20% nitric acid solution was used for regeneration (similar to the MACFF preparation process), the specific surface area and other characteristics of the regenerated MACFF change to a certain degree, and the number of adsorption sites may increase compared with that of the initial MACFF, resulting in a readsorption capacity greater than the initial adsorption capacity, that is, a regeneration rate more than 100%. With increasing regeneration times, the number of adsorption sites tends to be stable, so the regeneration rate shows a certain decline. With the increase of regeneration times, the final regeneration rate is basically maintained at approximately 96%. Compared with nitric acid, hydrochloric acid has weaker oxidation properties, and the degree of modification of MACFF is smaller in the regeneration process, and the increase in adsorption sites is also relatively small, so the regeneration rate obtained when hydrochloric acid is used as regeneration agent is relatively small. As distilled water cannot increase the adsorption sites of MACFF, the regeneration rate has no significant change and is basically maintained at approximately 71%.

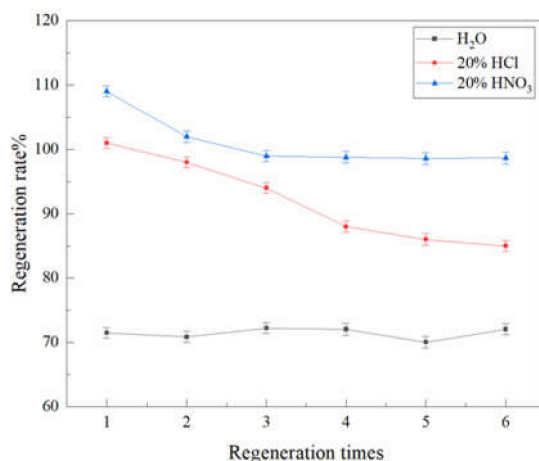


Figure 9. Regeneration rate of MACFF in different regeneration liquids.

Figure 10 shows the regeneration rate of different adsorption electrodes. It can be seen from the figure that the regeneration rates of AC and ACFF before and after modification are maintained at approximately 75%, 82%, and 96%, respectively, after five backwashing regeneration cycles. There is no obvious decrease, indicating that the carbon electrode material is suitable for electrosorption. The electrosorption method is highly efficient and allows spent MACFFs to be regenerated several times without losing their regeneration capacity [57]. The regeneration rate of MACFF is significantly higher than that of AC and ACFF, because the pores in the AC are easily covered by air, which affects the recovery rate. The main aim of regeneration is to remove NOR to recover the original adsorption capacity of the ACFF [57]. In the process of backwashing regeneration, the desalination cycle of the MACFF electrode is long and has a long service life. The reusability of the MACFF over several times is important from an economical point of view [58].

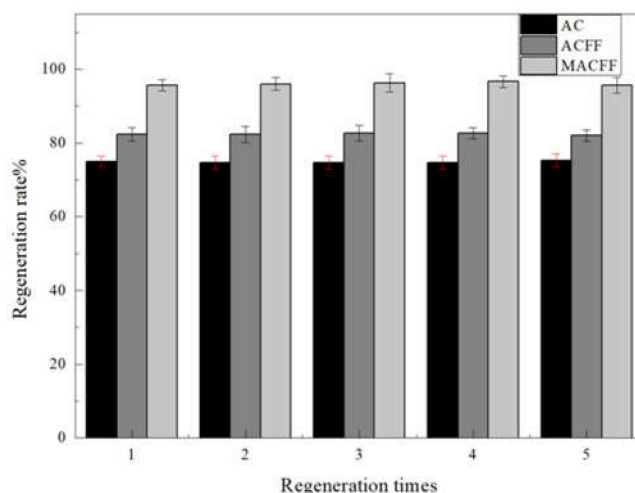


Figure 10. Regeneration rate of different adsorption electrodes.

4. Conclusions

For the electrosorption process studied here, the pH of the solution should be kept in weakly acidic to neutral conditions to obtain a better adsorption effect, and the optimal pH is 6, further indicating that hydrogen bonding plays a major role in the adsorption process. The optimal working conditions of the MACFF electrode are a voltage of 1.0 V and an electrode spacing of 10 mm. The maximum adsorption capacity of the MACFF for NOR was 128.55 mg/g. The results of particle diffusion analysis show that throughout the process, particle diffusion is not the only rate-controlling step and adsorption is controlled by both membrane diffusion and particle diffusion. In this study, it was found that the regeneration rate of the MACFF electrode was maintained at approximately 96% after several adsorption regeneration cycles with 20% nitric acid as the regeneration liquid, and the electrode had good regeneration, which could greatly reduce the application cost of this technology and provide theoretical support for the large-scale application of this technology.

Author Contributions: X.L., D.S., and W.-B.S. contributed to the conception and design of the study. X.L. and Y.H. performed the experiments and theoretical calculations, organized the database, and wrote the first draft of the manuscript. All authors have read and agreed to the published version of the manuscript.

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