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Rapid adsorption of diclofenac by polyaniline-coated carbon nanofiber

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Abstract: In this work, polyaniline-coated carbon nanofiber with acid treatment (named CNFA@PANI) composite was synthesized and used to eliminate diclofenac from the water environment. Thanks to the abundant amino functional groups and benzene-ring structures, the as-prepared CNFA@PANI composite presented the excellent adsorption capacity (q_e) of 202.9 mg/g and high distribution constant (K_d) value of 1.02×10^4 for diclofenac. The physical and chemical properties of the manufactured composites were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier-transformed infrared spectroscopy (FT-IR). The novel adsorbent possessed rapid and excellent adsorption performance for diclofenac. Moreover, in the wide pH range, the CNFA@PANI possessed well adsorption capacities. Meanwhile, after five adsorption-desorption cycles, the composite still showed excellent reusability performance. Furthermore, quantum chemical theory calculations indicated the possible adsorption sites of the composite for diclofenac. In total, this work provides an easy method to design novel composites for the efficient removal of diclofenac from the water environment.

Keywords: pharmaceuticals, diclofenac, polyaniline, carbon nanofiber, adsorption

1. Introduction

Diclofenac (DCF), one of the non-steroidal anti-inflammatory drugs (NSAIDs), has been widely used to treat many health problems like inflammation and pain (Shamsudin et al., 2022). However, diclofenac is harmful to human health and aquatic ecology with extended exposure (Moradi et al., 2022). Additionally, due to the extensive use, diclofenac is frequently detected in surface water, groundwater, and even drinking water (Ieamviteevanich et al., 2022). Thus, it is urgent to develop some efficient methods to remove diclofenac from the water environment.

Recently, advanced oxidation processes (Parra-Enciso et al., 2022), PMS activation (Zhao et al., 2022), bank filtration (de Carvalho Filho et al., 2022), and adsorption (Feng et al., 2022) have been conducted to remove diclofenac. Among them, adsorption is one of the most efficient, simple, nontoxic, and low-cost methods to remove pharmaceutical contaminants efficiently from the water environment. Excellent adsorbents should possess the advantage of rapid and efficient removal.

Carbon nanofiber (CNF) is an interesting material with distinctive properties such as nice flexibility, strong tensile strength, large surface area, and light weight (Tuzen et al., 2020). Thus, carbon nanofiber will be a potential material for pharmaceutical removal. Also, CNF is an ideal support for the in-site growth of functional materials. To further increase the adsorption capacity, CNF was acid-treated with nitric acid, increasing more oxygen-containing functional groups on the surface. Then, the acid-treated CNF will be easier modified. Polyaniline (PANI), one of the conducting polymers, possessed the advantages of simple synthesis, low cost, and excellent environmental stability (Samadi et al., 2021). Moreover, polyaniline has attracted much interest due to the favorable combination of its aromatic rings connected through nitrogen-containing groups, which was beneficial for the removal of benzene pollutants via hydrogen bond interaction (Samadi et al., 2021). Therefore, PANI is a promising material for pollutant removal from the water environment.

Inspired by the findings above, the composite material was produced by in-site growth of the polyaniline on the surface of nitric acid-treated carbon nanofiber. The synthesized CNFA@PANI composite was characterized by Scanning electron microscope (SEM), X-ray diffraction (XRD), and Fourier-transformed infrared spectroscopy (FT-IR). The prepared CNFA@PANI composite possessed abundant aromatic rings which were beneficial for the π-π conjugation interactions with benzene pollutants. Meanwhile, the CNFA@PANI composite was applied as the adsorbent for the removal of diclofenac from the water environment through the batch adsorption method. Multiple sorption/desorption cycles are applied to assess the stability and reusability of the adsorbent. This study provides novel perceptions for the application of CNF@PANI as an excellent adsorbent for the rapid and efficient removal of diclofenac from the water environment.

2. Experimental methods

2.1. Synthesis of CNFA@PANI

To achieve the acid-treated CNF, the initial CNF was pre-treated with 2 M nitric acid at 120 °C for 2 h. Then the CNFA@PANI composite was synthesized through the chemical oxidative polymerization of aniline onto the surface of the CNFA with the previously reported methods (Xu et al., 2022). In detail, 150 mg of CNFA was dispersed in 100 mL of 2 M HCl aqueous solution under sonication for 30 min. Next, 450 μL aniline was added to the suspension under vigorous stirring and continued for 30 min. Then, the oxidizing agent (50 mL of 0.1 M ammonium persulfate) was added into the above dark suspension drop by drop under stirring and continued for 12 h at room temperature. Finally, the dark-green product was collected via centrifugation, washed with DI water and absolute ethanol, and vacuum dried at 60 °C overnight.

2.2. Characterization

The microstructure morphology and element mapping images were obtained via scanning electron microscopy (SEM, FEI QUANTA FEG250, USA). The phase and crystal structures of the prepared materials were characterized by X-ray diffraction (XRD, Bruker, Germany) with Cu Kα radiation (1.5478 Å). The functional groups of the manufactured samples were recorded by Fourier-transformed infrared spectroscopy (FT-IR, ThermoFisher, USA).

2.3. Adsorption experiment

The adsorption abilities of the prepared CNFA@PANI for diclofenac were studied through batch adsorption experiments three times. The final concentrations of diclofenac after adsorption were measured by UV-1800 (Shanghai Instrument Co., Ltd.) at the maximum absorption wavelength (269 nm). The adsorption capacity (q_e, mg/g), distribution coefficient (K_d, mL/g), and removal efficiency (R, %) of diclofenac were calculated as equations (1-3).

$$q_e = \frac{C_0 - C_f}{m} V \quad (1)$$

$$K_d = \frac{C_0 - C_f}{C_f \times m \times 10^{-3}} \quad (2)$$

$$R = \frac{C_0 - C_e}{C_0} \times 100\% \quad (3)$$

Where C_0 (mg/L), C_f (mg/L), m (mg), and V (mL) correspond to the initial and final concentrations of diclofenac in solution, adsorbent mass, and solution volume, respectively.

To explore the reusability of the adsorbent, regeneration experiments were also conducted. The spent adsorbents were eluted with methanol, and the adsorption-degradation experiments were repeated in five cycles.

3. Results and discussion

3.1. Characterization Results

As displayed in **Figure 1a-b**, the CNFA possessed the rather smooth surface with the obvious nanofiber structure. After in-site coating, the surface of CNFA was completely covered with nano-size polyaniline spheres, effectively avoiding the agglomeration of polyaniline spheres and increasing the removal abilities. In **Figure 1c**, the XRD pattern of CNFA possessed two broad peaks at about 25° and 42°, ascribed to the (002) and (101) planes of graphitic carbon, respectively (Demiroğlu Mustafov et al., 2019). After polyaniline coating, the small peak appeared at around 23° attributed to the (110) plane, which indicated that the polyaniline layer possessed the amorphous structure (Hsini et al., 2021). Meanwhile, in the FT-IR spectra, CNFA@PANI had characteristic peaks distributed at 2000-1000cm^{-1}, owing to the stretching of quinone and benzene rings of the polyaniline layer (Wang et al., 2021). In total, the above characterization proved the successful synthesis of the CNFA@PANI composite.

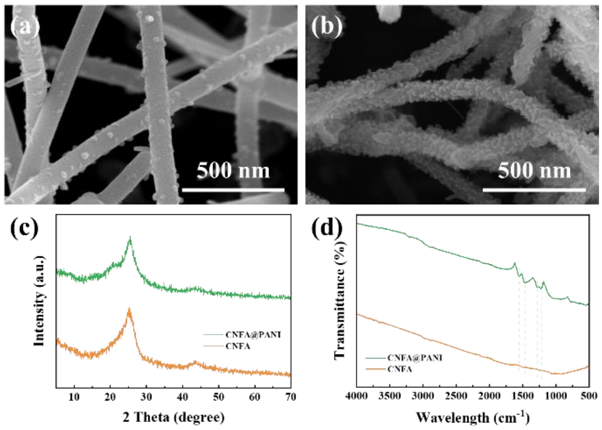

Figure 1. SEM images of (a) CNFA and (b) CNFA@PANI, (c) XRD pattern and (d) FT-IR spectra of CNFA and CNFA@PANI.

3.2. Batch Adsorption Experiments

As shown in **Figure 2a**, with the raising of diclofenac concentrations, the adsorption capacities of CNFA@PANI for diclofenac increased gradually. While the adsorption capacities of CNFA for diclofenac were limited, thus CNFA was not considered and compared in the following adsorption experiments. In addition, the adsorption capacities of CNFA@PANI composites presented good adsorption capacities at pH values ranging from 3 to 10 (**Figure 2b**), indicating the wide application of the novel materials.

3.3. Adsorption Kinetic

Figure 2d showed the adsorption kinetic behavior of diclofenac onto CNFA@PANI. The adsorption capacities increased continuously in 60 min and then reached the adsorption equilibrium, and the equilibrium adsorption capacity was around 138.4 mg/g. Besides, the experimental data were fitted with the non-linear pseudo-first-order, pseudo-second-order, and Elovich kinetic models. Among them, the pseudo-second-order model described the adsorption kinetic behavior better, because of the higher R^2 and approximative theoretical and experimental values (**Table 1**), indicating that the diclofenac adsorption onto CNFA@PANI favored the chemisorption process (Zhou et al., 2022).

3.4. Adsorption Isotherm

The adsorption capacities of CNFA@PANI at different initial concentrations of diclofenac were studied through non-linear Langmuir, Freundlich, and Temkin isotherm models. As shown in **Figure 2e**, with the increase of diclofenac concentrations, the adsorption capacities of CNFA@PANI increased gradually and then arrived at the adsorption equilibrium. The adsorption isotherm behavior of diclofenac onto CNFA@PANI was better matched with the Langmuir model owing to the higher correlation coefficients (**Table 2**), indicating the monolayer sorption behavior of CNFA@PANI for diclofenac (Chen et al., 2022). In addition, the maximum adsorption capacity achieved from the batch experiment was found to be 198.8 mg/g, which was very close to the theoretical value (202.9 mg/g) from the Langmuir model. Moreover, the distribution constant value of CNFA@PANI for diclofenac was 1.02×10^4, which indicated that CNFA@PANI was an excellent adsorbent (Li et al., 2022).

Furthermore, in the low diclofenac concentrations of 1-25 mg/L (**Figure 2c**), CNFA@PANI possessed excellent removal rates and the distribution constant value was 9.81×10^4, indicating that CNFA@PANI was an excellent and ideal adsorbent for the rapid and efficient removal of diclofenac.

3.5. Regeneration

In the regeneration experiments, five adsorption-desorption cycles were carried out to study the reusability of CNFA@PANI. According to the studied literature, methanol was chosen as the eluent to regenerate spent adsorbent. As shown in **Figure 2f**, the removal rate of CNFA@PANI for diclofenac reduced slightly with the conducting of each cycle. Additionally, the adsorption capacity of CNFA@PANI for diclofenac still possessed 90.4% of the initial after five cycles. In total, the prepared CNFA@PANI composite showed well regeneration performance during the adsorption removal of diclofenac from the water environment.

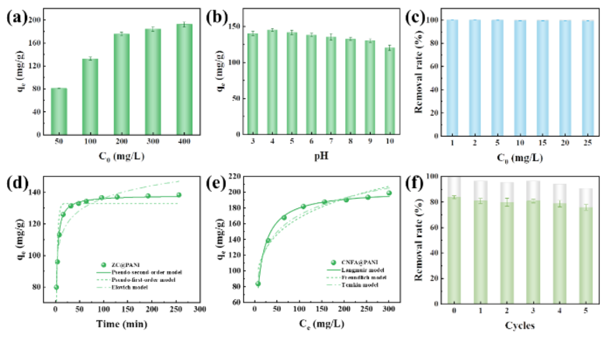

Figure 2. (a) Influence of initial concentrations, (b) Effect of solution pH, (c) Adsorption capacities at low concentrations, (d) Adsorption kinetics, (e) Adsorption isotherms, and (f) Regeneration performance.

3.6. Quantum chemical theory calculations

After optimizing the molecular structure through Gaussian 09, the 3D optimized molecular structures of diclofenac and polyaniline were shown in **Figure 3a-b**. To study the electrostatic potential (ESP) distribution quantitatively, the surface vertex color-filled molecular surface electrostatic potential distributions of diclofenac and polyaniline were conducted (Lu and Chen, 2012). As shown in **Figure 3c-d**, the cyan spheres represented the electrostatic potential surface minima points, while the yellow spheres represented the maxima points (Lu and Manzetti, 2014). Obviously, the oxygen atoms of diclofenac shared the blue areas and cyan spheres, while in polyaniline, the nitrogen atoms shared the red areas and yellow spheres, indicating the probable hydrogen bond interaction between diclofenac and CNFA@PANI.

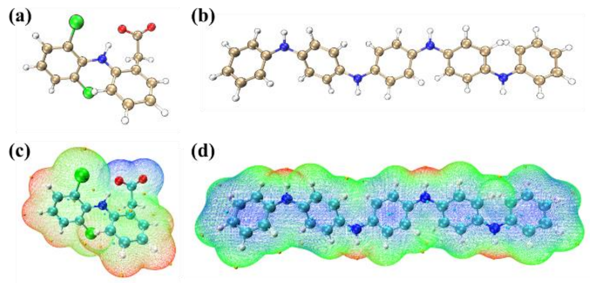

Figure 3. 3D optimized molecular structure of (a) diclofenac and (b) polyaniline, ESP colored molecular surface map of (c) diclofenac and (d) polyaniline (C-tan/cyan, O-red, H-white, N-blue, Cl-green).

4. Conclusion

The prepared CNFA@PANI composite possessed excellent adsorption performance for diclofenac. The adsorption kinetic and isotherm behavior conformed to the pseudo-second-order model and Langmuir model, respectively. ESP analyses indicated the possible hydrogen bond interaction between diclofenac and polyaniline. The further adsorption mechanism of CNFA@PANI for diclofenac removal will be explored in further work. In total, the novel CNFA@PANI composite presented the potential as an excellent adsorbent for the elimination of diclofenac from the water environment.

Table 1. Adsorption kinetic parameters of diclofenac onto CNFA@PANI.

Adsorbents	$q_{e,exp.}$ (mg/g)	Pseudo-first order model			Pseudo-second order model			Elovich model		
		$q_{e,cal.}$ (mg/g)	k_1 (1/min)	R^2	$q_{e,cal.}$ (mg/g)	k_2 (g/mg • min)	R^2	α (mg/g·min)	β (mg/g)	R^2
CNFA@PANI	138.4	133.1	0.360	0.869	138.2	0.00450	0.992	18788	0.088	0.851

Table 2. Adsorption isotherm parameters of diclofenac onto CNFA@PANI.

Adsorbents	T (K)	Langmuir isotherm model			Freundlich isotherm model			Temkin isotherm model		
		q_m (mg/g)	k_L (L/mg)	R^2	k_F ((mg/g)/(mg/L)$^{1/n}$)	n	R^2	A_T (L/mg)	b_T (J/mol)	R^2
CNFA@PANI	298	202.9	0.0778	0.992	67.9	5.11	0.906	2.39	79.4	0.960

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