Synthesis and Characterization of a Magnetic Carbon Nanofiber Derived from Bacterial Cellulose for the Removal of Diclofenac from Water

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ABSTRACT: Engineering and synthesis of novel materials are vital for removing emerging pollutants, such as pharmaceuticals from contaminated water. In this study, a magnetic carbon nanofiber (MCF) fabricated from bacterial cellulose was tested for the adsorption of diclofenac from water. The physical and chemical properties of the synthesized adsorbent were examined by field emission scanning electron microscopy (FESEM), field emission transmission electron microscopy (FETEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) analysis, energy-dispersive X-ray spectroscopy (EDS), a vibrating sample magnetometer (VSM), Raman spectroscopy, and Fourier transform infrared (FTIR) spectroscopy. The characterization results showed that the MCF is a carbon nanofiber with a three-dimensional interconnect network, forming a porous material (mesopores and macropores) with a specific surface area of 222.3 m$^2$/g. The removal of diclofenac (10 mg/L) by the MCF (0.75 g/L) was efficient (93.2%) and fast (in 20 min). According to the Langmuir isotherm model fitting, the maximum adsorption capacity of the MCF was 43.56 mg/g. Moreover, continuous adsorption of diclofenac onto MCF was investigated in a fixed-bed column, and the maximum adsorption capacity was found to be 67 mg/g. The finding of this research revealed that the MCF could be a promising adsorbent used to remove diclofenac from water, while it can be easily recovered by magnetic separation.

1. INTRODUCTION

Diclofenac is one of the nonsteroidal anti-inflammatory drugs (NSAIDs) that is widely used to treat acute and chronic pain in humans and animals. As arthritis and heart diseases have become more typical for an aging society, diclofenac usage is expanding. As a result, the diclofenac market has grown substantially, with its expected revenue up to $5.64 billion in 2025. Consequently, diclofenac contamination has been observed in several water sources, including river, ground-water, drinking water, hospital effluents, and sewage water. Although the diclofenac contamination is low, it can cause acute toxic effects to many organisms in water, like mussels, and can lead to chronic toxicological effects with extended exposure. Moreover, a diclofenac molecule can transform into a diclofenac ion by sunlight. The ion reactions with other contaminants in water lead to other forms of more toxic substances. Therefore, diclofenac should not be released into the environment, especially water resources.

Conventional processes used in wastewater treatment are not adequate to clean up diclofenac from water. The efficiency of these processes is less than 20%. Thus, alternative methods have been investigated to remove diclofenac from water, for instance, biodegradation, biological treatment, ion exchange, nanofiltration membrane, and adsorption. Among various techniques, adsorption is the most useful, simple, nontoxic, and cheap method to remove pharmaceutical contaminants from water. Significant parameters affecting the adsorption capacity are types of adsorbents and their structures. Carbon-based materials, such as carbon nanotube, graphene, graphene oxide, and activated carbon (AC), have been utilized for various contaminant adsorption because of their porous structure, high surface area, and hydrophobicity.

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Among these adsorbents, carbon nanofibers (CNFs) have attracted considerable attention due to their unique features such as low-cost synthesis, significant mechanical, electrical, and thermal properties.\textsuperscript{21} CNFs have been widely used in many applications, e.g., as an electrocatalyst for hydrogen and oxygen evolution reactions,\textsuperscript{22,23} oxygen reduction reaction,\textsuperscript{24} supercapacitors,\textsuperscript{25} and drug delivery.\textsuperscript{26} Additionally, they are widely used as safe and environmental-friendly adsorbents for the removal of dyes,\textsuperscript{27} oil,\textsuperscript{28} and volatile organic compounds (VOCs).\textsuperscript{29} Nevertheless, the carbon-based adsorbent in their intrinsic form are powders, making them difficult to recover, separate, and regenerate after wastewater treatment.\textsuperscript{30,31}

On the other hand, magnetic adsorbents have recently gained a lot of attention for treating contaminated water due to their ease of recovery and separation by applying an external magnetic field.\textsuperscript{30,32} Afterward, they can be subjected to regeneration for subsequent reuses. These magnetic adsorbents such as oak powder/Fe\textsubscript{3}O\textsubscript{4},\textsuperscript{33} organosilane polymer (PTMT)/Fe\textsubscript{3}O\textsubscript{4},\textsuperscript{34} and lignin/Fe\textsubscript{3}O\textsubscript{4}\textsuperscript{35} were used for the adsorption of heavy metals and dyes from contaminated water. Furthermore, the magnetic adsorbents were studied for the removal of pharmaceuticals in water, including the use of an amine/Fe\textsubscript{3}O\textsubscript{4}/AC nanocomposite for removing ciprofloxacin and norfloxacin,\textsuperscript{36} Fe\textsubscript{3}O\textsubscript{4}/polyacrylonitrile (PAN) for tetracycline adsorption,\textsuperscript{37} and chitosan/Fe\textsubscript{3}O\textsubscript{4} and Fe\textsubscript{3}O\textsubscript{4}/AC composites for treating diclofenac.\textsuperscript{30}

In this work, we fabricated a diclofenac adsorbent by combining the synergistic advantages of carbon-based materials and the ease of recovery by magnetic separation. We selected bacterial cellulose (BC) as a carbon source. BC is a natural cellulose produced by the cultivation of bacteria. Its structure comprises a three-dimensional (3D) network of a pure cellulose nanofiber with tremendous nanopores and numerous hydroxyl groups.\textsuperscript{38,39} Magnetic nanoparticles can be impregnated into the BC structure via several methods, adding magnetic functionality.\textsuperscript{30,31} With proper pyrolysis, the magnetic
BC is transformed into a magnetic carbon fiber (MCF), with a highly porous structure, a large surface area, extremely low density, and desired magnetic properties, which was demonstrated for its ability for oil/water separation. Here, the MCF was studied for its ability as an efficient diclofenac adsorbent. The interactive effects of adsorbent dosage, initial diclofenac concentration, and contact time on diclofenac adsorption were analyzed. Also, the isotherm and kinetic modeling were performed to understand the adsorption mechanism and the adsorption rate. Moreover, fixed-bed column adsorption experiments were conducted to mimic the industrial scale of diclofenac removal from water in a continuous mode.

2. RESULTS AND DISCUSSION

2.1. Characterization Results. The morphology of the adsorbent (MCF powder) is shown in Figure 1. The MCF sample consists of a three-dimensional interconnected network of carbon nanofibers. A number of nanopores can be observed in the SEM image Figure 1a, leading to a very high surface area of the MCF. In addition, the uniform distribution of Fe₃O₄ nanoparticles on the surface of MCF without any obvious aggregation was confirmed by transmission electron microscopy (TEM) images (Figure 1b). Moreover, the chemical composition of the MCF adsorbent was examined by the energy-dispersive X-ray spectroscopy (EDS) technique equipped with the SEM instrument. The EDS spectrum showed that carbon (C), oxygen (O), and iron (Fe) are the dominant elements present on the surface of an MCF adsorbent with atomic percentages of 63.40, 24.26, and 9.32% and weight percentages of 38.66, 19.70, and 26.44%, respectively. In addition magnesium (Mg), aluminum (Al), silicon (Si), calcium (Ca), potassium (K), chloride (Cl), and sulfur (S) with lower atomic percentages were detected by EDS. Figure 1c shows the weight and atomic percentages of the MCF elemental composition. Furthermore, based on the inductively coupled plasma mass spectrometry (ICP-MS) analysis, the iron content in the MCF sample was found as 284.7 mg/g (28.47%, wt %), which was close to EDS results.

The specific surface area ($S_{BET}$), total pore volume ($V_p$), and pore size distribution of the MCF were measured by nitrogen adsorption–desorption analysis (Figure 1d). The MCF exhibits a type II $N_2$ adsorption isotherm (multilayer adsorption) according to the IUPAC classification, with a visible hysteresis loop. The appeared H4 type hysteresis loop
in the adsorption isotherms suggests the presence of micropores and mesoporous in the MCF structure. It is worth noting that the isotherms rise remarkably near \( p/p_\infty = 1 \), suggesting that the MCF samples contain macropores. The BJH curve revealed the presence of pores classified into three groups, narrow micropores with pore size below 2 nm, a wider range of mesopores with the pore width in the range of 25–50 nm centered at around 50 nm, and macropores in the range of 50–170 nm centered at around 170 nm. Accordingly, specific surface area \( S_{\text{BET}} \), total pore volume \( V_p \), and average pore radius \( r = V_p/A_{\text{BET}} \) were measured to be 222.3 m\(^2\)/g, 0.025 m\(^3\)/g, and 11.5 Å, respectively. The size of the diclofenac molecule is 0.458 nm and they can penetrate into the porous structure of an MCF with a high specific surface area. Therefore, pore-filling could have a highlighted role in the removal of diclofenac from water by the MCF adsorbent.

The crystal structure of the MCF was examined by XRD, and its XRD pattern is shown in Figure 1e. Several peaks are observed at \( 2\theta = 30.16, 35.44, 43.28, 53.25, 57.44, \) and 62.99\(^\circ\). These peaks correspond to the \((220), (311), (400), (442), (511), (440)\) diffracted planes of the Fe\(_3\)O\(_4\) phase (ICDD: 01-075-1610). There is no other peak related to carbon nanofibers, indicating that the MCF adsorbent consists of amorphous carbon fibers coated with the crystalline Fe\(_3\)O\(_4\) nanoparticles.

Moreover, Figure 1f shows the measured FTIR spectra of the MCF before and after adsorption of diclofenac. The FTIR spectrum of MCF before adsorption shows several absorption bands, which are the characteristic bands of the carbon structure, namely, the \( \text{C} = \text{C} \) stretching at 2125 cm\(^{-1}\), the allene chain \((\text{C} = \text{C} = \text{C})\) stretching at 2029 and 1969 cm\(^{-1}\), the carbonyl group \((\text{C} = \text{O})\) stretching at 1766 cm\(^{-1}\), and the alkene chain \((\text{C} = \text{C})\) stretching at 1651 cm\(^{-1}\). In addition, the absorption band at 459 cm\(^{-1}\) is attributed to the Fe–O bonding from the octahedral side of Fe\(_3\)O\(_4\) nanoparticles. The FTIR spectrum of MCF after adsorption shows the same characteristic bands plus additional two bands located at 773 cm\(^{-1}\), assigned to the aromatic C–H bending and aromatic \( \equiv \text{CH} \) stretching at 2928 and 2856 cm\(^{-1}\). Both bands are attributed to the characteristic band of diclofenac. The findings confirm that MCF adsorbed diclofenac molecules successfully.

The Raman spectrum of MCF (Figure 1g) exhibits two strong peaks at 1354 cm\(^{-1}\) (D-band) and 1591 cm\(^{-1}\) (G-band)
that are attributed to the disorder in carbon nanofibers and the in-plane vibration of C–C bonds in the graphite lattice, respectively.\textsuperscript{50} Moreover, the broad peak at 670 cm\textsuperscript{-1} is assigned to the A\textsubscript{1g} mode, belonging to the magnetite nanoparticles.\textsuperscript{51}

In addition, the magnetic property of MCF was measured using a vibrating sample magnetometer (VSM) at room temperature. As shown in Figure 1h, magnetization (M) was plotted versus the magnetic field at −30 and 30 kOe. The hysteresis loop was not observed, implying superparamagnetism\textsuperscript{40,52,53} of MCF due to the nanosize of the magnetic particles. The saturation magnetization value of MCF was 80.0 emu/g, indicating that the adsorbent could be separated from the liquid phase using an external magnet, as shown in the inset of Figure 1h.

### 2.2. Batch Adsorption Experiments

Adsorbent dosage, adsorbate concentration, and contact time are three crucial variables that influence adsorption performance. To optimize these parameters, the maximum adsorption capacity and removal efficiency were evaluated in response to interactive effects of varying MCF dosages (0.25−0.75 g/L), initial diclofenac concentrations (10−50 mg/L), and contact times (20−120 min). The diclofenac removal efficiency and the adsorption capacity are represented as the 3D contour plots, as shown in Figures 2 and 3, respectively. These plots are very useful to illustrate the interaction between two variables, while the other factor is fixed.

As shown in Figure 2a−c, the MCF dosage was fixed, and the removal efficiency was studied as a function of the initial diclofenac concentration and the contact time. It shows that the removal efficiency decreases with increasing the initial diclofenac concentration. This finding is understandable since there is a finite amount of the MCF adsorbent and the specific proportions of available sites for adsorption. The increased diclofenac concentration reduces the ratio of the adsorbent's surface active sites to the total diclofenac molecules. The excessive diclofenac molecules cannot interact with the adsorbent and as such, they are not removed from the solution, and thus, the removal efficiency is decreased.\textsuperscript{54,55} On the other hand, increasing the contact time leads to higher removal efficiency. The longer contact time allows more time for the adsorbent sites to react with the diclofenac molecules. However, when the time is sufficiently long, the removal efficiency approaches the saturation point, as all of the available active sites of the MCF fully adsorb the diclofenac molecules.

Next, the initial diclofenac concentration was fixed, and the removal efficiency was plotted as a function of the MCF dosage and the contact time, as shown in Figure 2d−f. The general trend is that the removal efficiency increases with both the MCF dosage and the contact time. Also, there are more vacant sites for diclofenac adsorption at a higher MCF dosage and a fixed diclofenac concentration, which enhances the removal efficiency. For the contact time, the effect is more pronounced for the low initial diclofenac concentration. When the diclofenac concentration is low, it needs more time for the diclofenac molecules to diffuse to the adsorption site. However, at higher concentrations, there are already a lot of diclofenac molecules in the solution so that they can be adsorbed by the MCF almost instantly.

Figure 2g−i shows the removal efficiency for the fixed contact time. The removal efficiency is positively proportional to the MCF dosage but inversely proportional to the initial diclofenac concentration. The reason is straightforward. For the fixed time, increasing the MCF dosage means more active sites available for diclofenac adsorption and the increased diffusion pathway for diclofenac molecules.\textsuperscript{34} Conversely, the higher initial diclofenac concentration leads to the lower ratio of the available active sites of MCF to the diclofenac molecules, which implies that the removal of diclofenac is not efficient.

The effect of variables on the adsorption capacity is shown in Figure 3. For the fixed MCF dosage, the adsorption capacity increases with both the initial diclofenac concentration and the contact time (Figure 3a−c). As the initial diclofenac concentration increases, the diclofenac molecules have a larger driving force to overcome the mass transfer resistance at the solid−liquid interface.\textsuperscript{56} Thus, they can be adsorbed by the MCF more effectively and improve the adsorption capacity. On the other hand, increasing the contact time gives diclofenac molecules more time to interact with the active sites of the MCF. Nevertheless, the effect of the contact time is more pronounced only for a low diclofenac concentration and a low MCF dosage.

Figure 3d−f shows the variation of adsorption capacity with the MCF dosage and the contact time for the fixed initial diclofenac concentration. The longer the time, the more chance for diclofenac molecules to be adsorbed at the active sites of MCF, and thus the adsorption capacity increases with time. However, the adsorption capacity decreases when the MCF dosage is increased. This is understood from the definition of the adsorption capacity in eq 2. As the MCF dosage increases, the denominator in the equation also increases, resulting in the reduced q. Lastly, the adsorption capacity was studied for the fixed contact time, as shown in Figure 3g−i. The adsorption capacity increases with increasing initial diclofenac concentration but slightly decreases with increasing MCF dosage. The reasons are the changes, which are already discussed.

In addition to the interactive effects of the abovementioned variables, the initial pH of the solution is another important factor that affects the efficiency of adsorption. It does not only affect the surface charge of an adsorbent but also influences the degree of ionization and the charge state of an adsorbate.\textsuperscript{57,58} In this regard, the effect of the initial solution pH on the removal efficiency and the adsorption capacity of MCF toward diclofenac was investigated. Figure 4a shows the adsorption performance of MCF under a wide range of initial solution pH, viz., 4, 5, 6, 7, 8, and 9. The results showed that the removal efficiency increased from 77.61 ± 3.93 to 83.88 ± 0.91% as well as adsorption capacity increased from 12.43 ± 0.63 to 18.10 ± 0.20 mg/g as the initial solution pH increased from 4 to 5. The adsorption capacity was almost constant at an initial solution pH of 5, 6, and 7. Adsorption capacity and removal efficiency were found to decrease at pH > 7. Since the maximum adsorption capacity was observed at an initial solution pH of 5, 6, and 7, further batch (kinetic and isotherm) and continuous column experiments were conducted without pH adjustment at the initial solution pH of 6.41.

Overall, the batch adsorption experiments show that the highest removal efficiency of 98.3 ± 7.7% found for an MCF dosage of 0.75 g/L, and the initial diclofenac concentration of 10 mg/L, for the contact time of 120 min, whereas the maximum adsorption capacity of 48.8 ± 14.8 mg/g was observed for 0.25 g/L MCF dosage, 50 mg/L initial diclofenac concentration, and 120 min contact time. A comparison of
The maximum adsorption capacity of MCF is significantly higher than some adsorbents (e.g., polypyrrole/MWCNTs and MWCNTs modified by nitric acid), and comparable to others, such as magnetic-activated carbon and porous graphene, but it is still much lower than some adsorbents (magnetic chitosan multilayer, chitosan/Fe₃O₄, and sycamore ball-activated carbon). However, the most advantage of using the MCF adsorbent in this work is the fast adsorption. The time to reach the equilibrium level of MCF is only 30 min (based on kinetic experiment data), the lowest in Table 1. The other diclofenac adsorbents need a longer time (up to 300 min). In previous studies, fast adsorption kinetics has been considered an important property of a good adsorbent.  

2.3. Adsorption Isotherm. Isotherm experiments were performed to explain the adsorption behavior between an adsorbate and an adsorbent at equilibrium time. Figure 5a shows the correlation between the equilibrium diclofenac concentration ($C_e$) and the adsorption capacity ($q_e$) at equilibrium time. The experimental results are fitted with

![Figure 4](https://example.com/figure4.png) **Figure 4.** (a) Effect of the initial solution pH on the removal efficiency and the adsorption capacity and (b) plot of point of zero charge ($\text{pH}_{\text{pzc}}$) of MCF.

![Figure 5](https://example.com/figure5.png) **Figure 5.** (a) Adsorption isotherm plots for the adsorption of diclofenac onto the MCF adsorbent, fitted to the Langmuir, Freundlich, and Sips models; (b) adsorption kinetic plots for the adsorption of diclofenac onto MCF, fitted with the pseudo-first-order rate constant (PFORE) and pseudo-second-order rate constant (PSORE) models; and (c) resistance to intraparticle diffusion equation (RIDE) within the contact time of 180 min (initial diclofenac concentration: 50 mg/L, MFC amount: 0.5 g/L, pH: 6.41, and $T$: 22 °C).

| adsorbent                              | solution pH | initial diclofenac concentration (mg/L) | adsorbent dosage (g/L) | maximum adsorption capacity (mg/g) | equilibrium time (min) | refs |
|----------------------------------------|-------------|----------------------------------------|------------------------|------------------------------------|------------------------|------|
| magnetic chitosan multilayer           | 6.5         | 600                                    | 0.5                    | 434.8                              | 300                    | 60   |
| porous graphene                        | 7.5         | 100                                    | 0.25                   | 76                                 | 60                     | 18   |
| magnetic-activated carbon              | 7.5         | 4.16                                   | 0.35                   | 63.7                               | 60                     | 30   |
| chitosan/Fe₃O₄                        | 6           | 100                                    | 0.50                   | 103                                | 200                    | 54   |
| sycamore ball-activated carbon         | original    | 50                                     | 0.20                   | 178.9                              | 100                    | 14   |
| polypyrrole/ MWCNTs                   | 6           | 100                                    | 5                      | 19.7                               | 45                     | 55   |
| MWCNTs modified by nitric acid         | 50          | 5.40                                   | 8.6                    | 60                                 | 17                     |      |
| magnetic carbon fiber (MCF)            | 6.41        | 50                                     | 0.50                   | 45.7                               | 30                     | this work |

Table 1. Comparison of the Diclofenac Adsorption Properties for Various Adsorbents
Table 2. Parameters of Isotherm and Kinetic Models for Diclofenac Adsorption onto MCF (MFC Amount: 0.50 g/L, pH: 6.41, and T: 22 °C, Contact Time: 180 min (for Isotherm Studies) and Diclofenac Concentration: 50 mg/L (for Kinetic Studies))

| Isotherm Models | Langmuir | Freundlich | Sips |
|----------------|----------|------------|------|
| $q_m$ (mg/g)   | $K_L$ (L/mg) | $R^2$ | RMSE | SSE |
| 43.56          | 0.37     | 0.961     | 3.41 | 69.81 |
| $K_F$ [(mg/g)(L/mg)$^{1/n}$] | $n$ | $R^2$ | RMSE | SSE |
| 17.63          | 4.22     | 0.978     | 2.58 | 39.97 |
| $K_I$ (L/g)    | $\beta_i$ | $a_i$ (L/mg) | $R^2$ | RMSE | SSE |
| 22.36          | 0.43     | 0.33      | 0.986 | 2.22 | 24.76 |

| Kinetic Models | PFORE | PSORE | RIDE |
|----------------|-------|-------|------|
| $q_m$ (mg/g)   | $k_1$ (1/min) | $R^2$ | RMSE |
| 38.38          | 0.42   | 0.916  | 4.76 |
| $q_m$ (mg/g)   | $k_1$ (g/(mg·min)) | $R^2$ | RMSE |
| 40.73          | 0.02   | 0.957  | 3.34 |
| $C$ (mg/g)     | $K_d$ (mg/(g·min$^{1/2}$)) | $R^2$ | RMSE |
| 14.23          | 9.05   | 0.897  | 2.89 |

Different isotherm models: Langmuir, Freundlich, and Sips, as explained in Section 2.6. The fitting parameters are summarized in Table 2. All models appear to fit the experimental results pretty well. For example, the maximum adsorption capacity ($q_m$) from the experiment was found to be 45.8 mg/g, which is very close to the predicted value from the Langmuir model ($q_m = 43.6$ mg/g). Nevertheless, the best fit belongs to the Sips model ($R^2 = 0.986$). It implies that the diclofenac adsorption on the MCF surface is multilayer adsorption for a low diclofenac concentration. This agrees well with the nitrogen adsorption–desorption analysis (Figure 1d), in which the MCF exhibits a type II N2 adsorption isotherm for multilayer adsorption. However, when the diclofenac concentration is high, the monolayer adsorption is the major mechanism, according to the Sips model.

2.4. Adsorption Kinetics. Figure 5b,c shows the kinetic modeling plots of diclofenac onto the MCF. The MCF dosage and the initial diclofenac concentration were kept constant as 0.50 g/L and 50 mg/L, respectively. The adsorption capacity increases continuously with time up to about 30 min where the adsorption equilibrium is reached (Figure 5b), and the adsorption capacity is around 40 mg/g. The experimental data were fitted with the pseudo-first-order and pseudo-second-order models. The pseudo-first-order model represents the adsorption by diffusion of the adsorbate through a boundary (physical adsorption). The pseudo-second-order model describes the adsorption through a strong interaction force between the adsorbate and the adsorbent via chemical linkages. The adjusted kinetic parameters are summarized in Table 2. The best fit, determined from the $R^2$ and root-mean-square error (RMSE), is the pseudo-second-order model, indicating that the diclofenac adsorption on the MCF surfaces favors the chemisorption process.

Moreover, to study the mass transfer resistance at the boundary layer, which is crucial for the adsorption mechanism, the intraparticle diffusion model was applied by plotting the adsorption capacity versus the square root of time ($t^{1/2}$) (Figure 5c). The fitting parameters based on eq 8 are tabulated in Table 2. The value of C corresponds to the thickness of the boundary layer. If the C value is equal to zero, the linear line is passed through the origin, suggesting that there is no boundary layer. In this case, intraparticle diffusion is considered the only rate-controlling step. As shown in (Figure 5c) and Table 2, the $R^2$ value of the Weber and Morris intraparticle diffusion model was low and the regression line does not pass through the origin. Instead, two different segments of the curve could be related to the driving of adsorption diffusion by both the film and intraparticle diffusion.

2.5. Continuous Fixed-Bed Adsorption. Fixed-bed column experiments were studied to mimic the industrial scale of diclofenac adsorption onto an MCF in a continuous system. For this purpose, the performance of the column was evaluated at different concentrations of diclofenac (10 and 30 mg/L), while the other variables were kept constant. Figure 6 shows the effect of diclofenac concentrations on breakthrough curves. It can be seen that increasing the diclofenac concentration from 10 to 30 mg/L leads to the decrease of the exhaustion time from 400 to ca. 300 min. At a lower concentration, the exhaustion time is reduced, and the breakthrough is delayed. This indicates that the adsorption rate is higher at lower concentrations, leading to a faster breakthrough. Additionally, the column performance is evaluated by the breakthrough curves, which show the percentage of diclofenac remaining in the effluent at different times. The curves were obtained by plotting the dimensionless concentration of diclofenac in the effluent ($C_e/C_0$) against the dimensionless time ($t/T$), where $C_0$ is the initial concentration, $C_e$ is the concentration at time $t$, $T$ is the exhaustion time, and $t$ is the time elapsed.

Figure 6. Effect of adsorbate concentrations (10 and 30 mg/L) on breakthrough curves of diclofenac adsorption onto MFC (flow rate: 0.54–0.56 mL/min and MFC amount: 20 mg, pH: 6.41, and T: 22 °C).
diclofenac concentration, a longer time is required for the full saturation of the adsorbent due to the slower transport of lesser adsorbate molecules. Consequently, the breakthrough curve was extended near the saturation zone at a lower concentration. From a technical point of view, the gentle slope of 10 mg/L is less favorable than the steeper slope of 30 mg/L due to a wider mass transfer zone. Table 3 represents the parameters of columns operated under different diclofenac concentrations. With increasing the initial diclofenac concentration, the values of q_t and q_bed were increased from 1.08 to 1.34 mg and from 54 to 67 mg/g, respectively. Better column performance toward the maximum adsorption capacity at a higher diclofenac concentration could be due to a larger concentration gradient between the adsorbate and the adsorbent, which creates a greater mass transfer driving force. The similar pattern of increasing column adsorption capacity (from 3.44 to 7.12 mg/g) in response to increasing adsorbate concentrations (from 1 to 5 mg/L) has been reported by Feizi, Sarmah, and Rangsivek. Also, a decrease in the treated effluent (from 332 to 200 mL) and an increase in the total removal efficiency of the column (from 32.7 to 22.5%) were observed by increasing the diclofenac concentration, which could be related to a faster saturation of the MCF at a higher adsorbate concentration.

2.6. Adsorption Mechanism. Understanding the adsorption mechanism is important for identifying the fundamentals of adsorption and evaluating the commercial applicability of an adsorbent. In this regard, the physicochemical properties and structural features of the adsorbent and the adsorbate have critical roles in the adsorption mechanism. Accordingly, the results obtained from the SEM, Brunauer–Emmett–Teller (BET) analysis, FTIR analysis, pH of point of zero charge (pH_{pz}), and pK_a values were applied to describe the possible mechanisms of diclofenac adsorption onto the MCF adsorbent. Figure 7 shows pore-filling, complexation, and electrostatic, hydrophobic, and π–π interactions as the possible mechanisms in this study. The SEM image (Figure 1a) and BET analysis (Figure 1d) revealed that MCF is a porous material with a high surface area. Nanofibers with a three-dimensional structure of the MCF provide excellent physical adsorption sites for diclofenac molecules. As shown in Figure 5b, the experimental adsorption capacity was 19.58 mg/g after 30 s, which was almost half of the maximum adsorption capacity (43.42 mg/g) after 180 min. The high adsorption amount of diclofenac onto the MCF at the beginning of the process can be attributed to the fast occupation of empty pores of the adsorbent. Electrostatic interaction could also describe the adsorption mechanism according to the pK_a value of the adsorbate, pH_{pz} of the adsorbent, and pH of the experiment. The value of pH_{pz} of the MCF adsorbent was measured as 10.22. The surface charge of the MCF is negative at pH higher than pH_{pz} and it is positive at pH lower than pH_{pz}. On the other hand, the charge state of adsorbate molecules is defined according to their pK_a values. The pK_a values of diclofenac is 4.15. At pH above pK_a, diclofenac molecules are negatively charged because of the dissociation of the molecules into carboxylate anions. Here, the experiments were conducted at an initial solution pH of 6.41. At this pH, diclofenac molecules exist in an anionic form due to the deprotonation of −COOH groups in their chemical structure. In contrast, the surface of the MCF is positively charged at the same pH, which can attract the negatively charged species of diclofenac. Therefore, strong electrostatic attraction between the adsorbent and the adsorbate is a highly possible mechanism.

Table 3. Fixed-Bed Parameters for Diclofenac Adsorption onto MCF (Flow Rate: 0.54–0.56 mL/min and MFC Amount: 20 mg, pH: 6.41, and T: 22 °C)

| C_0 (mg/L) | M (mg) | V_total (mL) | t_total (min) | Q (mL/min) | q_total (mg) | Y (%) | V_eff (mL) | C_eq (mg/L) |
|---|---|---|---|---|---|---|---|---|
| 9.96 | 20 | 332 | 569 | 0.58 | 1.08 | 54 | 3.31 | 32.66 | 332 |
| 29.78 | 20 | 200 | 372 | 0.54 | 1.34 | 67 | 5.96 | 22.50 | 200 |

Figure 7. Proposed adsorption mechanism for diclofenac onto MCF.
Hydrophobic and π–π interactions could be the other mechanisms involved in diclofenac adsorption onto MCF. Hydrophobicity refers to the tendency of a substance for the minimum contact with water molecules due to its nonpolar properties. Hydrophobicity is determined by the octanol/water partition coefficient (log K_{ow}). Diclofenac sodium with a high value of log K_{ow} (3.91) is considered a hydrophobic compound.\(^{68}\) It implies that diclofenac molecules have a lower affinity with the aqueous phase and so would better adsorb onto MCF pores. On the other hand, the water contact angle of the pristine carbon fiber and MCF were measured as 98.6 and 107°, respectively (data not shown). The findings showed that the synthesized carbon fibers are hydrophobic (water contact angle ≥ 90°), and coating of the carbon fiber with magnetic nanoparticles slightly increased the hydrophobicity of MCF. In addition, the low ratio of O/C (0.38) evaluated by EDS analysis showed less hydrophilicity and more aromaticity of MCF. Therefore, hydrophobic interaction between diclofenac and MCF is another possible adsorption mechanism. In addition to hydrophobic interaction, the adsorption can occur through π–π electron donor–acceptor interactions between the aromatic rings (C=C bonds) of the MCF (Figure 1f) and the aromatic rings present in the diclofenac molecule.\(^{69}\)

Complexation between distributed magnetic iron nanoparticles on the surface of the MCF and carboxylic acid groups of diclofenac molecules could also participate in drug removal from water. Zhao, Liu, and Qin reported that bidentate \(^{70}\) effects of diclofenac molecules could also participate in drug removal from water. Zhao, Liu, and Qin reported that bidentate interactions could be the other mechanism of diclofenac adsorption onto MCF. The parameters of the fixed-bed column study revealed that the faster column saturation and the higher maximum adsorption capacity of the column occur at a higher diclofenac concentration.

### 3. CONCLUSIONS

Bacterial cellulose was used for fabricating a new magnetic carbon nanofiber by the facile coprecipitation method. Field emission scanning electron microscopy (FESEM), EDS, FTIR, XRD, and BET were employed for the characterization of the synthesized material. SEM images showed that the surface of carbon nanofibers is uniformly coated with Fe₃O₄ nanoparticles, which was furthermore confirmed by EDS analysis. Using bacterial cellulose with an aerogel structure as a precursor led to a porous structure of the synthesized MCF with a high surface area (222.3 m²/g). The distribution of mesopores and micropores on the surface of MCF was confirmed by BET analysis and SEM images. FTIR analysis revealed that the MCF consists of aliphatic, aromatic, and conjugated carbon doped with magnetic nanoparticles. In adsorption studies, it was observed that the interactive effects of MCF dosages, diclofenac concentrations, and contact times affect the removal efficiency and adsorption capacity, significantly. The Sips model was the most suitable isotherm model to describe diclofenac adsorption onto the MCF that implies multilayer adsorption of the adsorbate onto the adsorbent at a low diclofenac concentration. Well-fitting of experimental data to the pseudo-second-order kinetic model showed the chemisorption nature of diclofenac adsorption by MCF. The parameters of the fixed-bed column study revealed that the faster column saturation and the higher maximum adsorption capacity of the column occur at a higher diclofenac concentration.

4. MATERIALS AND METHODS

#### 4.1. Chemicals and Bacterial Strain

Bacterial strain (Komagataeibacter nataicola, TISTR 975) was purchased from the Thailand Institute of Scientific and Technological Research. Anhydrous D-glucose, 99% (CAS no. 50-99-7), and yeast extract powder, ≥95 (CAS no. 8013-01-2), were purchased from Thermo Scientific and HiMedia, respectively. Ferric chloride hexahydrate, 99% (CAS no. 10025-77-1), ferrous chloride tetrahydrate, ≥99% (CAS no. 13478-10-9), and sodium hydroxide, 99% (CAS no. 1310-73-2), were purchased from QReC, Merck, and RCI Labscan, respectively. The pharmaceutical used in this work was diclofenac sodium salt, ≥99% (CAS no. 15307-79-6), purchased from Sigma-Aldrich. All of the chemicals were of analytical grade and were used without further purification.

#### 4.2. Preparation of BC Aerogels

The BC hydrogel was fabricated from the cultivation of bacteria in a culture medium consisting of anhydrous D-glucose (100 g) and a yeast extract powder (10 g) in deionized water (1 L). The cultivation was controlled under a static condition at 30 °C for 14 days. The BC pellicle was then collected and purified in boiling water twice (for 1 h each time). After that, it was soaked in a NaOH solution (0.5 M) for 15 min. Afterward, it was further soaked in a NaOH solution (1.25 M) for 24 h to remove any impurities or contaminants. Finally, the BC was thoroughly washed with water until pH neutral to remove the remnant NaOH. The purified BC hydrogel was converted to the BC aerogel by freeze-drying and stored at room temperature prior to further use.

#### 4.3. Synthesis of Magnetic BC Aerogels and MCF Aerogels

The magnetic BC was prepared by immersing 3.5 g of a freeze-dried BC aerogel into a mixed solution containing 12.5 mmol FeCl₃·6H₂O (1.35 g) and 7.5 mmol FeCl₂·4H₂O (0.485 g) in 400 mL of deionized water. After 20 min, the white color of the BC pellicle changed to yellow. Then, the solution with the immersed BC was heated to 70 °C and kept at this temperature for 1 h to promote the homogeneous distribution of iron ions. Subsequently, the BC pellicle was transferred to another beaker containing the NaOH solution (100 mM) preheated at 70 °C for the coprecipitation process of iron oxide magnetic nanoparticles. The color of the BC changed rapidly from yellow to black, indicating the formation of magnetic nanoparticles in the BC structure. The magnetic BC was cleansed using deionized water until the pH was neutral. Following the previous step, the freeze-drying technique was applied to synthesize magnetic BC aerogels.

The magnetic BC aerogel was converted into a magnetic carbon fiber (MCF) aerogel through pyrolysis. The sample was placed in a tubular furnace and pyrolyzed with two-step heating in an argon atmosphere. The furnace was first heated to 500 °C (2 °C/min) and kept at this temperature for 1 h. The temperature was further increased to 700 °C (5 °C/min) and held for 2 h. The system was cooled to room temperature under an argon atmosphere. Finally, the obtained MCF aerogel pellicel was powdered using a blender before applying in adsorption experiments.

#### 4.4. Characterization of an Adsorbent

The adsorbent (MCF powder) was subjected to several characterization techniques. The surface morphology was studied using a field emission scanning electron microscope (FESEM) (JSM-7900F, JEOL). The distribution of iron particles in the MCF was performed using a field emission transmission electron microscope.
microscope (FETEM) (TALOS F200X, Thermo Scientific). The magnetization of the material was studied using a vibrating sample magnetometer (VSM) (VersaLab instrument, Quantum Design). The chemical composition was analyzed by energy-dispersive X-ray spectroscopy (EDS) equipped with the FESEM, while the functional groups were investigated using Fourier transform infrared (FTIR) spectroscopy (Frontier, Perkin Elmer). X-ray diffraction (XRD) (D8 Advance, Bruker) was used to collect information on the phase and the crystalline structure. The pore size and the surface area were measured using a surface area and porosity analyzer (Tristar II Plus, Micromeritics). Raman spectra were measured on a Thermo Scientific DXR3xi Raman Imaging Microscope (DXR3xi, Thermo Scientific) using a laser wavelength of 532 nm. All experiments were conducted in duplicate and mean values together with standard deviation (SD) are reported.

4.3. Adsorption Isotherm Studies. After the optimization test, isotherm experiments were performed with different initial diclofenac concentrations (1–50 mg/L) at a constant contact time (180 min) and MCF dosage (0.50 g/L). Langmuir (eq 4) and Freundlich (eq 5) as two-parameter isotherm models and Sips (eq 6) as a three-parameter isotherm model were applied to describe the adsorption mechanism of diclofenac onto MCF powders using the following equations

\[ q_e = \frac{q_m K_s C_e}{1 + K_s C_e} \]  

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

\[ q_e = \frac{K_s C_e^\beta}{1 + a_s C_e^\beta} \]

where \( q_m \) is the maximum adsorption capacity (mg/g), \( K_s \) is the Langmuir isotherm constant (dm^3/mg), \( K_f \) is the Freundlich isotherm constant (L/(mg)^1/n), 1/n is the adsorption intensity, \( K_s \) is the Sips isotherm constant (L/g), \( a_s \) is the Sips isotherm constant (L/mg), and \( \beta \) is the Sips isotherm exponent.

4.4. Adsorption Kinetic Studies. The adsorption kinetics reveals the mechanism of the adsorbate uptake into the adsorbent, optimum condition, and the possible rate-controlling step. In this work, a kinetic study was conducted at different initial times (0.5–180 min), while the amount of the MCF dosage (0.50 g/L) and initial diclofenac concentrations (50 mg/L) were kept constant. The pseudo-first-order rate equation (PFOR) (eq 6), the pseudo-second-order rate equation (PSORe) (eq 7), and the resistance to intraparticle diffusion equation (RIDE) (eq 8) kinetic models based on the following equations were used to fit experimental data

\[ q_t = q_e \left(1 - e^{-kt}\right) \]  

\[ q_t = \frac{q_e^2 k_s t}{(1 + q_e K_s t)} \]  

\[ q_t = K_{id} t^{0.5} + C \]

where \( q_t \) is the adsorption capacity at time (mg/g), \( q_e \) is the adsorption capacity at equilibrium (mg/g), \( k_s \) is the pseudo-first-order rate constant (1/min), \( t \) is contact time (min), \( k_{id} \) is the pseudo-second-order rate constant (g/(mg-min)^1/2)), \( K_{id} \) is the intraparticle diffusion rate constant (mg/(g-min^1/2)), and \( C \) is a constant related to the boundary layer thickness (mg/g).

4.6. Fixed-Bed Column Adsorption. The column experiments were designed to simulate the industrial water treatment process. Column studies were actuated with the Omnifit EZ chromatography column (100 mm height with a 6.6 mm inner diameter). Continuous adsorption mode experiments were carried out at different initial diclofenac

the desired values using 0.1 M NaOH and 0.1 M HCl solutions. Then, 10 mL of a diclofenac solution was added into 12 mL glass tubes containing 5 mg of the MCF powder. The samples were agitated at 150 rpm for 3 h at room temperature (around 22 °C). After that, the final concentration of the diclofenac solution was analyzed using a UV–vis spectrophotometer. Experiments were conducted in duplicate and mean values together with standard deviation (SD) are reported.

4.5. Adsorption Studies. 4.5.1. Batch Experiments. Batch adsorption experiments were investigated to reveal the interactive effects of three levels of three variables including MCF dosages (0.25, 0.50, and 0.75 g/L), initial diclofenac concentrations (10, 30, and 50 mg/L), and contact times (20, 70, and 120 min) on the removal efficiency and adsorption capacity. These experiments were conducted in a 12 mL glass tube containing a known amount of the adsorbent dosage and a certain volume of the adsorbate. The initial pH (without adjustment) and the desired initial concentration of the adsorbate solution were recorded before adding to the adsorbent. After mixing a diclofenac solution and the MCF powder, the mixture was shaken at a constant temperature (approximately 22 °C) (agitation speed 150 rpm) using an incubator shaker (KS 4000 I control, IKA). Immediately after the determined time, the adsorbent was filtered out using a syringe filter equipped with a 0.45 μm membrane. The concentration of diclofenac in the filtrate was measured using an ultraviolet–visible (UV–vis) spectrophotometer (Cary 5000 UV–vis–NIR, Agilent Technologies) at a wavelength of 276 nm. All experiments were conducted in duplicate and average values were reported. Consequently, the diclofenac removal efficiency (%) and the diclofenac adsorption capacity of the MCF adsorbent were calculated from eqs 1 and 2

\[ \text{removal efficiency} = \frac{(C_0 - C_e)}{C_0} \times 100 \]  

\[ q = \frac{(C_0 - C_e)V}{m} \]  

where \( C_0 \) is the initial concentration of diclofenac (mg/L), \( C_e \) is the diclofenac concentration at equilibrium (mg/L), \( C_i \) is the concentration of diclofenac (mg/L) at sampling time, \( q \) is the diclofenac adsorption capacity (mg/g) at sampling time, \( m \) is the mass of MCF (g), and \( V \) is the volume of the diclofenac solution (L).

4.5.2. Effect of Solution pH. The effect of the initial solution pH on the adsorption capacity was measured under six different pH values, viz., 4, 5, 6, 7, 8, and 9. For this purpose, the initial pH of a 10 mg/L diclofenac solution was adjusted to
concentrations (10 and 30 mg/L) and a constant flow rate of 0.5 mL/min and an adsorbent amount of 20 mg. The diclofenac solution was pumped through the column from top to bottom with a peristaltic pump. The diclofenac solution that passes through the column was collected at certain time intervals, and the residual concentration of diclofenac was measured by a UV–vis spectrophotometer. Several parameters can be evaluated from the column study as expressed in the equations shown below

\[ q_{\text{total}} = \frac{Q}{1000} \int_{t=0}^{t=\text{total}} C_{\text{ads}} \, dt \]  
\[ q_{\text{bed}} = \frac{q_{\text{total}}}{M_a} \]  
\[ m_{\text{total}} = \frac{C_0 \times Q \times t_{\text{total}}}{1000} \]  
\[ Y \ (%) = \frac{q_{\text{total}}}{m_{\text{total}}} \times 1000 \]  
\[ V_{\text{eff}} = \frac{Q \times t_{\text{total}}}{C_{\text{eq}} - q_{\text{total}}} \times 1000 \]

where \( q_{\text{total}} \) is the total adsorbed quantity (mg), \( Q \) is the flow rate (mL/min), \( t_{\text{total}} \) is the total time of operation (min), \( C_{\text{ads}} \) is the adsorbed diclofenac concentration on the adsorbent (mg/L), \( q_{\text{bed}} \) is the maximum adsorption capacity of the column (mg/g), \( M \) is the weight of the adsorbent in the column, \( m_{\text{total}} \) is the total amount of the adsorbate delivered to the column system (mg), \( C_0 \) is the initial diclofenac concentration (mg/L), \( Y \) is the total removal efficiency of the column (%), \( V_{\text{eff}} \) is the passed volume of the effluent through the column (mL), and \( C_{\text{eq}} \) is the concentration of diclofenac in the effluent.

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**Notes**

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