Research Article

Magnetic Fe_3O_4 @Chitosan Carbon Microbeads: Removal of Doxycycline from Aqueous Solutions through a Fixed Bed via Sequential Adsorption and Heterogeneous Fenton-Like Regeneration

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The adsorptive removal of antibiotics from aqueous solutions is recognized as the most suitable approach due to its easy operation, low cost, nontoxic properties, and high efficiency. However, the conventional regeneration of saturated adsorbents is an expensive and time-consuming process in practical wastewater treatment. Herein, a scalable adsorbent of magnetic Fe_3O_4 @chitosan carbon microbeads (MCM) was successfully prepared by embedding Fe_3O_4 nanoparticles into chitosan hydrogel via an alkali gelation-thermal cracking process. The application of MCM composites for the adsorptive removal of doxycycline (DC) was evaluated using a fixed-bed column. The results showed that pH, initial concentration, flow rate, and bed depth are found to be important factors to control the adsorption capacity of DC. The Thomas and Yoon-Nelson models showed a good agreement with the experimental data and could be applied for the prediction of the fixed-bed column properties and breakthrough curves. More importantly, the saturated fixed bed can be easily recycled by H_2O_2 which shows excellent reusability for the removal of doxycycline. Thus, the combination of the adsorption advantage of chitosan carbon with catalytic properties of magnetic Fe_3O_4 nanoparticles might provide a new tool for addressing water treatment challenges.

1. Introduction

In the past years, doxycycline (DC) has gradually become one of the most widely used antibiotics in the world especially in human therapy and livestock industry because of its specific antimicrobial properties and minor adverse side effects [1–3]. Regrettably, the metabolism of humans or animals cannot decompose the DC antibiotic thoroughly, and only 20–50% of DC can be absorbed into the organism. Thus, the residues of antibiotics have been frequently detected in soil, surface water, groundwater, and other aquatic environment [4]. It has been verified that exposure to low-level and accumulative DC may lead to a variety of dangerous effects,

including destruction of aquatic photosynthetic organisms and indigenous microbial populations and dissemination into antibiotic-resistant genes among microorganisms [5, 6]. Hereby, DC wastewater has drawn great attention and is especially targeted in the field of wastewater treatment. Compared with the traditional chemical and biological strategies to purify the antibiotic wastewater, the adsorptive removal of antibiotic from aqueous solution is the most suitable approach for the treatment of toxic antibiotic wastewater because of its easy operation, low cost, nontoxic properties, and high efficiency [7, 8]. A series of adsorbents, such as activated carbon [9], clays [10], graphene oxide [11], and zeolites [12], have been exploited extensively and applied widely for

the removal of organic antibiotics. In particular, the utilization of costless, renewable, and environmentally friendly activated carbon (AC) as adsorbents has become popular owing to its abundant porous structure and stable chemical property [13–15]. However, the adsorption of toxic organic compounds with activated carbon only transfers the pollutants from the wastewater to the surface of adsorbents rather than decomposing them, which limited the recycling of the adsorbents. In order to deal with such conundrums, the periodical regeneration by traditional physicochemical approaches should be executed for the pollutant-loaded adsorbents, such as thermal regeneration [16], oxidative catalytic regeneration [17], ultrasound-assisted sorbent regeneration [18], electrochemical method [19], and microwave regeneration [20].

The Fenton oxidation is the most powerful method to decompose organic pollutants because the $\cdot\text{OH}$ generated in the Fenton system (OH , oxidation potential: 2.8 V) is highly oxidative and nonselective, which can destruct many hazardous organic pollutants easily and effectively like azo dye [21], doxycycline [22], p-nitrophenol [23], sulfamethoxazole [24], and polyacrylamide [25]. In contrast, the heterogeneous Fenton oxidation, based on solid-liquid interface reactions, has more advantages than homogeneous Fenton reaction ($\text{H}_2\text{O}_2 + \text{Fe}^{2+}/\text{Fe}^{3+}$) with regard to less sludge formation, expanded pH range, and generation of highly potent chemical oxidants. More importantly, the removal efficiency through heterogeneous Fenton can be increased significantly by an enrichment or preconcentration sorption process and subsequent oxidation of the contaminants [26]. Specifically, organic contaminants are first adsorbed by adsorbents from a large volume of effluent, then separated from the wastewater system and mineralized by advanced oxidation. At the same time, the pollutant-loaded adsorbents are regenerated. For example, in our previous study, raspberry-like Fe_3O_4 @yeast shows excellent reusability for the removal of azo dyes because of the consecutive and synergistic effect of yeast biosorption and Fe_3O_4 nanoparticles [27].

Herein, we synthesized magnetic Fe_3O_4 @chitosan carbon microbeads (MCM) by a simple thermal cracking process under a nitrogen atmosphere at 350°C, aimed at combining the catalytic property of Fe_3O_4 with the adsorption capacity of chitosan carbon microbeads. Based on the XRD, SEM, and FT-IR characterization results, a possible mechanism for the formation of MCM was proposed. A fixed-bed column was employed to investigate the removal efficiency of doxycycline. The effects of pH, initial concentration, flow rate, and bed depth were also analyzed. Afterward, the regeneration/recycling tests were carried out by triggering the Fenton oxidation in the presence of H_2O_2 solution.

2. Materials and Methods

2.1. Materials. Chitosan, Fe_3O_4 nanoparticles, glutaraldehyde (25% (v/v)) aqueous solution, and acetic acid (36% (v/v)) were provided by Xi'an Chemical Agent Corp. All chemicals used in this work were of analytical grade and used without further purification. Deionized water was used throughout this study.

2.2. Preparation of Samples. 0.3 gram of chitosan was dissolved in 10 mL of 1% aqueous acetic acid solution to prepare the chitosan solution. Then, 0.9 gram of Fe_3O_4 nanoparticles was slowly added into the prepared chitosan solution. The homogenous solution was injected into a gently stirred sodium hydroxide solution using a syringe to form magnetic microspheres. After magnetic stirring for 4 h, the products were harvested by filtration, followed by washing with a copious amount of distilled water until the pH value was 7. Then, these magnetic microbeads were immersed in a cross-linking agent, 5% glutaraldehyde, for 8 h at room temperature. The cross-linked microbeads were filtered, washed, and dried at 60°C for 12 h. Finally, the resulting products were pyrolyzed in a tubular reactor at 350°C for 40 min under a nitrogen atmosphere. The synthesis of chitosan carbon microbeads (CSM) was also carried out in accordance with the above steps but without the adding of Fe_3O_4 .

2.3. Material Characterization of Samples. The size and surface morphology of the samples were determined by a Philips XL 30 field emission scanning electron microscope (FE-SEM). The crystallographic structure of the samples was measured by X-ray diffraction (XRD) on a Rigaku D/MAX-3C diffractometer operated at a voltage of 40 kV and a current of 20 mA, at a 0.028 scan rate with $\text{Cu K}\alpha$ radiation. Fourier transform infrared (FT-IR) spectra of samples were recorded on a Bio-Rad FTS135 spectrometer in the range 500–4000 cm^{-1} using a KBr wafer technique, to study the functional groups of the samples. To obtain N_2 adsorption/desorption curves (BET curves), adsorption-desorption experiments using liquid nitrogen were performed on a Micromeritics surface analyzer (WBL-8XX).

2.4. Continuous Fixed-Bed Experiments. The fixed-bed adsorption experiments were performed in up-flow columns with an internal diameter of 0.6 cm and a length of 15 cm. The influences of different initial concentrations of DC (20, 25, and 30 mg/L), flow rates (1.1, 2.1, and 3.1 mL/min), pH (2, 4, 7, 9, and 11), and bed depths (0.8, 1.2, and 1.6 cm) were studied. The pH of the DC solutions was adjusted by the addition of NaOH (0.1 mol/L) and HCl (0.1 mol/L). In order to exclude the trapped air and wet the porosity of activated carbon, water was pumped into the column at the flow rate of 8 mL/min for 10 min before starting the experiment. The column effluent samples were taken out at regular time intervals, and the concentration was analyzed by a Jenway 6405 UV-vis spectrophotometer at 351 nm.

The dynamic adsorption behavior of fixed-bed columns was investigated in terms of analyzing the shape of breakthrough curves. And the experimental breakthrough curves determined as the ratio of C_t/C_0 vs. t (min) (where C_0 is the inlet sample concentration, C_t is the outlet sample concentration, and t is the elapsed time) represent the loading of DC onto Fe_3O_4 /chitosan carbon microspheres. From a practical point of view, operation of the column was stopped when the concentration in the effluent is higher than 90% of the influent concentration because of the establishment of the saturation time, t_s .

SCHEME 1: Schematic of the adsorption and in situ regeneration mechanism of MCM in the removal of DC.

The volume of the effluent, V_{eff} (mL), was defined as

$$V_{\text{eff}} = Q \cdot t_{\text{total}}, \quad (1)$$

where t_{total} is the total flow time in min and Q is the flow rate which circulates through the column in mL/min.

The area above the breakthrough curve means the total mass of DC adsorbed, and q_{total} , in mg, was evaluated through the following equation:

$$q_{\text{total}} = \frac{Q}{1000} \int_{t=0}^{t=t_{\text{total}}} (C_0 - C_t) dt. \quad (2)$$

Equilibrium DC uptake per unit mass of adsorbent, q_e (mg/g), was calculated using the following equation when steady-state conditions were reached:

$$q_e = \frac{q_{\text{total}}}{m}, \quad (3)$$

where m (g) is the mass of adsorbent in the column.

The total amount of DC passed through the column m_{total} (mg) can be estimated from

$$m_{\text{total}} = \frac{C_0 \cdot Q \cdot t_{\text{total}}}{1000}. \quad (4)$$

2.5. Heterogeneous Fenton Oxidation Regeneration. After each adsorption cycle, the sorbent bed was washed by distilled water in the upward direction at a suitable flow rate (2.1 mL/min) to remove the residual DC. Then, the regeneration experiment was carried out by injecting various aqueous solutions through the column bed in an upward direction at a flow rate of 1.1 mL/min for 1.5 h. After the heterogeneous Fenton-like reaction, the column was rinsed again to remove the residual H_2O_2 . Finally, the bed was reused for the next adsorption/regeneration cycle, up to three consecutive cycles.

3. Results and Discussion

3.1. Formation Procedure of MCM and Characterization. The formation of magnetic Fe_3O_4 @chitosan carbon microbeads by alkali gelation-thermal cracking route was proposed in Scheme 1.

According to previous literatures, chitosan is insoluble in water but soluble in diluted acidic solution below its pKa (~6.3), in which the amine groups ($-\text{NH}_2$) of chitosan can be facilely converted into the soluble protonated form ($-\text{NH}_3^+$) [28]. In the current study, the chitosan was dissolved in 1% acetic acid with vigorously stirring to obtain a homogeneous quaternized chitosan solution and then intertwined together to form a three-dimensional network linked by hydrogen bonding or Van der Waals forces. Owing to the fact that the amine groups ($-\text{NH}_2$) of chitosan polymers were protonated easily, the chitosan network tends to expand due to the repulsive force among the protonation amine ions ($-\text{NH}_3^+$). Such network expansion provides a great opportunity for Fe_3O_4 nanoparticles to be fixed onto the linear scaffold of chitosan molecules. Thereafter, the mixture containing Fe_3O_4 nanoparticles and chitosan was injected into NaOH solution drop by drop. Under alkaline condition, $-\text{NH}_3^+$ groups were deprotonated and converted into insoluble forms ($-\text{NH}_2$) [29], resulting in the disappearance of electrostatic repulsion between chitosan molecules. Consequently, the magnetic Fe_3O_4 @chitosan hydrogel microbeads were formed through the sharing of the lone electron pairs from the nitrogen atom in amine with Fe irons [30, 31]. Then, the magnetic Fe_3O_4 @chitosan hydrogel microbeads were pyrolyzed in a tubular reactor at 350°C for 40 min under a nitrogen atmosphere to obtain MCMs. The content of Fe_3O_4 can be controlled precisely by tuning the dosage of reactants. Compared with the classical impregnation method, the present route by alkali gelation provides a better choice to synthesize functional composites containing Fe_3O_4 nanoparticles and carbon-related materials with higher content of Fe irons.

From the above analysis, chitosan polymers play a significant trifunctional role in the formation of the Fe_3O_4 @chitosan

composite. Firstly, the native entanglement or cross-linking property of chitosan chains helps Fe_3O_4 nanoparticles reunite together tightly and become a stable three-dimensional network due to the strong hydrogen bonding or Van der Waals forces. Secondly, the water absorption capacity of the three-dimensional network is partly retained, which is beneficial to the formation of pores or channels in the MCM during the thermal cracking process. Thirdly, chitosan polymers can act as a carbon source, providing lots of active sites for the adsorption of pollutants. Similarly, the Fe_3O_4 nanoparticles play two vital roles in the magnetic Fe_3O_4 @chitosan carbon microbeads. On the one hand, the mechanical stability of MCM can be strengthened by embedding hard Fe_3O_4 nanoparticles into chitosan. On the other hand, part of chitosan is replaced by Fe_3O_4 nanoparticles, offering additional catalytic active sites on the MCM substance. From this point of view, the prepared MCMs are demonstrated to not only preserve the adsorption performance of chitosan carbon but also possess an in situ regeneration ability of Fe_3O_4 nanoparticles.

The incorporation of Fe_3O_4 nanoparticles into the CSM matrix can be observed straightforwardly from the microscopy photos. The optical microscopy photos of MCM and CSM are presented in Figures 1(a) and 1(b), respectively. It can be seen that the MCMs inherited the spherical shape after the addition of Fe_3O_4 nanoparticles into the chitosan hydrogel microbeads. Correspondingly, the color of MCM substrates changed from white to black. Figures 1(a) and 1(b) show that the MCM outer surface was rough and interspersed with small bumps while the CSM outer surface was very smooth and flat. The loading of Fe_3O_4 nanoparticles onto the MCM scaffold led to a rough topographical surface for the CSM substrate. Such unique regular surface morphology usually contributes to the relatively more catalytic active sites, which is expected to favor the adsorption of contaminants. The absence of scattering Fe_3O_4 nanoparticles around the composite CSM implies a strong adhesion between the MCM scaffold and the Fe_3O_4 nanoparticles.

The incorporation of Fe_3O_4 nanoparticles into the CSM matrix can be further verified from the SEM images. SEM images of Fe_3O_4 nanoparticles, CSM, and MCM are shown in Figures 1(c)–1(h). Figures 1(c) and 1(d) display the primitive Fe_3O_4 nanoparticles, which exhibit irregular shape with the length of 0.2–0.3 μm . The inset image in the bottom right corner of Figures 1(e) and 1(g) demonstrated that both MCM and CSM samples were spherical. The average diameter of MCM was around 1.5–2.0 mm, which was much bigger than that of CSM about 1.2–1.5 mm, implying that the successful decoration of chitosan carbon with Fe_3O_4 nanoparticles enlarged the diameter size. On the other hand, the Fe_3O_4 nanoparticles in MCM also provided a mechanical strength against shrinkage during drying and consequently make the MCM denser. In contrast, the drastic shrinkage phenomenon happened under absolute drying conditions on the surface of CSM which is smaller in diameter. Figure 1(e) presents a typical SEM micrograph of CSM. It can be observed that the surface of CSM is completely smooth and flat. Figure 1(f) shows that the internal morphology of CSM exhibits an ordered incompact structure probably caused by the thermal cracking process [25, 32]. However, with the introduction of magnetic

Fe_3O_4 nanoparticles, there are significant changes on the outer surface morphology of MCM. The SEM micrograph of MCM (Figure 1(g)) shows a rough topographical surface decorated with some small bumps, which increase the surface area of the MCMs and provide more active sites for the adsorption of pollutant molecules. Hereby, the MCM adsorbent should have a better adsorption performance compared with the CSM. At higher magnification (Figure 1(h)), some clusters resulted from the aggregation of Fe_3O_4 nanoparticles distributed evenly in the MCM's core, suggesting that the Fe_3O_4 nanoparticles were successfully embedded into the MCM substrate.

To explain chemical binding between Fe_3O_4 and CSM, the Fourier transform infrared (FTIR) spectra of the pure Fe_3O_4 , CSM, and MCM were recorded. In Figure 2, the IR spectrum of MCM was very similar to that of CSM, indicating that the introduction of magnetic particles did not destroy the function groups of chitosan. For CSM, the peak at 3366 cm^{-1} resulted from axial stretching vibration of O-H superimposed on the N-H stretching band and intermolecular hydrogen bonds of the polysaccharide [33], and the adsorption peaks at 2919 and 2874 cm^{-1} are assigned to the stretching vibration of C-H. The typical band of primary amine groups ($-\text{NH}_2$) appears at 1655 cm^{-1} [34]. The biosorption bands around 1075 and 1027 cm^{-1} display the stretch vibration of the C-O bond. For magnetic Fe_3O_4 nanoparticles, the peak at 636 cm^{-1} relates to the Fe-O group [35]. The formation of a new peak at 636 cm^{-1} in MCM is related to the blending of Fe_3O_4 nanoparticles. The IR spectrum indicates that chitosan carbon and Fe_3O_4 both existed in MCM, and the Fe_3O_4 has been embedded into the MCM successfully. Notably, the N-H stretching vibration has a blue shift to 1637 cm^{-1} due to the sharing of the lone electron pairs from the nitrogen atom in amine with Fe iron [30, 31].

Figure 3 shows the XRD patterns of chitosan carbon, pure Fe_3O_4 nanoparticles, and the magnetic Fe_3O_4 /chitosan composite microspheres (MCM). Diffraction peaks of pure Fe_3O_4 nanoparticles at 2θ of 18.4° , 30.3° , 35.6° , 37.3° , 43.2° , 53.4° , 57.2° , and 62.9° corresponded to (110), (220), (311), (222), (400), (422), (511), and (440) in the face center-cubic phase of Fe_3O_4 , which agree with the literature data [36]. In Figure 3, chitosan is seen to show only a typical peak at around $2\theta = 18.3^\circ$. This broad peak indicates the existence of amorphous structure [37]. As expected, the broad peak at $2\theta = 18.3^\circ$ of MCM originates mainly from the amorphous structure of chitosan. Other diffraction peaks emerging in the XRD pattern of MCM are very close to the feature peak of Fe_3O_4 nanoparticles, which indicates the existence of Fe_3O_4 nanoparticles in the MCM, and no other diffractions are found, meaning the high purity of the samples.

The nitrogen adsorption isotherm of MCM is shown in Figure 4. Nitrogen adsorption isotherm is measured over a relative pressure (P/P_0) range from approximately 10^{-7} to 1. The BET surface area of MCM is estimated to be $3.278\text{ m}^2/\text{g}$ by the Brunauer-Emmett-Teller (BET) equation. A sharp increase in the isotherm at a high relative pressure indicates capillary condensation in the mesopores. Nonlocal density functional theory (NLDFT) [38] was applied to calculate the pore size distribution of MCM (inset image). It

FIGURE 1: Optical microscopy photos (40×) of MCM (a) and CSM (b); FE-SEM images: (c, d) Fe_3O_4 nanoparticles, (e) dissected CSM, (f) CSM under high magnification, (g) dissected MCM, and (h) MCM under high magnification.

FIGURE 2: FT-IR spectra of Fe_3O_4 nanoparticles, CSM, and MCM.

FIGURE 3: XRD spectra of Fe_3O_4 nanoparticles, CSM, and MCM.

reveals that the MCM has a high proportion of microspore volume and a low average pore diameter, and the average microspore volume is evaluated to be 0.0083 cc/g.

3.2. Removal of Doxycycline from Aqueous Solutions through a Fixed Bed via Adsorption. The fixed-bed adsorption requires very few devices and low operational cost. The fixed-bed columns are essential towards the industrial scale

design and scale-up of the continuous system for required applications and performances [39]. Generally, the column process is continuous and the influent wastewater comes in touch with a certain amount of adsorbents, hereby affording room for a large volume of flowing polluted fluid [40]. To evaluate the effect of operating conditions on the adsorption of DC, a batch of adsorption experiments including the effect of pH, initial feed solution concentration (C_0), bed depth (Z),

FIGURE 4: Nitrogen adsorption isotherm of the MCM.

and flow rate (Q) has been conducted. The results are displayed in Table 1.

3.2.1. pH Effect on the Adsorption Performance. pH is one of the dominant factors that affect the removal efficiency of antibiotic, because pH can affect the speciation of a DC molecule in solution and the surface charge of the adsorbent. The pH affects the prevalent chemical mechanisms by controlling the electrostatic interaction between the adsorbent and organic molecules, consequently changing the removal rate of DC from the aqueous solution and the breakthrough curves [41]. Thus, the effect of pH was investigated by varying the pH of the aqueous DC solution from 2.0 to 11.0, while the DC concentration, flow rate, and bed height were kept constant at 25 mg/L, 1.1 mL/min, and 1.2 cm, respectively. Breakthrough curves for DC uptake at various pH values are presented in Figure 5(a). The results extracted from the breakthrough curves are listed in Table 1. As can be seen in Table 1, the adsorption capacity of DC shows a significant increase from 0.934 to 4.816 mg/g with the increase in pH values from 2.0 to 11.0. From Figure 5(a), much sharper breakthrough curves of DC adsorption onto the MCM at lower pH conditions are observed. It is clear that the breakthrough and exhaustion times increase with the increase in pH.

Two vital factors are likely responsible for the remarkable effect of pH on DC adsorption. Firstly, pH can change the surface charge of ionizable organic compounds in chemical speciation [42, 43], and DC is an amphoteric molecule with ionizable groups such as tricarboxyl amide, phenolic diketone, and dimethyl amine moieties, which has three pKa values (3.5, 7.7, and 9.5) [43, 44]. In addition, DC exists in various forms in aqueous solution and its predominant species forms are different, showing as cations, zwitterions, and anions under acid, neutral, and alkaline conditions, respectively. Below pH 3.5, the DC molecule exists as DC^+ due to the protonation of the dimethyl ammonium group, while in the pH between 3.4 and 7.7, DC^0 appears and becomes a predominant form. As pH increases, this form transforms to anion (DC^- and DC^{2-} , respectively, above pH 7.7 and 9.5), owing to the deprotonation of phenolic

diketone moiety and tricarboxyl system. Secondly, in acidic condition, the hydrogen atoms can protonate amine groups of chitosan [45] forming a positively charged surface on MCM. As a result, the electrostatic repulsion between the positive DC ions and MCM with the positively charged surface is against the sorption process, whereas the protonation reaction gets weak with increasing the pH value and the sorption capacity is enhanced. Finally, when the pH is above 9, a good adsorption performance is obtained. This is due to the excellent adsorption capacity of MCM with abundant absorptive sites and outstanding porosity. The relatively ample activated sites and the porous structure of adsorbent can supply more binding sites to remove more organic contaminants from aqueous solution.

3.2.2. Effect of DC Concentration, Bed Depth, and the Feed Flow Rate. As the DC concentration decreases, the adsorption capacity of MCM increases, reaching saturation in the fixed bed only when the DC concentration is 30 mg/L, while at other concentrations, especially at 20 mg/L, the saturated time has been prolonged to achieve adsorption equilibrium (Figure 5(b)). When C_0 increased from 20 to 30 mg/L, the equilibrium adsorption capacity (q_e) decreased from 3.128 to 2.045 mg/L (Table 1). This can be explained that at higher DC concentration, the bed exhaustion was reached more rapidly before the saturation of MCM caused by a relatively smaller depth of the mass transfer zone. Moreover, the adsorption process depends on the intraparticle diffusion of the DC. On the other hand, increasing influent concentration leads to the increment of the driving force for the mass transfer for a fixed adsorption zone length [46]. It should be noted that the highest experimental adsorption capacity (4.18 mg/g) was achieved at the lowest C_0 (20 mg/L), which indicated that the adsorption process was favorable at lower solute concentration. The stronger driving force between the solute in the adsorbent and the solute in the solution makes the active sites of the adsorbent consume quickly, and finally an earlier breakthrough time and a sharper breakthrough curve were obtained [39]. The results obtained in the present study are in good agreement with the results obtained by Han et al. [47] where rice husk was used to adsorb methylene blue from the aqueous solution in a fixed-bed absorber at various inlet concentrations.

Figure 5(c) displays the results of the influence of the bed height on the breakthrough time. From Figure 5(c), it can be observed that with the increase in bed height, the breakthrough time increases and the slope of the breakthrough curve decreases, at a flow rate of 1.1 mL/min, a constant feed concentration of 25 mg/L, and a pH of 7. Under this situation, the highest DC adsorption capacity (2.787 mg/g) was obtained at the highest bed depth. The reason may be related to the situation that more effective adsorption on the surface of MCM had occurred with increasing bed depths. The BECT increases from 0.206 to 0.411 min as the bed depth increases, which suggests that more volume of DC solution could be treated and the enhanced contact time makes it possible to remove more contaminants. Furthermore, an increase in the bed depth results in a broadened mass transfer zone where the mass transfer zone formed can reach a deeper area,

TABLE 1: Parameters of Thomas and Yoon-Nelson models.

C_0 (mg/L)	Z (cm)	Q (mL/min)	pH	Thomas model			Yoon-Nelson model		
				$k_T \times 10^3$ (mL/(min·mg))	q_0 (mg/g)	R^2	k_Y (min ⁻¹)	τ	R^2
25	1.2	1.1	11	2.725	5.974	0.994	0.068	55.623	0.994
25	1.2	1.1	9	2.823	4.568	0.982	0.071	42.529	0.982
25	1.2	1.1	7	3.749	3.432	0.984	0.094	32.289	0.984
25	1.2	1.1	4	4.518	2.239	0.977	0.113	20.845	0.977
25	1.2	1.1	2	7.487	0.910	0.962	0.187	8.4716	0.962
20	1.2	1.1	7	4.107	4.168	0.983	0.082	48.139	0.983
25	1.2	1.1	7	3.749	3.432	0.984	0.094	32.289	0.984
30	1.2	1.1	7	2.834	2.168	0.985	0.095	16.806	0.985
25	0.8	1.1	7	4.647	2.487	0.998	0.116	15.286	0.998
25	1.2	1.1	7	3.749	3.432	0.984	0.094	32.289	0.984
25	1.6	1.1	7	2.817	3.538	0.982	0.070	45.545	0.982
25	1.2	1.1	7	3.749	3.432	0.984	0.094	32.289	0.984
25	1.2	2.1	7	4.108	2.959	0.996	0.103	14.429	0.996
25	1.2	3.1	7	5.518	0.840	0.929	0.138	2.775	0.929

and the diffusion phenomena are predominant compared with the axial dispersion phenomena in the mass transfer [48, 49]. In addition, an increase in the bed height leads to a larger specific surface of the adsorbent which provides more available binding sites. As expected, the adsorption capacity increases with an increase in the bed height, since the total surface area of the fixed-bed column increases [50, 51].

The effect of flow rate on DC biosorption by MCM was studied by varying it from 1.1 to 3.1 mL/min, keeping the bed height and initial solution concentration constant at 1.2 cm and 25 mg/L, respectively. A decrease in adsorption capacity from 2.448 to 2.282 mg/g by increasing the flow rate from 1.1 to 3.1 mL/min is shown in Table 1, from which it can be seen clearly that the flow rate has strong effects on the adsorption trend in a fixed-bed column. This behavior can be explained in terms of the fact that the high flow rate cannot provide the DC molecule enough time to migrate from the solution to the adsorbent surface and penetrate into the center of the adsorbent and then bind with the activated sites [52]. In other words, the contact time must be prolonged and the intraparticle diffusion is effective at a lower flow rate. Typical breakthrough curves are plotted in Figure 5(d) where a much sharper breakthrough curve with an increase in the flow rate was observed. An abatement removal efficiency and steeper breakthrough curve occurred, suggesting that the contaminant had inadequate time to react with the functional groups before the adsorption equilibrium is conducted [53]. This is because the adsorption process was affected by limited residence time of the adsorbate in the fixed bed. With increasing the flow rate, the residence time is longer as the DC molecule diffuses into the pore of the adsorbent. Additionally, an increase in the flow rate decreases the external diffusion mass transfer resistance at the surface of the adsorbents, finally leading to a fast saturation and an earlier breakthrough time.

3.3. Breakthrough Model Analysis. The design and scale-up of fixed-bed adsorption columns require the prediction of the

concentration-time profile or breakthrough curve for the effluent [54]. Many mathematical theory models with theoretical rigor are differential in nature and usually involve complex numerical methods. Because of this, in this study, we used the Thomas and Yoon-Nelson models to predict the dynamic performance of the column, which are empirical and semiempirical mathematical models. These semiempirical models are less rigorous than other theoretical models but easier to apply. All the model parameters are listed in Table 2.

3.3.1. Thomas Model. The Thomas model is one of the most popular and widely used to represent the behavior of the adsorption process. This model assumes that the main reason limiting the adsorption in a fixed-bed column is the mass transfer at the interface rather than the chemical reaction [55, 56]. The Thomas model is given in the following equation:

$$\ln \left(\frac{C_0}{C_t} - 1 \right) = \frac{k_T \cdot q_0 \cdot m}{Q} - k_t \cdot C_0 \cdot t, \quad (5)$$

where k_T (mL/(min·mg)) is the Thomas rate constant, q_0 (mg/g) is the predicted adsorption capacity of the fixed-bed column, m (g) is the mass of adsorbent, and Q (mL/min) is the flow rate. C_0 (mg/L) and C_t (mg/L) are the influent and the effluent concentrations of DC at interval time, respectively.

The adsorption capacity of the column q_0 and the Thomas rate constant k_T are determined from the plot of $\ln [(C_0/C_t) - 1]$ against t . The difference of the experimental and predicted adsorption capacity of DC in the fixed-bed columns is found to be not negligible. The fixed-bed columns did not reach their maximum capacity from the predicted results. But from the regression coefficient (R^2) which ranged from 0.929 to 0.998, it can be concluded that the Thomas model fitted the experimental data very well. The value of constant k_T tends to increase as the initial influent DC concentrations decreased from 30 to 20 mg/L, which implies a lower mass transfer and an enhanced adsorption capacity at

FIGURE 5: Breakthrough curve for adsorption of DC at different column conditions: (a) pH ($Z = 1.2$ cm, $Q = 1.1$ mL/min, and $C_0 = 25$ mg/L); (b) initial concentration ($Z = 1.2$ cm, $Q = 1.1$ mL/min, and pH = 7); (c) bed depth ($C_0 = 25$ mg/L, $Q = 1.1$ mL/min, pH = 7); (d) flow rate ($Z = 1.2$ cm, $C_0 = 25$ mg/L, and pH = 7).

a lower concentration. Furthermore, this phenomenon is because of an increase in the influence of mass transfer on the adsorption process [41]. These results suggest that the driving force is mainly coming from the concentration difference between the DC molecule on the sorbent and the DC molecule in the solution. A similar trend has been obtained where the bed depth shows a decrease. As the bed depth decreases from 1.6 to 0.8 cm, the k_T value increases from 2.817 to 4.647 whereas the theory adsorption capacity showed a reverse trend. With the increase in the flow rate, the theory adsorption capacity q_0 decreased but the k_T value increased. This phenomenon supposes that the contact time

is a predominant reason influencing adsorption capacity. The above results indicate that lower initial influent DC concentration, higher bed height, and lower flow rate are favorable for higher adsorption of DC onto MCM in a continuous column process.

3.3.2. Yoon-Nelson Model. The linearized Yoon-Nelson model is presented by the following equation [57–59]:

$$\ln \left(\frac{C_t}{C_0 - C_t} \right) = k_Y \cdot t - \tau \cdot k_Y, \quad (6)$$

TABLE 2: Experimental parameters of adsorptive removal of DC in a fixed bed.

C_0 (mg/L)	Z (cm)	Q (mL/min)	pH	t_{total} (min)	m_{total} (mg)	q_{total} (mg)	q_e (mg/g)	V_{eff} (mL)	EBCT (min)
25	1.2	1.1	11	108	2.970	1.233	4.816	118.8	0.308
25	1.2	1.1	9	93	2.558	0.839	3.281	102.3	0.308
25	1.2	1.1	7	72	1.980	0.627	2.448	79.2	0.308
25	1.2	1.1	4	54	1.485	0.426	1.666	59.4	0.308
25	1.2	1.1	2	30	0.825	0.239	0.934	33.0	0.308
20	1.2	1.1	7	96	2.112	0.801	3.128	105.6	0.308
25	1.2	1.1	7	72	1.980	0.627	2.448	79.2	0.308
30	1.2	1.1	7	63	2.079	0.523	2.045	69.3	0.308
25	0.8	1.1	7	48	1.320	0.396	2.333	52.8	0.206
25	1.2	1.1	7	72	1.980	0.627	2.448	79.2	0.308
25	1.6	1.1	7	96	2.640	0.989	2.787	105.6	0.411
25	1.2	1.1	7	72	1.980	0.627	2.448	79.2	0.308
25	1.2	2.1	7	51	2.678	0.598	2.334	107.1	0.162
25	1.2	3.1	7	30	2.325	0.585	2.282	93.0	0.109

where k_Y is the adsorption rate constant (min^{-1}), τ is the time required to reach 50% adsorbate breakthrough (min), and t is the time (min). The parameters k_Y and τ are obtained from the slope and intercept of the graph between $\ln [C_t/(C_0 - C_t)]$ and time (t).

Table 2 shows the results. The regression coefficient (R^2) values are higher than 0.9. Consequently, the calculated τ values are quite close to the time needed for 50% DC breakthrough from the experiments, which indicates that a good fitting has been obtained. The k_Y values increase with increasing DC concentration due to the increase in the force controlling the mass transfer between the liquid phase and solid phase [47]. In addition, the time necessary to reach 50% of the retention (τ) significantly increases with the decrease in DC concentration. This is because the bed exhaustion occurred more rapidly before the complete saturation of MCM at higher DC concentration. The k_Y values decrease but the 50% breakthrough time τ shows a reverse trend when the bed depth increases. The k_Y values increase and the τ decreases with an increasing flow rate.

3.4. Regeneration of MCM via Heterogeneous Fenton Oxidation Reaction. From an economic standpoint, the reusability of the adsorbents is one of the most important features to exemplify the potential of MCM for real applications. Moreover, both the magnetic and oxidation properties imparted by the mixing Fe_3O_4 nanoparticles are important for practical application. In this study, the regeneration experiments were carried out by using H_2O_2 solution to trigger the heterogeneous Fenton oxidation. According to the contrast experiments, the DC was hardly degraded in the absence of H_2O_2 (or Fe ion).

During the adsorption/regeneration process, the DC molecules are first removed from polluted water by the adsorption process and pre-concentrated on the surface of MCM adsorbent. Then, the regeneration processes are carried out by triggering the heterogeneous Fenton oxidation. Namely, the decomposition of H_2O_2 using Fe_3O_4 nanoparticles as Fenton catalysts was able to generate principal

oxidizing species like $\cdot\text{OH}$ radicals according to the following reactions:

In these ways, the saturated DC molecules on the surface of MCM adsorbent could be oxidized to degradation products.

To investigate the effect of H_2O_2 doses on the regeneration efficiency of MCM, the regeneration process was conducted with different amounts of H_2O_2 . And the performance of the continuous column was evaluated for three consecutive adsorption/regeneration cycles. The DC concentration, flow rate, bed depth, and pH were kept constant at 25 mg/L, 1.1 mL/min, 1.2 cm, and 7, respectively. The experimental results are shown in Figure 6.

In Figure 6, the regeneration efficiency is expressed as

$$\eta = \frac{t_r}{t_f} \cdot 100\%, \quad (9)$$

where η is the regeneration efficiency of the saturated MCM using H_2O_2 , t_r is the total flow time in the regeneration carbon, and t_f is the total flow time in the fresh carbon.

As shown in Figure 6, the regeneration efficiency can be easily controlled by adjusting the H_2O_2 dosage, and the optimal H_2O_2 concentration is 5% in this study. The regeneration efficiency is calculated as 78%, 93%, 72%, and 55% for H_2O_2 dosage in feed of 2%, 5%, 8%, and 11%, respectively. The regeneration efficiency increased with ranging H_2O_2 dosage from 2% to 5% and then decreased with ranging H_2O_2 dosage 5%–11%. This phenomenon can be well explained from two aspects. On the one hand, the Fe ions play a significant role as a catalyst leading to the rapid

FIGURE 6: Regeneration efficiency of the saturated MCM at different H_2O_2 concentrations and reusability of MCM with optimal H_2O_2 concentration.

regeneration of reactive oxygen species, such as $\cdot\text{OH}$ radicals which were mainly responsible for the degradation of organic contaminant [60]. Consequently, the heterogeneous Fenton oxidation process was carried out by degrading DC molecules easily in the presence of H_2O_2 solution. On the other hand, the reduced catalytic rate with higher H_2O_2 concentrations such as 8% and 11% was probably caused by the competition of the excessive H_2O_2 and target DC molecule against the active sites of the catalyst. Additionally, if the original concentration of H_2O_2 was higher, the H_2O_2 might scavenge the $\cdot\text{OH}$ radical seriously and hence the regeneration efficiency of the DC molecule decreased [61].

As seen in Figure 6, a saturated fixed bed can be easily restored by the $\text{Fe}_3\text{O}_4/\text{H}_2\text{O}_2$ Fenton-like oxidation process following a relatively low concentration of aqueous H_2O_2 (5%). And the good performance of a saturated fixed bed with 5% H_2O_2 was calculated for three consecutive adsorption/regeneration cycles. The regeneration efficiency was generally above 80% in two previous cycles. The excellent reusability of MCM is because of its strong affinity on DC and high degradation ability during the first and second adsorption cycle, implying that the MCM integrating the adsorption feature of chitosan carbon and the catalytic property of Fe_3O_4 may have a good application prospect on multiple adsorption cycles.

The embedding of Fe_3O_4 nanoparticles into the CSM substrate is beneficial to the easy separation of catalysts from the aqueous system. In order to verify magnetic separation of MCM, an external magnet was used to separate the samples from mixture solution. Figure 7(a) shows that MCM was settled at the bottom of the test vessel by self-gravity without a magnetic field. When an external magnetic field was introduced, the MCMs can be completely attracted to the sidewall from the aqueous solution within about 5 seconds, as seen in Figure 7(b). Such excellent magnetic property

FIGURE 7: Photographs of separation of MCM by gravity (a) and magnetism (b).

means that MCM can be easily be separated and collected from the adsorption system by a simple magnetic process after adsorption.

4. Conclusion

In summary, a low-cost magnetic chitosan@ Fe_3O_4 composite material, which integrates the adsorption features of chitosan with the magnetic and catalytic properties of Fe_3O_4 nanoparticles, was synthesized via an alkali gelation-thermal cracking process. The mechanism for the formation of the product was discussed in detail. These composites exhibited excellent properties for the effective removal and oxidative destruction of DC from aqueous solution via a fixed-bed column method. The optimum conditions were observed at an initial DC concentration of 20 mg/L, a flow rate of 1.1 mL/min, and a bed depth of 1.6 cm. The Thomas and Yoon-Nelson models showed a good agreement with the experimental data and could be applied for the prediction of the fixed-bed column properties and breakthrough curves. The MCM possesses a ferromagnetic characteristic allowing them to be easily

separated from the aqueous system by an external magnet. The regeneration of the saturated adsorbent after the adsorption process can be realized using H_2O_2 solution and could be controlled easily by adjusting the H_2O_2 dosage. Considering the abundant and low-cost raw materials, the facile fabrication route, the easy recovery and separation process, and the excellent reusability, the magnetic Fe_3O_4 @chitosan carbon microbeads may serve as a promising and scalable adsorbent for the removal and oxidation of organic compounds in practical applications.

Data Availability

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

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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