Research Article

Efficient Absorption of Antibiotic from Aqueous Solutions over MnO_2 @SA/Mn Beads and Their In Situ Regeneration by Heterogeneous Fenton-Like Reaction

Yu Luo,¹ Bo Bai,^{1,2} Honglun Wang,² Yourui Suo,² and Yiliang Yao¹

¹Key Laboratory of Subsurface Hydrology and Ecological Effects in Arid Region, Chang'an University, Ministry of Education, Xi'an 710054, China

²State Key Laboratory of Plateau Ecology and Agriculture, Qinghai University, Xining 810016, China

Correspondence should be addressed to Bo Bai; baibochina@163.com

Received 16 May 2017; Accepted 10 July 2017; Published 21 August 2017

Academic Editor: Run Zhang

Copyright © 2017 Yu Luo et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Alginate has been extensively used as adsorbents due to its excellent properties. However, the practical application of pure alginate has been restricted since the saturated adsorbent has weak physical structure and could not be regenerated easily. In this study, a low-cost and renewable composite MnO_2 @alginate/Mn adsorbent has been prepared facilely for the absorptive removal of antibiotic wastewater. FE-SEM, FTIR, and XRD analyses were used to characterize the samples. The norfloxacin (NOR) was used as an index of antibiotics. More specifically, the batch absorption efficiency of the adsorbents was evaluated by pH, contact time with different NOR concentration, and the temperature. Thus, the performance of absorption kinetic dynamics and isotherm equations were estimated for the absorptive removal process. Parameters including ΔG^0 , ΔH^0 , and ΔS^0 were utilized to describe the feasible adsorption process. To regenerate the saturated absorptive sites of the adsorbent, the heterogeneous Fenton-like reactions were triggered by introduction of H_2O_2 . The results showed that the in situ regenerating has exhibited an excellent recycling stability. The high activity and the simple fabrication of the adsorbents make them attractive for the treatment of wastewater containing refractory organic compound and also provide fundamental basis and technology for further practical application.

1. Introduction

Extensive usages of chemical antibiotics have played an important role in the health care for human and animals [1]. However, about 50~90% of ingested antibiotics are excreted into domestic sewage without being metabolized due to the incomplete metabolism [2, 3]. As a result, residual chemical antibiotic has been frequently found in the ground and drinking waters, which inevitably lead to some unfriendly environmental influences such as the effects of the toxicity to animal-culture and the threats to human health [4, 5]. In recent years, compared with the traditional strategies for removal of toxic antibiotics from wastewater, using absorptive approaches for the highly efficient degradation of stable antibiotics from wastewater treatment systems has been regarded as most efficient route owing to their interested features of simple operation, low budget, nontoxicity, and efficient removal

rate. Particularly, the application of low-cost, regeneration, and environmentally friendly adsorbent attracts much more attentions. For example, some wastes for economic crops, such as rice-bran [6], cacao-shell [7], maize-stalk [8], and peanut-shell [9], have been widely used as adsorbents to deal with various antibiotics wastewater. Sodium alginate (SA), a natural polysaccharide extracted from seaweed and comprised homopolymeric blocks of guluronate blocks and manuronate blocks, was used extensively as supported adsorbent owing to its advantages of biocompatibility, low toxic properties and budget, and ease of gelation [10, 11]. Several alginate-based adsorbents including alginate nanohybrids [12], alginate nanohydrogel [13], alginate fiber [14], alginate bead [15], and alginate film [16] have already been explored for organic pollution adsorption applications. In contrast, the alginate beads have been more widely used than the fiber,

nanoparticles, or film forms because of their simple fabrication and recovery process, controllable particle dimension, and excellent dispersion stability [17]. Unfortunately, practical application of pure alginate bead as adsorbent has been restricted since the adsorbent has weak physical structure and could not be regenerated easily, which needs extra process or complete replacement [18]. Therefore, the exploration of developing an effective and easy regeneration route for alginate bead is of particular significance in contemporary industry.

The degradation of contaminated organism from wastewater by traditional Fenton oxidation process using slurry suspensions of iron oxide as catalysts is considered as an expensive process since longer reaction times are usually required to entirely oxidize the pollutants due to their inefficient hydroxyl radicals' concentration inside reactions [19–21]. To overcome this dilemma, utilizing an enrichment method or prethickening adsorption way prior to the oxidation process has been ascertained that the removal efficiency of pollutants through the Fenton-like reaction has been significantly increased. Typically, the embedding of Fe_3O_4 nanoparticles of yeast has integrated biosorption properties from pure yeast cells under the Fenton performance from Fe_3O_4 nanoparticles, resulting in the high-effective degradation of cationic azo dye in wastewater treatment [22]. The enhanced efficiency of wastewater treatment is ascribed to the successive and synergistic effect on yeast biosorption and Fe_3O_4 nanoparticles over heterogeneous Fenton catalyzes performance and regeneration process. Compared with traditional iron oxide Fenton catalysts, MnO_2 exhibit most attractive transition metal oxides which predisposed to coordinate with oxidant forming the Fenton-like process reagent to remove the contaminants in water treatment. Such kind of catalyst possessed intriguing features such as widening operative pH ranges and high positive catalyst performance [23]. Furthermore, researches prove that decomposition of H_2O_2 can be catalyzed by MnO_2 nanoparticles to generate reactive oxygen species, like hydroxyl radicals, carboxyl radicals, and single oxygen, to remove organic pollutants [24–26]. As a consequence, the simultaneous utilization of MnO_2 and H_2O_2 has been considered as Fenton-like process reagent to oxidize the low-biodegradable organism. For instance, methylene blue [27], methyl orange [28], and azo dyes [29] have been removed using MnO_2 -involved hybrid composite as a catalyst in heterogeneous $\text{MnO}_2/\text{H}_2\text{O}_2$ Fenton-like system.

Thus, in this work, novel absorbents MnO_2 @alginate/Mn (MnO_2 @SA/Mn) beads were first fabricated. The adsorbents were characterized by a scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and powder X-ray diffraction (XRD), respectively. Norfloxacin (NOR), frequently detected in wastewater and surface water with high concentrations, was used on purpose as an index of antibiotics to evaluate the adsorption properties of MnO_2 @SA/Mn beads. The detailed absorptive removal processes for NOR antibiotic from aqueous solutions over MnO_2 @SA/Mn beads were investigated. Afterward, the in situ regeneration of the saturated MnO_2 @SA/Mn absorbents was triggered by introduction of H_2O_2 . The possible mechanism for in situ

regenerating norfloxacin-loaded MnO_2 @SA/Mn was discussed.

2. Experimental

2.1. Materials. Sodium alginate (SA) with the purity 0.95 was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Norfloxacin ($\text{C}_{16}\text{H}_{18}\text{FN}_3\text{O}_3$) was purchased from Sigma-Aldrich Co., Ltd. (Shanghai, China), and the purity is 0.98. The reagents in this experiment are analytical grade with mass fraction purity 0.99 and used as received. Manganese sulfate (MnSO_4) and potassium permanganate (KMnO_4) were purchased from Tianjin Yonghao Jingxi Chemical Co., Ltd. (Tianjin, China). Ethanol ($\text{C}_2\text{H}_5\text{OH}$) was purchased from Tianjin Fuyu Jingxi Chemical Co., Ltd. (Tianjin, China). Distilled water (18.3 M Ω cm) was used to make required aqueous solutions.

2.2. MnO_2 @SA/Mn Beads Preparation. MnO_2 nanoparticles were prepared via a hydrothermal method. Typically, 30 ml 0.2 mol·L⁻¹ MnSO_4 solution was added dropwise into 30 ml, 0.3 M KMnO_4 solution with continuous stirring for at least 30 min. Then the mixture was treated at 180°C with a Teflon-lined autoclave for 10 h. After cooling down to room temperature, the suspension was centrifuged and washed the precipitate with distilled water. After that, the precipitate was dried at 60°C in air for 6 h; the final MnO_2 nanoparticles were obtained. The reaction equation is as follows:

Subsequently, 1.000 g of MnO_2 nanoparticles was dispersed into 50 ml of 2.5 (w)% sodium alginate solutions at 298.15 K with continuous stirring for 2 h. After that, the sodium alginate solution was dropped into MnSO_4 solution (0.05 mg/L) with a peristaltic pump. After the hydrogel beads were stored at 4°C for 10 h to form MnO_2 @SA/Mn hydrogel beads, the obtained hydrogels were finally washed and stored at 4°C until use.

2.3. Adsorbents Characterization. The morphology of the MnO_2 @SA/Mn adsorbent was observed by a scanning electron microscopy (SEM, Hitachi S-4800, Japan). Element content and line-scanning analysis were investigated by energy-dispersive spectroscopy (EDS) analysis. To study the chemical structures, Fourier transform infrared spectra (FTIR, Bio-RAD FTS135, America) of the adsorbents were monitored by a Bio-Rad FTS135 spectrometer in the range 500–4500 cm⁻¹ using KBr. And the crystal phase was investigated by powder X-ray diffraction (XRD, Rigaku D/MAX-3C diffractometer, Japan) patterns which were conducted on X. Pert Pro diffractometer at a scanning rate of 10° per min using Cu K α radiations ($\lambda = 0.15418$).

2.4. Adsorption Experiments. In a typical run, the experiment was conducted in 200 mL conical flasks containing 100 mL of the desired NOR concentration at pH 4. Since

the adsorbents were primarily responsible for the adsorption, $2.0 \text{ g} \cdot \text{L}^{-1} \text{ MnO}_2/\text{SA}/\text{Mn}$ adsorbents were added in each flask. Then the solution was stirred using a magnetic stirrer for 85 min. 5 ml samples in solution were picked up at regular intervals to centrifuge in order to separate the adsorbents from the liquid, and then the supernatant was analyzed by a wavelength of 273 nm using an Evolution 201 ultraviolet-vis (Jenway, Cambridge, UK) spectrophotometer to confirm the residual concentration of NOR and the loading efficiency. After that, the samples were immediately reverted to the flask. The adsorption capacity (Q_e , $\text{mg} \cdot \text{g}^{-1}$) and loading efficiency (η , %) of NOR were determined as follows:

$$\eta = \frac{(C_0 - C_e)}{C_0} \times 100\%,$$

$$Q_e = \frac{(C_0 - C_e) \times V}{m},$$
(2)

where C_0 ($\text{mg} \cdot \text{L}^{-1}$) and C_e ($\text{mg} \cdot \text{L}^{-1}$) are the NOR concentration before and after adsorption, respectively. V (L) is the volume of the solution and m (g) is the weight of the adsorbent.

2.5. In Situ Regeneration of Absorbents. Typically in an adsorptive removal process, 100 mL $10 \text{ mg} \cdot \text{L}^{-1}$ NOR aqueous solution was conducted in conical flask, and $2.0 \text{ g} \cdot \text{L}^{-1}$ of $\text{MnO}_2/\text{SA}/\text{Mn}$ adsorbents was used as the absorbents, then analyzing the supernatant of the solution to determine the NOR loading efficiency when the adsorption equilibrium finished. After that, the solution was added by 5 mL 1 (w/v)% H_2O_2 and irradiated for 4 h using two ultraviolet lamps fixed directly above the flask. Then the absorbents were collected by centrifugation, washed thoroughly, and dried to be reused in the next run. Another cycle of sorption-regeneration process was repeated in the same manner as mentioned above.

3. Results and Discussion

3.1. Characterization of $\text{MnO}_2/\text{SA}/\text{Mn}$ Beads. An estimated formation pathway of $\text{MnO}_2/\text{SA}/\text{Mn}$ beads is shown in Scheme 1.

In this work, sodium alginate was dissolved ahead in distilled water with magnetic stirring for 10 h to get a homogeneous expansive solution which would intertwine each together forming a three-dimensional network through covalent and noncovalent interactions like hydrogen bond, electrostatic interactions and van der Waals forces [30, 31]. Then, the MnO_2 nanoparticles were introduced into the solution gradually with continuous stirring during the intertwined processes. Thus, the expansive solution of sodium alginate would provide a certain possibility for MnO_2 nanoparticles uniformly dispersing and embedding into the polymer network to obtain MnO_2/SA gel solution. After that, the composite was dropwise injected into MnSO_4 aqueous solution. When MnO_2/SA gel droplets were immersed into MnSO_4 aqueous solution, $\text{MnO}_2/\text{SA}/\text{Mn}$ hydrogel beads were achieved due to the ionic cross-linking interactions between carboxyl

SCHEME 1: Mechanism for the formation of $\text{MnO}_2/\text{SA}/\text{Mn}$ hydrogel beads.

group of the alginate chains and Mn^{2+} by chelation and covalent and noncovalent forces. It was conceivable that the impregnation of MnO_2 nanoparticles is an effective approach to enhance the physicochemical properties of hydrogel beads, and the physical $\text{MnO}_2/\text{SA}/\text{Mn}$ hydrogel beads acquired would be comprised of water, MnO_2 , Mn^{2+} ions, and alginate with abundant free carboxyl groups and hydroxyl groups.

Based on the previous analysis, we can infer that alginate molecule, MnO_2 nanoparticles, and Mn^{2+} ions have had their own extremely important contribution for the formation of $\text{MnO}_2/\text{SA}/\text{Mn}$ hydrogel beads, respectively. For the alginate material, the physical cross-linked property of the alginate polymer chains have assembled the dispersive MnO_2 nanoparticles into hydrogel beads, helping to fabricate the uniform and scattered spherical alginate gel microspheres. Besides, the generated alginate hydrogels have reserved sufficiently original groups including hydroxyl and carboxyl groups on the surface of alginate substrates, which can be used for capturing the chemical antibiotics compound from aqueous solutions by covalent and noncovalent forces. And thus, the enrichment or preconcentration adsorption of chemical antibiotics compound prior to the heterogeneous oxidation process could be fulfilled. As for the MnO_2 nanoparticles, they have acted as the inner skeleton to strengthen the mechanical stability of $\text{MnO}_2/\text{SA}/\text{Mn}$ hydrogel beads. Also, the MnO_2 nanoparticles within the inner and surface of $\text{MnO}_2/\text{SA}/\text{Mn}$ hydrogel beads can provide abundant catalytic active sites for the heterogeneous Fenton-like reaction, speeding up the degradation rate of norfloxacin antibiotics. Owing to the fact that coordination for divalent ions is permitted by the structure of guluronate blocks of alginate, the ample Mn^{2+} ions within the system hereby have

FIGURE 1: FTIR spectra of (a) AB, (b) MnO_2 , and (c) MnO_2 @SA/Mn beads.

functioned as a cross-linking agent to help to form alginate hydrogels in solution by binding solely with guluronate blocks from polymer chains. By these means, one polymer guluronate block could form junctions with the adjacent polymer guluronate chains, and finally the MnO_2 @SA/Mn beads with complicated cross-linking hydrogel and unique egg-box shape were constructed successfully [32].

To examine the chemical bonding structure and possible interactions of the MnO_2 @SA/Mn beads, FTIR analysis was employed to detect the chemical bonds transformation in parallel to MnO_2 , pure alginate hydrogel beads, and MnO_2 @SA/Mn beads. For the alginate hydrogel beads in Figure 1(a), the peaks at 3428, 2925, 2854, 1632, 1426, and 1163 cm^{-1} are ascribed to the -OH, -CH₂-, -CH₃, the asymmetric and symmetric stretching vibration of -COOH, and -CO vibrations, respectively [33–37]. In the case of the MnO_2 nanoparticles in Figure 1(b), the peak at 3429 cm^{-1} is mainly generated by -OH of the water molecule adhering to the surface of MnO_2 nanoparticles which indicates that the surface of synthesized MnO_2 nanoparticles has sufficient hydroxyl groups [38]. The two peaks around 716 and 523 cm^{-1} are aroused by Mn-O-Mn and Mn-O stretching vibration [39, 40]. In the FTIR spectrum of MnO_2 @SA/Mn beads (Figure 1(c)), the characteristic adsorption peaks of pure alginate hydrogel beads and MnO_2 were approximately maintained or even stronger. Moreover, an original peak at 1740 cm^{-1} probably caused by the absorption vibrations of the -COOH in alginate molecule [41, 42]. However, the peaks at 3428 cm^{-1} , 1632 cm^{-1} , 1426 cm^{-1} , and 1163 cm^{-1} of pure alginate hydrogel beads and 3429 cm^{-1} , 716 cm^{-1} , and 523 cm^{-1} of MnO_2 were changed to 3429 cm^{-1} , 1636 cm^{-1} , 1410 cm^{-1} , 1178 cm^{-1} , 670 cm^{-1} , and 594 cm^{-1} in MnO_2 @SA/Mn beads, respectively. These changes implied that the alginate network and MnO_2 /Mn in the MnO_2 @SA/Mn hydrogel beads were linked with the strong intermolecular forces of hydrogen bonding and chelation between Mn and hydroxyl groups, carboxyl groups, and such linkages resulted in forming a stable three-dimensional network.

Optical photographs and FE-SEM images of MnO_2 @SA/Mn beads are presented in Figure 2, respectively. Figure 2(a) indicates that the surface of MnO_2 @SA/Mn hydrogel beads in a gel state is smooth and the bead has a black spherical shape with a diameter approximately 2.0 ± 0.2 mm; simultaneously the average diameter after freezing drying is about 1.5 ± 0.2 mm. The shrinkage of the MnO_2 @SA/Mn hydrogel beads indicated that the obtained hydrogel beads have a definite adsorption capacity for water molecule. Theoretically, the water-holding capacity (WHC) can be calculated as follows:

$$\text{WHC (mg)} = \rho_W \times V_W = \rho_W \times \frac{4}{3}\pi (R_{\text{eq}}^3 - R_d^3), \quad (3)$$

where ρ_W is the density of water, V_W is the volume of MnO_2 @SA/Mn hydrogel beads, and R_{eq} and R_d are the radius of the gelatinous beads (eq) and dried (d) beads. After calculation, its water-holding capacity was theoretically about 73.27 $\text{mg}\cdot\text{bead}^{-1}$.

Figure 2(b) is the SEM photograph of a freezing dried MnO_2 @SA/Mn hydrogel bead. It shows that the surface of MnO_2 @SA/Mn hydrogel bead is relatively sags and crests with small concave depressions on; the reason should be attributed to two cases. For the one side, it is due to rough shrinkage of MnO_2 @SA/Mn hydrogels over complete freezing drying process. For another side, it is due to the impregnation of MnO_2 nanoparticles into alginate hydrogel beads in the aqueous solution. Figures 2(c) and 2(d) show that the local surface magnified and cross section magnified SEM photographs of samples. The photographs indicated that the MnO_2 nanoparticles, with an average size of 20.0 ± 2.0 μm widths and 400.0 ± 2.0 μm length, were successfully embedded on/in the three-dimensional cross-linked alginate hydrogel beads heterogeneously and deeply due to the intermolecular forces of hydrogen bond between MnO_2 nanoparticles and alginate polymers, and the chelation between Mn^{2+} ions and hydroxyl, carboxyl groups. Briefly, the stable and tight MnO_2 @SA/Mn hydrogel beads were acquired with abundant carboxyl and hydroxyl groups for NOR adsorption.

The distribution of elements of selected MnO_2 @SA/Mn zone was further investigated by EDS analysis and line-scanning. The experimental results were shown in Figure 3. As shown in Figure 3(a), the EDS analysis of MnO_2 @SA/Mn beads inferred that C, O, and Mn elements were the main components with weight percentage of 44.10%, 26.36%, and 29.54%, respectively, confirming the purity of MnO_2 @SA/Mn materials. Moreover, from the graph in Figure 3(b), the line-scanning for selected surface zone of MnO_2 @SA/Mn bead presented high homogeneity that, during the area with MnO_2 impregnation, the intensities of Mn and O are notable much stronger than C, while, in the other area, the intensities of C, O, and Mn trended towards stable values. These results further prove the successful immobilization of MnO_2 nanoparticles on/in the SA beads and lead to an enhancement of amount of available adsorption/regeneration sites.

The structural characterization of MnO_2 @SA/Mn beads are further determined by powder X-ray diffraction technology. The typical XRD analyses are shown in Figure 4. The

FIGURE 2: (a) Photograph of MnO₂@SA/Mn hydrogels in equilibrium gel state (left) and dried state (right); (b, c) SEM photographs of MnO₂@SA/Mn and surface of MnO₂@SA/Mn; and (d) cross section of MnO₂@SA/Mn.

FIGURE 3: Element content (a) and selected zone line-scanning analysis for C, O, and Mn elements of MnO₂@SA/Mn beads (b).

diffraction of alginate gel beads (Figure 4(c)) shows typical peaks around 13.1° and 20.6° [43]. Moreover, in Figure 4(b), the composites had similar diffraction peaks at $2\theta = 28.7^\circ$, 37.4° , 41.0° , 42.8° , 56.7° , and 59.4° , giving an index to a β -MnO₂ phase [44]. Therefore, Figure 4(a) exhibits the XRD

pattern of MnO₂@SA/Mn hydrogel bead including both the diffraction peaks of MnO₂ nanoparticles and alginate gel beads, correspondingly. And the successful impregnating of MnO₂ on/in the MnO₂@SA/Mn beads was confirmed since no further impurities peaks were found.

FIGURE 4: XRD patterns of (a) MnO_2 @SA/Mn beads; (b) MnO_2 nanoparticles; (c) pure alginate bead.

3.2. Adsorptive Removal of NOR Antibiotic from Aqueous Solutions. In this study, the applications of MnO_2 @SA/Mn beads were evaluated by the adsorptive removal of NOR compound from the simulated solution using batch reactor. The parameters of the adsorptive removal process determined in the experiments were pH (2–10), NOR concentration ($2\text{--}30\text{ mg}\cdot\text{L}^{-1}$), contact time (0–85 min), and temperature (288.15–318.15 K). In addition, parameters of adsorptive kinetic and thermodynamic were utilized to confirm efficiency for the adsorptive removal process.

3.2.1. Effect of pH in Solution. The effect of pH is a significant factor in adsorptive removal process since it is closely integrated with the surface charge of the adsorbent and the chemical structure of organic materials [45]. Herein, parameters of the NOR adsorptive removal experiments were performed with 10 mg/L NOR, $2\text{ mM H}_2\text{O}_2$ solution, and 2.0 g/L adsorbent at 30°C , and the adsorption properties including removal efficiency and adsorptive removal capacity were investigated by MnO_2 @SA/Mn and pure AB, respectively (Figure 5). The value of the maximum NOR adsorptive rate by catalyst MnO_2 @SA/Mn beads is 98.3% , while by catalyst AB the value is 55.2% at pH 4.0. However, with the pH of the solution (pH 4.0–10.0) further increasing, the efficiency of NOR adsorption decreases from 98.3% to 37.2% and 55.2% to 11.7% , respectively. The maximum adsorption capacities are 4.9 mg/g by catalyst MnO_2 @SA/Mn beads and 2.8 mg/g by AB beads individually. This observation gives the evidence that MnO_2 and Mn^{2+} ions can improve the NOR adsorption capacity in Fenton-like system.

Such phenomenon is probably ascribed to the causes below. For MnO_2 @SA/Mn beads adsorbents, their surface is apt to be adjusted at different pH since the pH_{pzc} of MnO_2 is 2.25 [46] and the pH_{pzc} of pure alginate bead is 4.2. For NOR adsorbate, each NOR molecule has two functional groups including acid carboxyl and basic piperazine. Therefore, the acid-base equilibrium of the NOR molecule was inevitably

influenced by the solution pH. More specifically, the piperazine group of the NOR exists as a protonated cation form in an acidic environment when pH is less than 6. On the contrary, a basic environment could cause a deprotonation when pH is greater than 9. Namely, the NOR performs as deprotonated anion form at a basic environment. While the solution pH is varied from 6 to 9, the NOR exists as zwitterions form [47, 48].

3.2.2. Effects of NOR Concentration. Effects of adsorption contact time with different initial NOR concentration ($2\text{--}30\text{ mg}\cdot\text{L}^{-1}$) were carried out for 85 min at 30°C with $2.0\text{ g}\cdot\text{L}^{-1}$ adsorbent and $2\text{ mM H}_2\text{O}_2$ in pH 4 solution in Figures 5(b) and 5(c). Figure 5(b) showed that the kinetics of NOR included two stages of behaviors during the adsorption process: a fast adsorption period over a short time followed by a slower adsorption period for a longer time. In the first stage, it is due to the adsorptive sites on the MnO_2 @SA/Mn adsorbent surface through the initial period of adsorption behavior. For the second stage, adsorption rate was probably by the molecular-repulsive interactions between NOR molecule on the absorbent surface and the solution. As time goes on, some adsorbed NOR molecules were desorbed from the adsorbent dispersing to the bulk phase again. Equilibrium adsorption capacity increased notably from 9.93 to $96.85\text{ mg}\cdot\text{g}^{-1}$ with the increasing of NOR concentration varying from 2 to $30\text{ mg}\cdot\text{L}^{-1}$. Such phenomenon can be probably contributed to the strong interactions of driving force among NOR ions during high concentration. From Figure 5(c), it indicates that a lower initial NOR concentration results in a higher adsorption efficiency. With NOR concentration varying from 2 to $30\text{ mg}\cdot\text{L}^{-1}$, the final degradation of NOR by MnO_2 @SA/Mn beads and pure AB beads at 85 min decreases from 99.3% to 57.9% and from 46.1% to 11.5% , respectively. The NOR removal efficiency and adsorption capacity by MnO_2 @SA/Mn beads are higher than those values by pure AB beads. These results indicate that MnO_2 @SA/Mn beads have more abundant adsorption sites than pure AB beads.

3.2.3. Kinetics of NOR. The kinetics is significant for the removal efficiency since it can provide the mechanism of adsorption process. For the reason that the adsorbate residence time is controlled by the kinetics, removal rate of the adsorption is so important that the design parameters of the process can be better optimized. Therefore, predicting removal rate in which adsorption behavior occurs is considered as the most significant element for the design of the adsorptive removal process [49].

To study the adsorption mechanism, linearized adsorptive kinetic equation is utilized to find the adsorption kinetics of NOR adsorbed by the MnO_2 @SA/Mn hydrogel beads [50]. The pseudo-first-order equation is as follows:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 \times t, \quad (4)$$

where Q_e and Q_t represent the amount of NOR adsorbed on the adsorbent at the equilibrium and at time t , separately. k_1 (min^{-1}) is rate coefficient for the pseudo-first-order.

FIGURE 5: Effects of (a) pH, $[\text{NOR}] = 10 \text{ mg}\cdot\text{L}^{-1}$, (b) and (c) contact time and initial NOR concentration, pH = 4. Reaction conditions: $[\text{catalyst}] = 2.0 \text{ g}\cdot\text{L}^{-1}$, $[\text{H}_2\text{O}_2] = 2 \text{ mM}$, $T = 30^\circ\text{C}$.

TABLE 1: Kinetic adsorption parameters of different initial concentration of NOR.

$C_0/(\text{mg}\cdot\text{L}^{-1})$	$Q_{\text{exp}}/(\text{mg}\cdot\text{g}^{-1})$	Pseudo-first-order			Pseudo-second-order		
		$Q_{\text{cal}}/(\text{mg}\cdot\text{g}^{-1})$	k_1/min^{-1}	R^2	$Q_{\text{cal}}/(\text{mg}\cdot\text{g}^{-1})$	$k_2/(\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1})$	R^2
2.0	9.933	10.057	0.088	0.955	10.135	0.097	0.998
5.0	24.530	24.965	0.081	0.963	25.026	0.039	0.996
10.0	48.523	50.481	0.065	0.961	49.485	0.020	0.994
15.0	64.799	65.527	0.090	0.988	66.100	0.015	0.996
20.0	73.691	74.191	0.100	0.989	75.190	0.013	0.997
30.0	86.779	87.914	0.087	0.910	88.455	0.011	0.997

The pseudo-second-order equation is as follows [51, 52]"

$$\frac{t}{Q_t} = \frac{1}{k_2 \times Q_e^2} + \frac{t}{Q_e}, \quad (5)$$

where Q_e and Q_t are the capacities at equilibrium and at time t (s), respectively. k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) is rate coefficient for the

second-order equation. The fitted curves for both two kinetics are presented in Figure 6; curve-fitting data and correlation parameters are shown in Table 1.

Figure 6 shows the plots of two kinetics of NOR adsorption on $\text{MnO}_2\text{@SA/Mn}$ with varied NOR concentrations. The rate coefficients and correlation coefficient for adsorption

FIGURE 6: Pseudo-first-order (a) and pseudo-second-order (b) adsorption kinetics for adsorption of NOR onto $\text{MnO}_2\text{@SA/Mn}$ at different initial NOR concentrations at reaction conditions: $[\text{catalyst}] = 2.0 \text{ g}\cdot\text{L}^{-1}$, $[\text{H}_2\text{O}_2] = 2 \text{ mM}$, $\text{pH} = 4$, $T = 30^\circ\text{C}$.

were simulated and summarized in Table 1. Table 1 revealed that the practical adsorption amount values (Q_{exp}) disagree with the theoretical values (Q_{cal}) although the constant values (R^2) for the pseudo-first and pseudo-second equations were in the range of 0.910~0.989 and 0.994~0.998, respectively. However, the values of correlation coefficient (R^2) for the pseudo-second-order are much closer to 1.0 than the values for pseudo-first-order, confirming that the adsorption process of $\text{MnO}_2\text{@SA/Mn}$ hydrogel beads for simulated NOR-solution fits the pseudo-second-order equation better.

3.2.4. Isothermal and Thermodynamic Experiments of Adsorption. Thermodynamic experiments on NOR adsorption were investigated in a temperature range of 15°C to 45°C with $\text{pH} 4$, $10 \text{ mg}\cdot\text{L}^{-1}$ NOR, $2.0 \text{ g}\cdot\text{L}^{-1}$ adsorbent, and $2 \text{ mM H}_2\text{O}_2$ solution. In order to study whether the adsorption process might take place spontaneously, parameters including the changes of enthalpy (ΔH^0), the entropy (ΔS^0), and the Gibbs free energy (ΔG^0) associated with adsorptive removal process were calculated as follows:

$$\begin{aligned} \ln K_d &= \frac{-\Delta H^0}{R \times T} + \frac{\Delta S^0}{R}, \\ K_d &= \frac{Q_e}{C_e}, \\ \Delta G^0 &= -R \times T \times \ln K_d, \end{aligned} \quad (6)$$

where K_d and T (K) are the equilibrium adsorption constant and temperature, respectively. Constant R ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) is the ideal-gas coefficient. In addition, parameters ΔH^0 and ΔS^0 are obtained from the plots of $\ln K_d$ versus $1/T$.

TABLE 2: Adsorption thermodynamic parameters of NOR by $\text{MnO}_2\text{@SA/Mn}$ beads.

Temperature/K	$\Delta G^0/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta H^0/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta S^0/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
288.15	-0.24	20.52	88.87
298.15	-2.71		
308.15	-8.76		
318.15	-6.84		

Table 2 exhibits the data of ΔG^0 , ΔH^0 , and ΔS^0 for the adsorptive removal process. From Table 2, the negative ΔG^0 indicates that, at temperature ranging from 15°C to 45°C , the spontaneous nature of adsorption occurs relatively easier at 35°C . Considering ΔG^0 is in the range -20 to $0 \text{ kJ}\cdot\text{mol}^{-1}$, the processes are dominated by the physical adsorption [53, 54]. Moreover, the positive ΔH^0 ($20.52 \text{ kJ}\cdot\text{mol}^{-1}$) reveals that such adsorptive removal process is the result of endothermic nature of adsorption and physical interactions, including van der Waals interactions, hydrogen-bonding forces, and electrostatic force [54]. Furthermore, the positive value of ΔS^0 ($88.87 \text{ kJ}\cdot\text{mol}^{-1}$) confirms that excellent affinity of NOR molecule towards adsorbent and randomness increases at the solid-liquid interface at $15\text{--}45^\circ\text{C}$ [55].

The Langmuir, Freundlich, and Dubinin-Radushkevich isotherms are selected to describe how adsorbents interact with adsorbate during the adsorption behavior. The Langmuir isotherm assumes that uniform adsorptive process occurs with the monolayer at the adsorbent surface [56]. While the Freundlich model is an empirical expression which describes the multilayer sorption behaviors that occurred in the heterogeneous system [57]. Compared with the isotherm equations above, Dubinin-Radushkevich isotherm model is

TABLE 3: Adsorption thermodynamic parameters of NOR by MnO₂@SA/Mn beads.

Temperature/K	$Q_m/\text{mg}\cdot\text{g}^{-1}$	Langmuir isotherm model		
		$b/\text{L}\cdot\text{mg}^{-1}$	R_L	R^2
288.15	173.2	0.54	0.48–0.06	0.9782
298.15	148.1	0.55	0.47–0.06	0.9824
308.15	249.9	0.40	0.56–0.08	0.9709
318.15	308.1	0.29	0.63–0.10	0.9787
Temperature/K	$K_F/\text{L}\cdot\text{g}^{-1}$	Freundlich isotherm model		
		n		R^2
288.15	67.6	2.82		0.9763
298.15	71.9	3.51		0.9813
308.15	75.7	4.57		0.9697
318.15	70.0	3.39		0.9778
Temperature/K	$Q_m/\text{mg}\cdot\text{g}^{-1}$	Dubinin-Radushkevich isotherm model		
		$k_{\text{DR}}/\text{kJ}^2\cdot\text{mol}^2$	$E/\text{kJ}\cdot\text{mol}^{-1}$	R^2
288.15	73.8	0.21	1.67	0.9052
298.15	58.2	0.19	1.69	0.9046
308.15	86.7	0.18	1.72	0.8965
318.15	101.6	0.16	1.74	0.8962

used to distinguish the adsorption mechanics as chemical and physical adsorption of NOR [58].

The Langmuir equation has the following form:

$$Q_e = \frac{Q_{\max} \times b \times C_e}{1 + b \times C_e}, \quad (7)$$

where C_e ($\text{mg}\cdot\text{L}^{-1}$) and $Q_{\max}$ ($\text{mg}\cdot\text{g}^{-1}$) are the equilibrium NOR concentration and maximum adsorptive capacity; and b ($\text{L}\cdot\text{mg}^{-1}$) is the coefficient of adsorption.

Moreover, the Freundlich isotherm equation is as follows:

$$Q_e = K_f \times C_e^{1/n}, \quad (8)$$

where K_f and n are the constants indicating the adsorption capacity and adsorption intensity, respectively.

Additionally, a dimensionless constant (R_L) can reflect the significant performance of Langmuir and is given by

$$R_L = \frac{1}{1 + b \times C_0}, \quad (9)$$

where the coefficient R_L implies the type of isotherm based on the following ranges: $R_L = 0$, irreversible; $0 < R_L < 1$, favorable; $R_L = 1$, linear; $R_L > 1$, unfavorable [59].

Furthermore, the Dubinin-Radushkevich isotherm model for the linear form is

$$\ln Q_e = \ln Q_m - k_{\text{DR}} \times \varepsilon^2, \quad (10)$$

$$\varepsilon = R \times T \times \ln \left(1 + \left(\frac{1}{C_e} \right) \right), \quad (11)$$

$$E = \frac{1}{\sqrt{2 \times k_{\text{DR}}}}, \quad (12)$$

where k_{DR} ($\text{mol}\cdot\text{J}^{-1}$) is the constant related to the mean free energy of adsorption; ε is Polanyi potential which can be

calculated from (11). Constant R ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and T (K) are the gas constant and absolute temperature. E ($\text{kJ}\cdot\text{mol}^{-1}$) is the mean energy of the adsorption.

The simulated data on the basis of the aforementioned models are shown in Table 3. It reveals the *determined coefficient* constant for the two isotherm models at different temperature. The result proves that the Langmuir model better fits the practical values of MnO₂@SA/Mn beads. From Table 3, we can find that the Langmuir constant Q_m indicating the maximum adsorption capacity of MnO₂@SA/Mn beads was increased, while the values of b indicating the energy of the adsorption were decreased with increasing temperature till 45°C. And the values of R_L range within 0.06–0.63 for different initial NOR concentrations at different temperatures. These phenomena once again confirm that the adsorption for NOR on MnO₂@SA/Mn beads was favorable.

Freundlich model could not explain the adsorption behavior as the Langmuir theory did since the constant R^2 was lower than the values in Langmuir model. The Freundlich constant n ranged from 2.28 to 4.57 at different temperatures, also revealing that the adsorption was favorable [60]. It confirmed that values of K_F increased with the temperature of the solution up to 308.15 K, proving that high NOR adsorption capacity easily occurred at relatively temperature.

From Table 3, it can be seen that the values of mean energy E simulated are all smaller than $2 \text{ kJ}\cdot\text{mol}^{-1}$, confirming that the adsorption of NOR by MnO₂@SA/Mn absorbent was dominated by physical adsorption during the process [61].

3.3. Regeneration of NOR-Loaded MnO₂@SA/Mn by Heterogeneous Fenton-Like Reaction. The migration of NOR antibiotics from aqueous solutions have been achieved by absorptive enrichment or preconcentration approach over MnO₂@SA/Mn beads. Then, the regeneration of the saturated absorptive sites by subsequent destruction of the

FIGURE 7: Reuse of the in situ regenerated alginate and $\text{MnO}_2\text{@SA/Mn}$ hydrogel beads. Reaction conditions: $[\text{NOR}] = 10 \text{ mg}\cdot\text{L}^{-1}$, $[\text{catalyst}] = 2.0 \text{ g}\cdot\text{L}^{-1}$, $\text{pH} = 4$, $T = 30^\circ\text{C}$.

adsorbed organic NOR pollutants are extremely crucial for the economic cost. In the present study, the reuse and regeneration of saturated adsorbent were performed by triggering UV assisted-heterogeneous Fenton-like reaction. The experimental results were shown in Figure 7.

Figure 7 showed the reuse performance of in situ regenerated alginate and $\text{MnO}_2\text{@SA/Mn}$. The cycling properties of alginate and $\text{MnO}_2\text{@SA/Mn}$ used for catalytic reaction were evaluated at $[\text{NOR}] = 10 \text{ mg}\cdot\text{L}^{-1}$, $[\text{catalyst}] = 2.0 \text{ g}\cdot\text{L}^{-1}$, $\text{pH} = 4$, and $T = 30^\circ\text{C}$. In Figure 7, the removal rate of pure AB after $\text{UV}/\text{H}_2\text{O}_2$ regeneration over four cycles was apparently dropped from 58% to 35%. This contributed to the fact that the removal of NOR in solution by pure alginate beads mainly depended on the adsorption properties. Herein, it is well known that decomposition of H_2O_2 could be catalyzed by UV radiation to create oxidizing radicals. The significant mechanisms include that NOR and H_2O_2 molecules occupied the bare active sites on the surface of the alginate; then NOR was removed by the oxidizing radicals created by the decomposition of H_2O_2 and dissolved into the solution, similar results were acquired by Tunç et al. [62]. Although NOR in solution could be removed by the pure alginate beads in the $\text{UV}/\text{H}_2\text{O}_2$ system, the adsorbed NOR could block the activated sites and decrease catalytic efficiency on the surface of the alginate towards the H_2O_2 decomposition [63]. However, compared with the pure alginate beads, the $\text{MnO}_2\text{@SA/Mn}$ has achieved a higher removal rate in the UV -Fenton-like system. The removal rate of $\text{MnO}_2\text{@SA/Mn}$ was 98%, 95%, 91% and 86%, respectively (Figure 7). It indicated that the $\text{MnO}_2\text{@SA/Mn}$ catalyst retained excellent activity and stability after recycle for four times. This probably can be attributed to the effects of alginate adsorption property, UV photolysis, and MnO_2/Mn -triggered heterogeneous Fenton-like oxidation. Comparing with pure alginate beads, the MnO_2/Mn -triggered heterogeneous Fenton-like oxidation process directs an ascendant position for the contributor

during regeneration process. The phenomena give a firm evidence that $\text{MnO}_2\text{@SA/Mn}$ catalyst can be reused at least four times without losing much effectiveness to remove NOR pollutant, which is significant in practical and long-term applications.

For UV/Fenton -like reaction system, $\bullet\text{OH}$, $\text{HOO}\bullet$, and $^1\text{O}_2$ were generated by decomposition of H_2O_2 , and they can powerfully and nonselectively oxidize or destroy the molecules structure of organic pollutants [64]. Nevertheless, organic pollutant, as NOR, can be removed from aqueous solutions only they were adsorbed on the catalyst surface [65]. Based on this assumption, possible formation mechanism for in situ regenerating NOR-loaded $\text{MnO}_2\text{@SA/Mn}$ is proposed to be a process of adsorption-decomposition-desorption. Firstly, H_2O_2 and NOR are adsorbed on the catalyst surface; secondly, under UV irradiation photolysis and MnO_2/Mn -triggered heterogeneous Fenton-like oxidation, H_2O_2 is decomposed into $\bullet\text{OH}$, $\text{HOO}\bullet$ and $^1\text{O}_2$ radicals ((13)–(21)). Part of the newly generated radicals diffuses on the surface and reacts directly with the adsorbed NOR molecules and decompose them into small organic molecules and inorganic substances. And the other radicals are desorbed from the surface, dispersed into the solution, and decomposed the NOR in the solution. Finally, the degraded small units of NOR are desorbed from the catalyst surface and enter into the solution, recovering the active potential site of the catalyst surface. Therefore, $\text{MnO}_2\text{@SA/Mn}$ could be in situ regenerated for the next catalytic reaction.

4. Conclusions

In this study, the present research attempted to develop a simple and ecofriendly approach to prepare a superabsorbent composite material via the modification of alginate hydrogel beads impregnating with MnO_2 nanoparticles. The abundant hydroxyl radicals and hydroperoxyl radicals derived from H_2O_2 and distinctive chemical/physical performance inherited from alginate have guaranteed the strengthened $\text{MnO}_2\text{@SA/Mn}$ composites with enhanced NOR adsorption and pH sensitivity. FE-SEM photographs displayed that the catalyst has a surface of relative sags and crests with small concave depressions. And FTIR analysis confirmed that the

composites have abundant carboxyl and hydroxyl groups for adsorption. The batch experiment was investigated by pH, contact time with different initial NOR concentration, and temperature. Moreover, the performance of kinetic dynamics and the kinetic data revealed that the adsorption of NOR onto $\text{MnO}_2\text{@SA/Mn}$ fitted pseudo-second-order kinetic model when compared with the pseudo-first-order kinetic equation confirming the rate determining step dominated by the chemical forces of attraction. The adsorption process was evaluated by Langmuir isotherm equation and Freundlich isotherm model, and it was found that the adsorption followed Langmuir isotherm equation well. This revealed that the adsorption process obeyed the monolayer sorption process. Thermodynamic parameters, such as negative value of ΔG^0 , indicated the spontaneous adsorption process. More importantly, the in situ regenerating tests justified the excellent recycling stability, reusability, and renewable ability. This study confirmed that NOR-containing solutions demonstrated high removal efficiency in the heterogeneous Fenton-like process over $\text{MnO}_2\text{@SA/Mn}$, the high activity of $\text{MnO}_2\text{@SA/Mn}$, and their simple preparation make them attractive for the treatment of antibiotics in wastewater treatment and provide fundamental basis and technology for further practical application.

Conflicts of Interest

The authors declare that they have no potential or actual conflicts of interest pertaining to this submission.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China (no. 21176031), Shanxi Provincial Natural Science Foundation of China (no. 2015JM2071), and Fundamental Research Funds for the Central Universities (no. 310829165027, no. 310829162014, and no. 310829175001).

References

- [1] C. G. Daughton and T. A. Ternes, "Pharmaceuticals and personal care products in the environment: agents of subtle change?" *Environmental Health Perspectives*, vol. 107, no. 6, pp. 907–938, 1999.
- [2] M. Gros, M. Petrović, A. Ginebreda, and D. Barceló, "Removal of pharmaceuticals during wastewater treatment and environmental risk assessment using hazard indexes," *Environment International*, vol. 36, no. 1, pp. 15–26, 2010.
- [3] R. Alexy, A. Schöll, T. Kümpe, and K. Kümmerer, *What Do We Know about Antibiotics in the Environment?* vol. 63, Springer, Berlin, Germany, 2004.
- [4] Y.-J. Lee, S.-E. Lee, D. S. Lee, and Y.-H. Kim, "Risk assessment of human antibiotics in Korean aquatic environment," *Environmental Toxicology and Pharmacology*, vol. 26, no. 2, pp. 216–221, 2008.
- [5] P. T. P. Hoa, S. Managaki, N. Nakada et al., "Antibiotic contamination and occurrence of antibiotic-resistant bacteria in aquatic environments of northern Vietnam," *Science of the Total Environment*, vol. 409, no. 15, pp. 2894–2901, 2011.
- [6] D. Kalderis, D. Koutoulakis, P. Paraskeva et al., "Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse," *Chemical Engineering Journal*, vol. 144, no. 1, pp. 42–50, 2008.
- [7] A. Obuge and M. Evbuomwan, "Adsorption of methylene blue onto activated carbon impregnated with KOH using cocoa shell," *Journal of Engineering Research*, vol. 2, pp. 11–18, 2014.
- [8] B. Xu, C. Wang, Q. L. Hao, Q. Z. Jia, G. J. Li, and Y. Wang, "Catalytic pyrolysis characteristics and kinetics of cotton stalk," *Chinese Journal of Bioprocess Engineering*, vol. 7, pp. 21–26, 2009.
- [9] Y. Liu, X. Sun, and B. Li, "Adsorption of Hg^{2+} and Cd^{2+} by ethylenediamine modified peanut shells," *Carbohydrate Polymers*, vol. 81, no. 2, pp. 335–339, 2010.
- [10] L. V. de Souza Santos, A. M. Meireles, and L. C. Lange, "Degradation of antibiotics norfloxacin by Fenton, UV and UV/ H_2O_2 ," *Journal of Environmental Management*, vol. 154, pp. 8–12, 2015.
- [11] J. H. Sun, J. L. Feng, S. H. Shi, Y. Q. Pi, M. K. Song, and Y. Shi, "Degradation of the antibiotic sulfamonomethoxine sodium in aqueous solution by photo-Fenton oxidation," *Chinese Science Bulletin*, vol. 57, no. 5, pp. 558–564, 2012.
- [12] G. Zelmanov and R. Semiat, "Iron(3) oxide-based nanoparticles as catalysts in advanced organic aqueous oxidation," *Water Research*, vol. 42, no. 1-2, pp. 492–498, 2008.
- [13] M. Gonçalves, P. Figueira, D. Maciel et al., "PH-sensitive Laponite®/doxorubicin/alginate nanohybrids with improved anticancer efficacy," *Acta Biomaterialia*, vol. 10, no. 1, pp. 300–307, 2014.
- [14] H. J. Lim, H. D. Ghim, J. H. Choi, H. Y. Chung, and J. O. Lim, "Controlled release of BMP-2 from alginate nanohydrogels enhanced osteogenic differentiation of human bone marrow stromal cells," *Macromolecular Research*, vol. 18, no. 8, pp. 787–792, 2010.
- [15] R. M. Wadowsky, S. Laus, T. Libert, S. J. States, and G. D. Ehrlich, "Inhibition of PCR-based assay for *Bordetella pertussis* by using calcium alginate fiber and aluminum shaft components of a nasopharyngeal swab," *Journal of Clinical Microbiology*, vol. 32, no. 4, pp. 1054–1057, 1994.
- [16] J. A. Rowley, G. Madlambayan, and D. J. Mooney, "Alginate hydrogels as synthetic extracellular matrix materials," *Biomaterials*, vol. 20, no. 1, pp. 45–53, 1999.
- [17] M. Oussalah, S. Caillet, S. Salmiéri, L. Saucier, and M. Lacroix, "Antimicrobial effects of alginate-based film containing essential oils for the preservation of whole beef muscle," *Journal of Food Protection*, vol. 69, no. 10, pp. 2364–2369, 2006.
- [18] V. N. Tirtom, A. Dinçer, S. Becerik, T. Aydemir, and A. Çelik, "Comparative adsorption of Ni(II) and Cd(II) ions on epichlorohydrin crosslinked chitosan-clay composite beads in aqueous solution," *Chemical Engineering Journal*, vol. 197, pp. 379–386, 2012.
- [19] N. M. Mahmoodi, "Binary catalyst system dye degradation using photocatalysis," *Fibers and Polymers*, vol. 15, no. 2, pp. 273–280, 2014.
- [20] T. Yuranova, O. Enea, E. Mielczarski, J. Mielczarski, P. Albers, and J. Kiwi, "Fenton immobilized photo-assisted catalysis through a Fe/C structured fabric," *Applied Catalysis B: Environmental*, vol. 49, no. 1, pp. 39–50, 2004.
- [21] M. B. Kasiri, H. Aleboyeh, and A. Aleboyeh, "Degradation of acid blue 74 using Fe-ZSM5 zeolite as a heterogeneous photo-Fenton catalyst," *Applied Catalysis B: Environmental*, vol. 84, no. 1-2, pp. 9–15, 2008.

- [22] R. Song, B. Bai, G. L. Puma, H. Wang, and Y. Suo, "Biosorption of azo dyes by raspberry-like Fe_3O_4 @yeast magnetic microspheres and their efficient regeneration using heterogeneous Fenton-like catalytic processes over an up-flow packed reactor," *Reaction Kinetics, Mechanisms and Catalysis*, vol. 115, pp. 547–562, 2015.
- [23] J. Fei, Y. Cui, X. Yan et al., "Controlled preparation of MnO_2 hierarchical hollow nanostructures and their application in water treatment," *Advanced Materials*, vol. 20, no. 3, pp. 452–456, 2008.
- [24] M. Fukushima, K. Tatsumi, and K. Morimoto, "Influence of iron(III) and humic acid on the photodegradation of pentachlorophenol," *Environmental Toxicology and Chemistry*, vol. 19, no. 7, pp. 1711–1716, 2000.
- [25] H. N. Alyea, "Chlorine from $\text{KMnO}_4 + \text{HCl}$," *Journal of Chemical Education*, vol. 46, no. 3, p. A218, 1969.
- [26] S. B. Kanungo, K. M. Parida, and B. R. Sant, "Studies on MnO_2 -III. The kinetics and the mechanism for the catalytic decomposition of H_2O_2 over different crystalline modifications of MnO_2 ," *Electrochimica Acta*, vol. 26, no. 8, pp. 1157–1167, 1981.
- [27] Z. Cai, D. Zhang, L. Gu et al., " MnO_2 nanosheets as a high-efficiency electrocatalyst for H_2O_2 reduction in alkaline medium," *RSC Advances*, vol. 6, no. 4, pp. 2546–2551, 2016.
- [28] Y. Li, J. Qu, F. Gao et al., "In situ fabrication of Mn_3O_4 decorated graphene oxide as a synergistic catalyst for degradation of methylene blue," *Applied Catalysis B: Environmental*, vol. 162, pp. 268–274, 2015.
- [29] H. Y. He, J. F. Huang, L. Y. Cao, and J. P. Wu, "Photodegradation of methyl orange aqueous on MnWO_4 powder under different light resources and initial pH," *Desalination*, vol. 252, no. 1–3, pp. 66–70, 2010.
- [30] A. A. Pandit, R. A. Pawar, and D. R. Shinde, "Colloidal MnO_2 catalysed degradation of two azo dyes methyl red and methyl orange from aqueous medium," *International Journal of Science and Research*, vol. 4, pp. 1119–1122, 2013.
- [31] X.-W. Shi, Y.-M. Du, L.-P. Sun, J.-H. Yang, X.-H. Wang, and X.-L. Su, "Ionically crosslinked alginate/carboxymethyl chitin beads for oral delivery of protein drugs," *Macromolecular Bioscience*, vol. 5, no. 9, pp. 881–889, 2005.
- [32] P. Degen, S. Leick, and H. Rehage, "Mechanical stability of ionotropic alginate beads," *Zeitschrift für Physikalische Chemie*, vol. 223, no. 9, pp. 1079–1090, 2009.
- [33] G. T. Grant, E. R. Morris, D. A. Rees, P. J. C. Smith, and D. Thom, "Biological interactions between polysaccharides and divalent cations: the egg-box model," *FEBS Letters*, vol. 32, no. 1, pp. 195–198, 1973.
- [34] Y. Dong, W. Dong, Y. Cao, Z. Han, and Z. Ding, "Preparation and catalytic activity of Fe alginate gel beads for oxidative degradation of azo dyes under visible light irradiation," *Catalysis Today*, vol. 175, no. 1, pp. 346–355, 2011.
- [35] S. K. Papageorgiou, E. P. Kouvelos, E. P. Favvas, A. A. Sapidis, G. E. Romanos, and F. K. Katsaros, "Metal-carboxylate interactions in metal-alginate complexes studied with FTIR spectroscopy," *Carbohydrate Research*, vol. 345, no. 4, pp. 469–473, 2010.
- [36] T. Kokubo, M. Hanakawa, M. Kawashita et al., "Apatite-forming ability of alginate fibers treated with calcium hydroxide solution," *Journal of Materials Science: Materials in Medicine*, vol. 15, no. 9, pp. 1007–1012, 2004.
- [37] C. Prabhu, S. Wanjari, S. Gawande et al., "Immobilization of carbonic anhydrase enriched microorganism on biopolymer based materials," *Journal of Molecular Catalysis B: Enzymatic*, vol. 60, no. 1–2, pp. 13–21, 2009.
- [38] T. Tripathy and R. P. Singh, "Characterization of polyacrylamide-grafted sodium alginate: a novel polymeric flocculant," *Journal of Applied Polymer Science*, vol. 81, no. 13, pp. 3296–3308, 2001.
- [39] M. Nakayama, M. Shamoto, and A. Kamimura, "Surfactant-induced electrodeposition of layered manganese oxide with large interlayer space for catalytic oxidation of phenol," *Chemistry of Materials*, vol. 22, no. 21, pp. 5887–5894, 2010.
- [40] S. Liang, F. Teng, G. Bulgan, R. Zong, and Y. Zhu, "Effect of phase structure of MnO_2 nanorod catalyst on the activity for CO oxidation," *Journal of Physical Chemistry C*, vol. 112, no. 14, pp. 5307–5315, 2008.
- [41] A. Vázquez-Olmos, R. Redón, G. Rodríguez-Gattorno et al., "One-step synthesis of Mn_3O_4 nanoparticles: structural and magnetic study," *Journal of Colloid and Interface Science*, vol. 291, no. 1, pp. 175–180, 2005.
- [42] D. Sannino, V. Vaiano, L. A. Isupova, and P. Ciambelli, "Heterogeneous photo-fenton oxidation of organic pollutants on structured catalysts," *Journal of Advanced Oxidation Technologies*, vol. 15, no. 2, pp. 1224–1226, 2012.
- [43] J. Zhou and L. Zhang, "Structure and properties of blend membranes prepared from cellulose and alginate in NaOH/urea aqueous solution," *Journal of Polymer Science Part B: Polymer Physics*, vol. 39, no. 4, pp. 451–458.
- [44] H. L. A. El-Mohdy, "Radiation-induced degradation of sodium alginate and its plant growth promotion effect," *Arabian Journal of Chemistry*, vol. 10, pp. S431–S438, 2017.
- [45] S. K. Das, J. Bhowal, A. R. Das, and A. K. Guha, "Adsorption behavior of rhodamine B on *Rhizopus oryzae* biomass," *Langmuir*, vol. 22, no. 17, pp. 7265–7272, 2006.
- [46] J. W. Murray, "The surface chemistry of hydrous manganese dioxide," *Journal of Colloid and Interface Science*, vol. 46, no. 3, pp. 357–371, 1974.
- [47] P. Zhang, H. Li, S. Yao, and W. Wang, "Effects of pH and polarity on the excited states of norfloxacin and its 4'-N-acetyl derivative: a steady-state and time-resolved study," *Science China Chemistry*, vol. 57, no. 3, pp. 409–416, 2014.
- [48] S. K. Swaina, T. Patnaik, P. C. Patnaik, U. Jha, and R. K. Dey, "Development of new alginate entrapped Fe(III)-Zr(IV) binary mixed oxide for removal of fluoride from water bodies," *Chemical Engineering Journal*, vol. 215–216, pp. 763–771, 2013.
- [49] A. M. Raichur and M. J. Basu, "Adsorption of fluoride onto mixed rare earth oxides," *Separation and Purification Technology*, vol. 24, no. 1–2, pp. 121–127, 2001.
- [50] Y. S. Ho, *Adsorption of Heavy Metals from Waste Streams by Peat*, University of Birmingham, 1995.
- [51] Y. S. Ho and G. McKay, "The sorption of lead (II) on peat," *Water Research*, vol. 33, pp. 578–584, 1999.
- [52] E. Bulut, M. Özacar, and I. A. Şengil, "Adsorption of malachite green onto bentonite: equilibrium and kinetic studies and process design," *Microporous and Mesoporous Materials*, vol. 115, no. 3, pp. 234–246, 2008.
- [53] T. Qiu, Y. Zeng, C. Ye, and H. Tian, "Adsorption thermodynamics and kinetics of p-xylene on activated carbon," *Journal of Chemical and Engineering Data*, vol. 57, no. 5, pp. 1551–1556, 2012.
- [54] A. A. Jalil, S. Triwahyono, M. R. Yaakob et al., "Utilization of bivalve shell-treated *Zea mays* L. (maize) husk leaf as a low-cost biosorbent for enhanced adsorption of malachite green," *Bioresource Technology*, vol. 120, pp. 218–224, 2012.

- [55] R. Sancha, J. Bajpai, and A. K. Bajpai, "Designing of fullers-earth-containing poly(vinyl alcohol)-g-poly(2-acrylamido-2-methyl-1-propanesulfonic acid) nanocomposites: swelling and deswelling behaviors," *Journal of Applied Polymer Science*, vol. 118, no. 2, pp. 1230–1239, 2010.
- [56] I. Langmuir, "The adsorption of gases on plane surfaces of glass, mica and platinum," *The Journal of the American Chemical Society*, vol. 40, no. 9, pp. 1361–1403, 1918.
- [57] V. Vimonses, S. Lei, B. Jin, C. W. K. Chow, and C. Saint, "Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials," *Chemical Engineering Journal*, vol. 148, no. 2–3, pp. 354–364, 2009.
- [58] A. A. Ahmad, B. H. Hameed, and A. L. Ahmad, "Equilibrium and kinetics of disperse dye adsorption on activated carbon prepared from rattan sawdust by chemical activation," *International Conference Environmental Engineering*, 2008.
- [59] A. Z. M. Badruddoza, Z. B. Z. Shawon, W. J. D. Tay, K. Hidajat, and M. S. Uddin, " Fe_3O_4 /cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater," *Carbohydrate Polymers*, vol. 91, no. 1, pp. 322–332, 2013.
- [60] Y. Liu, M. Chen, and H. Yongmei, "Study on the adsorption of Cu(II) by EDTA functionalized Fe_3O_4 magnetic nanoparticles," *Chemical Engineering Journal*, vol. 218, pp. 46–54, 2013.
- [61] J. Ma, F. Yu, L. Zhou et al., "Enhanced adsorptive removal of methyl orange and methylene blue from aqueous solution by alkali-activated multiwalled carbon nanotubes," *ACS Applied Materials & Interfaces*, vol. 4, no. 11, pp. 5749–5760, 2012.
- [62] S. Tunç, T. Gürkan, and O. Duman, "On-line spectrophotometric method for the determination of optimum operation parameters on the decolorization of Acid Red 66 and Direct Blue 71 from aqueous solution by Fenton process," *Chemical Engineering Journal*, vol. 181–182, pp. 431–442, 2012.
- [63] A. Bach and R. Semiat, "The role of activated carbon as a catalyst in GAC/iron oxide/ H_2O_2 oxidation process," *Desalination*, vol. 273, no. 1, pp. 57–63, 2011.
- [64] W. Zhang, Z. Yang, X. Wang, Y. Zhang, X. Wen, and S. Yang, "Large-scale synthesis of $\beta\text{-MnO}_2$ nanorods and their rapid and efficient catalytic oxidation of methylene blue dye," *Catalysis Communications*, vol. 7, no. 6, pp. 408–412, 2006.
- [65] C. Ye, Y. Bando, G. Shen, and D. Golberg, "Thickness-dependent photocatalytic performance of ZnO nanoplatelets," *The Journal of Physical Chemistry B*, vol. 110, no. 31, pp. 15146–15151, 2006.