Research Article

In Situ Synthesis and Characterization of ZnO/Chitosan Nanocomposite as an Adsorbent for Removal of Congo Red from Aqueous Solution

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ZnO/chitosan nanocomposite was successfully synthesized by in-situ precipitation method. The material was characterized by XRD, FESEM, TEM, FTIR, BET, and TGA. Results show that ZnO/chitosan nanocomposite has spherical shape with the average size of 20–25 nm. BET surface area and the average pore size of ZnO/chitosan nanocomposite are 2.2436 (m²/g) and 12.2 nm, respectively. The material was applied as an adsorbent for congo red removal from aqueous solutions. The congo red adsorption is better described by the Langmuir model \( R^2 = 0.996 \) than by the Freundlich model \( R^2 = 0.962 \). Therefore, it can be presumed that congo red was adsorbed in a single monolayer with the theoretical maximum adsorption capacity of 227.3 (mg/g). This is comparable to other available adsorbents. It can be suggested that ZnO/chitosan nanocomposite could serve as promising adsorbent for congo red in wastewater treatment technology.

1. Introduction

Despite of the fact that water resource is critical for the survival of living organisms, it is facing unprecedented challenges. Water pollution has become one of the most serious global issues. One of the leading sources of water pollutions is without doubt industrial activities. Every day, huge amounts of industrial wastewater are discharged into water body, and this severely affects not only the health of all living forms but also the quality of the whole ecosystem. Particularly, wastewaters from textile, pharmaceutical, food, cosmetics, plastics, photographic, paper industries, etc. are releasing large quantities of organic dyes into the environment. It was estimated that the world production of dyes in 1990s was 1,000,000 tons. For decades, it has rapidly increased with more than 100,000 types of commercial dyes. Approximately, the amount of 8–20% of the used dyes entered water environment. Numbers of them are toxic or are carcinogenic substances that are resistant to environmental degradation [1–3]. This results in the essential needs of effective and eco-friendly methods to remove these toxic chemicals from water.

Congo red dye, a benzidine-based anionic bisazo dye [1-napthalenesulfonic acid, 3,3-(4,4-biphenylene bis (azo) bis (4-amino-) disodium salt, is an interest subject to researchers due to its high toxicity to humans and its stability in the environment. In addition, after entering human bodies congo red can be metabolized into benzidine, a well-known carcinogen and mutagen in human [3, 4].

Several methods have been proposed in order to remove organic dyes from aqueous solutions such as adsorption, chemical coagulation, biodegradation, and advanced oxidation processes [5–8]. Compared to others, adsorption is considered as one the most popular methods with the advantages of being simple and cost-effective [9, 10]. Variety of materials have been investigated to be used as adsorbents for congo red, such as carbon-based materials, silica composites, cellulosic materials, and chitosan related materials [11–14]. Among them, chitosan would be a suitable candidate for producing the desirable adsorbents for congo red. Chitosan is an abundant biopolymer in nature. Its application as an adsorbent of heavy metal ions or colorants derives from its functional groups such as (–NH₂), (–OH). Nonetheless, chitosan has
several limitations such as poor adsorption capacity, low mechanical strength, low water solubility, and ease of decomposition under acidic conditions \cite{15}. For this reason, chitosan is usually combined with other substances such as hydroxyapatite, TiO$_2$, ZnO, Fe$_3$O$_4$ to form composites in order to overcome these disadvantages \cite{15, 16}. In this study, the aim was to synthesize ZnO/chitosan nanocomposite in situ from Zn$^{2+}$ by a simple and cost-effective precipitation method that allows to prepare the material in a large-scale. The material was thoroughly characterized and applied to remove congo red in aqueous solutions.

2. Materials and Methods

2.1. Materials and Method. Chitosan flakes (molecular weight $M_w = 32$ kDa and degree of deacetylation DD = 85\%) were prepared and characterized in our laboratory \cite{17}. All other chemicals including $\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$, $\text{CH}_3\text{COOH}$, and $\text{NaOH}$ were of analytical grade and used without further purification.

Chitosan solutions were prepared by completely dissolving 0.5 g of chitosan flakes in 100 mL of $\text{CH}_3\text{COOH}$ 1\% solution. ZnO/chitosan nanocomposite was produced by in situ precipitation method. The weight ratio of $m_{\text{chitosan}}/m_{\text{ZnO}}$ reported in former publications varies in a wide range from 0.084 to 1.0 \cite{18–20}. In this study, the weight ratio of about 0.3 was selected. The amount of 6.246 g of $\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ was added to 100 mL of chitosan solution. The mixture was stirred at 80°C for 30 min. The pH of the obtained solution was adjusted to 10 using sodium hydroxide solution 0.1 M. The mixture was additionally stirred for 2 hours at 80°C. The white precipitate was collected by centrifugation (Hettich Mikro 22R Centrifuges), washed with distilled water, and dried at 60°C overnight (8 hours). ZnO nanoparticles was synthesized by using similar procedure. However, $\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}$ was mixed in 100 mL of distilled water instead of chitosan solution.

2.2. Characterization Methods. The synthesized ZnO/chitosan nanocomposite was characterized by X-ray diffraction (XRD, Bruker D8 advanced X-ray diffractometer) with Cu Ka radiation ($\lambda = 1.54\AA$) and the scan rate of 0.02 $\text{s}^{-1}$ from 20° to 70°. Morphology of ZnO/chitosan nanocomposite was analyzed by Field Emission Hitachi S-4800 Scanning Electron Microscope (FE-SEM) and a transmission electron microscope (TEM), JEOL JEM-1010. Fourier transform infrared spectra (FT-IR) were obtained on a Nicolet iS10 Thermo Scientific spectrometer (USA). The thermal properties were studied by TGA (DSC131, Labsys TG/DSC1600, TMA, and Setaram, France). The nitrogen adsorption–desorption isotherms of the adsorbents (i.e. chitosan, ZnO nanoparticles and ZnO/chitosan nanocomposite) were recorded by the TriStar II 3020 nitrogen adsorption apparatus (Micromeritics Instruments, USA) at 77 K. The pore size distribution and the BET specific surface area ($S_{\text{BET}}$) of the samples were determined by the Barrett–Joyner–Halenda (BJH) method.

2.3. Adsorption Experiments. Chitosan used in adsorption experiment was prepared as the following: chitosan flakes were completely dissolved in $\text{CH}_3\text{COOH}$ 1\% solution and then precipitated by increasing the pH of the solution using NaOH 0.1 M. The mixture was stirred for 60 min. The precipitate was collected by centrifugation, washed with distilled water, and dried at 60°C overnight (8 hours).

The stock solution of congo red was prepared by dissolving 1 g congo red in 1000 mL distilled water. Desired congo red solutions were obtained by diluting the stock solution (1000 mg/L). Congo red concentrations of the solutions were confirmed by Agilent 8453 UV Vis-spectrophotometer at 497 nm before every adsorption experiment.

Batch experiments were carried out by mixing 0.02 g of the adsorbents with 40 mL of congo red solutions in 50 mL centrifuge tubes. The mixtures were ultrasonicated at 30°C (Elmasonic S100H Ultrasonic Bath) and then centrifuged at 6000 rpm. Congo red concentrations of supernatants were measured.

In order to find the equilibrium time of the congo red adsorption by ZnO/chitosan nanocomposite, the initial congo red concentration of 100 mg/L was applied. The supernatant was sampled at definite time intervals and measured for congo red concentration until negligible change in the congo red concentration was observed, signalling the equilibrium of the adsorption process. During the experiment, samples of supernatant were returned to the centrifuge tube after every measurement \cite{21}.

A series of solutions with different congo red concentrations varying from 100 to 550 mg/L was employed to determine the maximum congo red adsorption capacity of ZnO/chitosan nanocomposite. The reaction time was the equilibrium time of the congo red adsorption by ZnO/chitosan nanocomposite found in the previous experiment.

The congo red removal efficiencies of the three adsorbents were also compared by carrying out adsorption experiments with the initial congo red concentration of 100 mg/L.

The adsorbed amount of congo red per unit of weight of adsorbent, $q_t$ (mg/L), was calculated from the mass balance equation:

$$q_t = \frac{(C_0 - C_t)}{m},$$  \hspace{1cm} (1)

and percent of congo red removal:

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100,$$  \hspace{1cm} (2)

where $C_0$, $C_t$, and $C_e$ (mg/L) are initial congo red concentration, the congo red concentration after time $t$, and the congo red concentration at equilibrium, respectively; $V$ (L) is the volume of the solutions; and $m$ (g) is the mass of the adsorbents.

3. Results and Discussion

3.1. Characterization of ZnO/Chitosan Nanocomposite. XRD patterns of ZnO/chitosan nanocomposite are shown in Figure 1. The major peaks at scattering angles (2θ) of 31.8°, 34.4°, 36.2°, 47.5°, 56.6°, 62.8°, 66.3°, 68.1°, and 69.3° correspond to the lattice planes of (100), (002), (101), (102), (110), (103), (200),...
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These represent the wurtzite hexagonal phase of ZnO, confirming the formation of ZnO particles. The observed diffraction reflections are well-matched with the reported literature as well as standard JCPDS data card No. 36–1451 [18, 19, 22, 23]. Other diffraction peaks referring to any impurities were not detected, suggesting that precipitated Zn(OH)$_2$ was completely decomposed to ZnO.

The crystal size of ZnO/chitosan nanocomposite was calculated from the broadening of diffraction peaks using the Debye–Scherer formula [5]:

$$D = \frac{k\lambda}{\beta \cos \theta},$$  \hspace{1cm} (3)

where $D$ is crystal size, $k$ is constant (0.94), $\lambda = 0.154$ nm represents the wavelength of X-ray radiation, $\beta$ is the full width at half maximum of diffraction peaks (FWHM) in radian, and $\theta$ is the Bragg’s angle. The crystal size of the ZnO/chitosan nanocomposite was evaluated by measuring the FWHM of the most intense peak (101) because it has a relatively strong intensity and does not overlap with other diffraction peaks. Approximately, the average crystal size of ZnO/chitosan nanocomposite is of 22 nm.

Figure 1 shows the FE-SEM (a) and TEM (b) images of the ZnO/chitosan nanocomposite. As can be seen, the spherical particles appear to be quite distinct and uniform, and the size of the particles ranges from 20 to 25 nm.

Figure 3 shows the FTIR spectra of ZnO nanoparticles, chitosan, and ZnO/chitosan nanocomposite. In the FTIR spectrum of ZnO nanoparticles (Figure 3(a)), the peak at 3449 cm$^{-1}$ corresponds to the O–H stretching vibration of H$_2$O in ZnO; the peak at 1634 cm$^{-1}$ may be due to the O–H bending vibration; the H–O–H bending vibration or the absorbed CO$_2$ bands may be responsible for the peak at 1382 cm$^{-1}$; and the band in the range of 528–435 cm$^{-1}$ refers to the stretching mode of Zn–O [24–26]. In the spectrum of chitosan (Figure 3(b)), the broad peak at 3463 cm$^{-1}$ is due to the –OH/–NH$_2$ stretching vibration; the peaks at 2930 and 2860 cm$^{-1}$ are attributed to the C–H bending vibration; the peaks at 1651 cm$^{-1}$ and 1564 cm$^{-1}$ are attributed to the C–H stretching vibration; the peak at 1064 cm$^{-1}$ may be due to the deformation of amide II; and the peaks at 1023 cm$^{-1}$ may refer to the C–O stretching vibration [27–31]. Compared to the spectrum of chitosan, a new band from 528 to 412 cm$^{-1}$ referring to the Zn–O stretching appears in the spectrum of ZnO/chitosan.
strong intermolecular hydrogen bonding interaction between chitosan and ZnO [32].

The thermogravimetric (TG) curves of chitosan, ZnO nanoparticles and ZnO/chitosan nanocomposite were recorded (Figure 4). The TG curve of ZnO nanoparticles slightly went down as the temperature was increased from 25 to 800°C. The mass loss of 2.08% corresponds to the loss of absorbed water (Figure 4(a)). In the TG curve of chitosan, (c)). This indicates the existence of ZnO in the structure of the nanocomposite. In addition, the peak relating to the –OH/–NH₂ stretching vibration in chitosan (at 3463 cm⁻¹) is broader and shifted to the lower wavenumber (3446 cm⁻¹) in the nanocomposite, suggesting the presence of ZnO in the structure. The peak at 1643 cm⁻¹ in chitosan is not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 1428 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 1234 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 1130 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 1022 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 900 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 763 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 615 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 531 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 480 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 400 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 350 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 300 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 250 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 200 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 150 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 100 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 50 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure. The peak at 0 cm⁻¹ in chitosan is also not present in the nanocomposite, indicating the presence of ZnO in the structure.

![Graph](https://via.placeholder.com/150)

**Figure 4**: Thermo-gravimetric curves of ZnO nanoparticles (a), chitosan (b), and ZnO/chitosan nanocomposite (c).

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_BET (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO nanoparticles</td>
<td>9.7852</td>
<td>0.031169</td>
<td>11.3386</td>
</tr>
<tr>
<td>Chitosan</td>
<td>1.7461</td>
<td>0.010181</td>
<td>21.6846</td>
</tr>
<tr>
<td>ZnO/chitosan nanocomposite</td>
<td>2.2436</td>
<td>0.007779</td>
<td>12.2102</td>
</tr>
</tbody>
</table>

*BET surface area calculated from the linear part of the BET plot. BJH adsorption cumulative volume of pores between 17.0 Å and 3000.0 Å diameter. Adsorption average pore diameter (4 V/A by BET).

![Table](https://via.placeholder.com/150)

**Table 2**: Parameters of the Langmuir and Freundlich adsorption isotherms.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>q_m (mg/g)</th>
<th>K_L (L/mg)</th>
<th>R²</th>
<th>K_F (mg/g)</th>
<th>n</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>227.3</td>
<td>0.048</td>
<td>0.996</td>
<td>101.3</td>
<td>7.91</td>
<td>0.962</td>
</tr>
</tbody>
</table>

The thermogravimetric curves of chitosan, ZnO nanoparticles and ZnO/chitosan nanocomposite were recorded (Figure 4). The TG curve of ZnO nanoparticles slightly went down as the temperature was increased from 25 to 800°C. The mass loss of 2.08% corresponds to the loss of absorbed water (Figure 4(a)). In the TG curve of chitosan,
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The formation of hydrogen bonding between chitosan and zinc oxide in the composite may be responsible to this phenomenon [21].

Nitrogen adsorption–desorption isotherms of ZnO nanoparticles, chitosan, and ZnO/chitosan nanocomposite are displayed in Figure 5. The three materials have type IV isotherm (IUPAC classification) [34]. Moreover, the very narrow hysteresis loops at high (chitosan and nanocomposite) and moderate relative pressure (ZnO nanoparticles) indicate the presence of mesopores in their structure [34–36]. The similarity between the isotherms of chitosan, and ZnO/chitosan nanocomposite shows the similar porous structures of the two materials. BET surface areas of ZnO nanoparticles, chitosan, and ZnO/chitosan nanocomposite are 9.7852, 1.7461, and 2.2436 (m²/g), respectively (Table 1). The average pore size of the nanocomposite is 12.2 nm.

3.2. Congo Red Adsorption by ZnO/Chitosan Nanocomposite. The relationship between adsorption capacity of ZnO/chitosan nanocomposite and adsorption time is illustrated in Figure 6. The adsorption capacity sharply rises within the first 30 minutes and negligibly changes after 120 minutes. Therefore, the reaction time in other adsorption experiments is selected to be 120 minutes.

The two most common adsorption isotherms including the Langmuir and Freundlich adsorption isotherms were applied to characterize the adsorption of congo red by ZnO/chitosan nanocomposite. The Langmuir model assumes monolayer adsorption of the adsorbate with no interaction among adsorbate molecules, whereas the Freundlich model assumes multilayer adsorption of the adsorbate.

Corresponding mathematical expressions of the Langmuir and Freundlich adsorption isotherms are written as [37, 38]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_mK_L},$$  \hspace{1cm} (4)

$$\log q_e = \log K_F + \frac{1}{n}\log C_e,$$  \hspace{1cm} (5)

there are three stages of mass loss (Figure 4(b)). The first stage occurs from 50 to 120°C and reaches to the maximum degradation rate at 107.2°C with 13.49% mass loss, referring to the dehydration process. The second stage (from 220 to 350°C) with 26.50% mass loss may be due to the degradation and decomposition of the backbone chain of volatile fraction. The last stage (from 350 to 800°C) with 16.65% mass loss may relate to the decomposition of the backbone chain of residual chitosan [33]. A noticeable three-stage mass loss was also observed in the TG curve of ZnO/chitosan nanocomposite (Figure 4(c)). The first stage at the temperature from 50°C to 150°C is accounted for the thermal dehydration. The last two stages with the approximate total mass loss of 16.21% (from 220 to 350°C) and 8.67% (from 350 to 600°C) are presumed to be the thermal decomposition of volatile and residual chitosan in the nanocomposite, respectively. The maximum degradation rate of volatile chitosan is shifted from 251.8°C in chitosan to 261.2°C in the nanocomposite, while that of residual chitosan is shifted from 440.8°C in chitosan to 459.5°C in the nanocomposite. The formation of hydrogen bonding between chitosan and zinc oxide in the composite may be responsible to this phenomenon [21].

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$$\log q_e = \log K_F + \frac{1}{n}\log C_e,$$  \hspace{1cm} (5)

3.2. Congo Red Adsorption by ZnO/Chitosan Nanocomposite. The relationship between adsorption capacity of ZnO/chitosan nanocomposite and adsorption time (volume: 40 mL; adsorbent dose: 0.02 g; initial congo red concentration: 100 mg/L).

![Figure 5: Nitrogen adsorption–desorption isotherms of ZnO nanoparticles, chitosan, and ZnO/chitosan nanocomposite.](image)

![Figure 6: The relationship between adsorption capacity of ZnO/chitosan nanocomposite and adsorption time (volume: 40 mL; adsorbent dose: 0.02 g; initial congo red concentration: 100 mg/L).](image)

$\textbf{Table 3: Maximum congo red adsorption capacity of several adsorbents.}$

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$q_m$ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_3$O$_4$/Bi$_2$S$_3$ microspheres</td>
<td>92.24</td>
<td>[39]</td>
</tr>
<tr>
<td>MWCNTs/calcined eggshell</td>
<td>136.99</td>
<td>[40]</td>
</tr>
<tr>
<td>Magnetic CS/carrageenan ampholytic microspheres</td>
<td>212.7</td>
<td>[41]</td>
</tr>
<tr>
<td>Chitosan coated magnetic Fe$_3$O$_4$ particle</td>
<td>42.62–56.66</td>
<td>[42]</td>
</tr>
<tr>
<td>Zinc peroxide nanomaterial</td>
<td>208</td>
<td>[43]</td>
</tr>
<tr>
<td>ZnO microspheres</td>
<td>304</td>
<td>[44]</td>
</tr>
<tr>
<td>Mg-doped ZnO NPs</td>
<td>125</td>
<td>[45]</td>
</tr>
<tr>
<td>Hierarchical porous ZnO</td>
<td>334</td>
<td>[46]</td>
</tr>
<tr>
<td>ZnO/chitosan nanocomposite</td>
<td>227.3</td>
<td>This study</td>
</tr>
</tbody>
</table>

$\textbf{Figure 5: Nitrogen adsorption–desorption isotherms of ZnO nanoparticles, chitosan, and ZnO/chitosan nanocomposite.}$

$\textbf{Figure 6: The relationship between adsorption capacity of ZnO/chitosan nanocomposite and adsorption time (volume: 40 mL; adsorbent dose: 0.02 g; initial congo red concentration: 100 mg/L).}$
be concluded that the obtained nanocomposite has high potential to be applied for congo red removal.

Comparison among congo red removal efficiencies of ZnO/chitosan nanocomposite, ZnO nanoparticles, and chitosan are quite interesting (Figure 8). It is well known that the adsorption capacity strongly depends on the total surface area and the number of binding sites of adsorbents. Despite the fact that the total surface area of ZnO nanoparticles is approximately 5 times higher than that of chitosan and ZnO/chitosan nanocomposite, ZnO nanoparticles have the lowest congo red removal efficiency. More than 90% of congo red was removed by ZnO/chitosan nanocomposite after 2 hours and 78.1% of congo red was eliminated by chitosan, while only 39.2% of the dye was removed by ZnO nanoparticles. This suggests that the presence of chitosan in the nanocomposite is mainly responsible for the congo red adsorption capability of the material. In ZnO/chitosan nanocomposite, the ZnO may play a role as a rigid support for the thin film of chitosan, which contains –OH/–NH₂ groups. These functional groups probably play a role as binding sites to congo red molecules as proposed in numbers of publications [21, 47]. Further study, however, should be carried out in order to address the exact mechanism of the adsorption process.

### 4. Conclusions

In the present work, the ZnO/chitosan nanocomposite was successfully generated by direct simple, fast, and eco-friendly in situ precipitation method. XRD results reveal that the nanocomposite has wurtzite structure. The size of the nanocomposite is approximately 20–25 nm. The FESEM and TEM images show the spherical morphology of the material. The similarity in porous structures of chitosan and ZnO/chitosan nanocomposite was observed. BET surface area of ZnO/chitosan nanocomposite is 2.2436 (m²/g) and the average pore size of the nanocomposite is 12.2 nm. The material was applied as an adsorbent in order to remove congo red from aqueous solutions. According to the Langmuir isotherm model, the
theoretical maximum adsorption capacity of ZnO/chitosan nanocomposite is 227.3 (mg/g). From this result, it can be suggested that ZnO/chitosan nanocomposite could serve as a promising adsorbent for Congo red in wastewater treatment technology.

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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References


