



## Newly generated magnesium peroxide used for malodorous river water treatment

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### ABSTRACT

In this study, malodorous river water was treated by microwave enhanced composite technology. On this basis, the catalyst of iron hydrated oxide was developed. Newly generated magnesium peroxide was catalyzed by iron hydrated oxide. With total organic carbon (TOC) as the index, the water quality was improved significantly. The optimal operating conditions were as follows: the amount of iron of 15 mmol/250 mL wastewater, the calcination temperature of 500°C, the amount of hydrogen peroxide of 8 mL, the amount of magnesium sulfate of 6 g, and the microwave irradiation power of medium-high (539 W). The removal rate of TOC was the highest at 72.38% under these conditions.

*Keywords:* Magnesium peroxide; Malodorous river water; Iron hydrated oxide; Microwave enhanced composite technology

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### 1. Introduction

The course of urban river regulation in China is divided into three stages, namely, the primary regulation stage from 1950s to 1970s, the engineering application stage from 1980s to 1990s, and the ecological restoration and protection stage from the end of 1990s to present [1].

In the environmental quality standards of surface water (GB3838-2002), the surface water is divided into case 1 water, case 2 water, case 3 water, case 4 water, and case 5 water. In this study, the malodorous river water belonged to the inferior case 5 water. Conventional drinking water treatment technology no longer reaches the treatment requirements of surface water; thus, a new technology of wastewater treatment is an important subject worthy of attention. In this research, microwave, iron hydrated oxide, and magnesium peroxide had an intense synergistic effect; thus, the effect of microwave enhanced composite technology was studied and found belonging to a new technology of wastewater treatment [2–6].

Herein, we report for the first time that iron hydrated oxide and newly generated magnesium peroxide were Fenton-like reagents [7–9]. The preparation of iron hydrated oxide adopted isovolumetric impregnation method. Granular activated carbon (GAC) was adopted as the catalyst carrier. Cerium was added as the addition agent to ensure uniform distribution of iron hydrated oxide on the surface of the activated carbon [10–14]. Cerium usually has poor solubility in the solid phase. Thus, newly generated  $MgO_2$  was generated by  $MgSO_4$ , NaOH, and  $H_2O_2$ .

The microwave was adopted alone for wastewater treatment or connected with oxidant and catalyst to form a combination process [15–19]. Oxidation was carried out completely and rapidly, achieving an ideal removal effect in wastewater treatment. This study aimed to treat malodorous water by microwave enhanced composite technology. The influencing factors of the removal rate of organic compounds were optimized. The experimental results were described from the perspective of the average oxidation state of organic carbon of the effluent. This study provides

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necessary technical guidance for the application of microwave enhanced composite technology.

## 2. Materials and methods

The raw water was derived from an artificial river in a university campus. The water body was a malodorous river. The water quality indexes, as shown in Table 1, indicating that the pollution of raw water was serious.

Chemical oxygen demand (COD) comprised indicators reflecting the degree of water pollution. COD was determined by the oxidant of  $K_2Cr_2O_7$ . However, the standard method of COD determination has some defects, such as complex operation, long analysis time, high-cost, and secondary pollution. Therefore, total organic carbon (TOC) was the indicator used to determine organic pollutants. TOC was determined by a TOC detector made by Shimadzu. Hydrogen peroxide was an analytical pure agent with a concentration of 30%.

The average oxidation state of organic carbon was expressed by COD and TOC. It was relevant to the degree of change in the structure of organic compounds after oxidation. Therefore, the effect of chemical oxidation was expressed as follows.

$$\frac{4(\text{TOC}-\text{COD})}{\text{TOC}} = \text{average oxidation state of organic carbon [20]}$$

where the unit of TOC is mol C and the unit of COD is mol  $O_2$ .

The corresponding valence of carbon in  $CH_4$  was  $-4$ , and the corresponding valence of carbon in inorganic carbon ( $CO_2$ ) was  $4$ . The average oxidation state of organic carbon of raw water was  $-0.214$ , which indicated the presence of many reducing substances in the raw water.

Newly generated  $MgO_2$  was generated by  $MgSO_4$ ,  $NaOH$ , and  $H_2O_2$ . Catalyst preparation adopted isovolumetric impregnation method, and distilled water dosage was determined as 4 mL/10 g GAC. First, ferric nitrate was weighed quantitatively. Next, cerium nitrate was weighed quantitatively. All were placed into a beaker, and 4 mL of distilled water was added to dissolve them completely. Quantitative granular activated carbon was added into the beaker, which was heated in an autoclave at  $120^\circ\text{C}$  for 20 min to achieve adequate hydrolysis. The reactor was opened, semi-finished products were placed in a muffle furnace at a certain temperature, and the calcination time was 1.5 h. Thus, the catalyst of iron hydrated oxide ( $FeO_x$ ) was

successfully prepared. The temperature of  $120^\circ\text{C}$ , the heating time of 20 min, and the calcination time of 1.5 h were selected based on many experimental experiences.

## 3. Results and discussion

### 3.1. Major factor optimization experiment

Pollutants in river water are mainly composed of starch, protein, fat, and other soluble compounds [21]. In this study, extensive research was conducted on microwave enhanced composite technology, including catalyst preparation and Fenton-like reaction mechanism. On this basis, microwave enhanced composite technology was defined, and the effect of the treatment was studied.

#### 3.1.1. Effect of iron molar quantity on the efficiency of microwave enhanced composite technology

The iron molar quantities were 5, 10, 15, 20, and 25 mmol. The  $Fe(NO_3)_3$  dosages were 1.2, 2.4, 3.6, 4.8, and 6.0 g/250 mL wastewater. The reaction time was 6 min. The TOC amounts of influent and effluent were determined, as shown in Figs. 1 and 2, respectively.

Fig. 1 shows that numerous catalysts enhanced the ineffective decomposition of hydrogen peroxide. Notably, 15 mmol  $Fe(NO_3)_3$  corresponded to 72.13% TOC removal. Thus, 3.6 g (15 mmol) was the best value of  $Fe(NO_3)_3$  dosage.

Fig. 2 shows that when the  $Fe(NO_3)_3$  dosage was 15 mmol, the average oxidation state of organic carbon in the effluent was the highest. This finding indicated that starch, protein, fat, and other soluble compounds were decomposed into organic acid of a small molecule by microwave enhanced composite technology. Thus, the organic acid of the small molecule was dominant in the effluent.

#### 3.1.2. Effect of calcination temperature on the efficiency of microwave enhanced composite technology

Isovolumetric impregnation method was adopted in the experiment. The calcination temperatures were  $300^\circ\text{C}$ ,  $400^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $600^\circ\text{C}$ , and  $700^\circ\text{C}$ . The reaction time was 6 min.

Table 1  
Monitoring results of artificial river water on campus

Analysis item	Water quality index
pH	7.26
Dissolved oxygen (mg/L)	0
Total organic carbon (mg/L)	48.35
Chemical oxygen demand (mg/L)	139.1
$NH_4^+-N$ (mg/L)	21.8
Total phosphorus (mg/L)	2.32

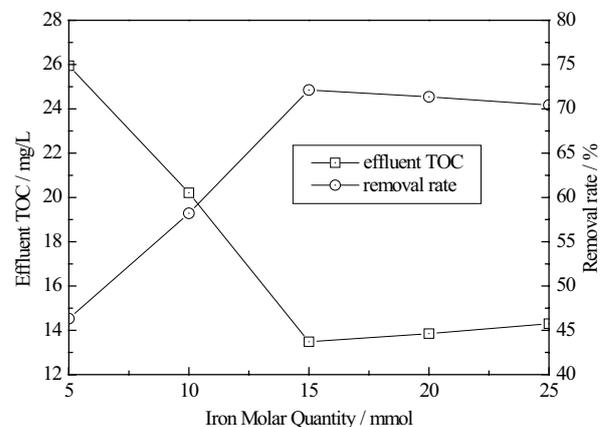


Fig. 1. Effect of iron molar quantity on TOC removal.

The TOC amounts of influent and effluent were determined. The average oxidation states of organic carbon of influent and effluent were determined, as shown in Figs. 3 and 4, respectively.

Fig. 3 shows that the removal rate of TOC corresponding to 500°C was the highest at 72.34%. The decomposition of  $\text{Fe}(\text{NO}_3)_3$  was complete under this condition.

Fig. 4 shows that when the calcination temperature was 500°C, the average oxidation state of organic carbon in the effluent was the highest. Therefore, the yield of  $\text{FeO}_x$  was the largest under 500°C.

### 3.1.3. Effect of hydrogen peroxide dosage on the efficiency of microwave enhanced composite technology

The hydrogen peroxide dosages were 4, 6, 8, 10, and 20 mL/250 mL wastewater. The reaction time was 6 min. After the reaction was completed, the TOC amounts of influent and effluent were determined, as shown in Figs. 5 and 6, respectively.

Fig. 5 shows that, when the hydrogen peroxide dosage was 4 mL/250 mL wastewater, the removal rate of TOC was only 42.33%. The removal rate of TOC was low because the hydrogen peroxide dosage was relatively low. When the hydrogen peroxide dosage was 10 mL/250 mL wastewater, the removal rate of TOC was 72.55%. However, the removal rate of TOC was 72.45% when the hydrogen peroxide dosage was 8 mL/250 mL wastewater. The hydrogen peroxide dosage of 8 mL/250 mL wastewater was appropriate when considering the reagent cost.

Fig. 6 shows that when the hydrogen peroxide dosage was 8 mL/250 mL wastewater, the average oxidation state of organic carbon in the effluent was the highest. This result indicated that the production of  $\cdot\text{OH}$  was the largest under this condition.

### 3.1.4. Effect of $\text{MgSO}_4$ dosage on the efficiency of microwave enhanced composite technology

$\text{MgSO}_4$  dosages were 2, 4, 6, 8, and 10 g/250 mL wastewater. The TOC amounts of influent and effluent were determined, as shown in Figs. 7 and 8, respectively.

Fig. 7 shows that the maximum value of the removal rate of TOC of 72.41% appeared at 6 g/250 mL. When the  $\text{MgSO}_4$  dosage was over 8 g, the removal rate of TOC declined because excessive  $\text{MgSO}_4$  was not beneficial to the formation of  $\text{MgO}_2$ . Thus, the  $\text{MgSO}_4$  dosage was fixed at 6 g/250 mL wastewater.

Fig. 8 shows that when the  $\text{MgSO}_4$  dosage was 6 g/250 mL wastewater, the average oxidation state of organic carbon in the effluent was the highest. Therefore, the generation of  $\text{MgO}_2$  was the largest under this condition.

### 3.1.5. Effect of microwave irradiation power on the efficiency of microwave enhanced composite technology

The following experiments were conducted to investigate the effect of microwave irradiation power on the efficiency of the aforementioned technology. The microwave irradiation power was adjusted from low to high, namely, medium-low (281 W), medium (385 W), medium-high

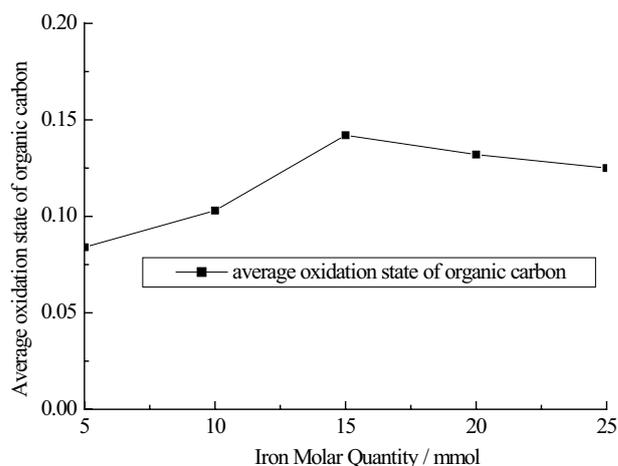


Fig. 2. Effect of iron molar quantity on the average oxidation state of organic carbon.

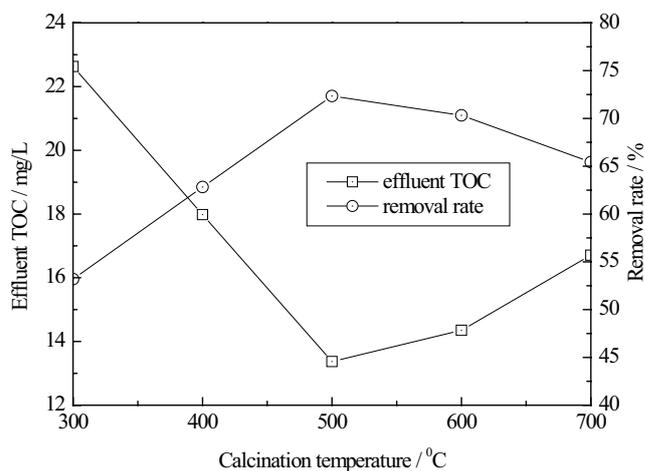


Fig. 3. Effect of calcination temperature on TOC removal.

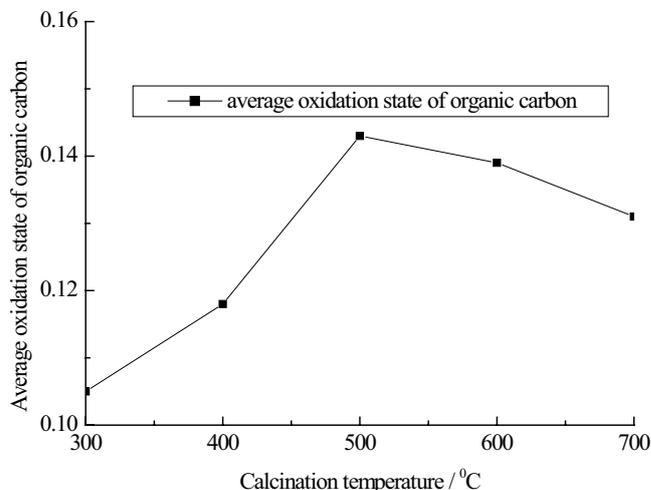


Fig. 4. Effect of calcination temperature on the average oxidation state of organic carbon.

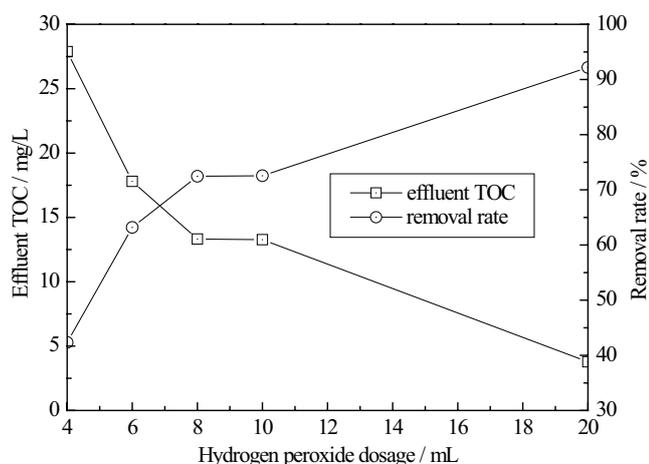


Fig. 5. Effect of hydrogen peroxide dosage on TOC removal.

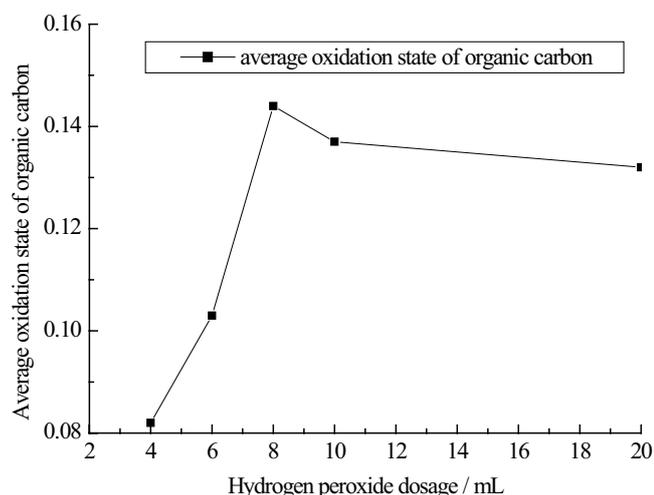


Fig. 6. Effect of hydrogen peroxide dosage on the average oxidation state of organic carbon.

(539 W), and high (700 W). After the reaction was completed, the TOC amounts of influent and effluent were determined, as shown in Figs. 9 and 10, respectively.

Fig. 9 shows that, when the microwave irradiation powers were medium-low, medium, medium-high, and high, the removal rates of TOC were 54.61%, 65.22%, 72.38, and 71.22%, respectively. When the microwave irradiation power was medium-low (281 W), the removal rate of TOC was low. When the microwave irradiation powers were medium (385 W) and medium-high (539 W), the removal rate of TOC increased by a large margin. When the microwave irradiation power continued to increase to high (700 W), the removal rate of TOC decreased slightly. Therefore, the most appropriate microwave irradiation power was identified as medium-high (539 W).

Fig. 10 shows that, when the microwave irradiation power was medium-high (539 W), the average oxidation state of organic carbon in the effluent was the highest. This

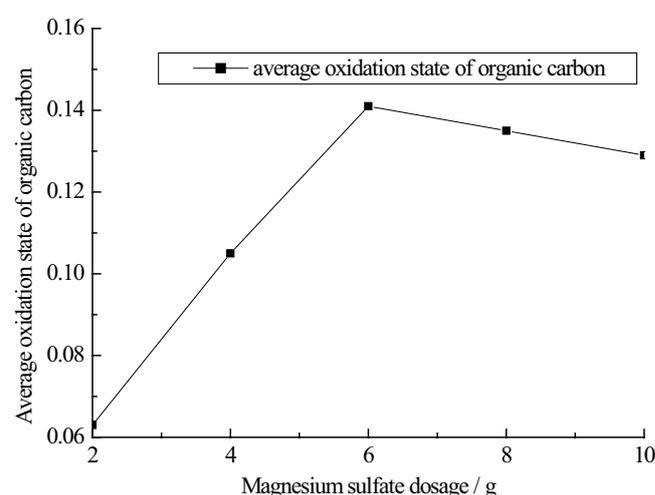


Fig. 8. Effect of  $MgSO_4$  dosage on the average oxidation state of organic carbon.

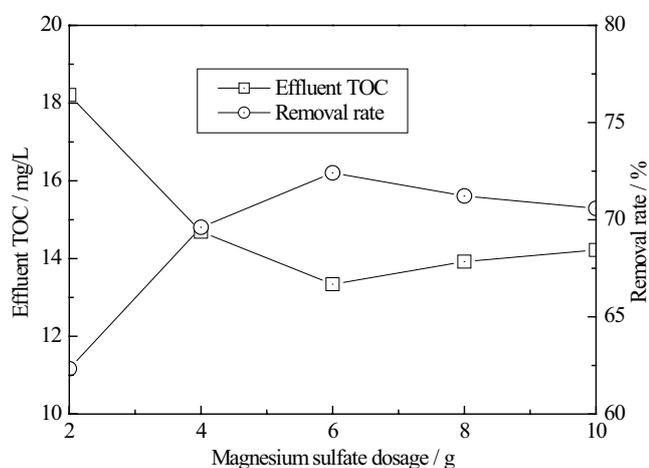


Fig. 7. Effect of  $MgSO_4$  dosage on TOC removal.

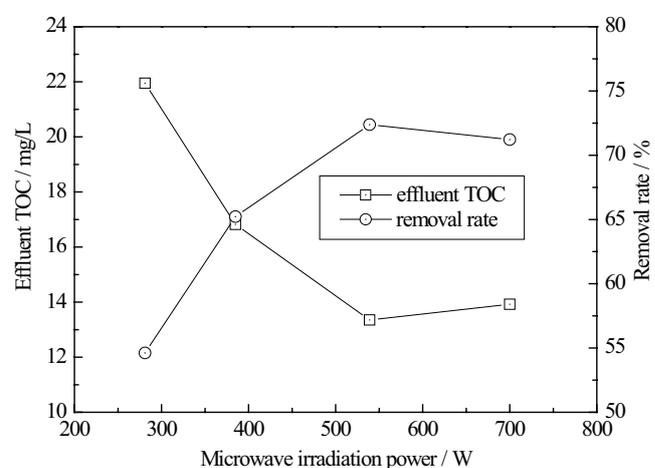


Fig. 9. Effect of microwave irradiation power on TOC removal.

result indicated that the production of  $\cdot\text{OH}$  was the largest under this condition.

### 3.2. Catalyst characterization

The internal structure and properties of the catalyst were studied by Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD), and other methods. As verified,  $\text{FeO}_x$  could catalyze  $\text{MgO}_2$  to produce  $\cdot\text{OH}$  with high efficiency.

#### 3.2.1. BET test for catalyst and catalyst carrier

The BET specific surface area of original activated carbon was  $42.9286 \text{ m}^2/\text{g}$ , and the pore volume was  $0.016768 \text{ cm}^3/\text{g}$ . When the calcination temperature was  $500^\circ\text{C}$ , the BET specific surface area and pore volume of catalyst support were the largest at  $232.3237 \text{ m}^2/\text{g}$  and  $0.126388 \text{ cm}^3/\text{g}$ , respectively. Thus, the catalyst was the most active at this time. The effect of the newly generated  $\text{MgO}_2$ , which acted as an oxidant, was the best when it was used in combination with the catalyst.

#### 3.2.2. SEM test for the catalyst

Fig. 11 shows that the sizes of surface particles were consistent. The preparation of the catalyst was successful. Furthermore, the water losses were less at  $300^\circ\text{C}$  and  $400^\circ\text{C}$  and were more at  $600^\circ\text{C}$  and  $700^\circ\text{C}$ . The water loss was acceptable at  $500^\circ\text{C}$ . These results indicated that the dewatering process of the catalyst greatly influenced its active structure formation.

#### 3.2.3. XRD test for the catalyst

Metal oxides in the catalyst remained amorphous because the particle size was very small. It was called bulk floc and was one of the important reasons for the high efficiency of  $\text{FeO}_x$ .

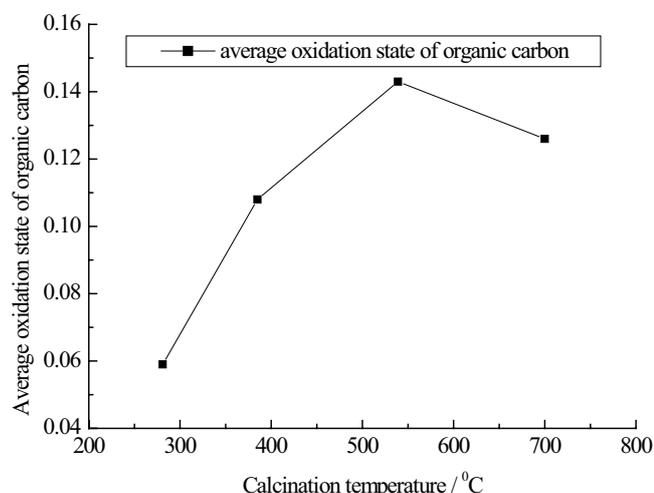


Fig. 10. Effect of microwave irradiation power on the average oxidation state of organic carbon.

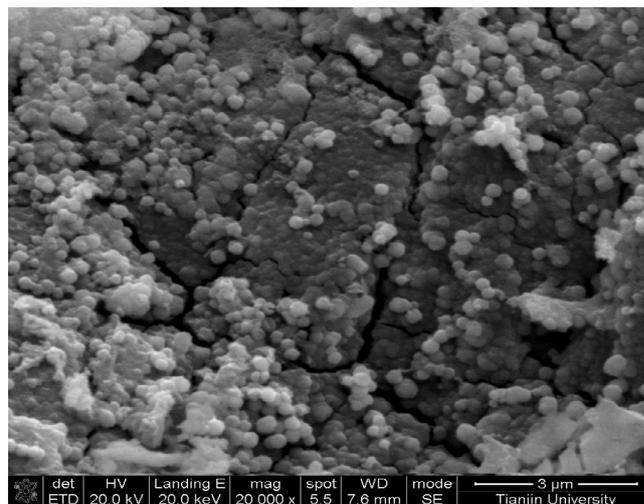


Fig. 11. SEM images of the catalyst (20,000 $\times$ ).

Under the microwave action, the bulk floc turned into a certain amount of polymerized iron. The form of polymerized iron was the same as that formed by the traditional Fenton system. Moreover, it had difficulty in escaping from the activated carbon carrier for bulk floc.

## 4. Conclusion

Microwave enhanced composite technology highly affected the pollutant removal in malodorous river water due to the newly generated  $\text{MgO}_2\cdot\text{FeO}_x$ , which acted as the catalyst, was highly effective for advanced oxidation. Microwave irradiation also greatly improved the degradation efficiency of pollutants. Microwave, iron hydrated oxide, and magnesium peroxide had an intense synergistic effect. Therefore, the efficiency of microwave enhanced composite technology was satisfactory. The optimal operating conditions were as follows: the amount of  $\text{Fe}(\text{NO}_3)_3$  of 3.6 g, the calcination temperature of  $500^\circ\text{C}$ , the amount of  $\text{H}_2\text{O}_2$  of 8 mL, the amount of  $\text{MgSO}_4$  of 6 g, and the microwave irradiation power of medium-high (539 W). The removal rate of TOC was the highest at 72.38% under these conditions.

The newly generated  $\text{MgO}_2$  reacted with the bulk floc, that is, catalysis and synergy occurred. Thus, the production of  $\cdot\text{OH}$  increased, and the effect of microwave enhanced composite technology was improved.

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