Experimental study of manganese dioxide doped with metal for the treatment of phenolic wastewater

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Abstract—The wastewater containing phenol is harmful, and the process is complicated, photocatalytic oxidation technology is believed to be the greenest and promising strategy for contaminants removal because of the solar energy utilization and no additional oxidants. Herein, manganese dioxide (MnO2) doped with metal was fabricated by a low-temperature hydrothermal method, the specific surface area of MnO2 photocatalyst was significantly enhanced by doping metal ion. This making the photocatalytic performance improved obviously, and further applying for phenol degradation under visible light irradiation at room temperature.

1. Introduction
Phenolic wastewater seriously inhibits the growth and normal metabolic activities of microorganisms. Organic pollutants in the wastewater lead to the decline of their biochemical properties, which is very difficult to treat and poses a threat to human health and environmental development [1]. Moreover the reports on its toxicity and persistence have aroused great concern worldwide [2,3]. Conventional water treatment processes including biodegradation and adsorption, can remove most organic compounds from wastewater [4]. Nevertheless, the biodegradation process is nonideal for the treatment of toxic organics [5]. Although these pollutants can be transferred from the polluted water to the solid by adsorption technology, it still needs further treatment. Among various remediation approaches, photocatalysis is considered to be a promising method for the treatment of phenolic wastewater [6]. Thus, developing a facile and green method for constructing highly efficient photocatalysts is vitally important and highly desirable. Polyvalent manganese has attracted growing attention in the photocatalytic field because it could be sensitized by visible light [7,8]. Manganese dioxide (MnO2) has a narrow bandgap and high specific surface area, which can improve the utilization of visible light. The doping of metals allows manganese dioxide to provide valuable advantages such as strong visible light absorption, more active sites, and enhanced charge separation performance [9]. The effects of metal doping types and ratios on bandgap structure and specific surface area of manganese dioxide and the environmental conditions for maintaining high photocatalytic efficiency were investigated herein.

2. Experimental
2.1. Chemicals and instrument
All chemicals used are analytical grade without further purification. (The chemical reagents utilized in this study were analytical grade (≥99.7%) unless stated otherwise.) Deionized (DI) water was used as a
solvent. A UV-Vis spectrophotometer (Shanghai Jing Hua Technology Instruments Co.) was used to determine the adsorption efficiency of the samples for phenol.

2.2. Synthesis.
In this paper, pure manganese dioxide and metal-doped manganese dioxide were prepared using a low-temperature hydrothermal method. An appropriate amount of this photocatalyst was used for the photocatalytic oxidation of 200 mg/L phenol solution. The spectrophotometric values of the photocatalytically treated phenol solution were measured by UV-Vis spectrophotometer and compared with the phenol standard curve to analyze the photocatalytic performance of the prepared photocatalyst.

3. Test Results and Discussions

3.1. Comparison of the photocatalytic efficiency of MnO2 doped with different metals
From the phenol degradation experiments, it is established that photocatalytic degradation efficiency of different dopants (shown in Table 1), it can be seen that the photocatalytic efficiency of pure MnO2 can reach 52%, but the photocatalytic performance of doped MnO2 is not necessarily enhanced. For example, when the doping is calcium oxide, the photocatalytic efficiency is reduced to 26.8%, while when the doping is iron oxide, iron oxide, and titanium dioxide, the photocatalytic efficiency of the new catalysts is improved to varying degrees. In particular, when the doped metal is iron oxide, the photocatalytic efficiency can reach 72.30%.

|                | MnO2 | MnO2+TiO2 | MnO2+CaO | MnO2+Fe2O3 | MnO2+Fe3O4 |
|----------------|------|-----------|----------|------------|------------|
| Spectrophotometric values for control group | 0.213 | 0.213     | 0.213    | 0.213      | 0.213      |
| Spectrophotometric values for the experimental group | 0.103 | 0.09      | 0.156    | 0.059      | 0.082      |
| Photocatalytic efficiency | 52%   | 57.70%    | 26.80%   | 72.30%     | 61.50%     |

3.2. Comparison of the adsorption efficiency of different doping levels of Fe2O3 on MnO2
Fig. 1 shows the effects of different doping ratios of MnO2 on photocatalytic degradation of phenol. In the doping process, metal cations may replace the six-coordinated Mn$^{3+}$/Mn$^{4+}$, thus changing the coordination environment, generating oxygen vacancies, or affecting the bond energy of adjacent Mn-O bonds, resulting in changes in the activity of the reaction site and enhancing the photocatalytic efficiency. When the doping amount of Fe2O3 is too much, it may inhibit the formation of MnO2 crystal and lead to the decrease of photocatalytic performance. It can be seen from Figure 1 that when the molar ratio of MnO2 and Fe2O3 is 5:1, the photocatalytic performance is the best.

![Fig. 1 Photocatalytic efficiency of MnO2 doped with different metals](image_url)
3.3. Comparison of adsorption efficiency at different temperatures
As shown in Fig. 2, with the increase of temperature, the photocatalytic reaction rate and efficiency increased, and the photocatalytic reaction efficiency reached a peak at 20–30 °C. Subsequently, with the increase of temperature, the photocatalytic reaction efficiency began to decline. Due to the melting point of phenol is 40.3 °C, the high temperature makes the phenol solution evaporate faster, resulting in the decrease of photocatalytic efficiency. Therefore, the optimal reaction temperature for the photocatalytic reaction was determined to be 20 °C.

![Fig.2 Effect of temperature and pH on photocatalytic efficiency](image)

3.4. Comparison of adsorption efficiency at different pH
The pH value of the solution shown in Fig.2 is a parameter in the photocatalytic degradation of semiconductors. The pH value determines the surface charge property of the photocatalyst, thereby affecting the adsorption behavior of pollutants. High or low pH will reduce the photocatalytic efficiency, and the photocatalytic performance is the best when pH is 7. Considering that the pH of wastewater containing phenol is generally 8–9, the photocatalytic performance of the photocatalyst can be maintained at a high level. It can be determined that MnO₂ doped iron oxide photocatalyst can be better applied to the treatment of wastewater containing phenol.

4. Specific surface area and pore structure (BET) analysis
Through the BET analysis and comparison of MnO₂ and MnO₂ composite iron oxide (Table 2), the pore size analysis and comparative adsorption-desorption curve of MnO₂ and MnO₂ doped iron oxide are drawn in the Fig.3. The specific surface area of MnO₂ doped with iron oxide was 253.81 m²/g, which was improved compared with that of pure manganese dioxide, the larger the specific surface area of manganese dioxide, the better its photocatalytic performance, and the pore size of MnO₂ composite iron oxide was larger than that of manganese dioxide. Its adsorption-desorption curve was significantly higher than that of pure manganese dioxide, with significantly higher specific surface area, and porosity the MnO₂ doped iron oxide photocatalyst can effectively provide more active sites and accelerate the photocatalytic process. These characterization analyses are consistent with the experimentally measured photocatalytic efficiency data, so we believe that the photocatalytic performance of our MnO₂ doped iron oxide is better than that of pure MnO₂ and is a more suitable photocatalyst.

| Sample        | S BET/(m²·g⁻¹) | r/nm | V/(cm³·g⁻¹) |
|---------------|----------------|------|------------|
| MnO₂          | 88.39          | 20.68| 0.46       |
| (Fe₂O₃)-MnO₂  | 253.81         | 9.71 | 0.62       |
Fig.3 (a) Pore size analysis diagram of manganese dioxide. (b) Pore size analysis diagram of manganese dioxide doped iron oxide. (c) Photocatalyst adsorption-desorption contrast diagram.

5. Conclusion
In this experiment, phenol simulated wastewater containing phenol was used as the treatment object. Pure MnO$_2$ and different metal oxides doped modified MnO$_2$ photocatalyst were prepared by low-temperature hydrothermal method, and the preparation conditions and process conditions were explored.
In addition, the prepared photocatalysts were characterized by BET, which provided a basis for in-depth analysis of experimental data. After data collation, analysis, and summary, the following conclusions:

1. The optimum preparation conditions of MnO₂ and doped metal prepared by low-temperature hydrothermal method were determined, and the photocatalytic properties of various doped metals were determined. It was determined that the different doping ratios of Fe₂O₃, and the optimal doping ratio was 5:1.

2. The specific surface area and pore size of MnO₂ and MnO₂ doped iron oxide were measured by the BET method. It was found that the specific surface area and pore size of iron oxide doped photocatalyst were significantly higher than that of pure manganese dioxide, indicating that the doped photocatalyst has more photocatalytic reaction sites on its surface, which improves the photocatalytic performance.

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