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Research Paper

# Evaluation of $MnO_2$-templated iron oxide-coated diatomites for their catalytic performance in heterogeneous photo Fenton-like system

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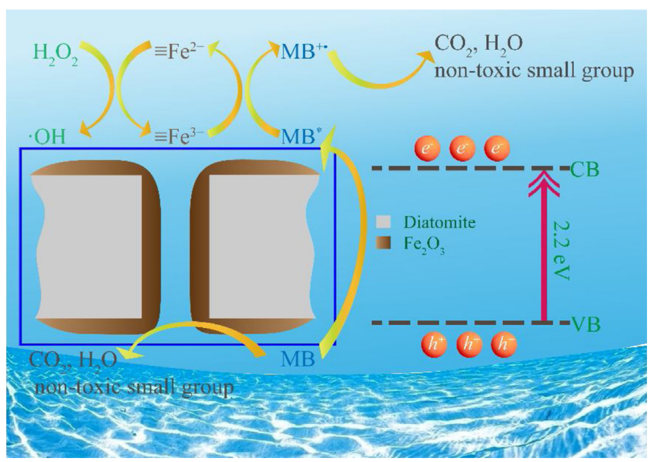
## HIGHLIGHTS

- Simple preparative strategy for $Fe_2O_3$@diatomite.
- $MnO_2$ template precisely controlled.
- High MB removal of 99% (120 min) in the pH 3 and 80.8% (120 min) in pH 11.
- Lower energy light source requirement, less hydrogen peroxide consumption and less time to decolorize a higher initial dye concentration.
- Good stable reusability.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Herein, iron oxide-coated diatomites were prepared through hydrothermal synthesis and sacrificial template redox etching reaction. The microstructure characterization results revealed that the $Fe_2O_3$ nanorods were uniformly distributed on the surface of diatomite. The effects of diverse synthetic parameters on morphology of as-synthesized $Fe_2O_3$@diatomite were investigated. When the reaction time was prolonged from 12 h to 24 h, the morphology of FeOOH would change from nanorods into nanoflowers. Two different crystal phases of $Fe_2O_3$@diatomite were obtained from the FeOOH@diatomite samples calcined under different atmospheres. The catalytic activity of $\alpha$-$Fe_2O_3$@diatomite was evaluated by the heterogeneous photo Fenton-like system through degradation of methylene blue (MB, $10-40\,mg\,L^{-1}$) in the presence of hydrogen peroxide ($H_2O_2$, 9 mM – 120 mM) under UV light irradiation. It was found that $\alpha$-$Fe_2O_3$@diatomite composites showed very excellent degradation efficiency, which was about 99% within 120 min under UV irradiation. This catalyst extended the range of pH values of homogeneous Fenton reaction, in which the MB removal rate was maintained over 80.8%. Moreover, the $\alpha$-$Fe_2O_3$@diatomite catalyst still showed sound reusability after 5 rounds of degradation of MB dye. In principles, a possible photo-catalytic mechanism was proposed to testify metal oxides composites for heterogeneous photo Fenton-like reaction.



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## 1. Introduction

Water pollution caused by organic dye coming from textile, printing and leather industries has attracted a worldwide concern [1]. Traditional treatment methods such adsorption, coagulation, biological treatment are not radically effective as they just transfer the pollutants from one phase to another phase [2]. To cover the shortages of traditional methods, chemical oxidation techniques such as advanced oxidation processes (AOPs) have emerged as promising alternative strategies for water treatment. Among the AOPs, Fenton reaction between hydrogen peroxide and iron ions/salts generates hydroxyl radicals ($^{\bullet}$OH) with powerful oxidizing capacity to decompose many organic compounds [3]. However, traditional homogeneous Fenton reaction works effectively only under highly acidic conditions, leading to the accumulation of ferric oxide sludge [4,5]. Considering the reusability of catalyst, many efforts have been made to develop heterogeneous Fenton catalysts which make the iron ions or iron oxides immobilized onto the surfaces of different supports [6–9] and to exploit photo-Fenton catalysts which accelerate the cycling of $Fe^{III}/Fe^{II}$ under the UV–vis light irradiation [10,11].Most of the previous studies have reported that clays [12], zeolites [13], mesoporous silicas [14], and carbon materials [15], can act as supports to anchor iron ions or iron oxides. In addition, as an abundant non-metallic material in spherical, laminar, annular, cylindrical shapes and in sizes from $10\sim200\,\mu m$, diatomite can also be used as a catalyst support [16]. This inartificial material enjoys unique properties such as high porosity, low density, high absorption capacity, low thermal conductivity, chemical inertness, and relatively low price [17,18].

Iron oxides are preponderant candidates as Fenton reagents due to its abundant sources, cost-effectiveness, eco-friendly properties and band-gap of 2.0-2.2 eV. Among the highly used iron oxides, $Fe_2O_3$ (hematite $\alpha$-$Fe_2O_3$ and maghemite $\gamma$-$Fe_2O_3$) is the most explored due to their chemical and physical properties [19,20]. Hematite $\alpha$-$Fe_2O_3$ is the most thermodynamically stable phase of $Fe_2O_3$ under ambient conditions and shows weak ferromagnetism at room temperature [21]. The unit cell of $\alpha$-$Fe_2O_3$ is hexagonal, containing only octahedral coordinated $Fe^{3+}$ atoms (corundum structure), which can cause regular displacement of either Fe ions or other metallic ions, serving as the active sites, greatly contributing to the catalytic ability [22]. Maghemite $\gamma$-$Fe_2O_3$ is a metastable phase of $Fe_2O_3$ and shows ferromagnetism at room temperature [23]. It exhibits cubic spinel structure with both octahedral and tetrahedral coordinated $Fe^{3+}$ sites. The cationic vacancies exist in the crystal structure of $\gamma$-$Fe_2O_3$ hold great potential in accelerating electron transfer efficiency and increasing promising active sites for catalytic reaction [24].Besides, many reports have proven that the catalytic property of $Fe_2O_3$ particles is determined by their size, shape, surface structure, and surface active sites [25–27]. For example, Liu et al. prepared $Fe_2O_3$ nanocrystals in various morphologies (nanocubes and nanorods in different particle sizes) by a facile hydrothermal process. The results showed that $Fe_2O_3$ nanorods had a higher catalytic performance for CO oxidation than the $Fe_2O_3$ in other morphologies, which is attributed to that $Fe_2O_3$ nanorod has a more reactive crystal plane (110) and higher density of Fe atoms [28]. To enhance the catalytic performance and improve the reusability of catalyst, the $Fe_2O_3$ nanorods have been used to fabricate hybrid materials with diatomite for environmental remediation as a photocatalyst [29,30].

In this work, a novel $Fe_2O_3$ nanorods coated diatomite ($Fe_2O_3$@diatomite) composite was prepared by a two-step synthesis method including hydrothermal synthesis and sacrificial template redox etching reaction using $MnO_2$ as the template because of its easy synthesis, structural versatility and precisely controlled size, unique dimension and morphology [31], which provides reference for coating diatomite with metal oxide uniformly. Meanwhile, this sacrificial template redox etching method may be generalized to the preparation of other metal oxides. Synthetic parameters relating to the morphology of as-synthesized $Fe_2O_3$@diatomite were investigated and the possible formation mechanism of $Fe_2O_3$@diatomite was proposed. Two crystal phases of $Fe_2O_3$ ($\alpha$-$Fe_2O_3$ and $\gamma$-$Fe_2O_3$) were obtained by a slight experimental variation of calcination and still remained the nanorods morphology. The catalytic performance of $\alpha$-$Fe_2O_3$@diatomite was checked by degradation of cationic dyes MB through a series of comparative tests under UV irradiation. Results showed that $\alpha$-$Fe_2O_3$@diatomite catalyst extends the range of pH values and has stable reusability, this composite may become a promising material for wastewater treatment.

## 2. Materials and experimental methods

### 2.1. Preparation of $MnO_2$ @diatomite

The natural diatomite employed in this study was procured from Tianjin Damao Chemical Reagent Company. The chemicals were of analytical grade and used without further purification.

Before the hydrothermal process, first purify the diatomite according to a reported chemical method [32]. Secondly, disperse 40 mg of the purified diatomite into 30 mL of $KMnO_4$ (0.05 M) solution to form a homogeneous suspension. After that, transfer the mixture to a 50 mL Teflon-lined stainless steel autoclave to be heated to 160 °C for 24 h. Finally, collect the precipitate, wash it with distilled water and ethyl alcohol, and then dry it at 60 °C.

### 2.2. Preparation of $Fe_2O_3$@diatomite

The strategy for synthesizing $Fe_2O_3$@diatomite is schematically depicted in Fig. 1. Firstly, conduct hydrothermal method to make $MnO_2$ nanosheets vertically grown on the surface of diatomite. Secondly, perform solvothermal treatment for the obtained $MnO_2$@diatomite composite as the sacrificed template to synthesize the $Fe_2O_3$@diatomite by a previously reported method with slight modifications [33] in a mixed solution of deionized (DI) water, ethylene glycol (EG) and dissolved $FeSO_4$. Partial hydrolysis of $Fe^{2+}$ generates an acidic environment which facilitates the subsequent redox reaction expressed by the equation of $[Fe(H_2O)_6]^{2+} \rightarrow [Fe(OH)\,(H_2O)_5]^{+} + H^{+}$. Simultaneously, the $MnO_2$ is reduced by the $Fe^{2+}$ and etched by $H^+$, which can be expressed by the equation of $2Fe^{2+} + MnO_2 + 4H^{+} \rightarrow 2Fe^{3+} + Mn^{2+} + 2H_2O$. The hydrolysis and redox etching preferentially occur at the interface between $MnO_2$ nanosheets and the solution [33]. This consumption of $H^+$ accelerates the reaction $Fe^{3+} + 2H_2O \rightarrow FeOOH(s) + 3H^{+}$ and progressive hydrolysis of $Fe^{2+}$, thus eventually leading to an enhanced redox etching in the vicinity of $MnO_2$ and the formation of well-oriented FeOOH coated diatomite [34]. After drying in the air, a post annealing process is applied to transform the FeOOH into $\alpha$-$Fe_2O_3$ phase or $\gamma$-$Fe_2O_3$ phase coated diatomite with a slight experimental variation.

Detail processes can be described as follow: first dissolve 450 mg of $FeSO_4{\cdot}7H_2O$ in 64 mL of mixed solution of ethylene glycol and deionized water (1:7 in volume), and keep stirring for about 10 min. After that, transfer this translucent solution and the as-prepared $MnO_2$@diatomite into a 100 mL Teflon-lined stainless steel autoclave, and heat them at 120 °C for 12 h, before cooling the autoclave to room temperature. Finally, collect the precipitate, wash with absolute ethanol, and then dry it at 60 °C to obtain FeOOH@diatomite. The $\alpha$-$Fe_2O_3$@diatomite was obtained by annealing the FeOOH@diatomite at 350 °C in air for 2 h, while the $\gamma$-$Fe_2O_3$@diatomite was obtained by annealing the