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Regular Article

# Synergistic effect of manganese dioxide and diatomite for fast decolorization and high removal capacity of methyl orange

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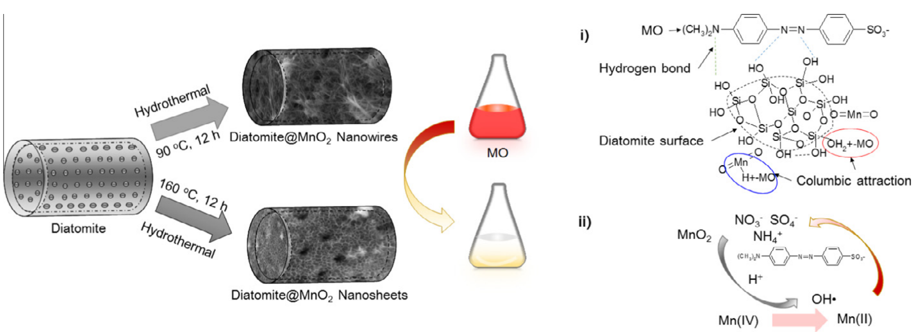
## GRAPHICAL ABSTRACT

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## ABSTRACT

$MnO_2$ nanostructures with two different morphologies (nanowires and nanosheets) were uniformly deposited on diatomite via a one-pot hydrothermal method. The fast decolorization and high removal capacity for anionic dye-MO over synthesized composites had been clarified. The results revealed that the equilibrium time was shortened to as low as 10–30 min, and the maximum adsorption capacities were 325 mg $g^{-1}$ and 420 mg $g^{-1}$ for nanowires and nanosheets composites, respectively, under the condition of initial pH 3 and ambient temperature. Indeed, the proposed decolorization mechanism was considered to be simultaneous multi-processes during the dye removal, including physical, physicochemical and chemical process. In principle, well-controlled cost-effective composites have promising ability to remove anionic dye pollutants for environmental remediation.



## 1. Introduction

Global occurrence in water resource of industrial and organic effluents, such as metolachlor (pesticide), ethinyl oestradiol (pharmaceutical), methylene blue (MB, thiazine dye) and methyl orange (MO, aromatic azo dye), has raised great concerns about

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their potential negative effects on human health and aquatic ecosystems [1–5]. Traditional wastewater treatment methods, like physical, chemical and biological techniques, have been widely investigated in this respect [6–8]. In recent years, adsorption methods and catalytic degradation using various assembled nanocomposites to remove organic pollutants from water have been broadly researched due to the advantages of low energy requirement, wide applicability and simple operation [9–13]. However, the key challenge is still to find cost-effective, high-performance and environment-friendly materials in wastewater treatment, as well as to clarify the removal mechanism of various pollutants by different composites in practical applications [14,15].

Diatomaceous earth (so-called bio-silica or diatomite) consisting principally of skeletal remains of a unicellular photosynthetic plant is a non-metallic, highly porous and chemically inert mineral [16]. It has a unique combination of physical and chemical properties, which make it applicable as a promising substrate for the preparation of porous composites. It is against this background that the feasibility of using diatomite or diatomite-based composites for the removal of pollutants has been attempted, such as purified diatomaceous earth for adsorption of MB [2], natural diatomites for catalytic oxidation of Orange II [17], and diatomite-$Fe_2O_3$ for catalytic degradation of Rhodamine B [7]. Additionally, manganese dioxide ($MnO_2$), an inexpensive, abundant and environmentally friendly mineral with unique layered and tunneled structure and high specific surface areas, are likewise of interest for wide applications in adsorption [18,19], catalysis [10], energy storage [20] and so forth. Therefore, an emerging interest has been raised to combine manganese dioxide with diatomite due to their individual properties in order to improve the performance [21–24]. However, for environmental applications, the decolorization mechanism of color dyes (e.g. MO) onto diatomite-$MnO_2$ composites, to the best of our knowledge, has not been well-clarified.

Herein, we fabricated $MnO_2$-deposited diatomite composites with two different $MnO_2$ morphologies (nanowires and nanosheets) via a one-pot hydrothermal method. The preparation process is depicted in Scheme 1. Furthermore, the resulting composites were used to investigate the removal behaviors for anionic dye-MO at different pH 2–7.5, which exhibited fast decolorization and high removal capacity at pH 3 and ambient temperature (303 K). Finally, a novel decolorization mechanism was proposed, which was composed of simultaneous multi-processes including physical, physicochemical and chemical process. Thus, the as-prepared composites can be used as an outstanding candidate for the removal of anionic dye pollutants in practical applications.

## 2. Experimental section

### 2.1. Materials and reagents

The purified diatomite sample was provided by Mount Sylvia Diatom Pty Ltd (Queensland, Australia). Potassium permanganate and ammonium persulphate were purchased from Chongqing Chuandong Chemical Co. Ltd, China. Others were purchased from Alfa Aesar. All chemical reagents used in this work were analytical grade without any further treatment. Deionized water was used throughout all experimental processes.

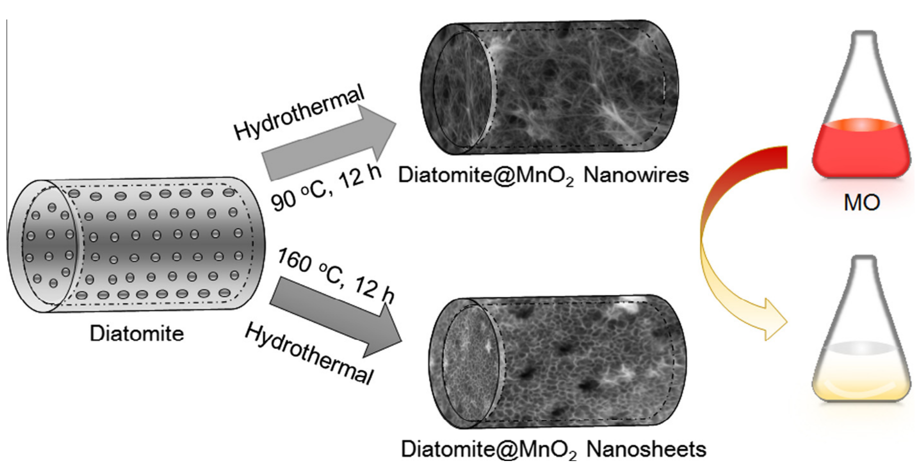
### 2.2. Synthesis of $MnO_2$ nanowires/nanosheets-deposited diatomite

$MnO_2$ nanowires and nanosheets-deposited diatomite were synthesized through modified one-pot hydrothermal methods from our previous works [21,25]. In a typical synthesis, for $MnO_2$ nanowires-decorated diatomite, 2.1 g of diatomite powders were dispersed into deionized water (30 mL) to form a homogeneous solution by vigorously stirring. Then, $KMnO_4$ (0.01 mol) and $(NH_4)_2S_2O_8$ (0.01 mol) were added to the abovementioned solution under continuous vigorously agitating for about 10 min. Next, the mixture was transferred into a Teflon-lined stainless steel autoclave and hydrothermally treated at 90 °C for 12 h. After being cooled to ambient temperature, the resulting black precipitate was centrifuged and washed thoroughly with deionized water and ethanol for several times, and then dried at 60 °C over night. Finally, the $MnO_2$ nanowires-decorated diatomite composites (denoted as MwD) were obtained.

Comparatively, for $MnO_2$ nanosheets-decorated diatomite, the synthetic procedure was similar. Briefly, diatomite (30 mg) was dissolved in $KMnO_4$ aqueous solution (30 mL, 0.05 M) to form a homogeneous solution by vigorously stirring. Then, the mixture was transferred into a Teflon-lined stainless steel autoclave (50 mL) and hydrothermally treated at 160 °C for 12 h. After a similar centrifugation and washing procedure, the $MnO_2$ nanosheets-decorated diatomite composites (denoted as MsD) were obtained. After measured, the average $MnO_2$ loading mass of MwD and MsD were 25.80 wt% and 28.33 wt%, respectively.

### 2.3. Characterization

The morphological and structural information of the as-prepared samples were characterized by focused-ion-beam scanning electron microscopy (Zeiss Auriga FIB/SEM). The crystallographic information and chemical composition of the samples




**Scheme 1.** Schematic representation of the synthesis and application of the samples in this work.