A designed Mn$_2$O$_3$/MCM-41 nanoporous composite for methylene blue and rhodamine B removal with high efficiency

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Abstract

The authors report a facile chemical precipitation method for the fabrication of a highly ordered mesoporous Mn$_2$O$_3$/MCM-41 composite. Examination of the acquired samples using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and nitrogen adsorption–desorption measurement has provided fundamental insight into the structure and properties of the Mn$_2$O$_3$/MCM-41 composite. It is found that the as-prepared Mn$_2$O$_3$/MCM-41 composite has a highly ordered mesoporous structure with a specific surface area of 793 m^2 g^{-1}. The performance of Mn$_2$O$_3$/MCM-41 composite as a remover was further demonstrated in the removal of azo dyes of methyl orange (MO), Congo red (CR), methylene blue (MB), and rhodamine B (RB) with/without visible light irradiation at room temperature. The results show that the Mn$_2$O$_3$/MCM-41 composite has an excellent removal performance for MB and RB, making it a promising candidate for wastewater treatment.
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1. Introduction

The contamination of water due to color effluents coming from different industries is a current problem all over the world [1–4]. The wastewater of the textile industries is known to contain a considerable large amount of non-fixed dyes, azo dyes, and inorganic salts [5]. Among these pollutions, azo dyes are frequently used for colorization in textile industries. Therefore, azo dyes removal in wastewater has attracted considerable attention because of their long-term environmental toxicity and short-term public health damage which can lead to hypersensitivity, allergy [6], and even intestinal cancer [1,7,8]. However, the traditional physical, chemical and biological means of wastewater treatments often have little removal effect on the azo dyes pollutants with physicochemical, thermal and optical stability owing to the quite stable and complex aromatic structures. Thus, there is an urgent requirement for the development of innovative but low-cost processes, by

which dye molecules can be effectively removed. Adsorption and degradation are very promising methods that are widely used for the removal of azo-dyes in wastewater [9]. Up to now, various adsorbents and photocatalysts, such as nanoporous silica [10], TiO$_2$-loaded zeolites [11], Fe$_2$O$_3$–MCM-41 [12], AgBr/nano AlMCM-41 [13], Cr (IV) on mesoporous TiO$_2$ [14], and so on, have been investigated. Generally the removal capacity of an adsorbent or photocatalyst mainly depends on its surface properties, including surface area and surface ion exchange sites [6]. As a result, it is necessary for adsorbents and photocatalysts to have many ion exchange sites and high surface area. The synthesis of mesoporous materials offers the possibility of preparing catalysts that are applicable in many industrial processes. The characteristics of high surface area, large adsorption capacity and porous structure make them great promising candidates in oil refining, petrochemistry, organic synthesis and waste treatment [15,16]. In particular, the mesoporous silicate MCM-41 has the potential to be used as an adsorbent or support for catalyst due to its hexagonal arrangement of pores with typical diameter of 1.5–10 nm, high surface area, large pore volume, and high thermal stability [17–21]. To improve

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their catalytic activities, transition metals and some main group elements and their oxides were introduced isomorphously into the mesoporous framework as the active sites by direct synthesis or impregnation methods [22–32].

Mn_2O_3–SiO_2 composite has been extensively studied for many applications in terms of catalysts and adsorption [33,34]. However, to the best of our knowledge, little work has been carried out to investigate its removal behavior for organic dyes in wastewater. With this aim, in the present work we have studied the removal properties of organic dyes (methyl orange (MO), Congo red (CR), methylene blue (MB), rhodamine (RB)) utilizing Mn_2O_3/MCM-41 mesoporous composite. The obtained data are discussed in connection with the differences in the removal of the azo dyes.

2. Experimental

2.1. Synthesis of Mn_2O_3/MCM-41 mesoporous composite

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification. Mn_2O_3/MCM-41 composite was prepared in base condition at room temperature as follow: NH_4OH (205 mL 25 wt% solution) was firstly mixed with 270 mL distilled water; then 2.0 g CTAB surfactant was dissolved into the solution with stirring and heating. Subsequently, 10 mL TEOS was added when the solution became homogeneous, and the solution was stirred for 2 h. $MnCl_2 \cdot 4H_2O$ (same quality as TEOS) was mixed with the suspension and continually stirred for further 4 h. After aging for 20 h, the solid product was filtered with distilled water, dried in an oven at 50 °C, and calcined in air at 550 °C for 4 h. For the purpose of comparison, Mn_2O_3 particles and MCM-41 were prepared using the same method without TEOS or $MnCl_2 \cdot 4H_2O$, respectively.

2.2. Characterization

Powder X-ray diffraction (XRD) data were collected using a Rigaku TTRIII diffractometer by Cu K_α radiation (λ=1.5406 Å). The accelerating voltage and applied current were 40 kV and 200 mA, respectively. The samples were scanned from 1.0° to 8.0° and 10° to 90° (2θ). Scanning electron microscopy (SEM) analysis was performed by means of a FEI QUANTA200 with the microscope operating at 15 kV. The samples for SEM were prepared by dispersing the final powders in a conductive glue; this dispersion was then sprayed with gold. Transmission electron microscopy (TEM) measurement was carried out with a Zeiss EM 912 Ω instrument at an acceleration voltage of 120 kV. The samples were prepared by spreading an ultrasonicated suspension in ethanol onto a grid and evaporating the solvent. N_2 adsorption–desorption isotherms at 77 K were recorded on a Micromeritics ASAP 2010 automated sorption analyzer. The samples were outgassed for 20 h at 150 °C before the analysis. X-ray photoelectron spectroscopy (XPS) was utilized to investigate the surface chemistries of the samples in an ESCALAB 250

system. During XPS analysis, an Al Kα X-ray beam was adopted as the excitation source and the vacuum pressure of the instrument chamber was 1×10^{-7} Pa. Bonding energy was calibrated with reference to C 1s peak (285.0 eV). Measured spectra were decomposed into Gaussian components by a least-square fitting method.

2.3. Dye removal

The removal experiments were carried out in an aqueous solution at room temperature using as-synthesized Mn_2O_3/MCM-41 mesoporous composite as catalyst. In a typical removal experiment, 50 mg of the catalyst was added into 50 mL of methyl orange (MO), Congo red (CR), methylene blue (MB) and rhodamine (RB) aqueous solutions with a concentration of 25 or 50 mg L^{-1} in a quartz beaker under stirring. At different time intervals, 4 mL of the dispersion was extracted and subsequently centrifuged to separate catalyst and dye solutions at 4000 rpm for 30 min. The initial concentrations (C_o) and concentrations (C) in the filtrate of CR, MB, MO, and RB solutions were monitored immediately by measuring the absorption intensity of the different supernatants at 498, 664, 463 and 550 nm using a spectrophotometer (Model no. JH722N). The removal rates (R) of azo dyes were calculated from the following relation:

$$R = \frac{C_0 - C}{C_0} \times 100\% \qquad (1)$$

3. Results and discussion

The small angle X-ray diffraction (LAXRD) patterns of MCM-41 and Mn_2O_3/MCM-41 nanoporous composite are shown in Fig. 1(A). As shown in Fig. 1(A), it exhibits a strong peak around 2.55°, and two weak peaks at 4.42° and 5.09°, corresponding to diffraction of (100), (110), and (200), respectively. These equidistant diffraction peaks are attributed to rational reflections, characteristic of mesostructure, which are recognized to arise from a pore nanostructure. The observed three well-resolved diffraction peaks are consistent with a typical 2-D hexagonal mesostructure, and with MCM-41 reported before [35]. It confirms both mesoporosity and order of the silica matrix in Mn_2O_3/MCM-41 nanoporous composite. By taking a close look, one can see that the diffraction peaks shift to the large angle and become weaker when the Mn_2O_3 particles are introduced into MCM-41. These phenomena are reasonably attributable to the tunnel size, the increase of lattice defect resulting from the agglomerates of Mn_2O_3 particles and the interaction with MCM-41 framework [36]. Fig. 1(B) illustrates the wide-angle X-ray diffraction (WAXRD) patterns of the Mn_2O_3/MCM-41 nanoporous composite. A broad diffusion peak centered at $2\theta = 22.9°$ ranging from 10° to 30° (2θ) can be observed, suggesting that the main substance of MCM-41 is amorphous silica. The experimental XRD patterns demonstrate well-developed diffraction lines of Mn_2O_3 (ICDD PDF no. 65-1798), space group $Ia\overline{3}$ (206). Besides, no other crystalline by-products such as MnO, MnO_2,