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High temperature synthesis of interfacial functionalized carboxylate mesoporous TiO_2 for effective adsorption of cationic dyes

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HIGHLIGHTS

- The mesoporous TiO_2 was grafted with carboxylate groups at high temperature.
- Bidentate carbonate species were also detected.
- The surface chemical properties impact the dye adsorption behaviors of TiO_2.
- The MB adsorption was highly dependent on the electrostatic interaction.
- TiO_2 can be easily regenerated up to 9 times by high temperature treatment.

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ABSTRACT

This study reported a facile method to enhance the adsorption capacity of TiO_2-based mesoporous material for the removal of methylene blue (MB) as a cationic dye from aqueous solution. The mesoporous surface of the modified TiO_2 was successfully grafted with interfacial carboxylate groups by using the sol–gel method with ethylenediaminetetraacetic acid (EDTA) as a template at high temperature. Properties of the as-synthesized adsorbents were characterized by FTIR, XPS, FE-SEM, TGA and BET analysis. The MB uptake by adsorption was highly dependent on the electrostatic interaction between the adsorbent and the adsorbate. Basic media was favorable for greater MB deposition on the modified TiO_2 surface, which related to uncoordinated carbonyl groups. The maximum capacity was reported as 32.15 mg/L. The removal efficiency was maintained at 83% even after 9 adsorption–desorption cycles, which supported the reusability of the adsorbent for cationic dyes removal from aqueous solutions.

1. Introduction

The rapid growth of many industries such as textile, paper, printing, leather, food and cosmetics has resulted in the extensive use of dyes for coloring substrates [1]. Treatment of discharged wastewater containing dye compounds has become challenging due to their stable and complex chemical structures, and their low biodegradability. Qada et al. reported that less than 1 ppm of dyes can make colored wastewater [2]. Moreover, the presence of dyes in industrial effluents has seriously deteriorated the environment. Once dyes enter aquatic liquefiers, they can prevent the sunlight from penetrating into the water and hence impede the photosynthesis of the aqueous ecosystem [3]. Some dyes are also carcinogenic, mutagenic, teratogenic and harmful to the human respiratory system [4,5]. Therefore, the removal of dyes has attracted much attention. Methylene blue (MB) is a cationic dye with a heterocyclic aromatic structure. Like other dyes, its adverse impacts on the aqueous media are inevitable. Hence, studies on the decolorization of MB in aqueous solutions are of significant practical importance.

The numerous methods used to treat dye – loaded effluents can be divided into three categories: chemical (e.g., oxidation, photochemical), physical (e.g., adsorption, membrane filtration, ion exchange) and biological (e.g., aerobic and anaerobic biodegradation) [6–9]. Among them, adsorption has been found to be superior to others in terms of its simplicity, low cost, acceptable removal efficiency and ease of operation. Various adsorbents have been used for dye removal from wastewater. From a purely practical point of view, adsorbents themselves should be effective and nontoxic. TiO_2, an inexpensive and nontoxic material, has been propagated for use as a photocatalyst in environmental and energy-related fields, particularly in air and water purification-related fields. However, even when TiO_2 is used as a

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photocatalyst, the adsorption of pollutants on TiO_2 plays an important role as a prerequisite for the effective photodegradation [10]. The adsorption capacity of TiO_2 is limited due to their intrinsic disadvantages such as narrow pore diameter, low surface area, thermal instability and less active sites [11]. Recently, several studies have focused on methods to enhance the adsorption ability of TiO_2 for effective removal of pollutants by functionalizing the TiO_2 surface with carboxylic acids [12,13]. However, most of synthesis have been performed at low temperature. Synthesis, in which interfacial functional groups can be survival at high temperature, is essential for an extension of TiO_2 applications as an adsorbent and a photocatalyst under visible light.

Mesoporous TiO_2 has been investigated with the expectation of improved performance in terms of photocatalytic activity [14–16]. However, extensive studies on the adsorption performance of functionalized mesoporous are favored in a viewpoint of application to water treatment.

Therefore, the current study aimed to synthesize interfacial functionalized mesoporous TiO_2 (hereafter, modified TiO_2) with carboxylate groups at high temperature by using EDTA as a template. Effects of functional groups on the enhanced MB adsorption of the modified TiO_2 were discussed in detail. The feasibility of thermal treatment for regenerating the adsorbent was also investigated.

2. Methods and materials

2.1. Material synthesis and analysis methods

First, 3.60 g of EDTA (99%, Sigma–Aldrich) was dissolved in 100 mL of deionized water. A 50.0 mL mixture (1:2) of titanium (IV) isopropoxide precursor (97%, Sigma–Aldrich) and isopropanol was then added dropwise to the prepared EDTA solution to make the sol form under vigorous stirring at 4 °C for 3 h. The as-prepared solution was aged in the dark for 24 h to induce gelation. Afterwards, the solvent was evaporated at 70 °C for 1 h to obtain the modified TiO_2 sample. The sample was further calcinated at 400 °C for 5 h and ground into powders. For comparison, the pristine TiO_2 was synthesized using the same process but in the absence of EDTA. All reagent-grade chemicals were used without pretreatment.

To study the nature of the chemical bonding, Fourier Transform Infrared (FTIR) transmittance spectra in the region 4000–400 cm^{-1} were recorded on a Perkin–Elmer Nicolet Nexus 470 FTIR spectrometer at room temperature. The thermogravimetric (TG) analyses were performed on Setaram Labsys Evo in N_2 flow and at a heating rate of 10 °C/min. The chemical states of elements in the samples was analyzed based on X-ray photoelectron spectroscopy (XPS) data recorded on a Thermo Scientific Sigma Probe spectrometer with a monochromatic AlKα source (photon energy 1486.6 eV), spot size 400 μm, pass energy of 200 eV and energy step size of 1.0 eV. The specific Brunauer–Emmett–Teller (BET) surface area and pore size measurements of the samples were conducted on a Micromeritics ASAP 2020 apparatus under nitrogen air. Field Emission – Scanning Electron microscopy (FE-SEM) was used to check the morphology of the as-synthesized materials. The solution pH was monitored through a pH meter. A Genesis 10S UV–Vis spectrophotometer was used to obtain the absorbance of the MB solution at 665 nm.

2.2. MB adsorption study

Batch mode was applied throughout triplicate MB adsorption experiments under dark condition. To optimize the adsorption conditions, 0.01–0.10 g of the adsorbent was shaken with 20 mL of solution containing 0.06, 0.1, 0.2, 0.3, 0.4, 1.2, 1.6, and 2.0 g of MB at 30 ± 1 °C at a shaking speed of 150 rpm for 210 min. The solution pH was adjusted in the range of 1–12 by adding a small amount of 0.1 M HCl or 0.1 M NaOH while other parameters were kept constant.

The adsorption isotherm studies were also carried out by mixing 0.02 g of modified TiO_2 with 20 mL of MB solution in which the amount of MB was varied (0.06–2.0 g), for 210 min at pH = 10 and 30 ± 1 °C. The same experimental conditions were applied when investigating the adsorption capacity as a function of time. The remaining MB – concentration was determined using a UV–vis spectrophotometer. Before the measurement, aliquots of MB were taken out at specific intervals of time, and centrifuged at 3000 rpm for 5 min to remove solids. The amount of MB removed per gram of adsorbent (q_t) and the removal ratio (H%) were obtained according to Eqs. (1) and (2), respectively [17]:

$$q_t = \frac{V_s \times (C_0 - C_t)}{1000 \times m} \tag{1}$$

$$H\% = \frac{100 \times (C_0 - C_t)}{C_0} \tag{2}$$

where C_0 and C_t (mg/L) are the concentrations of MB before and after the adsorption, respectively, V_s (mL) is the volume of MB solution, and m (g) stands for the mass of the adsorbent.

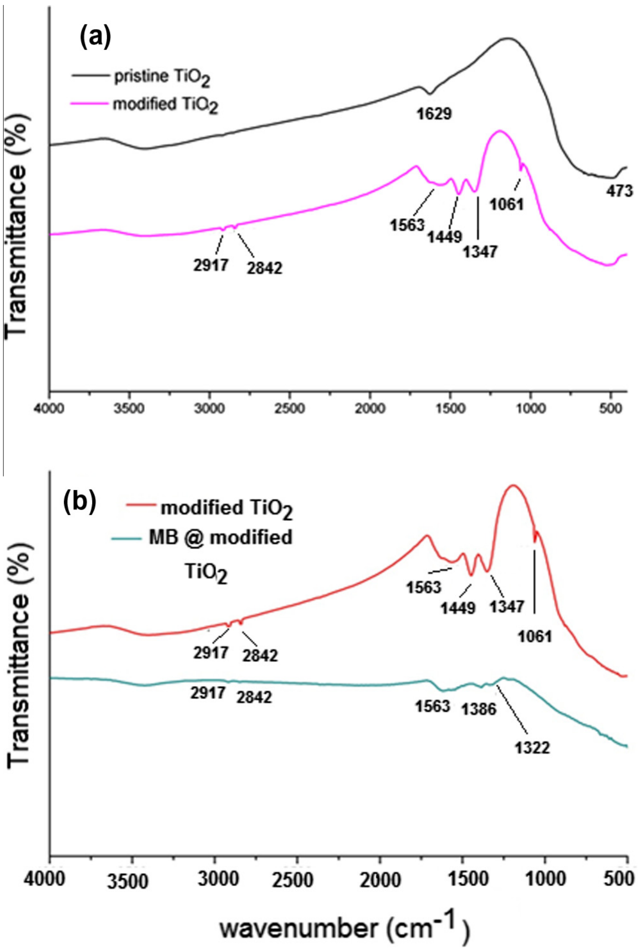

Fig. 1. (a) FTIR spectra of modified and pristine TiO_2. (b) FTIR spectra of modified TiO_2 before and after adsorption.