



# Magnetised nanocomposite mesoporous silica and its application for effective removal of methylene blue from aqueous solution



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## ARTICLE INFO

### Article history:

Received 2 April 2015

Received in revised form 10 August 2015

Accepted 12 August 2015

Available online 13 August 2015

### Keywords:

Silica

Magnetite

Nanocomposite

Mesoporous

Adsorption

Reuse

## ABSTRACT

Via a new synthetic route, magnetized nanocomposite mesoporous material (MNCM) was prepared using silica (SiO<sub>2</sub>) and nano-magnetite (Fe<sub>3</sub>O<sub>4</sub>). The formation mechanism of MNCM was determined using various spectroscopic analyses. Among the synthesized materials, MNCM-1, prepared with a molecular weight ratio of Fe<sub>3</sub>O<sub>4</sub> to SiO<sub>2</sub> of 0.14:1, had a homogeneous mesopore structure with a mean pore size of 4.68 nm, specific surface area of 576 m<sup>2</sup> g<sup>-1</sup>, and a pore volume of 0.65 cm<sup>3</sup> g<sup>-1</sup>. MNCM-1 had magnetic properties (2.9 emu) and structural strength, as well as higher and faster adsorptive MB removal than other mesoporous materials. The removal of MB by MNCM-1 was found to be a physisorption process with an electrostatic interaction between negatively charged silanol (Si–O<sup>-</sup>) and positively charged MB, and was thermodynamically favorable at higher temperatures. The economic assessment revealed that treatment costs for MB-containing water using MNCM-1 were 16–80 times lower than those with other mesoporous materials, due to the use of the cheap Si precursor and the higher sorption capacity. Furthermore, MNCM-1 can be reused and regenerated without any defects after easy separation using a magnet. Because MNCM-1 can be produced economically on a large scale, it may have significant effects for adsorption-based treatment systems with regard to the removal of MB from waste water.

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## 1. Introduction

Waste water discharged from various industries, such as textiles, paper manufacturing, wool coloring, and paint production, contains high level of organic dyes, such as methylene blue (MB). MB belongs to a group called the azo dyes and has a chemical formula of [(CH<sub>3</sub>)<sub>2</sub>N(C<sub>6</sub>H<sub>3</sub>) NS<sup>+</sup>(C<sub>6</sub>H<sub>3</sub>)N(CH<sub>3</sub>)<sub>2</sub>]. MB has been reported to cause adverse health effects to humans, wildlife, and microorganisms and also to increase dangers in the environment by releasing toxic substances [1–3]. In particular, in humans, MB can cause adverse health effects such as eye burns, cyanosis, methemoglobinemia, convulsions, tachycardia, dyspnea, and skin irritation [3]. MB has a complex aromatic molecular structure with high thermal and light stability and poor biodegradability, so it is difficult to degrade. There is a continuing need to develop an

effective and cheaper way to remove MB from waste waters before releasing them into the environment.

Numerous physicochemical treatment techniques, such as chemical oxidation [4], biodegradation [5], ultrafiltration [6], photodegradation [7], extraction [8], and adsorption [9,10], have been developed to treat MB. Among these methods, adsorption systems offer promising results for the removal of MB because they are simple, economical, and easy to operate. As adsorbents, activated carbons, nanoporous silicas, zeolites, and iron oxides have been studied extensively for MB removal. However, application of these materials in waste water treatment has been limited due to separation difficulties, low sorption capacities, and risk of secondary environmental contamination caused by fine particles. To overcome these drawbacks, it is important to develop sorption materials with high sorption capacities, low production costs, high reusability, and thermal stability.

Over the last decade, mesoporous silica materials (MSMs) have been of great interest in the field of water treatment. MCM-41, MCM-48, and SBA-15 have been studied as possible adsorbents because of their simple preparation process and high stability

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[11,12]. Furthermore, the physical characteristics of MSMs, such as high surface area, large pore volume, even pore size distribution, and open pore structures, make them suitable adsorbents for large-scale organic pollutants such as MB [3,13–15]. However, the synthesis of MSM requires the use of expensive silica sources, such as tetraethylorthosilicate (TEOS) [2,3]. Moreover, MSM has a very fine particle size, causing disadvantages such as separation difficulties and expensive filtering costs [16].

To improve the separation and recovery process of the adsorbent, scientists have recently tried to develop highly porous and magnetized adsorbents [17]. However, to our knowledge the production costs of these adsorbents remain very high and the synthesis routes are complex. Thus, they are not yet suitable for large-scale industrial application.

In this report, we describe an optimized, economical, and facile synthesis process for magnetized nanocomposite mesoporous material (MNCM) using silicon dioxide ( $\text{SiO}_2$ ), which is inexpensive, abundant, and readily available, compared with TEOS. The main objective of this research was to optimize the synthesis of MNCM through incorporation of various amounts of nano-magnetite. Not only did we study the formation mechanism of MNCM, but we also identified the best mesostructured material by studying pore properties. The selected MNCM was used to adsorb MB and the removal mechanism was examined. The adsorption behavior of MB by MNCM was investigated at various pHs, concentrations, and temperatures. Finally, the reusability and thermodynamics of MB removal by MNCM were also investigated.

## 2. Materials and methods

### 2.1. Materials

Iron (II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and potassium permanganate ( $\text{KMnO}_4$ ) were purchased from Merck and used to synthesize nano-magnetite. Pluronic P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) and  $\text{SiO}_2$  were obtained from Sigma–Aldrich (USA) and R&M (United Kingdom), respectively. MB (99% purity) was purchased from R&M.

### 2.2. Methods

#### 2.2.1. Synthesis of nano-magnetite

The nano-magnetite was synthesized using a modified version of the method set out by Schwertmann and Comell [18,19]. First, 40 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was dissolved in 500 mL deionized water (DI) at room temperature. The solution was heated to 80 °C and the alkaline solution was added slowly. Separately, the alkaline solution was prepared using 22.4 g NaOH and 3.3 g  $\text{KNO}_3$  in 415 mL of DI water. The color of the solution changed from yellowish to dark purplish, and then to black. The solution was stirred at 80 °C for 1 h and then stirred overnight at room temperature. The precipitated nano-magnetite was obtained by centrifugation, then washed with deionized water several times, and dried in an oven at 60 °C.

#### 2.2.2. Synthesis of mesoporous silica material and magnetized nanocomposite mesoporous materials

Synthesis of MSM and MNCM was prepared by a sequence of dissolving  $\text{SiO}_2$  in 1 M NaOH and stirring at 45 °C for 20 h. To prepare MNCMs, a predetermined mass (0.25, 0.5, or 1 g) of nano-magnetite was added into the acidic solution containing the pore-templating agent Pluronic P123 and hydrochloric acid (2 M). The suspension was heated to 45 °C. Then, 30 mL of silicate solution was added into the 60 mL suspension containing magnetite. The mixed solution was stirred at 200 rpm from 40–45 °C for 3 h.

The mixture was then stirred vigorously at room temperature overnight, and then was transferred to an autoclave container and aged at 90 °C for 20 h. The precipitated solid and liquid were centrifuged (2000 rpm) and the solution was decanted. The solids were washed with DI water and ethanol (50%), and dried at 60 °C for 24 h. The dried samples were calcined at 500 °C for 6 h using a Western furnace. The synthesis ratio for 1 g nano-magnetite added MNCM (designated as MNCM-1) was 0.14  $\text{Fe}_3\text{O}_4$ :1  $\text{SiO}_2$ :1 NaOH:0.1 HCl:0.013 Pluronic:167  $\text{H}_2\text{O}$ . The synthesis was repeated with 0, 0.25, and 0.5 g of nano-magnetite, which are referred to as MSM, MNCM-0.25, and MNCM-0.5, respectively.

### 2.3. Characterization of MNCM

XRD was performed with a PANalytical Empyrean X-ray diffractometer (Panalytical, Netherlands). The scanned angle was from 0.5–2.5° of  $2\theta$ , and the step size and scanning time were 0.0070° and 19.9260 s, respectively. Small-angle X-ray scattering (SAXs) was performed to determine the particle size distribution of the nano-magnetite. Nitrogen adsorption and desorption isotherms were measured using a Micromeritics TriStar II 3020 system (Micromeritics Instrument Corporation, United States). The samples were analyzed at 77.35 K. Brunauer–Emmett–Teller (BET) theory was used to determine the specific surface area of the samples. The Barrett–Joyner–Halenda (BJH) method was used to measure the pore size distributions and pore volumes of the samples. IR spectra were obtained using a NICOLET IS 10 spectrometer (Thermo Scientific, USA). Microscopic images of nano-scale pore structures were taken using transmission electron microscopy (Hitachi HT 7700 TEM, Japan) at 120 kV. An ultra-high-resolution FESEM (Hitachi SU 8000, Japan) fitted with an EDX analyzer was used to capture the images of the samples. A Netzsch-brand TGA (Netzsch Holdings, Germany) was used to perform the thermal analysis of the samples, scanning from 25 to 1100 °C. The zeta potential of the samples was measured using a Malvern Zetasizer nano-series (Malvern Instrument, UK). A magnetometer was used to determine the magnetic properties of the sample.

### 2.4. Adsorption of MB

#### 2.4.1. pH effect of MB adsorption

Physicochemical characterization of MNCM revealed that MNCM-1 had the best mesopore structure in terms of surface area, pore structure, and volume. Thus, all MB adsorption tests were performed using MNCM-1. In a conical flask, 200 mL of MB was prepared at 20  $\text{mg L}^{-1}$ . The initial pH of the MB solution was adjusted from 2 to 10, and 15 mg of MNCM-1 was dispersed in the solution. The pH adjustment was conducted using either 0.1 M HCl or NaOH solutions. The conical flasks were placed into an electric shaker and agitated at 200 rpm and 25 °C for 100 min. At regular intervals, samples were collected and the suspended solids were separated using a magnet. The solution left was analyzed for MB concentration using a UV–vis spectrophotometer (Shimadzu, Japan).

#### 2.4.2. Concentration effect of MB adsorption by MNCM-1

To investigate the concentration effect of MB, further batch tests were conducted using MB solutions with 20–40  $\text{mg L}^{-1}$ . The initial pH was adjusted to 10, and other experimental conditions were similar to those described in Section 2.4.1.

#### 2.4.3. Reusability of MNCM-1

To determine the reusability of the MNCM-1, three cycles of MB adsorption tests were conducted using 25  $\text{mg L}^{-1}$  MB and 15 mg MNCM-1 at pH 10. After each cycle, the adsorbent was collected using a magnet and calcined in the furnace at 500 °C for 3 h in air.

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