Dyes and Pigments 131 (2016) 177–185

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Rhodamine 6G assisted adsorption of metanil yellow over succinamic acid functionalized MCM-41

Aneesh Mathew, Surendran Parambadath, Mary Jenisha Barnabas, Hyun Jin Song, Jae-Sung Kim, Sung Soo Park, Chang-Sik Ha*

Department of Polymer Science and Engineering, Pusan National University, Geumjeong-gu, Busan 46241, Republic of Korea

ARTICLE INFO

Article history:
Received 21 September 2015
Received in revised form
1 April 2016
Accepted 2 April 2016
Available online 13 April 2016

Keywords:
MCM-41
Mesoporous silica
Rhodamine 6G
Methylene blue
Metanil yellow
Adsorption

ABSTRACT

The adsorption properties of succinamic acid functionalised MCM-41 (SA-MCM-41) towards dyes aqueous solution, such as rhodamine 6G (R6G), methylene blue (MB) and metanil yellow (MY), were studied. SA-MCM-41 was synthesised using a three step synthesis strategy, starting with the preparation of MCM-41 through a sol–gel methodology. Succinamic acid functionality was introduced through a ring opening reaction of succinic anhydride (SA) over the propyl amine functionality of A-MCM-41 in presence of trimethylamine. The materials at each synthesis step were characterised by X-ray diffraction, transmission electron microscopy, scanning electron microscopy, N_2 adsorption–desorption isotherms, Fourier transform infrared spectroscopy, and ^{29}Si and ^{13}C nuclear magnetic resonance spectroscopies. SA-MCM-41 exhibited good adsorption capacity towards R6G and MB but poor adsorption for MY from the individual dye solutions. The competitive adsorption from binary and ternary dye mixtures showed that SA-MCM-41 can remove MY effectively in the presence of R6G. The adsorption behaviour of R6G and MY over SA-MCM-41 from binary and ternary mixtures highlight the possibility of multilayer adsorption. The MY removal efficiency of pristine MCM-41 from R6G-MY binary mixture was also tested.

1. Introduction

Dyeing is an essential and unavoidable process in modern life. The dyeing industries depend on chemicals to impart colour to various materials. The extensive discharge of such dyes through wastewater effluents have had detrimental effects on the ecosystem of evoked considerable environmental concerns. Wastewater containing dyes are quite difficult to treat as the dyes are recalcitrant molecules, resistant to aerobic digestion, and stable to oxidising agents. The main sources of dye pollution in water are textiles printing, dyeing, dyestuff manufacturing, and food plants [1–4]. The contamination of water sources through dye disposal is a serious issue due to the fact that degradation products may be carcinogens and toxic to mammals [5]. Moreover, the colour produced by organic dyes in water is of great concern since the colour in water is aesthetically unpleasant [6]. This has prompted an exhaustive search for the best methodology of dye removal. Some physicochemical methods, such as advanced oxidation and biological process, coagulation, membrane filtration, electrochemical, and adsorption techniques have been proposed to satisfy the above requirements [1,7]. For both environmental and health reasons, it is essential to remove these dyes completely before they reach the effluent stream to the discharge water supply. Among the different dye removal strategies, adsorption has attracted considerable attention owing to its low cost and high efficiency. Recently, modified porous materials were introduced for the adsorption study [8].

The discovery of mesoporous materials in 1990 has opened a wide range of applications, such as catalysis, medical usage, ecology and nanotechnology, sensing, adsorption, and separation [9–13]. As one of these materials, MCM-41 provides excellent textual properties, such as high surface area, large pore volume, tunable pore diameter, and narrow pore size distribution [14]. The Si–OH groups imparted a negatively charged surface to pristine MCM-41, and will adsorb positively charged dyes, whereas it has less favourable interactions with negative dyes [15]. Surface functionalization has also attracted intense interest in the use of MCM-41 materials as a solid support in a variety of dye adsorption applications.

Azo dyes are important colorants with extensive applications

---

* Corresponding author.
E-mail address: csha@pnu.edu (C.-S. Ha).

http://dx.doi.org/10.1016/j.dyepig.2016.04.007
0143-7208/© 2016 Elsevier Ltd. All rights reserved.

worldwide. Approximately 10–15% of azo dyes with respect to the total production are released to environment via wastewater. Azo dyes containing aromatic amines are generally non-degradable and accumulate under anaerobic conditions. Although azo dye molecules are biologically inactive, microorganisms in the skin and in the environment can cleave the azo linkages and release the respective amines [16]. Few studies have reported effective methods to remove azo dyes from contaminated water sources [17,18]. The limited references for azo dye adsorption, even by the functionalised silica, highlight the need for effective adsorbents from a mixture of dyes. Most industrial waste water contains many types of dyes in a single effluent. The need for the use of separate adsorbents in a treatment plant to remove individual dyes from a mixture is a tedious process. Therefore, it is necessary to generate a general adsorption strategy for removing cationic and anionic dyes simultaneously using a single entity.

The objective of the present study is to evaluate the dye removal efficiency of the succinamic acid [propyl-1-N,N-di-(4-carbonyl-butanoic acid)] modified MCM-41 (SA-MCM-41) from aqueous solutions. A three step synthesis strategy was adopted for the realization of the adsorbent, which include the succinamic acid formation through ring opening reaction of succinic anhydride with the propyl amine functionalized MCM-41. We have used rhodamine 6G (R6G), methylene blue (MB) and metanil yellow (MY) as model dyes. The SA-MCM-41 material was used effectively for dye adsorption from the individual, binary and ternary dye aqueous solutions. The effects of the initial sorbent loading, initial pH and the contact time on the adsorption capacity of SA-MCM-41 were also measured to obtain more information on the adsorption characteristics. Generally, carboxylic acid functionality is quite active for adsorbing cationic dyes owing to its negative charge [19]. We report the R6G assisted enhanced adsorption of MY over SA-MCM-41, a phenomena which was not observed with pristine MCM-41. The complete adsorption of MY in presence of R6G from binary and ternary mixtures highlighted the possibility of multilayer adsorption.

2. Experimental

2.1. Chemicals

Cetyltrimethylammoniumbromide (CTABr), tetraethyl orthosilicate (TEOS), (3-aminopropyl)triethoxysilane (APTES), succinic anhydride (SA), Triethylamine (TEA) rhodamine 6G (R6G), methylene blue (MB), metanil yellow (MY) and dry toluene were used as received from Aldrich.

2.2. Synthesis of MCM-41

MCM-41 was synthesised using CTABr as the structure directing agent and TEOS as the silica source. The reaction procedure was as follows: CTABr (0.5 g, 1.4 mmol) and an ammonia solution (26.7 g, 27%) were placed in distilled water (105 g). The mixture was stirred for 30 min at 50 °C in an oil bath. TEOS (2.35 g, 11 mmol) was then added drop wise to the clear solution. The mixture was allowed to stir for a further 3 h at 75 °C the white precipitate was separated by filtration and washed well with deionised water and ethanol. The obtained material was dried at 50 °C under vacuum overnight. Surfactant removal was carried out by calcination at 550 °C for 6 h at a heating rate of 1 °C/min [20].

2.3. Preparation of amino-functionalised MCM-41 (A-MCM-41)

The silanization of MCM-41 by APTES was carried out using the grafting method reported elsewhere [21]. Briefly, MCM-41 (1 g) was heated with APTES (1 g, 4.51 mmol) in dry toluene (100 ml) for 24 h under reflux. The solid product was filtered off and washed with toluene, ethanol and dried in an oven at 50 °C for overnight. The material obtained was labelled A-MCM-41 (Scheme 1).

2.4. Preparation of succinamic acid tailored A-MCM-41 (SA-MCM-41)

Carboxyl groups were introduced quantitatively onto A-MCM-41 via a ring–opening reaction of succinic anhydride (SA) with A-MCM-41 [22,23]. Briefly, A-MCM-41 (1 g) was heated to 60 °C with SA (1.32 g, 13.2 mmol) in dry toluene under a nitrogen atmosphere in the presence of TEA (0.2 g, 2 mmol). 1:2 ratio for amino functionality in MCM-41 and SA was used to replace the hydrogen atoms in the amino group. After 24 h, the solid product was separated by filtration and washed several times with toluene and dichloromethane, dried under vacuum for overnight at 50 °C and labelled SA-MCM-41 (Scheme 1).

2.5. Adsorption of dyes using SA-MCM-41

Stock solutions of R6G, MB and MY dyes were prepared in 0.08 mM concentration. The experimental solutions were prepared by diluting the stock solution with distilled water to the required concentration. The initial pH of each solution was adjusted to the required values with diluted HCl or NaOH solutions before adding the adsorbent. The adsorption behaviour was examined using a batch adsorption method, which permits a convenient evaluation of the parameters that influence the adsorption process, such as the pH of the solution, chemical contact time and adsorbent dosage. Fig. 1 presents the chemical structure of the dyes used in the adsorption study. In each adsorption experiment, 10 mg of adsorbent was added to 5 ml of the dye solutions and shaken mechanically to the required time. After adsorption, the residual concentration of the dyes in the filtrate was determined using a UV–Vis spectrophotometer at the wavelength corresponding to the maximum absorbance at 436, 527 and 664 nm, respectively for MY, R6G and MB [24]. The UV–Vis spectrophotometer was calibrated against a standard solution before each analysis.

2.6. Characterization techniques

XRD (Bruker AXN) was performed using Cu-Kα radiation. The XRD patterns were collected over the low-angle range from 1.2° to 10° 2θ. TEM (JEOL 2010) was performed at an accelerating voltage of 200 kV. The SEM (JEOL 6400) images were collected at an operating voltage of 20 kV. The N_2 adsorption–desorption isotherms were measured using a Nova 4000e surface area and pore size analyser. The samples were degassed at 120 °C for 12 h prior to the measurements. The Brunauer-Emmet-Teller (BET) method was used to calculate the specific surface area. The pore size distribution was obtained from an analysis of the adsorption branch using the Barrett–Joyner–Halenda (BJH) method. The Fourier transform infrared (FT-IR, JASCO FTIR 4100) spectra were measured from KBr pellets over the frequency range, 4000-400 cm^{-1}. The ^{13}C CP and ^{29}Si MAS NMR (Bruker DSX 400) spectra were obtained using a 4 mm zirconia rotor spinning at 6 kHz (resonance frequencies of 79.5 and 100.6 MHz for ^{29}Si and ^{13}C CP MAS NMR, respectively; 90° pulse width of 5 ms, contact time of 2 ms, recycle delay of 3 s for both ^{29}Si MAS and ^{13}C CP MAS NMR, Korea Basic Science Institute Daejeon Center). Elemental analysis for C, H and N was performed by combustion analysis on a Perkin Elmer CHN Analyser (Model 2400). The absorption spectra of the samples were obtained using a UV–Visible spectrophotometer (U-2010, HITACHI Co.). The zeta potential measurements were carried out using Zetasizer Nano ZS