



# Synthesis and adsorption properties of mesoporous material for the removal of dye safranin: Kinetics, equilibrium, and thermodynamics



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## ABSTRACT

A highly ordered large pore mesoporous adsorbent MCM-41 is synthesized and characterized by XRD, BET, FTIR and SEM. Effect of contact time, initial dye concentration, adsorbent dose, pH and temperature were studied for adsorption of dye safranin on MCM-41. Experimental data were investigated for various thermodynamic models and kinetic models and corroborated that adsorption followed second order kinetic model. Langmuir model evidenced the maximum adsorption capacity as  $68.8 \text{ mg g}^{-1}$  at 303 K. Thermodynamic parameters surmised that adsorption of safranin on MCM-41 is spontaneous, exothermic and feasible.

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## Introduction

There is growing public concern over the contamination of wastewater by dyes. The removal of dyes and pigments from wastewater has become a major focus of research. This is due to the fact that presence of dyes and pigments in water, even at very low concentrations, is highly undesirable [1]. Total annual dyes production in the world is more than  $7 \times 10^5$  tons and about 2% of dyes produced annually are discharged in effluent from manufacturing operations [2]. During the past 35 years, India has become a major producer of dyes and pigments to cater to the needs of not only the textile industries but also of other industries such as paper, rubber, plastics, paints, printing inks, art and craft, leather, food, drug and cosmetics [3]. Discharge of dye effluents into the environment is currently one of the world's major environmental problems for both toxicological and esthetic reasons.

Safranin is one of the most commonly used cationic, azine dye, which is among the oldest known synthetic dyes. Safranin is a water-soluble reddish brown powder, which is mainly used as

food dye in flavoring and coloring candies and cookies. It is also used for dyeing tannin, cotton, bast fibers, wool, silk, leather and paper [4]. The presence of safranin causes several acute effects on health like irritation to mouth, throat, tongue, lips and pain in stomach which may lead to nausea, vomiting and diarrhea [5]. So the removal of dye safranin from the aqueous solution is highly significant.

Dye laden wastewaters are usually treated by physical or chemical processes. The conventional methods for treatment processes such as physical separation, oxidation, biological degradation, coagulation and flocculation have been widely investigated to remove dyes from wastewaters [6–8]. Among all these, adsorption has shown to be one of the most efficient physicochemical processes. Activated carbon is the most widely used adsorbent for removal of dyes from aqueous solution. However, the high cost of production and regeneration make it uneconomical [9]. Review of literature shows the adsorption behavior of dyes with different adsorbent such as activated carbon, clay, ion exchanger resin and zeolite has been thoroughly investigated [10–15]. Recently developed ordered mesoporous materials like ZSM-5, MCM-22,  $\text{NH}_4$ -Beta, etc. with desirable properties such as unique ordered structure, large uniform and tunable mesopore size, high specific surface area, and large pore volume opened up a new era in this field and have showed

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remarkable improvement in the adsorption of bulky dyes over commercial activated carbons [16–19].

Mesoporous silica MCM-41 has negative charge density due to presence of Si–O and Si–OH group. In the present study, our objective is to examine the possible effect of interactions between large positively charged dye safranin and MCM-41. The synthesized material is characterized with XRD, FTIR and SEM. The adsorption experiments with respect to pH, contact time, temperature and adsorbent dose were done to congregate more information about the adsorption process. In addition kinetic and thermodynamic studies are carried out to interpret the adsorption mechanism.

## Experimental

### Materials

Tetraethylorthosilicate (TEOS) was purchased from Sigma (Aldrich). Ethanol, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were procured from Merck, India. Triethylamine (TEA), *n*-cetyl trimethylammonium bromide (CTAB, chemical formula =  $C_{19}H_{42}BrN$ , Mol. wt. = 364.45) and safranin (C.I. 50240, chemical formula =  $C_{20}H_{19}N_4Cl$ , Mol. wt. = 350.8) was purchased from S.D Fine Chemicals (Mumbai, India).

### Adsorbate

An accurate weighed quantity of the dye safranin was dissolved in double-distilled water to prepare a stock solution ( $500 \text{ mg L}^{-1}$ ). Desired concentrations were obtained by successive dilutions with double distilled water. Concentration of dye solution before and after adsorption was deduced from the calibration curve (absorbance vs concentration) of the dye at absorption maximum.

### Synthesis of MCM-41

MCM-41 was prepared by using tetraethylorthosilicate (TEOS) as silicon source, and CTAB as surfactant [20,21]. It was crystallized from gel composed of TEA:TEOS:CTAB:NaOH:H<sub>2</sub>O = 10:2:0.5:0.5:170 in a Teflon container. The composition was left to age for 20 h at room temperature then heated at  $150^\circ\text{C}$  for 48 h. The solid product was obtained by filtration, washed with distilled water and dried at room temperature.

Template removal was done by solvent extraction method. Synthesized product was suspended and refluxed in 1 M HCl in ethanol for 6 h, then filtered, washed and dried at  $100^\circ\text{C}$  for 10 h.

### Characterization of adsorbent

FTIR spectra of the samples were recorded in a Perkin Elmer FTIR spectrophotometer in the range of  $400\text{--}4000 \text{ cm}^{-1}$  taking KBr as the reference. Surface morphology was studied by scanning electron microscopy (Carl Zeiss Supra 55), equipped with Energy dispersive X-ray analysis (EDX) using gold sputtering process. The materials are further characterized by using the X-ray diffraction in the scanning mode on XRD 7000 (Shimadzu, Japan) analytical instrument operated at 40 kV and a current of 30 mA with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The N<sub>2</sub> adsorption–desorption isotherms of the adsorbent was measured using an automatic adsorption instrument (Micromeritics Chemisorb ASAP 2020) at liquid nitrogen temperature (77 K). Prior to measurements, sample was degassed at  $300^\circ\text{C}$  for 12 h under vacuum. The specific surface area (SBET) of the adsorbent was calculated using the Brunauer–Emmett–Teller (BET) equation by assuming the area of

the nitrogen molecule to be  $0.162 \text{ nm}^2$ . The total pore volumes were estimated from the liquid volume of adsorbate adsorbed (N<sub>2</sub>) at a relative pressure of 0.99. In addition, the pore size distribution (PSD) was determined by using the Barrett–Joyner–Halenda (BJH) method applied on the adsorption/desorption hysteresis loop assuming a model of cylindrical open-ended pores.

The pH of zero point charge ( $\text{pH}_{\text{zpc}}$ ) was determined for MCM-41 by the method given by Rivera-Utrilla et al. [22]. 50 ml of a 0.01 M sodium chloride (NaCl) solution was placed in a 100 ml Erlenmeyer flask. The pH was then adjusted to successive initial values between 2 and 12, by using either sodium hydroxide or hydrogen chloride (0.1 N), and 0.15 g MCM-41 was added to the solution. After a contact time of 24 h, the final pH was measured and plotted against the initial pH. The pH at which the curve crosses the line  $\text{pH}(\text{final}) = \text{pH}(\text{initial})$  is taken as the  $\text{pH}_{\text{zpc}}$ .

### Adsorption experiment

Adsorption experiments were carried out by stirring 25 mg of MCM-41 in 25 mL of the aqueous solutions of dye safranin at different temperatures. The flasks with their contents were shaken for different time intervals. After adsorption the supernatant was centrifuged for 5 min at 4000 rpm. The concentration of each dye in the supernatant solution before and after the adsorption was determined with a UV Visible spectrophotometer (1800, Shimadzu, Japan) at a wavelength of maximum absorption,  $\lambda_{\text{max}}$  (518 nm).

Adsorption capacity,  $q_t$  ( $\text{mg g}^{-1}$ ), of the adsorbent was calculated by a mass balance relationship, which represents the amount of adsorbed dye per amount of adsorbent:  $q_t = V(C_0 - C_t)/m$ , where  $C_0$  is the initial dye concentration ( $\text{mg L}^{-1}$ ),  $C_t$  is the dye concentration in solution ( $\text{mg L}^{-1}$ ) at time  $t$ ,  $V$  is the volume of the solution (L), and  $m$  is the mass of the mesoporous MCM-41 (g). The percent removal (%) of dye was calculated using the equation:  $\% \text{ removal} = ((C_0 - C_t)/C_0) \times 100$ .

## Results and discussion

### Characterization of MCM-41

Fig. 1 shows the FT-IR spectra of the MCM-41 samples. In the hydroxyl region ( $3600\text{--}3200 \text{ cm}^{-1}$ ), a broad band is seen around  $3458 \text{ cm}^{-1}$ , which is attributed to surface silanols and adsorbed water molecules. The absorption bands close to  $1634 \text{ cm}^{-1}$  is due to the bending vibration of adsorbed water molecules. The asymmetric stretching vibrations of Si–O–Si are observed by the absorption bands at  $1035 \text{ cm}^{-1}$ . The band at  $971 \text{ cm}^{-1}$  is attributed to Si–OH vibrations. The absorption peaks around  $467$  to  $795 \text{ cm}^{-1}$

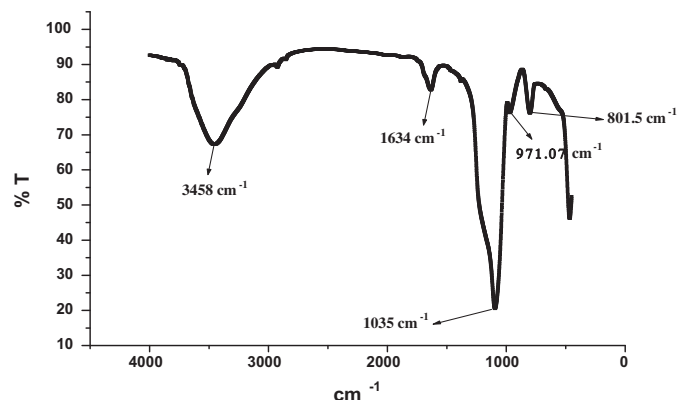


Fig. 1. FTIR spectra of calcinated MCM-41.

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