

An Efficient Removal of Erioglaucine Dye using MCM-41 Synthesized from Waste Coal Fly Ash

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Abstract

MCM-41 have been synthesized by developing simple hydrothermal route using waste coal fly ash (CFA) as a starting material. The synthesized MCM-41 was characterized by XRD, FT-IR and SEM. The catalysis showed the remarkable photocatalytic activity for high and quick removal of the Erioglaucine dye from its aqueous solutions using Photocatalytic degradation method. The MCM-41 catalyst was further tested for its recyclability and it shows good photocatalytic activity after five cycles.

Keywords: Hydrothermal, MCM-41, Erioglaucine, Photocatalytic degradation. Fly ash

INTRODUCTION

India's increasing demand for water for intensive integrated agriculture, for generating electricity and for consumption in urban areas and industries like textile, paper, rubber, petroleum, food and drugs for fabricating, processing, washing, diluting, cooling and transporting the product. Industrial effluent containing pollutants that are extremely harmful to flora and other environmental elements. Dyes are one of the component of paints, textile, printing inks, paper, and plastic industries. The effluent from these industries are the most polluting element [1-3].

Worldwide more than 100000 variants of dyes are produced and about 8×10^5 tons consumed annually [4]. The highly water soluble dyes like methylene blue, indigo carmine, acid violet, rhodamine B, erioglaucine have toxic, hazardous and a destructive effect on living things, because they have organic sulphonic acid group. Therefore, the removal of dye from water is necessary [5].

Many techniques have been used to remove these dyes from wastewater, like photochemical oxidation, coagulation, membrane filtration, electrochemical degradation, photocatalytic degradation and adsorption etc [6]. Out of these techniques, photocatalytic degradation is the most effective technique for removal of these toxic dyes. The dyes which are stable and intractable towards chemical oxidation and these characteristics leave them resistant towards decolorization. These dyes can be degraded by using photocatalytic degradation. It is substituted technique for adsorption method and able to operate effectively under the UV-visible light irradiation.

In coal based generation of electricity India is third largest country in the world [7]. The coal used in India is having low calorific value as well as high ash content. Near about 120-150 million tons coal fly ash is produced in India per annum [8]. Out of the total production of coal fly ash (CFA) more than 38% of CFA is utilized for making bricks, manufacture of cement, etc. Therefore large quantity of CFA still remains unutilized. Since, CFA is acidic in nature the disposal of CFA is major

environmental issue therefore this paper reports eco-friendly hydrothermal synthesis of MCM-41 from coal fly ash and its applicability for removal of EG dye from the aqueous medium.

The characteristics of MCM-41 is its large pore size and special surface property [9]. It consists of a regular arrangement of cylindrical meso-pores that form a one- dimensional pore system [10]. MCM-41 is a type of meso-porous zeolitic material having hexagonal structure, large specific surface area and large pore volume [11-12]. This paper first time reports the hydrothermal synthesis of MCM-41 by using waste CFA and its application as an efficient photocatalyst for removal of EG dye from its aqueous solution by photocatalytic degradation method.

EXPERIMENTAL WORK

Materials and Methods

A commercial grade Sodium hydroxide, NaOH with 97% purity, ethylene glycol and methanol was purchased from Molychem (India). The dye used are Erioglaucine (EG) with high purity was purchased from Sigma Aldrich. These chemicals and materials used in this study were commercially available and used with further purification. Deionized water was used throughout the experiments for preparation of various solutions. The coal fly ash (CFA) was collected from the thermal power plant Eklahre, Nashik, Maharashtra, (India). 2

Hydrothermal synthesis of MCM-41

The raw CFA used for synthesis of MCM-41 was analyzed by inductively coupled plasma (ICP) spectroscopy for quantitative determination of its composition. Which shows, Na₂O - 0.23 %, Al₂O₃- 29.03 %, SiO₂ - 55.0 %, K₂O - 1.38%, CaO - 2.52%, Fe₂O₃ - 7.36%, MgO - 0.80% and other LOI - 3.68%. The ICP data obtained showthat, %SiO₂/ %Al₂O₃ ≈ 2. Therefore CFA can be used as a source of Si and Al.

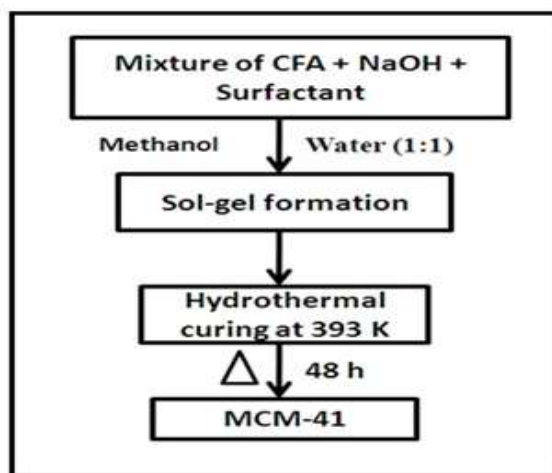


Fig. 1: Flow sheet diagram for Hydrothermal Synthesis of MCM-41

The Fe₂O₃ present in the fly ash was removed by magnetic separation method. Then CFA was washed with distilled water and dilute HCl to remove the soluble impurities and unburned carbon. 10.0 g of dried and treated CFA was taken in a Teflon lined autoclave of 250 ml capacity. To this 16.0 g of NaOH, 4.0 ml ethylene glycol, 50.0 ml methanol and 50.0 ml distilled water was added to form gel. The autoclave was kept in the oven for 48 h at 120^oC. After 48 h the cement like solid mass was formed, this material was then washed with distilled water filtered and dried in the oven at 120^oC for 24 h. The crystalline product was heated at 550^oC for 2 h in the furnace. The product thus obtained was used for further characterization and application to remove the dyes from their aqueous solutions. Figure (1) depicts the flow sheet for the hydrothermal synthesis of MCM-41 from CFA.

RESULTS AND DISCUSSION

FT-IR analysis

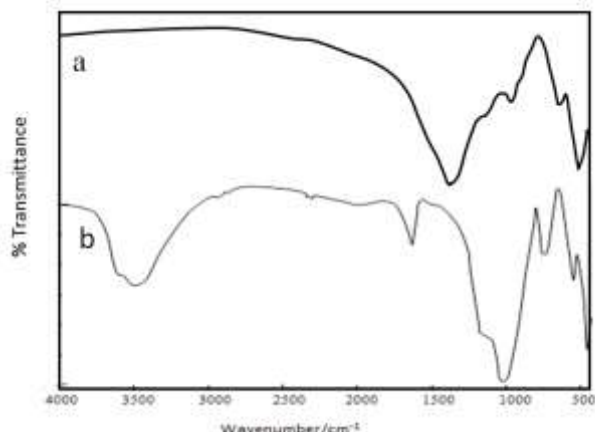


Fig. 2: FT-IR of (a) CFA and (b) MCM-41

The FT-IR spectrum (Fig.2a) of CFA shows peak at 1045 cm^{-1} is due to T-O asymmetric stretching vibrations and may be attributed to the presence of quartz (Where T = Si or Al). The bands corresponding to 800 and 557 cm^{-1} are due to quartz and mullite present in the fly ash. The band at 420 cm^{-1} is due to T-O bending vibrations [13]. Figure 2 (b) shows FT-IR spectrum for MCM-41 with broad peak at $\sim 963\text{ cm}^{-1}$ is due to asymmetric stretching vibrations of Al-O-Si bonds, two low intense peaks $\sim 750\text{-}650\text{ cm}^{-1}$ are due to symmetric stretching vibrations of Al-O-Si bonds and broad peak at $\sim 450\text{-}400\text{ cm}^{-1}$ is due to bending mode of vibrations of O-T-O bonds.

XRD analysis

The X-ray powder diffraction pattern of CFA mainly shows various peaks of low intensity due to presence of quartz (SiO_2) and mullites ($\text{Al}_6\text{Si}_2\text{O}_{13}$) (Fig.3a). After alkali fusion and hydrothermal process the original peaks disappeared and various sharp peaks are observed which depicts the formation of MCM-41 (Fig. 3b).

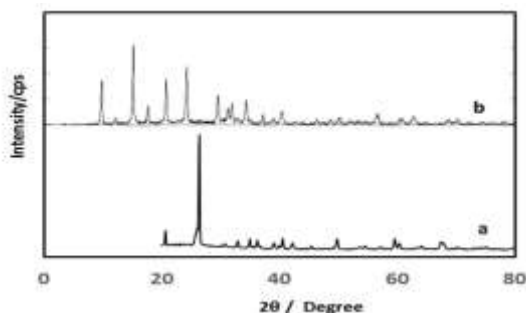


Fig. 3: XRD pattern of (a) CFA and (b) MCM-41

SEM analysis

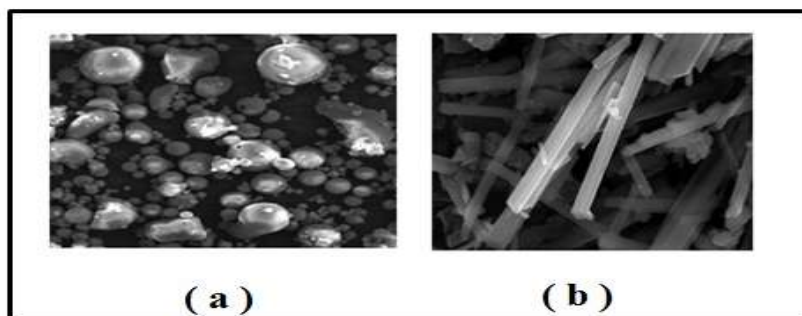


Fig. 4: SEM images of (a) CFA and (b) MCM-41

The SEM image of coal fly ash shows that most of fly ash particles are globular in shape with smooth surface (Fig. 4a). SEM image of MCM-41 shows change in the surface morphology from globular to rod like structure and it confirms the formation of MCM-41(Fig. 4b). The observed crystal morphology supports the hexagonal crystal structure.

Removal of EG dye by Photocatalytic Degradation

The photocatalytic activity of hydrothermally synthesized MCM-41 catalyst was studied by photodegradation of EG dye on exposure to UV-Visible radiation.

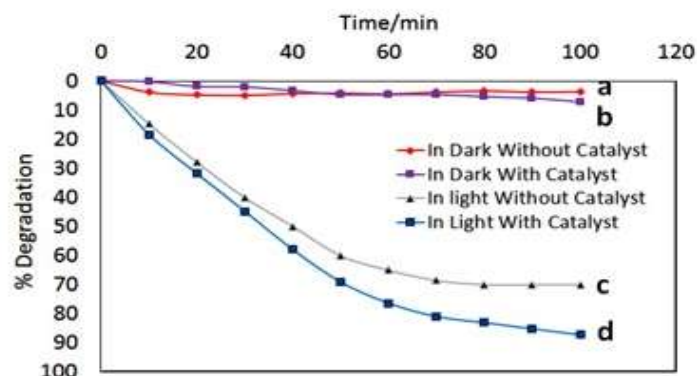


Fig. 5: Degradation of EG dye with different experimental conditions.

The close observation of Fig. 5 depicts that in the first case in which EG dye in absence of catalyst as well as UV-Visible light shows only 3.75 % degradation within 100 min. exposure by UV-Visible light (Curve (a)). In the second case in which EG dye in presence of 0.2 g. MCM-41 photocatalyst and in absence of light shows only 7.19 % degradation (Curve (b)). In the third case i.e. 6 ppm EG dye solution in absence of catalyst but in presence of UV-Visible light shows 70.19 % of degradation (Curve (c)). Where as in the last case where 6 ppm EG dye solution along with 0.2 g. MCM-41 photocatalyst shows 87.41 % degradation within 100 min (Curve (d)).

The light blue color of EG dye ($\lambda_{\max} = 630 \text{ nm}$) is due to the chromophoric and auxochromic groups present in the structure of EG dye. The photocatalyst MCM-41 consists of Al and Si atoms. As we irradiate the photocatalyst by UV-Visible light the electron gets excited from valence band to the conduction band leaving hole behind in the valence band. The electron from the conduction band is taken by adsorbed oxygen molecule to form superoxide radical anion $\text{O}_2^{\cdot-}$ and the hole takes electron from adsorbed water molecule to give H^+ ion OH^{\cdot} radical. The $\text{O}_2^{\cdot-}$ formed from adsorbed oxygen further combines with H^+ formed from water to form HOO^{\cdot} . Two such HOO^{\cdot} radicals further forms excited H_2O_2 and oxygen molecule. The excited H_2O_2 further breaks in to two OH^{\cdot} radicals. These OH^{\cdot} radicals responsible for breaking of the bonds giving different fragments and therefore the blue colour of the EG dye diminishes slowly and gradually and finally colourless. Figure6 shows the actual photograph of the fraction of solutions taken at time interval of 10 min. during EG dye degradation.



Fig. 6 Actual photograph showing change in colour intensity of EG dye at interval of 10 min.

The mechanism of degradation of EG dye may be explained with the help of following reactions-

- 1) $\text{MCM-41} + h\nu \text{ (UV radiation)} \longrightarrow \text{MCM-41} (e^-_{\text{conduction band}} + h^+_{\text{valence band}})$
- 2) $\text{MCM-41} (h^+_{\text{valence band}}) + \text{H}_2\text{O} \longrightarrow \text{MCM-41} + \text{H}^+ + \text{OH}^\bullet$
- 3) $\text{MCM-41} (e^-_{\text{conduction band}}) + \text{O}_2 \longrightarrow \text{MCM-41} + \text{O}_2^{\bullet-}$
- 4) $\text{O}_2^{\bullet-} + \text{H}^+ \longrightarrow \text{HOO}^\bullet$
- 5) $\text{HOO}^\bullet + \text{HOO}^\bullet \longrightarrow \text{H}_2\text{O}_2 \text{ (ads)} + \text{O}_2$
- 6) $\text{H}_2\text{O}_2 \text{ (ads)} \longrightarrow 2 \text{OH}^\bullet \text{ (ads)}$
- 7) $\text{EG dye} + \text{OH}^\bullet \text{ (ads)} \longrightarrow \text{Products of degraded EG dye}$
- 8) $\text{EG dye} + e^-_{\text{conduction band}} \longrightarrow \text{Products of degraded EG dye}$
- 9) $\text{EG dye} + h^+_{\text{valence band}} \longrightarrow \text{Products of degraded EG dye}$

These photocatalytic reactions are possible because of presence of dissolved oxygen in water. By taking view of the above reactions we propose the following mechanism for degradation of EG dye (Fig. 7).

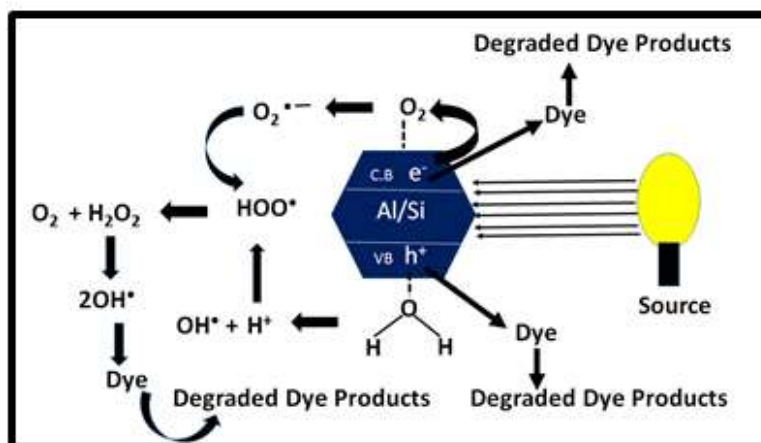


Fig. 7: Proposed mechanism of degradation of EG dye by MCM-41 in presence of UV-Visible light.

Recyclability of MCM-41 for photocatalytic degradation of EG dye:

To study the recyclability of photocatalyst, 0.2 g MCM-41 was taken with 6ppm EG dye solution. After the use of photocatalyst it was washed three times with deionized water and then with ethanol and dried in the oven at 60⁰C for 2 h and further used for the next cycle. The % degradation was calculated by measuring the initial and final concentrations in terms of its absorbance. This procedure was repeated for 5 cycles. The % degradation was plotted versus number of cycles (Fig. 8). The small decrease in the % degradation of EG dye can be attributed due to loss of small amount of catalyst MCM-41 during its recovery and washing.

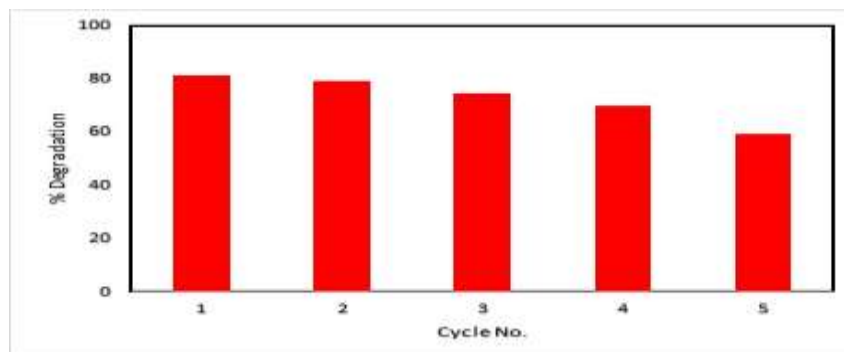


Fig. 8: Recyclability of MCM-41 photocatalyst against EG dye.

CONCLUSION

High % of Si and Al in CFA make possible to synthesize MCM-41 by hydrothermal treatment. This method requires very less energy as well as reagents. FT-IR, Powder X-ray diffraction pattern, SEM analysis confirms the conversion of CFA into MCM-41. This is the first report to use MCM-41 as efficient photocatalyst for the removal of EG dye from its aqueous solution. MCM-41 shows very good photocatalytic activity even after using it almost five times.

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