

Effect of poly(ethylene glycol) surfactant on carbon-doped MoO₃ nanocomposite materials and its photocatalytic activity

M E NAVGIRE[†], M K LANDE^{*}, A B GAMBHIRE, S B RATHOD, D V AWARE[†] and S R BHITRE[†]

Department of Chemistry, Dr Babasaheb Ambedkar Marathwada University, Aurangabad 431 004, India

[†]Jijamata College of Science and Arts, Bhende, Ahmednagar 414 605, India

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Abstract. Carbon-doped MoO₃ samples were prepared by impregnation method. The effect of addition of polyethylene glycol-400 (PEG-400) and carbon (0, 1, 2 and 3 wt. %) as substrates, were investigated systematically to get the desired phase of carbon-doped MoO₃ material. The carbon used was prepared from the natural sources such as *Acacia arabica* plant wood. The resulting samples were calcined at 500°C. The effect of PEG-400 and carbon composite on the structure, particle size and morphology of MoO₃ was investigated. The samples thus prepared gave better control of particle size and porosity. The prepared samples were characterized using XRD, SEM-EDS and FT-IR techniques. Photocatalytic activities of the samples were studied with degradation of methylene blue. The 3 wt.% carbon-doped MoO₃ modified by PEG-400 (CMP3) sample showed enhanced photocatalytic activity in comparison with the undoped samples.

Keywords. Carbon substrate; nanostructure; MoO₃; PEG; impregnation method; photocatalytic degradation.

1. Introduction

Nanocrystalline materials have received considerable attention because of their structural, electronic, optical properties and their potential applications (Lee *et al* 2002; Sian and Reddy 2004). In the past decade, a large number of nanocrystalline metal oxides, such as TiO₂, Cr₂O₃, MoO₃ (Kasuga *et al* 1999; Zach *et al* 2000; Lota *et al* 2007), have been widely synthesized. These nanomaterials have been used as photocatalyst (Jose *et al* 2007; Gambhire *et al* 2009), dye sensitized solar cells (Gratzel 2004), rechargeable lithium batteries (Wen *et al* 2006), gas sensors (Taurino *et al* 2006), field emitters (Zhou *et al* 2003) and in heterogeneous catalysis (Rathod *et al* 2009; Gambhire *et al* 2011).

Among these nanostructured metal oxides, MoO₃, a wide bandgap *n*-type semiconductor, is particularly interesting due to its potential applications. It has been extensively investigated as a key material for fundamental research and technological applications in optical devices, smart windows, catalysts, sensors, lubricants, electrochemical storage batteries, information displays and optical filters. Molybdenum oxides and molybdenum oxide based materials are of great technical interest (Li *et al* 2002; Mai *et al* 2003; Prasad *et al* 2003; Patil *et al* 2008).

The present work is an attempt to prepare realistic catalytic model system based on molybdenum oxide, which should

preserve the chemical and structural complexity of real catalysts but at the same time stay accessible to both surface science and bulk analytic techniques and hence contribute to bridge the materials gap. A combination of metal-organic synthesis, sol-gel chemistry and inorganic aqueous solution chemistry was used to synthesize molybdenum oxide based powders and thin films. Majority of the molybdenum containing heterogeneous catalysts described in the literature was prepared by co-precipitation of an aqueous ammonium heptamolybdate (NH₄)₆Mo₇O₂₄ solution (Juarez *et al* 2003).

Generally small surface areas of the resulting catalysts have attracted chemists to seek alternative preparation methods, which allow better control of the structure, size, and morphology of the molybdenum oxide. In this study, a new additive using polyethylene glycol (PEG) was introduced. The PEG is water soluble organic polymer having structure HO-(CH₂-O-CH₂)*n*-OH (molecular weight ranging from 200–100000 g/mol).

The present study investigates the effect of polyethylene glycol-400 i.e. molecular weight around 400 g/mol (PEG-400) additions on morphology of the molybdenum oxide. The improved desired properties of MoO₃ by addition of carbon substrate were explained by the high adsorption of impurities on the surface of added carbon and their transfer to MoO₃ surface. The carbon substrates were prepared and utilized from natural sources like *Acacia arabica* plant. This study describes a parametric design to determine the effect of PEG and natural carbon obtained *Acacia arabica* plant on morphology of the molybdenum oxide calcined at 500°C.

* Author for correspondence (mkl_chem@yahoo.com)

The degradation or decomposition by photocatalysis is a novel method for the treatment of air and water pollutant. Most of the photocatalytic studies use TiO_2 as a photocatalyst (Noorjahan *et al* 2002; Gandhe and Fernandes 2005). Recently some studies have been carried out to evaluate the priority of other metal oxides such as ZnO , In_2O_3 , SnO_2 and TiO_2 (Hu *et al* 1999; Carlos *et al* 2000; Byrappa *et al* 2006; Talebian and Nilforoushan 2010). The photocatalytic activities of TiO_2 doped MoO_3 have also been reported (Baiju *et al* 2005; Agarwal *et al* 2010). Here we report the photocatalytic activity of carbon doped MoO_3 catalysts.

2. Experimental

The reagent grade chemicals were used in the preparation of samples, ammonium heptamolybdate (Ranbaxy Fine Chemicals), oxalic acid (Ranbaxy Fine chemicals), ammonia (Ranbaxy) and polyethylene glycol (PEG-400) (Qualigens Fine chemicals), without further purification.

2.1 Preparation of carbon substrate

Carbon was prepared from *Acacia arabika* plant as a natural source. In the first step dried wood was burnt in absence of air, then the resulting charcoal crushed into fine powder. Finally, the obtained powder material was calcined at 500°C in high temperature muffle furnace in air atmosphere.

2.2 Preparation of carbon-doped MoO_3

Carbon-doped MoO_3 catalysts were prepared by conventional standard impregnation method. To impregnate carbon-doped MoO_3 the solution was obtained by dissolving ammonium heptamolybdate (0.2 M) in deionized water. The system was kept under constant stirring and sustaining the $\text{pH} = 8$ by simultaneous addition of 1:1 NH_4OH (Reddy *et al* 2000). The fine powdered carbon was added with 0 wt% (M), 1 wt% (CM1), 2 wt% (CM2), 3 wt% (CM3), respectively. The excess water was evaporated on the water bath with continuous stirring. The resultant precursor was then dried at 110°C for 12 h and calcined at 500°C for 2 h in air atmosphere.

2.3 Preparation of carbon-doped MoO_3 with PEG

To impregnate 0, 1, 2, 3 wt. % carbon-doped MoO_3 modified by PEG-400 i.e. MP, CMP1, CMP2, CMP3, respectively were obtained by a mixture of solutions of ammonium heptamolybdate (0.2M), oxalic acid (0.2M) and PEG-400 (0.5M) (Laigashetty *et al* 2005). The carbon addition, evaporation, drying and calcination steps followed were the same as in the above mentioned procedure.

2.4 Characterization technique

X-ray diffraction analysis (XRD) of the calcined samples were obtained with a Philips X-ray diffractometer in the diffraction angle range $2\theta = 20^\circ$ to 80° using $\text{CuK}\alpha$ radiation of wavelength 1.5405 \AA . Surface morphology and elemental analysis of the samples were carried out using scanning electron microscopy with electron dispersion spectroscopy (SEM-EDS) characterization conducted using a JEOL JED 2300 (LA) instrument. The Fourier transformation infrared spectra (FT-IR) were recorded on FT-IR spectrometer (JASCO FTIR/4100), Japan in the range $4000\text{--}500 \text{ cm}^{-1}$.

3. Results and discussion

3.1 XRD analysis

In order to understand the phase symmetry of the calcined samples a systematic study on the XRD was undertaken. Figure 1 shows that highly intense peaks were obtained at $2\theta/\text{degree} = 22.98, 25.36, 29.33, 35.94, 39.40, 43.19$ and 47.35 , giving corresponding planes of (320), (400), (421), (440), (532), (542) and (552) which predict the cubic crystal symmetry of carbon substrate or fullerene. It was found that all XRD reflections of carbon substrate were matched using JCPDS card No. 79-7015 (David 1991) and lattice parameter ($a = b = c = 14.0408$).

Figures 2a–d show the XRD patterns of carbon doped MoO_3 without PEG-400 addition giving highly intense and sharp peaks at $2\theta/\text{degree} = 23.36, 25.75, 27.30, 33.61$ and 38.96 , corresponding to the planes (110), (040), (021), (111) and (060) indicating orthorhombic crystal structure. The average crystallite sizes of the powder were calculated using Debye–Scherrer formula (Taylor 1961) (table 1, entries 1–4), showing the crystallite size without addition of PEG-400 in the range of $\approx 11.80\text{--}12.98 \text{ nm}$ for M, CM1, CM2

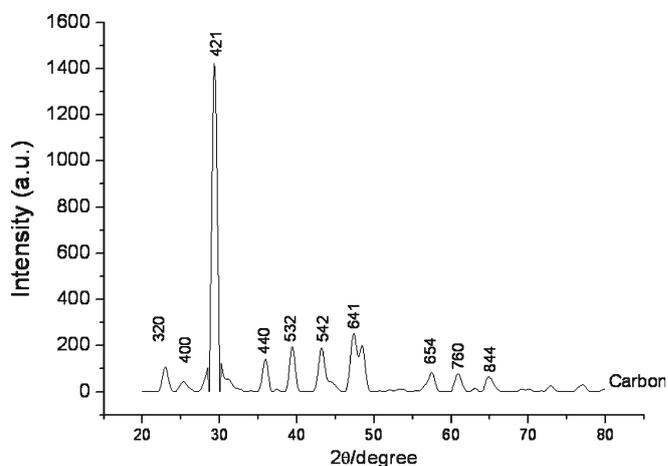


Figure 1. XRD pattern of carbon.

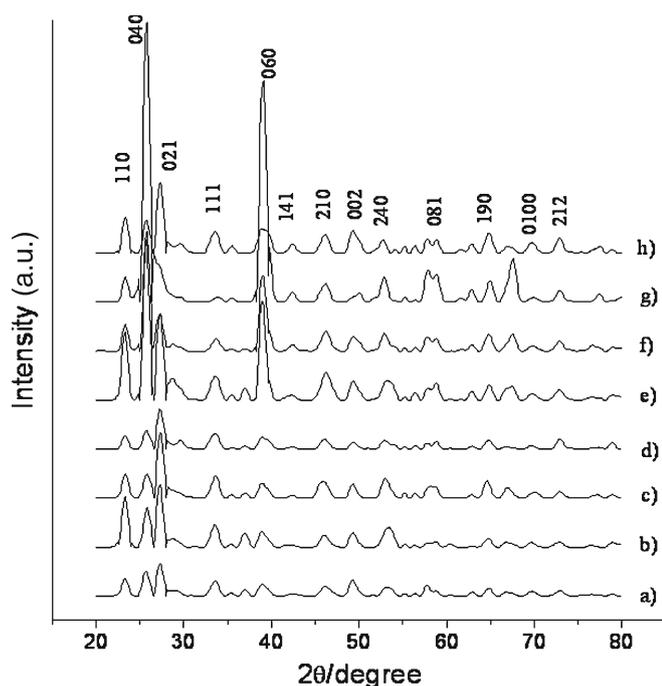


Figure 2. XRD patterns of (a) MoO₃, (b) 1%, (c) 2%, (d) 3% carbon doped MoO₃, (e) 0%, (f) 1%, (g) 2% and (h) 3% carbon doped MoO₃ with PEG-400.

and CM3. It was noted that all the XRD peaks are identified as MoO₃ peaks from the JCPDS card 76-1003 (Kihlberg 1963), with lattice parameters $a = 3.9628$, $b = 13.8550$ and $c = 3.6964$. The strong and sharp peaks suggest that the as-prepared materials are crystalline.

Figures 2e–h show the XRD patterns of carbon doped MoO₃ with PEG-400 addition identifying the planes (110), (040), (021), (111) and (060) corresponding to orthorhombic crystal symmetry. Same structure was found for the entire range of concentration of carbon. The crystallite size calculated from XRD data is as large as 9.96 to 11.28 nm (table 1, entries 5–8) for MP, CMP1, CMP2 and as small as 9.85 nm for the sample CMP3. This apparent fall in the crystallite

Table 1. Crystallite size calculated using Debye–Scherrer formula.

Entry	Catalyst	2θ/degree	FWHM	Size (nm)
1	Carbon	29.33	0.7968	10.79
2	M	25.754	0.7356	11.80
3	CM1	25.764	0.6970	12.48
4	CM2	25.771	0.7285	11.91
5	CM3	25.738	0.6701	12.98
6	MP	25.824	0.7684	11.28
7	CMP1	25.839	0.8923	9.96
8	CMP2	25.714	0.8139	10.64
9	CMP3	25.785	0.8783	9.85

size will have many potential applications of these catalysts (Oyama *et al* 2003).

3.2 SEM and EDS studies

To study the surface topography and elemental composition, the SEM with EDS were investigated systematically. Figure 3(a) shows flakes structure of carbon like fullerene. Figures 3b–g show the variation in morphology of MoO₃ samples with and without PEG-400 and carbon addition. Figures 3b–c show morphology of pure MoO₃, which is highly crystalline in nature. It can be seen that the sample CM3 shows agglomeration and randomness in the crystallite size without porosity (figures 3d–e). Further, the sample CMP3 shows decrease in the crystallite size and development of porous surface figures 3f–g. From the SEM micrograph it can be seen that effect of addition of PEG-400 as a surfactant clearly shows alteration in crystallite size and morphology with increasing porosity.

Elemental compositions of carbon doped MoO₃ with and without PEG-400 i.e. CM3 and CMP3, were represented in table 2. The observed Mo : C : O atomic ratios are fairly close to the expected bulk ratios indicating also a rather good distribution of the metal species inside the samples. From this analysis it was shown that, the minimum stoichiometric ratio of desired 3 wt% carbon doped MoO₃ with and without PEG-400 were maintained.

3.3 FT-IR study

Figure 4(a) shows the FT-IR spectra of the carbon substrate. The spectrum of the carbon substrate shows broad peak at 3400 cm⁻¹ due to –OH stretching vibration modes of the adsorbed water, the peak at 1384 and 1576 cm⁻¹ could be assigned for C–C and C=C vibrations, respectively (Ganguly and George 2007).

Figure 4(b) shows the FT-IR spectra of MoO₃. A band at 878 cm⁻¹ is characteristic of terminal molybdenum oxygen double bond (Mo=O). The bands at 1439 and 1577 cm⁻¹ were attributed due to C–C and C=C vibrations. The broad band around 3499 cm⁻¹ is due to O–H stretching vibration modes of the adsorbed water on the surface of the powder (Cheng *et al* 2006).

Figures 4c–e show the FT-IR spectrum of CM1, CM2 and CM3, respectively. Sharp bands appear in the range 875–885 cm⁻¹ due to the terminal molybdenum–oxygen double bond (Mo=O). The bands at 1410–1600 cm⁻¹ were attributed due to C–C and C=C vibrations, the additional band around 2926 cm⁻¹ probably may be due to CH₂ and or C (OH) stretching mode. While broad band around 3381–3464 cm⁻¹ may be due to O–H stretching vibration modes of the adsorbed water (Luo *et al* 2009).

Figure 5f–i show the FT-IR spectrum of MP, CMP1, CMP2 and CMP3. Similar bands were observed without addition of PEG-400 samples.

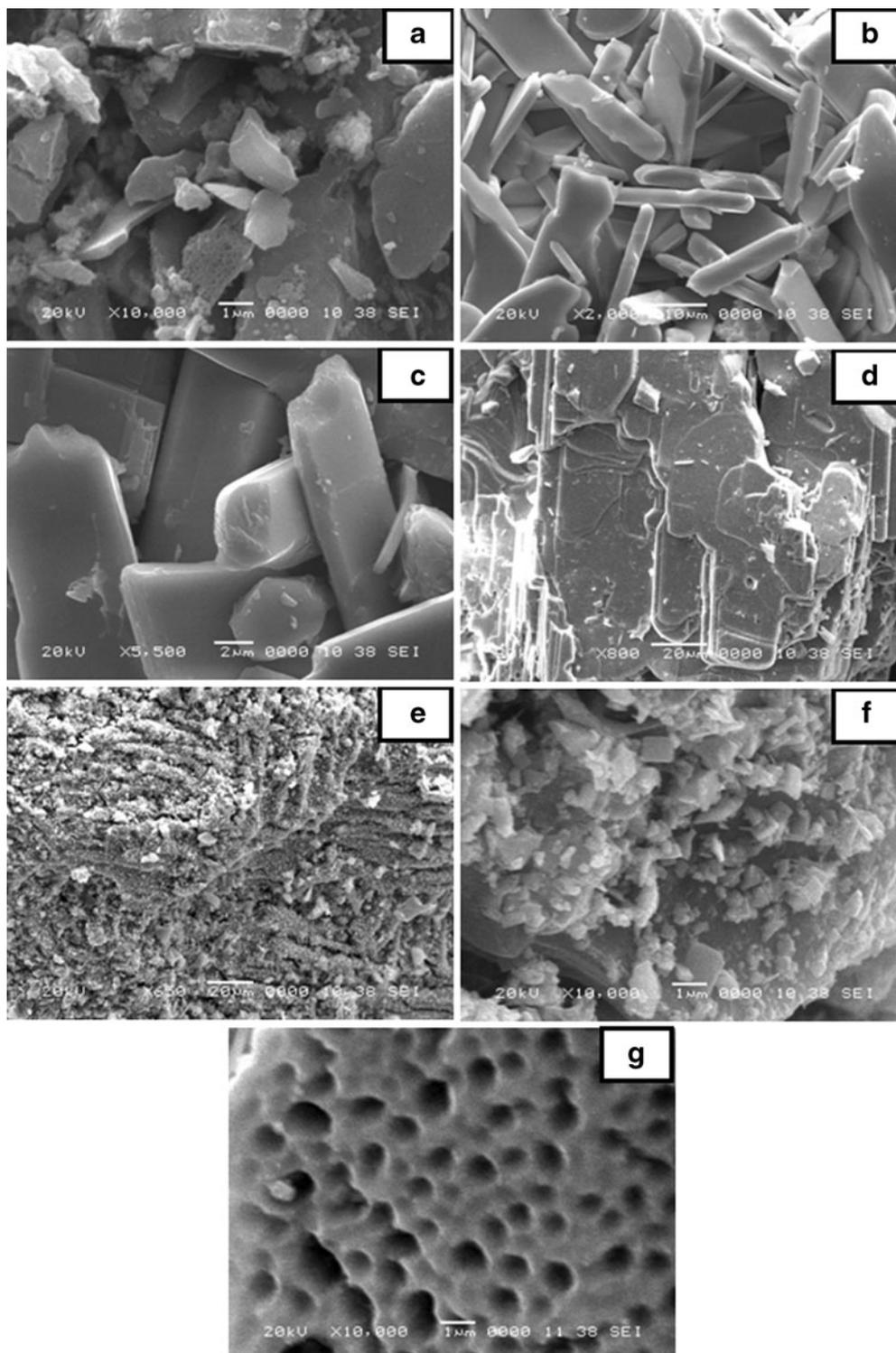


Figure 3. SEM images of **a.** carbon, **b–c.** MoO_3 , **d–e.** 3% carbon doped MoO_3 , **f.** and **g.** 3% carbon doped MoO_3 with PEG-400.

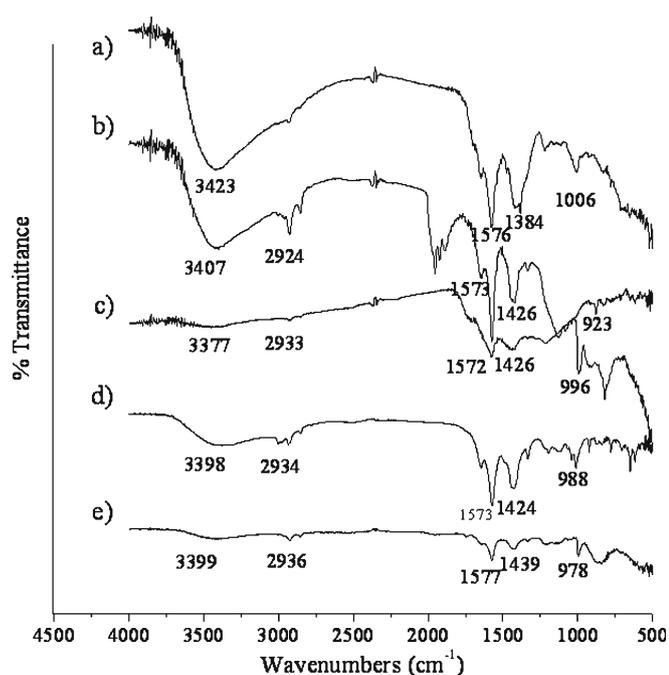
3.4 Photocatalytic activity measurements

To evaluate the photocatalytic activity of prepared series of carbon-doped MoO_3 modified by PEG-400 towards dye

degradation, photocatalysis experiments were carried out in round-bottomed pyrex glass cells with a cut off wavelength of 320 nm. The irradiation system was equipped with mercury lamps, 250W (Philips UV), light bulb. Methylene blue

Table 2. EDS elemental quantitative analysis.

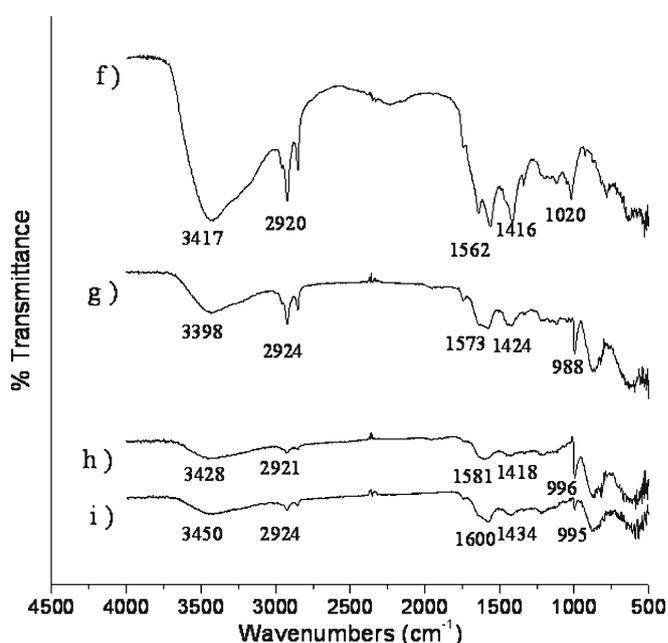
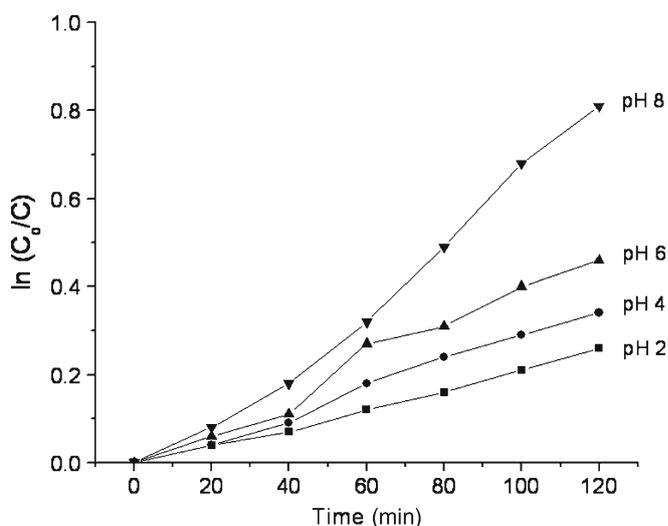
Entry	Catalyst	Elemental atomic wt %		
		Mo	O	C
1	CM3	13.12	44.09	42.79
2	CMP3	9.58	34.51	55.91

**Figure 4.** IR spectra of (a) carbon, (b) MoO₃, (c) 1%, (d) 2% and (e) 3% carbon doped MoO₃.

(MB) was used as the model pollutant for degradation. The suspensions of catalyst in dye solution were subjected to UV light radiation for 120 min. The solution of the dye with desired concentration (5 mgL⁻¹, pH 8) and 0.2 g of the catalyst was prepared in double distilled water. For irradiation experiment, 100 mL aqueous solution was taken in the photoreactor. The pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HCl or NaOH. The solutions were stirred intermittently. After every 20 min, 2 ml aliquots were pipetted out and then centrifuged. The photocatalytic degradation of the dye was monitored using UV spectroscopic analysis technique (Varian Cary 500 spectrophotometer). The absorbance of the clear supernatants was determined at 660 nm wavelength against appropriate blanks. The rate of decolorization was observed in terms of change in intensity at λ max of the dye. The decolorization efficiency (%) has been calculated as:

$$\text{Efficiency} = \ln(C_0 - C),$$

where C_0 is the initial concentration of dye and C the concentration of dye after photoirradiation.

**Figure 5.** IR spectra of (f) 0%, (g) 1%, (h) 2% and (i) 3% carbon doped MoO₃ with PEG-400.**Figure 6.** Photodegradation kinetic of MB on 3% carbon doped MoO₃ with PEG-400 as catalyst at different pH and dye concentrations (5 mgL⁻¹).

First, the photocatalytic experiments were carried out using different catalysts and pH values (2, 4, 6, and 8) at dye concentration (5 mgL⁻¹). The percentage of degradation increased with increasing UV exposure time as shown in figure 6. The variation of photodegradation % of MB using different catalysts under the UV irradiation for 120 minutes is shown. The observed photocatalytic efficiency increased with addition of carbon and PEG-400. The photocatalytic efficiency of various catalysts at 8 pH values is shown in

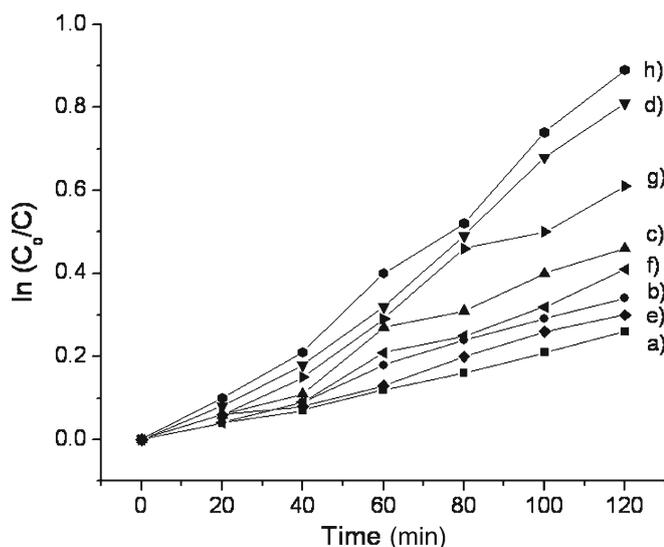


Figure 7. Photocatalytic efficiency of various catalysts (a) MoO_3 , (b) 1%, (c) 2%, (d) 3% carbon doped MoO_3 , (e) 0%, (f) 1%, (g) 2%, and (h) 3% carbon doped MoO_3 with PEG-400 for MB degradation at pH 8 (dye concentration, 5 mgL^{-1} ; irradiation time, 120 min).



Figure 8. Photograph of MB degradation.

figure 7. The same trend was observed for photocatalytic efficiencies of different catalysts. The difference between photoactivities of these samples is possibly due to their different microstructures, as shown from SEM results. It was seen that, the 3 wt. % carbon-doped MoO_3 modified by PEG-400 sample showed maximum dye degradation in 120 min. The rate of degradation was found to be higher in the CMP3 sample shown in figure 8. The catalyst prepared without carbon and PEG-400, was found to be photocatalytically less active. This may be due to the comparatively increased porosity and decreased crystallite size of the CMP3 sample. It seems a great ability to capture photons is exhibited efficiently by nanocrystalline CMP3; it is due to rough and porous surface area.

4. Conclusions

In the present investigation, we have introduced for the first time carbon substrate obtained from *Acacia arabika* wood

plant and used it for the preparation of carbon-doped MoO_3 nanocomposite material. The PEG-400 and carbon composites have played an important role as structure directing agents in the designing of highly porous materials. This certainly allows alteration in crystallite size and morphology. The effect of variation of wt. % of carbon substrate calcined at 500°C for 2 h on the MoO_3 morphology was successfully evaluated. From the results, it was found that, increase in weight % of carbon substrate and addition of PEG-400 increases the porosity, crystalline nature and also which will improve the surface area of the nanocomposite material. The 3 wt.% carbon-doped MoO_3 modified by PEG-400 (CMP3) sample showed enhanced photocatalytic degradation of methylene blue activity in comparison with the undoped samples.

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