Visible Light Induced Photocatalytic Degradation of Methylene Blue using Polyaniline Modified Molybdenum Trioxide

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ABSTRACT. Polyaniline/Molybdenum trioxide composite was prepared by a chemical oxidative polymerization method. The obtained Polyaniline/Molybdenum trioxide composite was characterized by X-ray diffraction analysis (XRD), Fourier transform infrared (FT-IR) spectroscopy and transmission electron microscopy (TEM). The XRD pattern showed the diffraction peaks to be in good agreement with the structure of MoO₃. The obtained results confirm the successful formation of the Polyaniline/Molybdenum trioxide composite. Finally, the composite was employed as photocatalyst for the photodegradation of methylene blue under visible light irradiation. Further the photodegradation mechanism also discussed in detail.

Introduction. In recent years, synthetic organic dyes have become one of the leading pollutants in wastewater because of their extensive use in various industries such as plastic, rubber, cosmetics, textile, printing and paper industries as colouring agents [1]. The release of these coloured waste water in the ecosystem cause various environmental issues such as, biochemical oxygen demand (BOD), chemical oxygen demand (COD), increase of toxicity and colour of the water. As a result, the removal of organic pollutants like Methylene Blue (MB), Congo red (CR) and Rhodamine B has been the subject of various researches using different techniques such as chemical oxidation, reverse osmosis, electrochemical process or photochemical degradation, adsorption[2, 3]. Among them, photodegradation and adsorption are the two main reliable and effective methods for the removal of the toxic dyes. Recently, adsorption process has been proved to be an excellent method which offers significant advantages like easy operations, low cost and reusability of the adsorbent. But this technique transfers pollutants merely from aqueous to solid phase rather than their degradation and generates secondary waste problems. Compared with adsorption, Photocatalysis technology is considered as one of the most promising method for the removal of the carcinogenic pollutants because of mineralization of dyes based on solar energy [4].

Recently, a lot of studies have been carried out on the degradation of organic pollutants via photocatalysis of various semiconductors [5] such as ZnO, TiO₂, CeO₂ etc., Among them, MoO₃ a n-type semiconducting material has received considerable amount of attention due to its large surface area, inexpensive and pollution-less. Various methods such as hydrothermal process and template free solution growth technique have been employed for the fabrication of different MoO₃ morphologies such as nanofibers, nanorods, etc., Recently, Ying Ma et al. and A. Chithambararaj et al., have reported the removal of organic dye using MoO₃ [6, 7]. Improving the catalytic performance of MoO₃ and its composites has been the major aim of many researchers.
There are many literature reports that report the combination of semiconducting photocatalyst with electrically conducting materials such as carbon nanotubes and graphene to enhancing their photocatalytic performances [8]. Recently, conducting polymers such as Polythiophene, polyindole, polypyrrole and polyaniline have extensively studied for some applications such as gas sensors, biosensors, solar cells and battery applications [9]. Among these, polyaniline (PANI) has elicited great attention because of its unique electrochemical stability, optical properties, low cost and simple synthesis. Previously, PANI was reported to effectively improve the photocatalytic performance of many metal oxides such as TiO$_2$, ZnO and MnO$_2$ [4]. It has been reported that incorporation of PANI with metal oxides not only reducing the recombination rate of electron-hole pairs but also enhancing the photocatalytic activity. Considering the advantages of PANI, it was incorporated with the MoO$_3$ in this study to enhance the photocatalytic performance.

**Materials and methods**

Aniline (99%) and ammonium heptamolybdate tetrahydrate (98%) were purchased from Rankem. Camphor-10-sulphonic acid (98% pure) and ammonium peroxydisulphate (98% pure) were obtained from Sigma Aldrich chemicals. Methylene Blue (MB) was obtained from Qualigens. All experiments were done using double distilled water.

**Preparation of PANI/ MoO$_3$ composite photocatalyst**

Initially, MoO$_3$ nanoparticles were synthesized from ammonium heptamolybdate tetrahydrate through solid state decomposition method at 500 °C as per previous report [3]. The obtained powder was washed with distilled water and dried. Then, 1g of MoO$_3$ nanoparticles were dispersed in 50 mL of deionized water containing aniline (0.3 g). To this, camphor-10-sulphonic acid (aniline: CSA = 1:0.5, molar ratio) solution was mixed. Then, ammonium persulfate (APS) (aniline: APS = 1:1) solution was added drop wise to the above solution and allowed to react for 12 h with constant stirring at 0-4 °C. A dark green precipitate was obtained and washed with water followed by ethanol and dried in an air oven.

**Photocatalytic experiments**

The photocatalytic activity under visible light in the literatures is followed [7]. The photocatalytic performance of PANI/ MoO$_3$ composite was evaluated by the degradation of methylene blue which was taken as a model organic compound. Reaction suspensions were prepared by adding 500 mg of the catalyst into the 500 ml of MB solution with an initial concentration of $1.5 \times 10^{-5}$ mol l$^{-1}$. Prior to the irradiation, the suspensions were magnetically stirred in the dark for about 30 min to ensure the establishment of an adsorption-desorption equilibrium between the MB dye and photocatalyst. Visible light irradiation for this experiment was carried out using projection lamp (7748XHP 250 W, Philips, 532 nm) in a photocatalytic reactor. Then the prepared suspension was kept under the irradiation under continuous stirring at room temperature. During the irradiation, the suspensions were sampled at every 30 min and immediately centrifuged to remove the catalyst particles. Then the absorption of MB aqueous solution was measured by UV-Vis spectrophotometer.

Degradation efficiency can be calculated using the following equation:

$$\eta = (1 - C_t / C_0)$$

where $C_t$ and $C_0$ are the concentrations of the solution after illumination for $t$ minutes and before illumination ($t = 0$) respectively.

**Characterization of the photocatalysts**

X-ray diffraction (XRD) pattern was recorded using GE X-RAY Diffraction System-XRD 3003 TT with CuK$\alpha$ radiation ($\lambda = 1.5406\text{Å}$ ) for $2\theta = 10-70\degree$. Fourier transform infrared (FTIR) spectrum
was obtained from Perkin-Elmer FTIR system. The optical absorption properties of photocatalysts were obtained ANALYTIK JENA SPECORD 200 PLUS. HRTEM analysis was carried out using TECHNAI INSTRUMENT operating at operating voltage of 200 kV.

Results and discussion

Structural and morphological characterization

XRD pattern of MoO$_3$ and PANI/ MoO$_3$ is presented in Fig. (1). For the MoO$_3$, all the diffraction peaks are attributed to the orthorhombic structure of MoO$_3$ (JCPDS card No. 05-0508) indicating well crystallization. The XRD pattern of PANI/ MoO$_3$, clearly shows the maintenance of MoO$_3$ crystal structure even after the addition of polyaniline. Moreover, also there is no change in the peak position. It implies that, the polymerization of aniline monomers takes place on the surface of metal oxide. While adding the polyaniline, amorphous nature was observed with the crystalline pattern which indicates the formation of PANI/ MoO$_3$ composite [3].

![Fig. 1. XRD Pattern of MoO$_3$ and PANI/ MoO$_3$.](image1.png)

![Fig. 2. HRTEM image of PANI/ MoO$_3$.](image2.png)
Fig. 2 shows the HRTEM image of PANI/ MoO₃. It can be observed that MoO₃ particles wrapped by the grey colored layer. It clearly shows that MoO₃ particles were covered by the PANI. The obtained result is in good agreement with the XRD results. The size of the particles was measured using imagej software. It was found to be in the range of ~100 - 400 nm.

**FTIR analysis**

![FTIR Spectrum of PANI/MoO₃](image)

Fig. 3. FTIR spectrum of PANI/MoO₃.

FTIR spectrum of PANI/MoO₃ in the range of 4000 – 400 cm⁻¹ is shown in Fig. 3. FTIR spectrum shows peaks at ~3236, 1570, 1487, 1302, 1243 and 1146 and 630 cm⁻¹. The peak at around ~3236 cm⁻¹ attributed to the N-H stretching vibrations. The peaks observed at ~1570 and ~1487 cm⁻¹ assigned to the stretching vibration of quinonoid ring and benzenoid ring respectively. The peak at ~1243 cm⁻¹ corresponds to the C-N⁺ stretching vibration. Peaks at ~1302 and ~1146 cm⁻¹ corresponds to the C–N stretching of an aromatic amine and C–H in plane bending mode respectively. The peak appearing at ~630 cm⁻¹ attributed to the bending mode vibration of the Mo–O–Mo [3, 7].

**Evaluation of Photocatalytic activity**

Initially, PANI/ MoO₃ composite was added to the MB solution under dark condition to establish adsorption–desorption equilibrium between the dye molecules and PANI/ MoO₃. The concentration of the MB in the supernatant solution was analyzed using UV-Vis spectrophotometer at the wavelength of maximum absorbance at 665 nm. The decrease in the peak intensity suggests that MB dye was removed by the PANI/ MoO₃.

Fig. 4 shows the MB removal percentage at regular interval of time. Nearly, 46% percentage of the dye was adsorbed on to the composite. It is due to the electrostatic interactions between cationic dye and negatively charged metal oxide surface. Also the presence of negatively charged sulphonic group present in the system as well as by the presence of pi–pi stacking interactions between aromatic ring of PANI and MB is reasonable for the migration of dye molecules onto the surface of composites [3, 7].

The photocatalytic activity of PANI/ MoO₃ composite catalyst was evaluated by measuring the decomposition rate of MB dye under visible-light irradiation. The decontaminating efficiency of the catalyst was calculated using the equation (1). Upon visible light irradiation, PANI can absorb visible light delivering the excited-state electrons of the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Then, the excited-state electrons in the LUMO of PANI molecules can drift into the CB of MoO₃ subsequently, they migrate to the surface of MoO₃...
and react with water to produce superoxide radical, which could oxidize the organic molecules. Here PANI acting as a photosensitizer which contribute to the higher photocatalytic activity. i.e hydroxyl radicals and superoxide anions were produced by the composite catalyst leading to the decomposition of organic dyes [4, 7]. The results demonstrate that 95.4% of the dye was removed in 150 min from the initial concentration.

**Summary.** Polyaniline/Molybdenum trioxide composite was successfully prepared by a chemical oxidative polymerization method. The formation of composite was confirmed from the FTIR analysis. Polymerization of aniline monomers on the surface of MoO$_3$ was confirmed from the XRD and HRTEM analysis. The decontaminating (including photocatalytic degradation and adsorption) activity of PANI/MoO$_3$ was demonstrated and evaluated on MB.

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**References**


Cite the paper