

Synthesis of MoO₃ Nanostructures by Solid State Reaction Method for Selective Adsorption of Cationic Dyes

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Received 21 June 2023; accepted 4 August 2023

The ecosystem and living things are severely hampered by the water pollution caused by organic compounds containing dyes and pigments. The cost-effective removal of organic dyes has therefore attracted a lot of attention in recent years. Herein, we report the removal of textile dyes from water via effective adsorption by nanostructured MoO₃ material. The MoO₃ have been synthesized via the solid state reaction method. The adaptation to multi-phases at effectively high temperatures and solvent-free conditions, as well as their scalability and simplicity, offers a lot of potential for this method. Powdered X-ray diffraction technique (PXRD) confirms the formation of pure-orthorhombic phase of MoO₃ (o-MoO₃). Field emission scanning electron microscope (FESEM) micrographs reveals the formation of stacking layer structure of MoO₃. The surface charge and surface area has been investigated by using Zeta potential and BET-BJH technique. The adsorption capacity of MoO₃ has been investigated for two common dyes: Methylene Blue (MB), and Methyl Orange (MO). The adsorption studies show that the material effectively and quickly adsorbs MB dye with adsorption capacity (759.3 mg/g), which is attributed to strong electrostatic interaction of O⁻ ions of MoO₃ with MB dye. Further, isotherm and kinetic studies suggest that adsorption follows Langmuir and Pseudo-second-order kinetics model respectively.

Keywords: Water pollution; Cationic dyes; MoO₃; Electrostatic interaction

1 Introduction

Dyes are essential part of industrial processes for a wide range of products. But their discharge in hydrosphere produces undesirable colour and restricts the penetration of sunlight, which compromises the photochemical and biological activities of aquatic life. That needs to be treated to reduce their toxic content before being released into water bodies. Thus, researchers and scientists are searching for different methods that can treat these dyes before releasing to the environment¹. Adsorption procedure is one kind of surface phenomenon where adsorbate is amassed on the adsorbent's active surface portion. Therefore, adsorbent with high surface area and charge are highly recommendable. Among various transition metal oxides, MoO₃ has received particular attention to remove dye from aqueous solutions, due to its high adsorption effectiveness, low cost, and effective synthesis².

The present report discusses the synthesis and characterization of o-MoO₃, which selectively adsorbs a primary amine containing MB dye from its aqueous solution. The adsorption studies show that MoO₃

material exhibits significantly higher adsorption capacity and can be reused in multiple cycles without undergoing any considerable loss in adsorption activity. Further, adsorption phenomenon has also described by using kinetic and isotherm models.

2 Materials and Methods

2.1 Synthesis

High purity AHM (Ammonium Heptamolybdate Tetrahydrate) ((NH₄)₆Mo₇O₂₄·4H₂O) was used for the synthesis of MoO₃ nanoparticles. Solid-state synthesis is commonly used to cause a chemical reaction from solid starting materials to form a new solid with a well-defined structure. In this method, raw material grinded properly in the dry-grinding mode for 1h followed by wet grinding using methanol for another 1h by agate mortar and pestle to obtain homogeneous mixtures of nanoscale size. The calcinations of the prepared mixtures was carried out at an optimized temperature of 400 °C by using covered alumina crucibles in a high-temperature muffle furnace with a 3 °C/min heating rate for 4 h. After cooling, the powder was grinded again thoroughly for half an hour. The greyish colored MoO₃ nanostructures are to be obtained.

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2.2 Characterizations

The structural characterization of prepared material has been done by X-ray diffractometer at ambient temperature using Panalytical X'Pert Pro at a speed of 8° per min with $\text{CuK}\alpha$ radiation ($\lambda=1.5418\text{\AA}$) in the 2θ range from 10° to 80° . Zeta potential readings were made using a Malvern Zetasizer Nano ZS Zen3600 device. Using Microtrac BEL equipment, the BET surface area and BJH pore distribution analyses were carried out.

2.3 Dye removal by adsorption

The adsorption study has been investigated by preparing MB stock solutions (1000 mg/L). The experimental steps for dye adsorption are as follows: First, 40 mL of the MB solution (20 mg/L - 450 mg/L) was taken in a beaker. Second, MoO_3 samples weighing 20 mg of material were then added to above mentioned MB solution. Third, this mixture was shook continuously in the dark at 250 rpm. The 2 mL supernatant was taken for UV-Vis measurements after centrifugation (for 2 min at 5000 rpm).

3 Results and Discussions

Figure 1 displays the prominent X-ray diffraction peaks at $2\theta = 12.83^\circ, 23.44^\circ, 25.94^\circ, 27.40^\circ, 33.72^\circ,$ and 39.06° , which correspond to (200), (101), (400), (210), (410), and (002) planes of MoO_3 . The identified pattern is well matched with the standard data card no JCPDS 01-089-7112³ of MoO_3 , having lattice planes $a = 12.38 \text{\AA}$, $b = 3.33 \text{\AA}$, and $c = 3.53 \text{\AA}$ for orthorhombic phase which are in good agreement with standard results and previously reported values. The crystallite size (D) can be determined from Debye-Scherrer's equation⁴ and the calculated value of average crystallite size for preferential orientation was 25.1 nm. The FESEM images of MoO_3

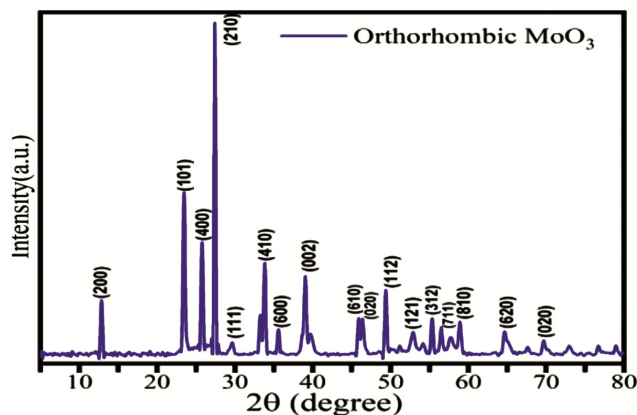


Fig. 1 — PXRD pattern of pure o- MoO_3 .

nanoparticles with different magnification shown in Fig. 2(a-b). It reveals that MoO_3 nanoparticles having polygon like structure with diameter 5.3 nm and length of about 450 nm. Higher negative surface charge around -19.0 mV reveals that the opposite interactions takes place between cationic dye and O^- ions of MoO_3 as shown in Fig. 3.

The higher distribution of mesopores around 2-4 nm with surface area $6.43 \text{ m}^2/\text{g}$ proposed adsorption mechanism of dye on MoO_3 as cleared from Fig. 4. The ability of MoO_3 to adsorb dyes on its surface, leading to the dye removal of aqueous dye solutions was investigated towards MB and MO by UV-Vis

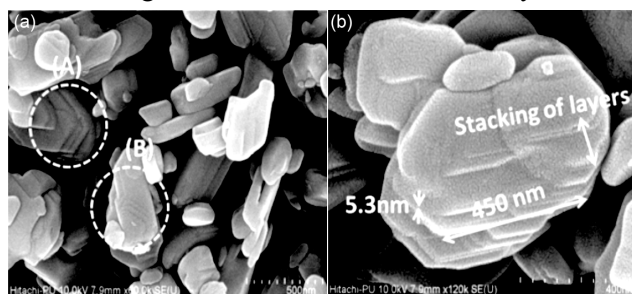


Fig. 2 — (a-b) FESEM images of MoO_3 nanostructures.

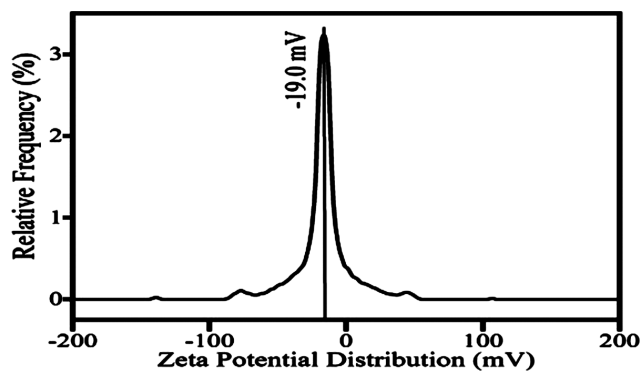


Fig. 3 — Zeta analysis of MoO_3 nanostructures.

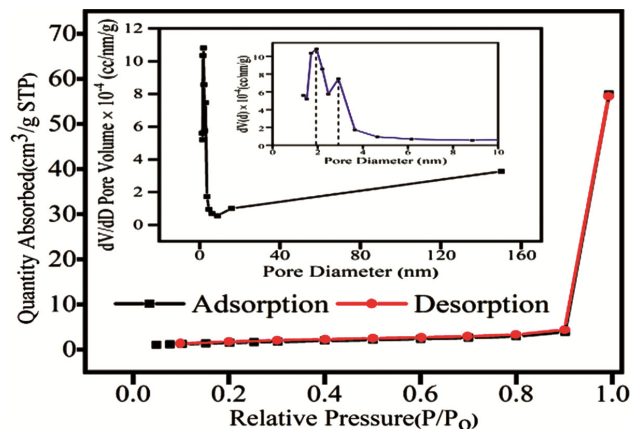


Fig. 4 — BET-BJH analyses of MoO_3 nanostructures.

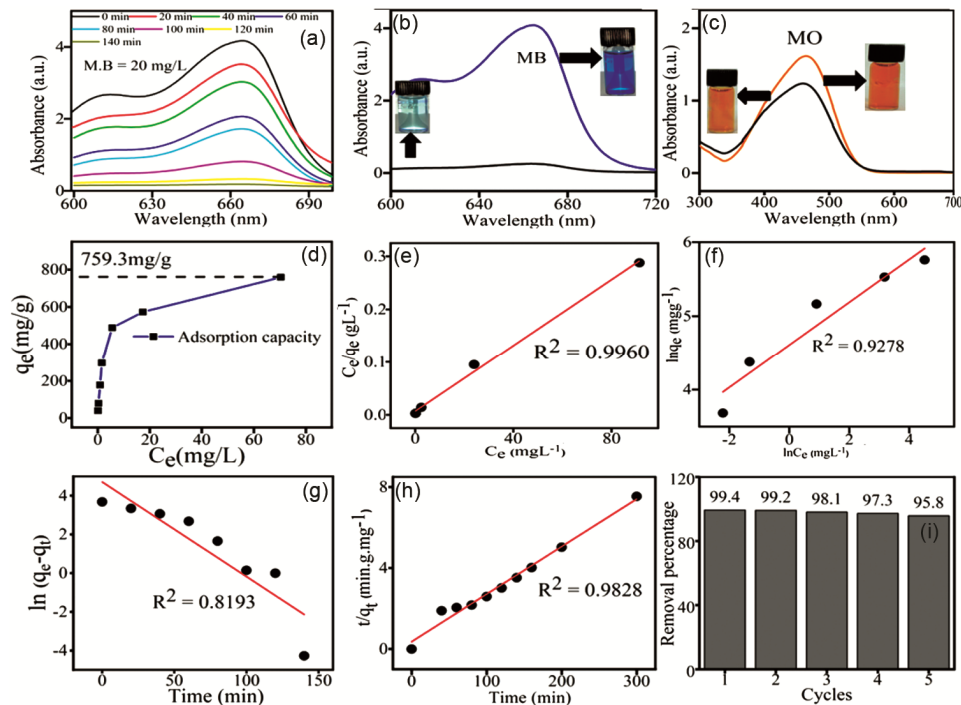


Fig. 5 — (a-c) UV-Vis spectra of MB dye with increasing time, MB and MO respectively (d) Experimental maximum adsorption capacity of MB dye (e-f) Langmuir and Freundlich adsorption isotherm (g-h) Pseudo-first and second-order kinetic plot (i) Percentage of dye removal of MB dye after 5 cycles.

absorption spectroscopy. It is evident that MoO₃ does selective adsorption of MB dye leading to 99.4% dye removal. However, in case of MO only 13-14% dye removal was observed under similar adsorption conditions; suggesting selective adsorption of MB cationic dye as shown in Fig. 5(a-c) calculated from dye removal equation⁵. The adsorption capacity was found to be 759.3 mg/g as shown in Fig. 5(d) calculated from studied literature⁶. Fig. 5(e-f) illustrates the Langmuir model for MoO₃ sample, a high degree of linearity was observed, with a correlation coefficient (R^2) of 0.99 as compared to Freundlich model as calculated from isotherm model⁷. According to Langmuir model, the maximum adsorption of MB was 787.4 mg/g, which is not far from experimental value (759.4 mg/g). Upon fitting the value of q_e and that of q_t obtained at different time intervals in straight line as shown in Fig(g-h), the best fitting (0.98) was obtained the pseudo second order adsorption rather than first-order as calculated from kinetic model⁸. Besides this, sorbent should have the ability to be recycled without undergoing any considerable reduction in its removal percentage. The reusability test of MoO₃ was studied for 5 cycles by adsorption desorption and regenerated as shown in Fig. 5(i). No significant change in removal percentage

has been observed. The obtained negative surface charge of O⁻ of MoO₃ interact with positively charged cationic dye through electrostatic interactions, reveals the mechanism of adsorption

4 Conclusion

The orthorhombic phase of MoO₃ with stacked layers has been obtained by a simple, facile and cost effective solid state approach. The nanostructures exhibit higher surface charge (-19.0mV) and surface area (6.43 m²/g) leading to the greater dye adsorption activity. The synthesized MoO₃ offers 99.4% removal efficiency with 759.3 mg/g adsorption capacity towards MB dye with good recyclability. Adsorption isotherm and kinetics studies reveal that the adsorption takes place by Langmuir adsorption model and follows second order adsorption kinetics.

Acknowledgement

One of the authors (Jaspreet Kaur) is thankful to the CSIR and CIL/SAIF, department of Punjab University for the financial support through fellowship and in carrying out various characterizations respectively. The authors acknowledge the SERB/DST, India for providing funds under research project (EEQ/2021/000933).

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