



Evaluation of Visible Light Photocatalytic Activities of MoO₃, Cu₂O And V₂O₅ For Degradation of Rhodamine-B, Methylene Blue And Methyl Orange

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ABSTRACT

Photocatalytic activities of three binary metal oxides MoO₃, Cu₂O and V₂O₅ are evaluated and compared with that of Degusa P25 for the degradation of Rhodamine-B, Methylene blue and Methyl orange in presence of an external oxidant H₂O₂. UVDRS of MoO₃, Cu₂O and V₂O₅ indicated band gaps of 2.93 eV, 2.38 eV and 2.08 eV respectively. The enhanced photocatalytic activity due to Cu₂O and V₂O₅ as compared to MoO₃ and TiO₂ is attributed to their higher visible light absorption efficiency as well as to the presence of H₂O₂ which generates more ·OH radicals that facilitate faster degradation process.

Keywords: Rhodamine-B, Methylene blue, Methyl orange, Photocatalytic degradation.

INTRODUCTION

There has been a growing interest in the study of semiconductor metal oxide mediated photocatalysis for remediation of organic pollutants because of its potential as an inexpensive clean technology. In this context, the n-type semiconductor TiO₂ is projected as highly useful since it is inexpensive, easy to synthesize, stable towards photo corrosion, biologically and chemically inert, and exhibit good photocatalytic efficiency towards degradation of several hazardous organic pollutants. However, the wide band gap of 3.2 eV associated with TiO₂ restricts its absorption to U.V. region which is < 5% of solar radiation. In order to shift the absorption maximum of TiO₂ into visible region, three different approaches have been reported in literature in terms of (i) doping TiO₂ with metal atoms/ cations and/or anions (ii) modifying TiO₂ surface with a sensitizer having higher quantum efficiency in the visible region and (iii) forming a composite in nano, meso or hallow structure with materials of suitable band potential [1]. Each of the above routes has its own advantages and limitations in terms of versatility, cost effectiveness and wide range applicability. In view of this, several other binary oxides such as ZrO₂, SnO₂, ZnO, Fe₃O₄, Co₃O₄, CuO and Bi₂O₃ were also studied. Recently, Yuping Chen et al [2] reported photocatalytic evolution of single crystalline MoO₃ nanobelts for the degradation of Methylene blue. Zhiri Yu et al [3] reported photocatalytic degradation of Methylene blue, Methyl red, Malachite green and Bromo phenol blue over MoO₃. Liying Huang et al [4] reported fabrication of g-C₃N₄/MoO₃ for photocatalytic evaluation of Methylene blue. Lei Huang et al [5] studied visible light photocatalytic degradation of Methyl orange over Cu₂O particles of different sizes. Madina Shoeib et al [6] reported photocatalytic degradation of methyl orange over nanocrystalline Cu₂O. Ru Li et al [7] reported morphology dependence of Cu₂O on the

photocatalytic degradation of Methyl orange. Yim Lang Chen, S.Y. Pung and S. Sreekantan [8] evaluated degradation of Rhodamine-B over V_2O_5 nano flakes on PET fiber. Arguine Tes Raj et al [9] reported photocatalytic degradation of Methyl orange over V_2O_5 nanoparticles under U.V irradiation. The present study is taken up to evaluate the photocatalytic activities of as purchased samples of MoO_3 , V_2O_5 and Cu_2O in comparison with Degusa P-25 (TiO_2) for the degradation of Rhodamine-B (Cationic trimethylene dye) , Methylene blue (Thiazene dye) and Methyl orange (Azo dye) under visible light irradiation in presence of an external oxidant H_2O_2 .

MATERIALS AND METHODS

Samples of A.R grade MoO_3 , V_2O_5 , Cu_2O and TiO_2 (Degusa P-25) as purchased are used in the photocatalytic studies.

Characterization Techniques: Phase purity of purchased MoO_3 was investigated with X-ray diffractometer (PANalytical- X' Pert PRO, Japan) at room temperature, using Nickel filtered $Cu-K_{\alpha}$ radiation ($\lambda= 1.54059 \text{ \AA}$), with a scan rate of 2° min^{-1} . UV-visible diffuse reflectance spectrum (UVDRS) of the sample was obtained with the dry pressed disk samples using Shimadzu UV-visible spectrophotometer (UV-3600) between 200 to 800nm range. Spectral grade $BaSO_4$ was taken as reference for the reflectance spectra.

Photocatalytic Studies: 100 mg of the catalyst powder was added into 100 mL Rh-B aqueous solution (5 mg L^{-1}). Before irradiation the suspension was magnetically stirred for 30 min in dark. The suspension was then exposed to 400 watts metal halide lamp; 5mL aliquots were pipetted at periodic time intervals and filtered through 0.45 micron Millipore filters to remove the suspended powder. Progress of discoloration was followed by recording the corresponding absorption spectrum. The same procedure has been adopted for (10 mg L^{-1}) MB and (10 mg L^{-1}) MO dyes. All the experiments were conducted under ambient conditions. Extent of degradation of dye is calculated by using the expression.

$$\% \text{ degradation} = (A_0 - A_t / A_0) 100$$

Where A_0 and A_t are respectively initial absorbance and absorbance at time 't'.

RESULTS AND DISCUSSION

MoO_3 is known to exist in three different polymorphic forms namely- α (Orthorhombic), β (Monoclinic) and h (Hexagonal). Among these, α - MoO_3 has attracted much attention because of its double layered planar structure. XRD pattern and the FTIR of MoO_3 used in this study are shown in Fig. 1. All the observed diffraction peaks shown in Fig 1 (a) agreed well with the orthorhombic form of MoO_3 of JCPDS file 76-1003. The lattice parameters $a=3.9634$, $b=13.8336$ and $c=3.6917$ calculated from XRD pattern agreed well with the reported values of $a=3.9628$, $b=13.855$ and $c=3.6964$. Similarly the observed peaks in FTIR are also in agreement with those reported in literature [2]. Accordingly the peaks at 988, 876, 624 cm^{-1} are ascribed to $Mo=O$, $Mo-O-Mo$ stretching vibrations and $Mo-O-Mo$ bending mode respectively, while the peaks at 1630 and 3445 are due to water. U.V-visible diffuse reflectance spectra (UVDRS) of MoO_3 , V_2O_5 and Cu_2O are shown in Fig. 2. It is apparent from the figure that both V_2O_5 and Cu_2O show considerable absorption in the visible region as compared to MoO_3 . The corresponding band gaps computed from UVDRS are 2.93 eV, 2.38 eV and 2.2 eV for MoO_3 , V_2O_5 and Cu_2O respectively.

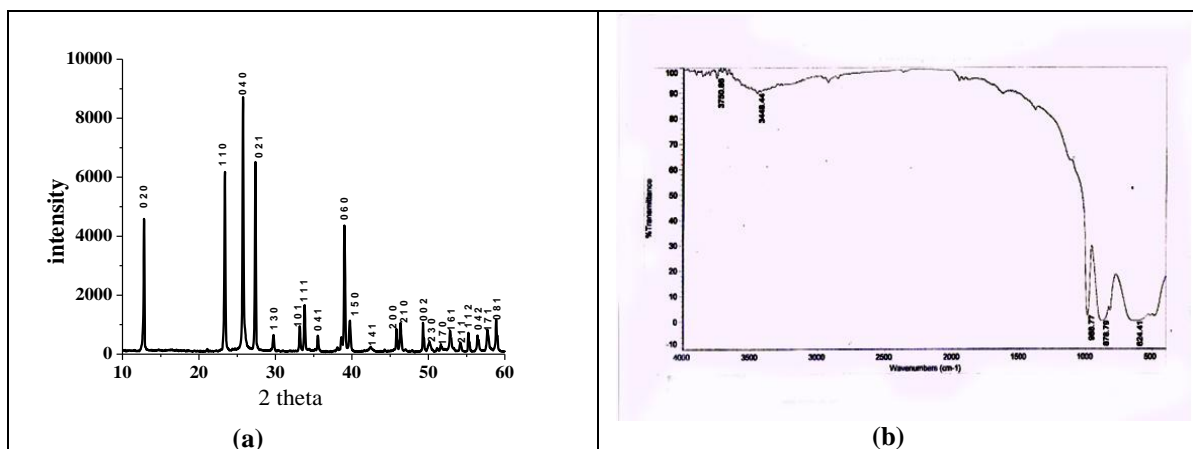


Figure 1. (a) XRD pattern and (b) FTIR Spectrum of MoO₃ sample used in this study

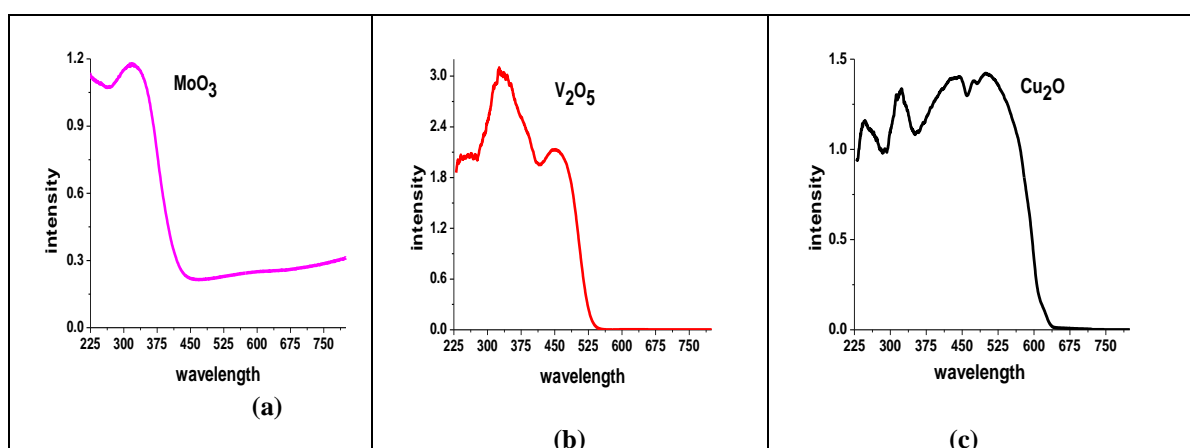


Figure 2. UV-visible diffuse reflectance spectra of (a) MoO₃, (b) V₂O₅ and (c) Cu₂O

Photocatalytic degradation of Rhodamine-B (Rh-B) was reported under U.V. irradiation over ZnO [10-11], TiO₂/ZnO [12], TiO₂ and ZnO [13] and the corresponding degradation times varied in the range 60 to 240 minutes. Temporal variations of spectral contours as a function of irradiation time for degradation of Rh-B over MoO₃, Cu₂O, V₂O₅ and TiO₂ are shown in Fig. 3. From the figure, it can be seen that absorption intensity decreased with progressive irradiation and respective degradation times of 120, 60, 60 and 180 minutes are obtained for complete discoloration. The observed photocatalytic efficiency is in the order TiO₂ < MoO₃ < V₂O₅ = Cu₂O

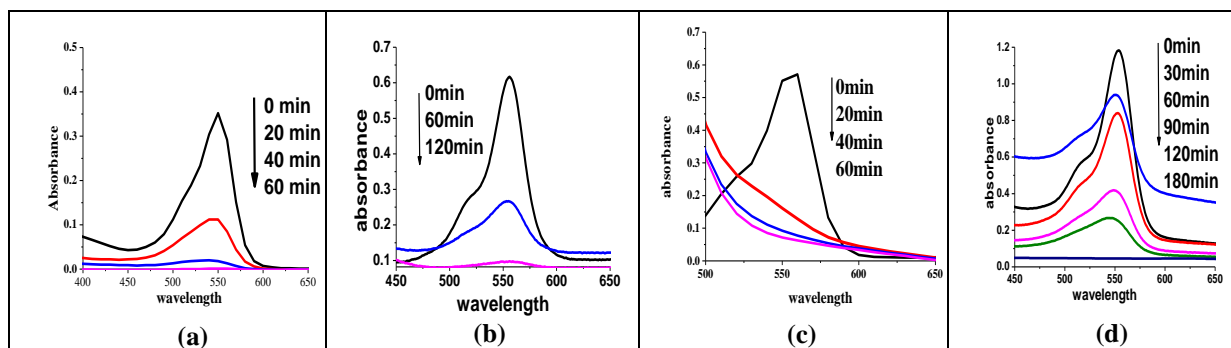


Figure 3. Temporal variation of spectral contours as a function of irradiation time for Rhodamine-B over (a) Cu₂O, (b) MoO₃, (c) V₂O₅ and (d) TiO₂

Photocatalytic degradation of Methylene blue (MB) was reported using ZnO [14], TiO₂ [15-17] under U.V. irradiation and solar irradiation. Temporal variations of spectral contours as a function of irradiation time for degradation of MB over MoO₃, Cu₂O, V₂O₅ and TiO₂ are shown in Fig. 4. It is apparent from the figure, the absorption intensity in each case decreased with progressive irradiation and 100% degradation is noticeable for all four photocatalysts with degradation times of 120, 120, 30 and 180 minutes for MoO₃, Cu₂O, V₂O₅ and TiO₂ respectively. The photocatalytic efficiency is noticed in the order TiO₂ < MoO₃ ~ Cu₂O < V₂O₅.

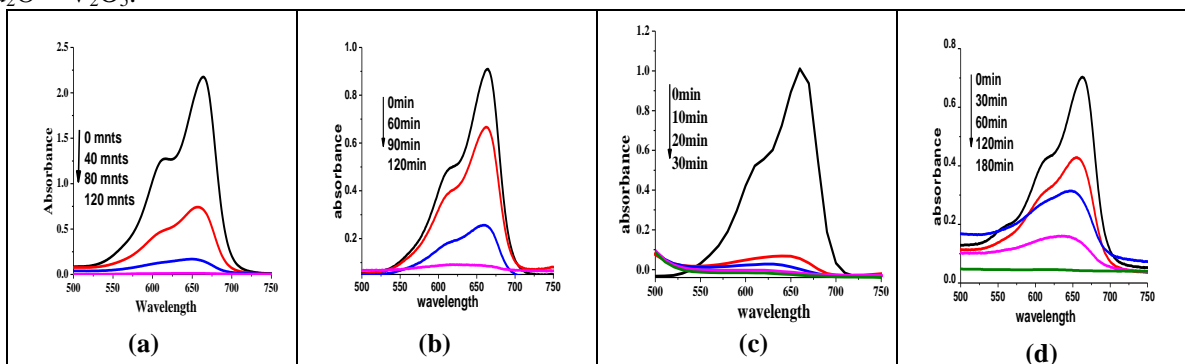


Figure 4. Temporal variation of spectral contours as a function of irradiation time for Methylene blue over (a) Cu₂O (b) MoO₃, (c) V₂O₅ and (d) TiO₂

Photocatalytic degradation of Methyl orange (MO) was reported over SnO₂ [18], TiO₂ [19], CuO doped ZnO [20], Ag/N-TiO₂ [21], nano ZnO [22], and α -Fe₂O₃ [23]. In all these studies, the irradiation source is U.V. and the reported photocatalytic times varied between 80-540 minutes. Temporal variations of spectral contours as a function of irradiation time for degradation of MO over MoO₃, Cu₂O, V₂O₅ and TiO₂ are shown in Fig. 5. From the figure, it can be noticed that, absorption intensity decreased with progressive irradiation, and 100% degradation is obtained for MoO₃, Cu₂O and V₂O₅ for 300, 160 and 30 minutes respectively. Degradation of Methyl orange over TiO₂ is incomplete even after irradiation up to 160 min. The photocatalytic efficiency varied in the order TiO₂ < MoO₃ < Cu₂O < V₂O₅.

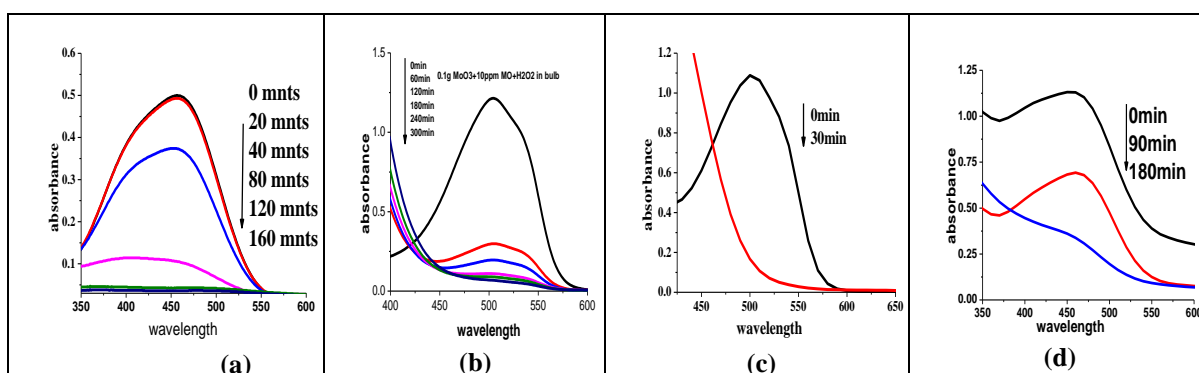


Figure 5. Temporal variation of spectral contours as a function of irradiation time for Methyl orange over (a) Cu₂O, (b) MoO₃, (c) V₂O₅ and (d) TiO₂

In the above degradation studies, V₂O₅ showed consistently higher photocatalytic activity followed by Cu₂O. This can be understood in terms of their extent of absorption in the visible region as seen in the UVDRS (Fig. 2). Since TiO₂ has least absorption in the visible region, its photocatalytic efficiency is found to be least. Besides the extent of visible light absorption, the enhanced degradation can also be attributed to the presence of external oxidant H₂O₂ which is responsible for generation of more \cdot OH free radicals that expedite disintegration of the molecular frame work of dyes [24-26].

CONCLUSIONS

Bulk samples of as purchased MoO₃, Cu₂O and V₂O₅ showed higher visible light activated photocatalytic efficiency for degradation of Rhodamine-B, Methylene blue and Methyl orange than Degusa P-25. The enhanced degradation is attributed to two factors – (i) higher absorption of Cu₂O and V₂O₅ in the visible region as compared to either MoO₃ or TiO₂, and (ii) the presence of external oxidant H₂O₂ which generates more ·OH radicals to expedite dye degradation.

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REFERENCES

- [1] A.V. Prasada Rao, A.M. Umabala, P. Suresh, *J. Aplic. Chem*, **2015**, 4 (4), 1145-1172
- [2] Y. Chen, Ch. Lu, L. Xu, Y. Ma, W. Hou, J. Jie Zhu, *Cryst. Eng. Comm*, **2010**, 12, 3740-3747.
- [3] Z. Yu, D. Chu, Q. Li, L. Wang, *Adv. Mater. Res*, **2012**, 535, 345-348.
- [4] L. Huang, H. Xu, R. Zhang, X. Cheng, J. Xia, *Appl. Surf. Sci*, **2013**, 283, 25-32.
- [5] L. Huang, F. Peng, H. Yu, H. Wang, *Solid state Sci*, **2009**, 11, 129-138.
- [6] M.A. Shoeib, O.E. Abdelsalam, M.G. Khafagi, R.E. Hammam, *Adv. Powder Tech*, **2012**, 23, 298-304.
- [7] R. Li, X. Yan, L. Yu, Z. Zhang, Q. Tang, Y. Pan, *Cryst. Eng. Comm*, **2013**, 15, 10049-10058.
- [8] Y.L. Chan, S.Y. Pung, S. Sreekantan, *J. Catalysis*, **2014**, <http://dx.doi.org/10.1155/2014/370696>.
- [9] A. Tes Raj, K. Ramanujan, S. Thangavel, S. Gopalakrishan, N. Raghavan, G. Venugopal, *J. Nanosci. Nanotech*, **2015**, 15, 3802-3808.
- [10] S. Hiremath, C. Vidya, M.A. Lourdu Antonyraj, M.N. Chandraprabha, R. Srinidhi, R. Manjunath, Padmanabha, Agrawal, H., *Int. Rev. Appl. Biotech. Biochem*, **2014**, 2, 207-213.
- [11] Md. Amad Ali, Md. Rahman Idris, Md. EmranQuayum, *J. Nanostruct. Chem*, **2013**, 3:36, 1-6.
- [12] D. Zhang, *Acta Chimica Slovaca*, **2013**, 6(2), 245-255.
- [13] Pi. Du, Li. Song, Ji. Xiong, Hb. Cao, *J. Mater. Sci*, **2013**, 48, 8386-8392.
- [14] S. Kuriakose, N. Bhardwaj, J. Singh, B. Satpati, S. Mohapatra, *Beilstein J. Nanotechnol*, **2013**. 4, 763-770.
- [15] M. Aliabadi, M. Hajiabadi, *J. Bio & Env. Sci*, **2013**, 3, 8-12.
- [16] K. Balachandran, S. Rajeswari, R. Venkatesh, *J. Environ. Nanotech*, **2013**, 2 (1), 32-39.
- [17] S.S. Al-Shamali, *Australian J. Basic Appl. Sci*, **2013**, 7(4), 172-176.
- [18] H. Yuan, J. Xu, *Int. J. Chem. Eng. Applications*, **2010**, 1 (3), 241-246
- [19] Q. Hu, B. Liu, Z. Zhang, M. Song, X. Zhao, *J. Wuhan University Technol. Mater. Sci. Ed*, **2010**, 25 (2), 210 – 213.
- [20] N.Z. Razali, A. Halim Abdullah, Md. Jelas Haron, *Environ. Eng. Manag. J*, **2011**, 10, 1523-1528.
- [21] D. Wu, M. Long, *Water Sci. Technol*, **2012**, 65 (6), 1027-1032.
- [22] A.R. Daniel Souza, M. Gusatti, C. Sanches, V.M. Moser, N.C. Kuhnen, H.G. Riella, *Chem. Eng. Trans*, **2013**, 32, 2275-2280.
- [23] P. Sharma, R. Kumar, S. Chauhan, D. Singh, M.S. Chauhan, *J. Nanosci. Nanotech*, **2014**, 14, 1-5.
- [24] P. Suresh, A.M. Umabala, T. Siva Rao and A.V. Prasada Rao, *J. Aplic. Chem*, **2014**, 3 (2), 696-701.

- [25] P. Suresh, A.M. Umabala and A.V. Prasada Rao, 3rd international conference on Chemistry, Chemical Engineering and Chemical Process (CCECP 2015) in Singapore, **2015**, doi: 10.5176/2301-3761_CCECP15.59
- [26] P. Suresh, T. Narasimha murthy, A.V. Prasada Rao, *Int. J. Sci. Res*, **2015**, 4(6), 2372-2378.

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