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SYNTHESIS AND CATALYTIC STUIDES OF LAYERED AND OMS TYPE NANO MANGANESE OXIDE MATERIAL

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Nano structured layered and octahedral molecular sieve type Manganese Oxide (MO) was synthesized by ultrasonic method. The prepared MOs were characterized by using FTIR, Powder X–ray Diffraction, Surface area, Scanning Electron Microscopy techniques. The characteristic FTIR peaks at 3348 & 1597 cm^{-1} confirm the presence of water molecules present in the sample and the peaks at 510 cm^{-1} confirms the formation of layered manganese oxide. Scanning Electron Microscopic (SEM) study reveals that the synthesized materials are in the form of nanotubes and nanoparticles. The catalytic activity of the manganese oxide was tested for the decolorization of methylene blue and Amido black 10 dyes. The catalytic efficiency on both the materials was tested and the results are discussed.

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Keywords: Manganese oxide, ultrasonication, catalytic studies, methylene blue

1. Introduction

Manganese oxides are one of the largest families of porous materials with various structures as found in manganese oxide minerals all over the world. Two major structures are important (1) Octahedral layer (OL) constructed by edge sharing MnO_6 to form sheets with cations (Na^+,K^+) and in which water is present in between any two adjacent sheets and (2) octahedral molecular sieve (OMS) materials constructed by the edge and corner shared octahedral MnO_6 [1,2]. The diverse structures, chemical properties of manganese oxides are taken advantage of in potential applications such as cation–exchange [2], ion and molecule separation [2–4], adsorbents [5], sensor [6], battery [7], catalysis [8] etc. Manganese oxide materials have been used for a wide catalytic applications, such as degradation of dyes [9, 10], photocatalytic oxidation of organic pollutants and waste water treatment [11], nitric oxide reduction [12], ozone decomposition [13], selective oxidation of CO [14], alcohols [8] etc., Recently Manganese oxide has been used as a substitute for the noble metal catalysis, but, because of the lower surface area the catalytic activity was often disturbed [15,16,], Therefore, there has been tremendous research interest on the laboratory synthesis of manganese oxides with various structures to improve the catalytic ability. The wide spread of dye industries, which amounts to more than one million tons annually, combined with the potential carcinogenic risk, cause severe environmental pollution. More than half of the used dyes are organic dyes, which are extensively used in textile, paper, leather, petroleum, food and cosmetics industry [17]. It is essential to develop methods that can lead to destruction of such compounds. Several methods are available for color removal from wastewater such as membrane separation, aerobic and anaerobic degradation using various microorganisms,

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chemical oxidation, coagulation and flocculation, adsorption using different kind of adsorbents and reverse osmosis [18, 19]. Significant attention have been focused on the use of hydrogen peroxide as the active oxidant for several commercial and industrial processes. The destructive oxidation of organic dyes with H_2O_2 has been studied, [20]. A major drawback to the use of H_2O_2 is its low activity at room/lower temperatures. In order to overcome these problem various metal and metal oxide have been used in order to improve the catalytic efficiency of H_2O_2. Manganese oxide materials have shown interesting properties dues to its nanosize, porosity, high surface area and different structural forms [9, 4]. The present work focuses on the ultrasonic assisted synthesis of layered manganese oxides, which was tested for the catalytic oxidation of Methylene blue dye and Acid black in the presence of H_2O_2 in aqueous solution.

2. Experimental

The synthesis of manganese oxide is given as follows: about 6.5 g $KMnO_4$ (Merck) was dissolved in 150 ml of (1:1) water ethanol mixture and was placed in the ultrasonic bath (Pci, India, 35 kHZ) for 3 hrs. In order to complete the reaction, 1 ml of H_2O_2 (30v/v) was added. The black precipitate of manganese oxide was separated and washed several time with water. A part of the sample was dried at 400ºC (MO1) in a furnace for two hours and another part of the sample was dried using a domestic microwave oven (MO2). The synthesized manganese oxide was characterized by means of FT – IR (Shimadzu,), Powder XRD (Schimadzu, LAB X, XRD – 600), Scanning Electron Microscope (SEM, JEOL 6390).

The catalytic studies were carried out in a 250 ml glass flask, which contained 100 ml of MB dye solution (320 mg/L), and 100 mg of catalyst. After adding 1 ml of H_2O_2 (30 v/v) solution, the mixture was allowed to react at room temperature with continuous stirring. For a given time interval, 1 ml of the mixture solution was pipette out into a volumetric flask and diluted with distilled water to 25 ml prior to the analysis. For optical absorption measurements, the diluted solution was immediately centrifuged in order to remove the catalyst particles. The centrifuged dye solution was then put into a quartz cell (path length 1.0 cm) and the absorption spectrum was measured with a Shimadzu UV-1800 ultraviolet–visible (UV–Vis) spectrophotometer at a λ_{max} of 664nm The degradation products of MB dye were analyzed using an (TOC –V CPH/CPN, Shimadzu, Japan) equipment.

3. Results and discussion

The FTIR spectra recorded for the manganese oxide samples show significant IR signals at different frequency range (supplementary data). The broad and strong peak at 3384 cm^{-1} and the one at 1597 & 1420 cm^{-1} correspond to the O–H_{str}, and O–$H_{bending}$ frequencies respectively for the adsorbed water present in the manganese oxide sample. The bands at 515 and 480 cm^{-1} correspond to the Mn–O bond [22–24]. From the above result we conclude that the synthesized material is in the K–OL–1 form, and there is no much difference for both MO1 and MO2.

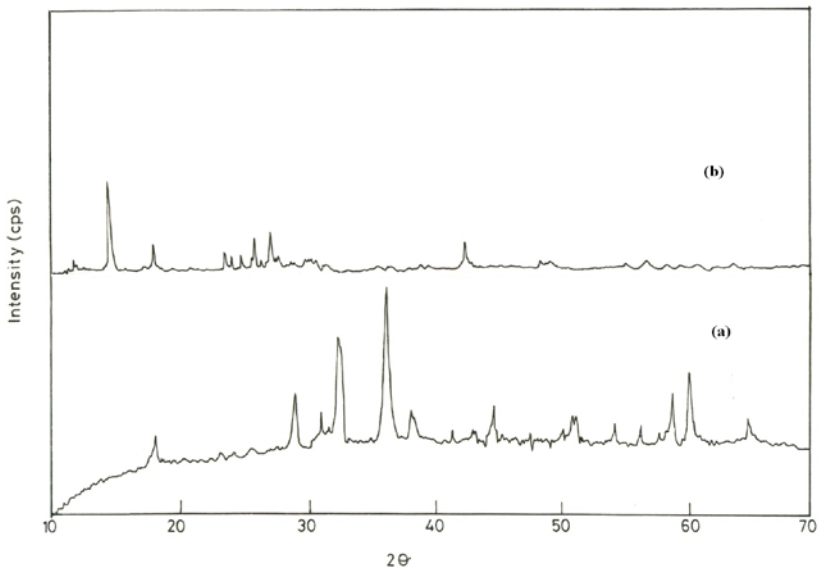

Fig 1. X–ray diffraction pattern of ultrasonic assisted synthesized manganese oxide heated at (a) 400 ºC in oven and (b) microwave.

The crystalline nature of manganese oxides were checked by powder XRD. The sample before and after calcination was checked for the formation of manganese oxide. Initially the gel was formed in the nanoparticles range. The ultrasonication of $KMnO_4$ results in the formation of manganese oxide gel. Fig. 1 (a&b) shows the sharp peak of 2θ of 12 indicative of the formation of layered type (K–OL–1, interlayer spacing of 7 Å) type of manganese oxide calcined at 400º C. The MO2 sample exhibits the formation of octahedral molecular sieve (OMS) (JCPDS# 29–1020), because, on thermal calcinations it leads to the slow rise in temperature and formation of layered structure, where as in the microwave condition the heat generation is quick to reach the maximum, so the layered structure collapses to the OMS structure.

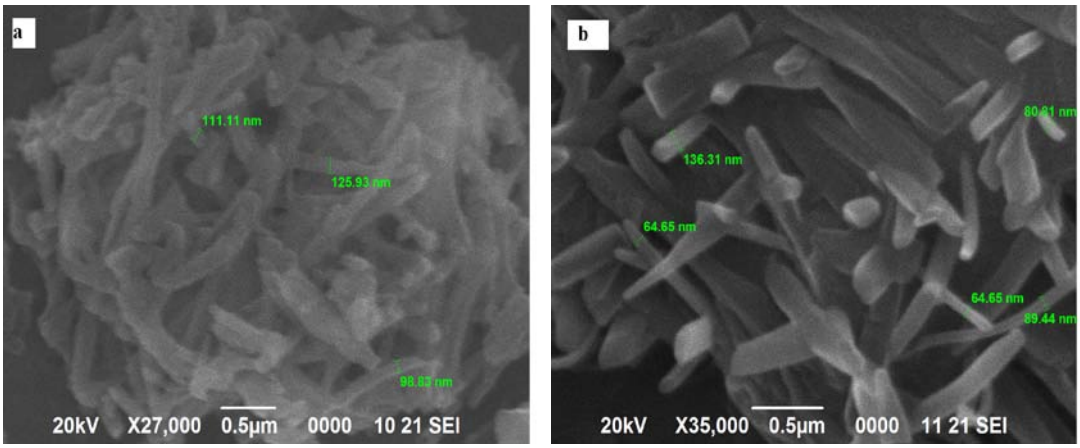

Fig 2. Scanning Electron Microscopic images of ultrasonic assisted synthesized manganese oxide heated at (a) 400 ºC in oven and (b) microwave.

The surface morphologies of the manganese oxide were examined by SEM observations and are shown in figure2. Fig. 2(a) shows the presence of several bundles of nanobelts. A careful analysis of Fig. 2(a) indicates that the Manganese oxide has grown uniformly as nanobelts or needle like nanoclusters. This clearly demonstrates that the growth of Manganese oxide is in one

direction and that it extends uni-dimensionally as nanotubes. This is due to the cavitations effect of ultrasonic irradiation.

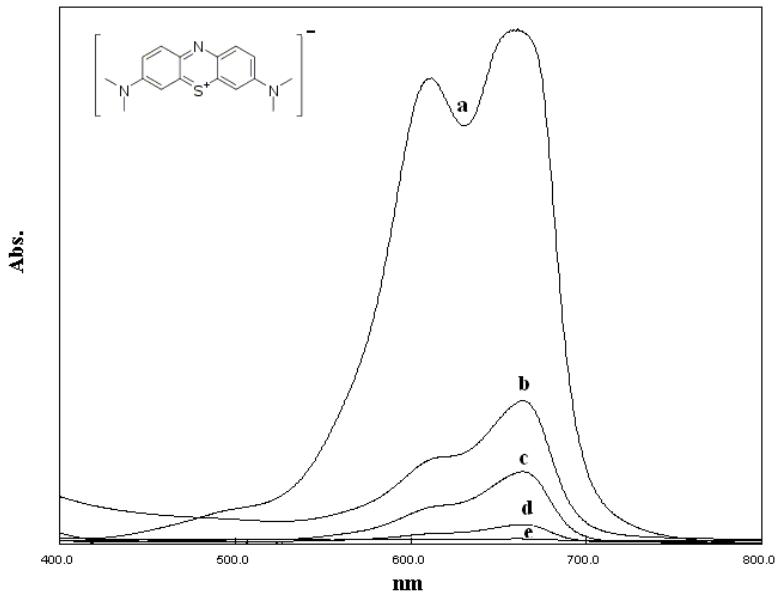

Fig 3a.UV–Vis spectrum of (a) MB dye and manganese oxide catalytic decolorization of MB dye in presence of H_2O_2 (b-h) from 2, 5, 10 and 30 min.

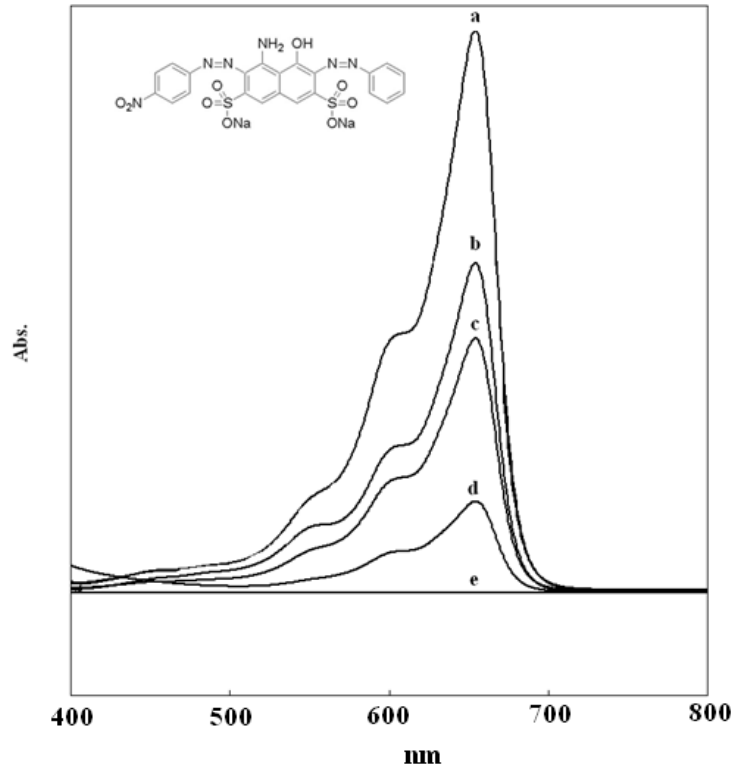

Fig 4. UV–Vis spectrum of (a) AB dye and manganese oxide catalytic decolorization of AB dye in presence of H_2O_2 (b-h) from 2, 5, 10 and 30 min.

The presence of uni – dimensional structure such as nanoclusters of nanobelts, in the prepared manganese oxide, can serve as an excellent catalyst towards the oxidation of Methylene Blue dye. On adding manganese oxide and H_2O_2 oxidant to the MB solution, the expected

decoloration occurred. Remarkably, the use of manganese oxide as a catalyst allowed the degree of decoloration to reach 90% in 2 min, which is better than that of commercial manganese oxide. The saturated degree of decoloration was as high as 99.1%, when compared to commercial MnO_2 in which it was 90% efficient. In the case of AB dye the decolorization was 55% in 5 min. Which is due to the presence of the bulky sized dye molecule. After 30 min the AB dye solution is decolorized completely. Both MO1 and MO2 show almost equal efficiency towards the decolorization of MB and AB dye (figure 4 a & b). The decolorization was tested by Photoluminescence spectrum of MB and AB. Fig. 6, exhibits the dye was completely removed from the aqueous solution.

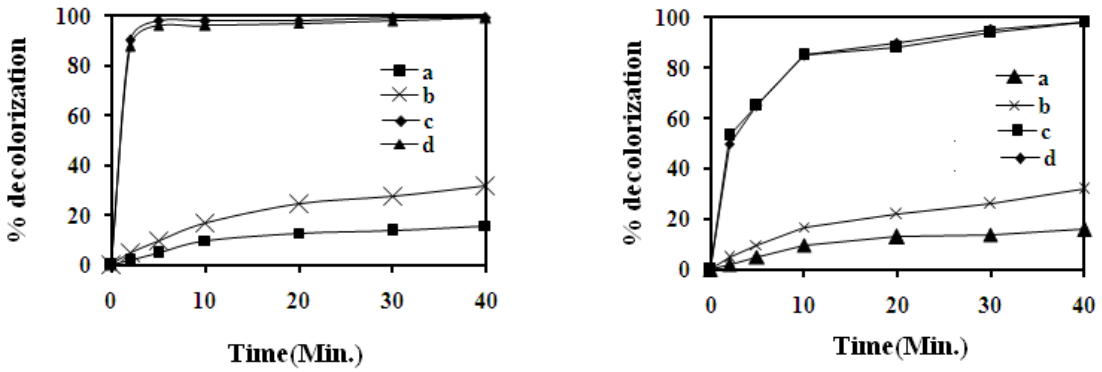

Fig. 5.UV–Vis decolorization profile of different nanostructured manganese oxide as a function of time. Decolorization in presence of (a) Commercial MnO_2 (b) H_2O_2 (c) MO1+H_2O_2 and (d) MO2 +H_2O_2.

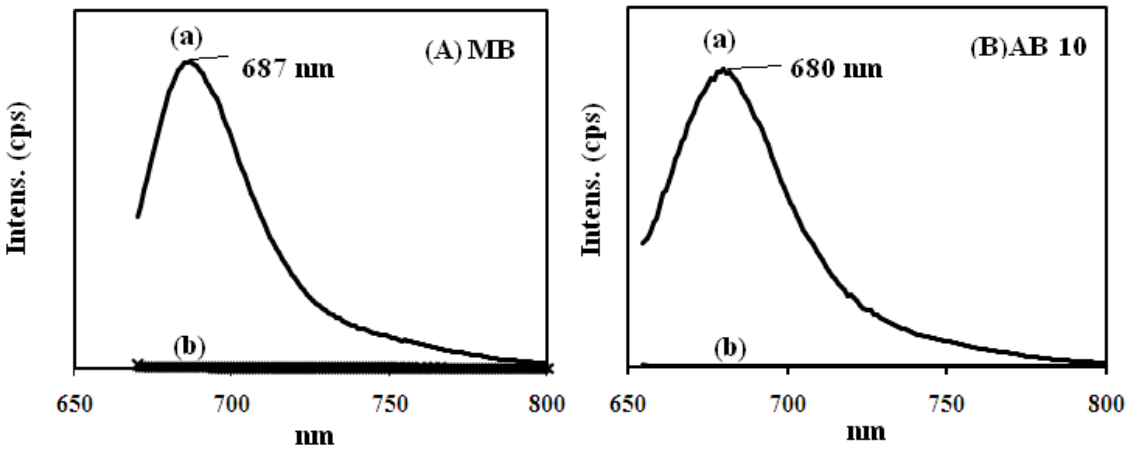

Fig 6. Fluorescence Emission spectrum for the (a) pure (MB & AB 10) dye, (b) MB+MO+H_2O_2.

Catalytic degradation of MB and AB dye must have occurred here, because the adsorbed dyes immediately react with the peroxide and degrades the MB dye at a fast rate as compared to AB. The degradation behavior of MO1& MO2 on MB was tested by the total organic carbon (TOC) experiment. For an initial concentration of 148 mg/L, the degradation was 48% within 5 min. The maximum degradation of 98% occurred within 30 min. This shows that the material is an effective catalyst for decolorizing and decomposing the dye. The degradation efficiency of MO2 is slightly higher than that of the MO1. This is due to the intercalation of MB dye into the MO1 layers. After the first experiment, the catalyst was recovered and used for further experiments. The results showed that the catalyst efficiency was decreased by about 2% in the second cycle and up

to 5^{th} cycle the catalyst showed only a decrease of 7% in the efficiency. This fact clearly proves that the catalyst is very efficient and reusable. The study on the kinetics of the decolorization will be carried out in the future.

4. Conclusion

In short, by a simple method both layered and OMS type manganese oxide was synthesized. The powder XRD patterns confirm the formation of Manganese oxide. The characteristic FTIR spectra shows, a band of Manganese oxide at 515 cm^{-1}, which corresponds to the Mn-O stretching modes of octahedral layers. SEM images show the presence of uniform nanotubes clusters and nanoparticles of manganese oxide. Manganese oxide of both types (layer and OMS) proves to be an excellent material for the decolorization of MB & AB 10 dye. Among the two OMS type shows slightly better efficiency than layer MnO_2 , which can be attributed to the intercalation of the dye molecule into the layered structure.

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References

[1] S. L. Suib and J. Mater. Chem. **18**, 1623 (2008)
[2] Q. Feng, H. Kanoh and K. Ooi, J. Mater. Chem. **9**, 319 (1999)
[3] Q. Feng, H. Kanoh, Y. Miyai and K. Ooi, Int. Conf. Ion Exchange, Proceedings, (1995), p. 141.
[4] Y. F. Shen, R. P. Zerger, R. N. DeGuzman, S. L. Suib, L. McCurdy, D. I. Potter and C. L. O'Young, Science, **11**, 260 (1993)
[5] L. A. Attar, A. Dyer and J. Maer. Chem. **12**, 1381 (2002)
[6] Y.H. Bai, Y. Du, J.J. Xu and H.Y. Chen, Electrochem. Commun. **9**, 2611 (2007)
[7] M. Nakayama, T. Kanaya, J.W. Lee and B.N. Popov, J. Power Sources **179**, 361 (2008).
[8] X. Shen, Y. Ding, J. Liu, K. Laubernds, R. P. Zerger, M. Polverejan, Y. C. Son, M. Aindow S. L. Suib, Chem. Matet. **16**, 5327 (2004)
[9] S. R. Segal, S. L. Suib and L. Foland, Chem. Mater. **9**, 2526 (1997)
[10] W. Zhang, Z. Yang, X. Wang, Y. Zhang, X. Wen and S. Yang, Catal. Commun. **7**, 408 (2006)
[11] J. Chen, J. C. Lin, V. Purohit, M. B. Cutlip and S. L. Suib, Catal. Today **33**, 205 (1997)
[12] L. Chen, T. Horiuchi and T. Mori, Appl. Catal. A, **209**, 97 (2001)
[13] R. Rahakrishnan and S. T. Oyama, J. Catal. **199**, 282 (2001)
[14] G. G. Xia, Y. G. Yin, W. S. Willis, J. Y. Wang and S. L. Suib, J. Catal. **185**, 91 (1999)
[15] C. E. Langley, C. Biljana, C. E. Banks, R. G. Compton, Jpn. Soc. Anal. Chem. **23**, 165 (2007).
[16] C. Xia, W .Ning, G. Lin , Sens. Actuators B **137**, 710 (2009).
[17] M.S. Reisch, CHEM. Eng. News **66**, 7 (1988).
[18] A. Jumasiah, T.G. Chuah, J. Gimbon, T.S.Y. Choong and I. Azni, Desalination **186**, 57 (2005)
[19] A. Gurses, C. Dogar, S. Karaca, M. Acikyildiz and R. Bayrak, J. Hazard. Mater. B **131**,254 (2006)
[20] Z. Ai, L. Zhang, F. Kong, H. Liu, W. Xing and J. Qiu, Mater. Chem. Phys. **111**,162 (2008)
[21] T. S. Liu, T. F. Kang, L. P. Lu, Y. Zhang, S. Y. Cheng, J. Electroanal. Chem **632**, 197 (2009).
[22] L. Kang, M. Zhang, Z.H. Liu and K. Ooi, Spectrochim. Acta. A **67**, 864 (2007)
[23] L. Li, Y. Pan, L. Chen and G. Li, Solid State Chem. **180**, 2896 (2007)
[24] R. M. Potter and G. R. Rossman, Am. Mineral. **63**, 1199 (1979)