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MnO_2 SUPPORTED POM–A NOVEL NANOCOMPOSITE FOR DYE DEGRADATION

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Manganese oxide xerogel was prepared by the sol-gel method and a composite with POM (phosphomolybdic acid) was prepared using ultrasonic irradiation. The prepared composite was characterized by means of powder X–ray diffractrogram and Scanning Electron Microcopy. The catalytic activity towards the degradation of organic molecule (Methylene blue dye) was tested. The composite exhibits excellent degradation of MB to about 93% within 10 min. The decolorization and degradation was tested with different quantities of loaded POM, by varying the contact time and having different initial concentration of the dye. The results are discussed in detail.

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Keywords: Manganese oxide, Methylene blue, Photocatalyst, Sol-gel, Xerogel

1. Introduction

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 azo dyes which are extensively used in textile, paper, leather, petroleum, food and cosmetics industry [1]. It is essential to develop methods that can lead to destruction of such compounds. Colour removal from industrial effluents has been a major concern in waste water treatment. Physical methods [2], biological methods [3, 4] and chemical methods [5] are the most frequently employed treatment techniques. The presence of Methylene blue, an organic dye in discharged dye effluents is hazardous for human beings and limits light diffusion and consequently the photosynthesis processes are reduced [6, 7, 8]. Activated carbon is suitable for removing minor amounts of such organic dyes from aqueous solution. Unfortunately this effective absorbent is expensive and has high regeneration cost. For these reasons different studies have been carried out in order to find out inexpensive materials to remove and degrade the organic dyes.

There are a number of research results which show that the functional activity of semiconductor materials depends on the structure. Manganese oxide (MnO_2) is one of the most interesting materials, which has a wide variety of structure with large surface area. The diverse chemical properties makes the MnO_2 material unique [9]. These materials find extensive application in the field of catalysis, batteries, photocatalytic materials [10] etc.

A more complex class of photo catalytically active material that has received less attention is the poly oxo metalate (POM) [11, 12]. Most POM clusters share the general photochemical characteristics of the semiconductor photo catalysts. POM anions include a large variety of oxygen bridged metal clusters well known for their rich photo catalytic action analogous to that of semiconductors. The POM are relatively non toxic and inexpensive. Their excited state, produced after absorption of UV – near visible light is a strong oxidant which is able to mineralize either directly or by radicals mediated oxidation of organic species including organic pollutants.

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The photo reduced POM species can deliver the electrons to a great variety of chemical species. [13]. Soluble POM can photo catalyze a much large variety of reaction types but suffer from their inability to be recycled. Moreover, the specific area of the solid POM are very low (< 10 m^2 g^{-1}) [14] leading to very few active sites on their surfaces. Thus to overcome these problems, the immobilization of POM onto solid support to create novel hybrid catalysts have been attempted. This has the advantages of high surface area compared to pure POM, which enhances catalytic activity, contact recovery and possible recyclability [15]. Recently Qu et al studied $H_3PW_{12}O_{40}/ZrO_2$ for the photocatalytic degradation of nitrophenol and Methylene Blue dye [16]. Consequently, the most relevant researches focus on seeking efficient and cost effective catalysts for decolorization reactions. In this communication we report the synthesis of POM ($H_3PMo_{12}O_{40}$) / Manganese oxide and the study on the catalytic efficiency of the composite for the photocatalytic decolorization of Methylene blue dye.

2. Experimental

Synthesis of MnO_2 xerogel was carried out by already reported method [17] with a slight modified procedure. The synthesis was done by taking about 50 ml of 0.38M $KMnO_4$ to which 20 ml of 1.4 M D-glucose and 2 ml of 30% H_2O_2 were added quickly. After few seconds a blackish brown gel was formed, which was heated in the hot air oven at 100° C for about 12 hrs. The impregnation of POM ($H_3PMo_{12}O_{40}$) of various weight percentiles [1, 2, 5, and 10] was carried out on the gel and the contents were sonicated for about 3 hrs and later dried. This sample was used for the photo catalytic studies. The composite was characterized by an XRD instrument Shimadzu X-600 Japan, with Cu -Kα radiation, and Scanning Electron Microscope equipment (SEM, JEOL 6390, Japan). Total Organic Carbon determination was carried out using an (TOC –V CPH/CPN, Shimadzu, Japan) equipment.

The catalytic studies were carried out in a 250ml beaker which contained 100 ml of MB dye solution (140 mg/L) and 50mg/L of MnO_2 – POM (1%,2%,5%,10%) . The pillaring of the materials was tested by the elemental analysis (ICP-OES). The reaction solution was irradiated with U.V light of wave length 365nm. For a given time interval, about 3ml of the reaction solution was taken out and centrifuged. The centrifuged solution was taken into a quartz cell (path length 1.0 cm) and the initial absorption spectrum was measured using a Shimadzu UV –VIS double beam spectrophotometer (model No. 1800) and the variation of absorbance was followed using a Systronic minispec (Systronic, India) single beam spectrophotometer.

3. Results and discussion

Retention of the structural integrity of POM in the Manganese oxide was confirmed by powder X-ray studies. The gel was heated to 100° C. The xerogel formed by the continuous heating of the gel, up to 300°C, later collapsed, and was transformed into hausmannite (Mn_3O_4) (fig 1 (a)) with a spinal-like structure. The reason for this is possibly because of the difference in types and amounts of tunnel cations which are formed [17]. After the formation of the gel, the POM was added and sonicated, which led to the trapping of POM in the tunnel and which finally resulted in MnO_2 – POM nano composite material formation. The formation of nanocomposite shows the typical layered structure. Here POM acts as an electron reservoir for decolorization, as well as degradation of the dye molecule. This composite shows excellent catalytic activity towards the photochemical decolorization of the dye. The structural morphology of MnO_2 gel and composites were studied using the SEM. The SEM images show, that the prepared gels were platelike shaped particles and the MnO_2 – POM composites were plate structures with nanobelts or strips of average size of 100nm. It is also clearly revealed that these belts are between the plates and uniformly mixed together. The elemental analysis of the prepared composite before and after the studies show that the composite was stable. After fifth cycle about 2% of POM was either lost or leached out for the composite.

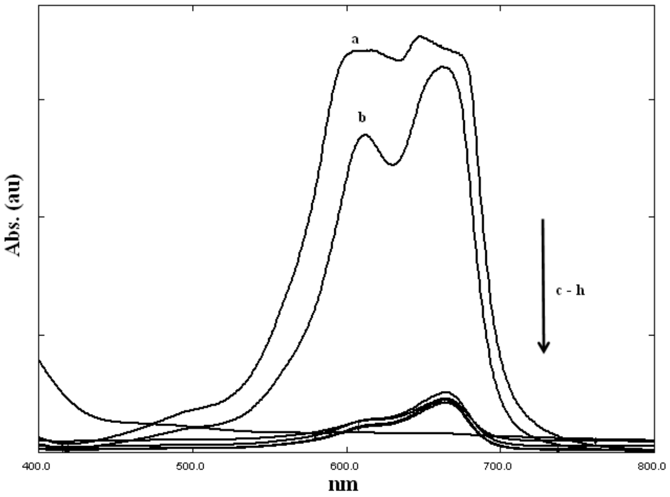

Fig. 1. UV-Vis spectrum of (a) MB dye, (b) adsorption of MB on Composite and (c) Photocatalytic decolorization of MB dye catalyzed by MnO_2/HPA nanocomposite from 5 – 30 min.

The catalytic performance of MnO_2 – POM nanocomposite on the decolorization of MB dye was studied. All the reactions were carried out at room temperature. The absorbance of the MB with the initial concentration of 140 mg/L was recorded (t=0). Four characteristic peaks of 664nm, 640nm, 245nm, 292 nm were observed using a specific amount of catalyst (about 50 mg/L). In order to check the catalytic efficiency, three different experiments were carried out as follows: one in which the dye without the catalyst was irradiated, the second one in which the dye and xerogel as catalyst was irradiated with UV light and the third one in which the dye and the MnO_2 – POM composite as catalyst was irradiated with UV light. The results show that in the first experiment there was no appreciable change in the absorbance. In the 2nd experiment in which the xerogel was the catalyst, in the absence of UV irradiation it showed little change in the absorbance, of about 15%, which was due to simple adsorption. This was tested by the TOC experiment and did not show any degradation and the third experiment showed that in the presence of the composite and UV irradiation, about 93% decolorization took place within 10 min. Initially within 5 min. about 50 % of the dye was decolorized and the complete discoloration took place after another 5 min. The second experiment shows that the adsorption of the composite was about 15%, since the preadsorption of dyes before irradiation is very important for the photocatalysis process [18], so the degradation was facilitated by adsorption of dye on the composite. Zahang et al [19] have reported that the catalytic efficiency of MnO_2 for the oxidative decolorization of MB in the presence of H_2O_2, and Troupis et al [13] have studied the photocatalytic efficiency of various POM for degradation of acid orange 7. The above studies have shown that both act as good catalysts for decolorization, but both the methods have their own disadvantages. The decolorization in the presence of H_2O_2 is problematic due to the facile decomposition and little utilizable rate of active oxygen. In the POM degradation the catalyst recovery was not possible. But the composite which we have used shows excellent catalytic activity towards decoloration without any external catalytic agent and the recovery of the catalyst was also very easy.

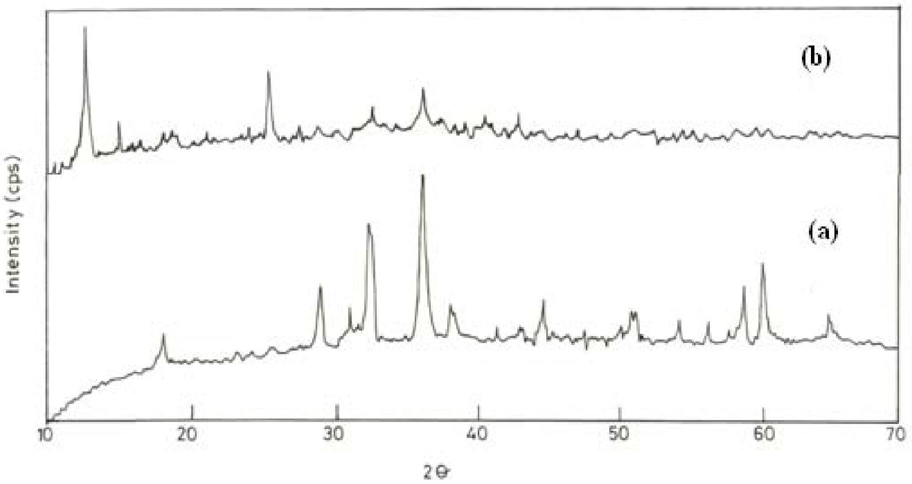

Fig. 2. Powder XRD spectrum of manganese oxide xerogel heated up to 300° C (a) in absence and (b) in presence of HPA.

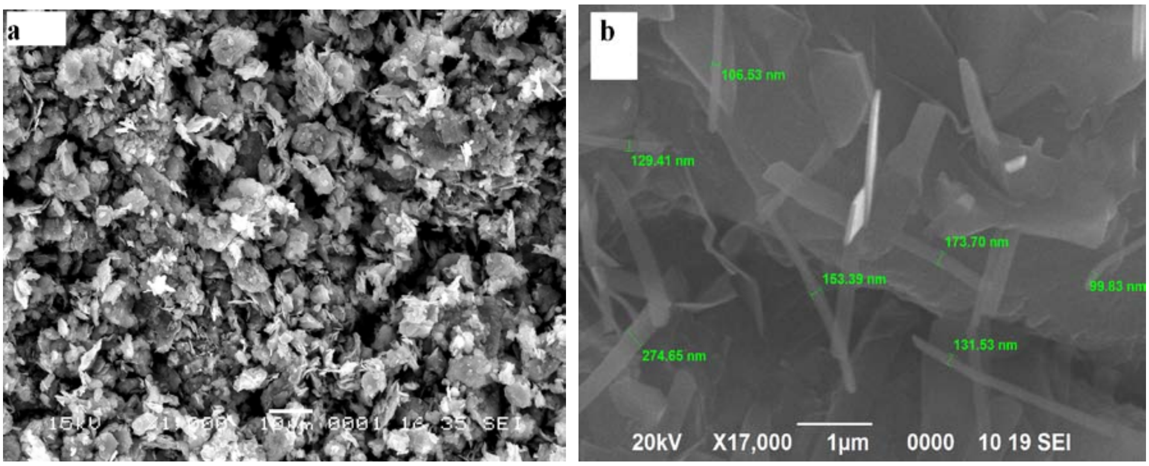

Fig. 3: Scanning Electron Microscopic image of (a) MnO_2 xerogel, and (b)Mn_3O_4-POM nanocomposite

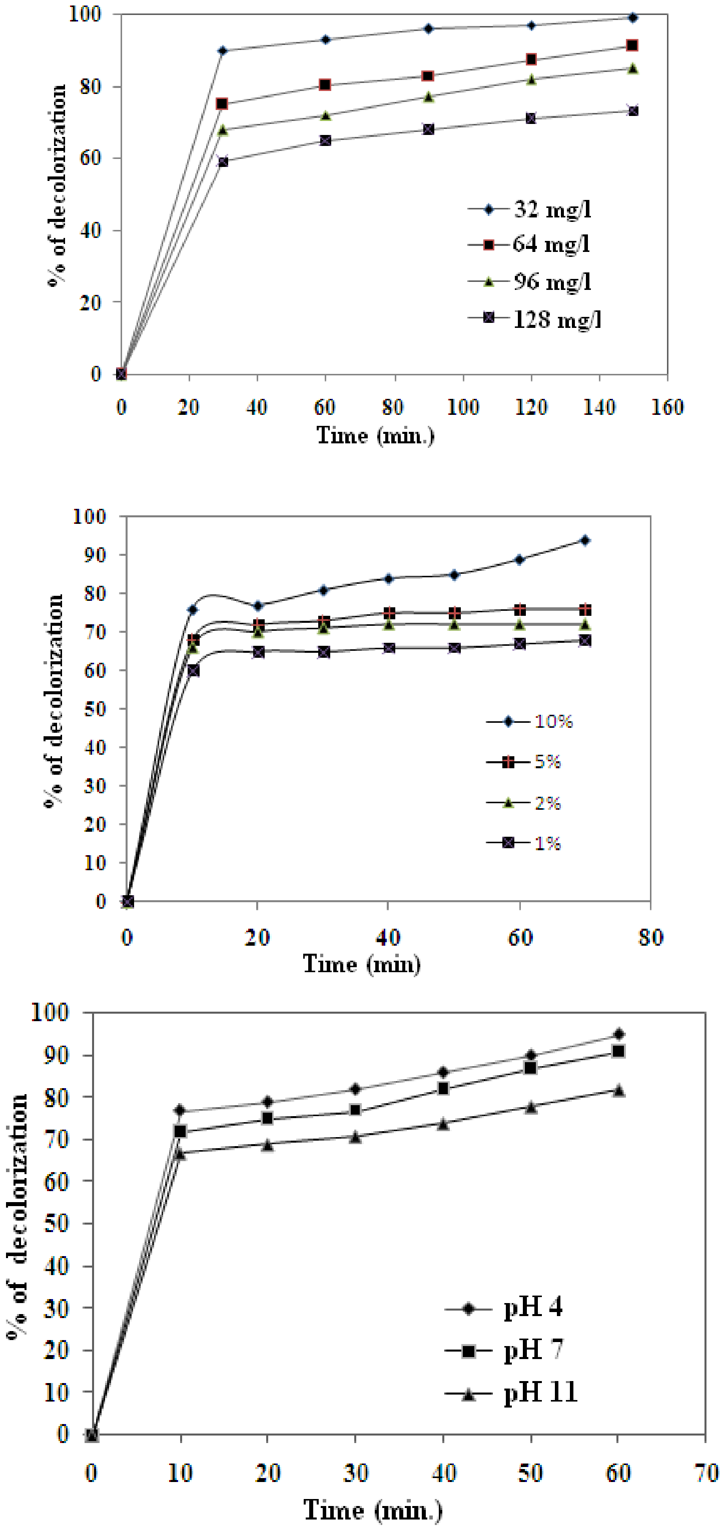

Fig. 4 (a): Effect of initial concentration for the decolorization of MB dye. (b): Effect of POM on the decolorization of MB dye. (c): Effect of pH on the decolorization of MB dye.

The initial concentration of the dye varied form 32 mg/L to 140 mg/L, and in the dark we could not observe any decolorization. Decolorization was observed only after UV light was irradiated. When the initial concentration was low, the decolorization and degradation were fast, but once the concentration of the dye increased the activity got reduced. At low concentration the dye molecules easily get adsorbed on the composite, which facilitates the composites to decolorize in a fast manner, whereas at high concentration the multilayer formation and the dimer of the dye molecules on the composite took time for decolorization. More over, the photocatalytic activity increases with increasing the POM from 1, 2, 5, 10 wt %, however above 15 % the decolorization was slow, which may be due to the aggregation of POM molecules on the MnO_2. The homogeneous dispersion of POM into MnO_2 plays an important role to improve the photo catalytic activity. When higher amount of POM aggregates into the MnO_2 and reduce the active sites for contact between the dye molecule and the composite, the activity got decreased. The pH also plays an important role on the decolorization experiments, because of the hydroxyl and hydrogen molecules which enable the dye to actively get absorbed on the catalyst. The decolorization studies were carried out at pH 4, 7 and 11. From the results we conclude that the decolorization was effective at the lower pH of (4 & 7), because the absorption of the molecules would be facilitated by the hydrogen ion. At a higher pH of (11), the decolorization was less. In higher concentration the degradation profile was decreased due to the formation of $-NH_4^+$, $-SO_4^{2-}$ ions which disturb the dye molecules absorption on the composite. Apart from the decolorization of MB, the compound also gets degraded which was confirmed by performing the Total Organic Carbon (TOC) experiment. In the lower concentration the compound was fully degraded. The initial concentration of 140 mg/L, after irradiation with UV light with and without catalyst is 138 and 48 mg/L respectively within 10 min. The irradiation completely degraded the dye in only 25 min. It showed that the catalyst effectively decolorizes and decomposes the dye. After the first photocatalytic cycle was completed, 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 the 5th cycle the catalyst showed only 8% decrease in its efficiency, which clearly goes to prove that the catalyst is very efficient and reusable. The study on the kinetics and mechanistic details of the decolorization and degradation will be carried out in the future.

4. Conclusion

The Manganese Oxide xerogel was synthesized by simple sol-gel method and POM was impregnated on it and a novel nanocomposite was synthesized for the first time. The sonication of the composite makes it uniform. The resultant nanocomposite shows excellent photocatalytic activity towards the decolorization of MB. The degradation of the molecule is observed to be 66% within the first 10 min. The present study reveals that the MnO_2–POM nanocomposite has great potential for practical photo decolorization and degradation of dyes in effluents.

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