

Colloidal MnO_2 Catalysed Degradation of Two Azo Dyes Methyl Red and Methyl Orange from Aqueous Medium

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Abstract—Colloidal MnO_2 has been synthesized and characterized by chemical and spectroscopic methods. Chemical analysis showed that synthesized MnO_2 is 99.21% pure and X-ray spectroscopic analysis indicated that it is amorphous in nature. Scanning electron microscopy observation revealed that amorphous MnO_2 consists of fine-particles of roughly spherical in shape with the average particle size 210 nm. Degradation of the dyes from aqueous solution is accounted in terms decolorization of the dye solution. Preliminary experiments showed that synthesized MnO_2 is capable of decolorize selected azo dyes efficiently from aqueous solution. Then further experiments were carried out to optimize reaction conditions. pH dependent degradation of these dyes showed that pH below five support the decolorization of both the azo dyes. Kinetics of degradation of dyes showed that time 60 to 75 minutes is sufficient for the complete decolorization of both azo dyes from aqueous solution. Effect of temperature was investigated and it has been observed that rate of degradation of azo dyes increases with increase in temperature of the dye solution.

Index Terms— azo dyes, degradation, colloidal MnO_2 , decolorization, catalyst, methyl orange, methyl red.

1 INTRODUCTION

AZO dyes are characterized by $-\text{N}=\text{N}-$ and chromophoric group attached to nitrogen atoms which are responsible for the characteristic colours of the azo dyes [1]. More than 10,000 dyes are used in textile, leather, paper, food, petroleum, etc. industries, and from them about 50% dyes are azo dyes [2]. From the total amount of dyes used in the textile industries 10 to 20% dyes are released into effluent either in solution or suspended form [3]. It was estimated that about 280,000 tonnes of dyes are discharged every year into effluent worldwide [4]. Disposal of azo dyes in natural water sources cause many issues regarding water pollution. Such as aerobic degradation of azo dyes in water leads to the formation of aromatic amines which are more toxic in nature than original dye [5]. Chemical oxygen demand (COD) of azo dyes is very high as compared to biological oxygen demand (BOD) which indicates that they are not easily biodegradable. Moreover azo dyes and their degradation product are toxic, mutagenic, and carcinogenic in nature [6]. Dyes possess high absorbance. Hence even though dyes are present in minute quantity they are clearly visible in water. This property of dyes limits passing of the light through water and directly affects life of phytoplanktons by showing adverse effect on photosynthesis process [7]. Therefore it is of prime importance to remove dyes from industrial effluent. For removal of organic compounds biological methods are used however, these methods are not much more effective for removal of dyes due to resistance of dyes towards biodegradation [5, 8, 9]. Many dye stuffs are designed so that they are resistance to degrade by light as well as by microorganism. Today advanced oxidation process are used which are proven to be more effective and able to de-

grade dye completely from waste water [10, 11, 12]. However, these processes has drawback such as high enegy and chemical requirement, formation of side products, etc. [13]. In advanced oxidation process like Fenton's oxidation process formation of $\text{Fe}(\text{OH})_3$ takes place while in persulfate method formation of NH_4SO_4 takes place as a side products. Side products are not desired into treated effluents hence formation of side products increases the load on the treatment process. In present investigation we are proposing simple and cost effective catalytic method for degradation of two azo dyes by using manganese dioxide as a catalyst. There are very few reports on manganese dioxide based degradation of azo dyes hence we have tried to explore use of MnO_2 as a catalyst for dye degradation. Methyl orange and methyl red are selected as model azo dyes in our study.

2 EXPERIMENTAL

2.1 Preparation of Catalyst:

Colloidal MnO_2 was prepared by the reaction between MnSO_4 and KMnO_4 under neutral pH. To definite volume of 0.1M MnSO_4 solution 0.1M KMnO_4 solution was added drop wise with constant stirring till supernatant solution acquire faint pink color. Then resulted brown colored solid was separated by filtration using Whatman filter paper No-41 under vacuum. Precipitate was washed on filter paper with distilled water till it become free from sulfate ions. Brown colored solid was dried in an oven at 110°C for 2 hr. and used as catalyst.

2.2 Characterization of Colloidal MnO_2 catalyst:

Weighed quantity of catalyst was dissolved in 1:2 conc. HCl : HNO_3 and Mn content in solution was determined by Volhard's method [14]. SEM, XRD spectrum of synthesized MnO_2 was recorded.

2.3 Primary Experiment:

Solutions of dyes methyl red (MR) and methyl orange (MO) were prepared at the concentration 1×10^{-4} M. Both dyes are of high purity and purchased from Sigma-Aldrich Chemical Company. To 100 ml dye solution 200 mg synthesized

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MnO₂ was added and resulted suspension was stirred at 200 rpm on magnetic stirrer for 90 minutes then suspension was centrifuged and analyzed spectrophotometry for dye content in the solution. The residue of MnO₂ in the centrifuge tube was washed with water, then stirred with 15 ml 2M CH₃COOH for 10 minutes and finally centrifuged. Supernatant was collected and analysed by spectrophotometry for dye content.

2.4 pH Dependent Degradation of Dyes:

pH of 100 ml dye solution was adjusted to desirable value ± 0.1 by 1 or 0.1N H₂SO₄, to it 100 mg MnO₂ was added and stirred at 200 rpm for 60 minutes. After 60 minutes suspension was filtered and quantity of dye remaining was determined by spectrophotometric method. This experiment was performed at different pH of dye solution from pH 2 to 7 at the interval of one unit.

2.5 Time Required for Complete Decolorization:

pH of 200 ml effluent was adjusted to requisite value (pH at which degradation of dye was observed maximum) and 200 mg MnO₂ was added to it. Resulted suspension was stirred at 200 rpm on magnetic stirrer till complete decolorization of dye solution take place. During experiment 5 ml suspension was withdrawn at definite time interval, centrifuged and analyzed for dye content by the spectrophotometric method.

2.6 Recovery of Catalyst:

To the treated dye solution 1M KMnO₄ was added till solution shows slightly pink color. This solution was centrifuged to separate solid MnO₂. Brown colored solid MnO₂ was dried and reused for next catalytic cycle.

2.7 Determination of Dye Concentration

Methyl orange has λ_{\max} 490 nm methyl red has λ_{\max} 510 nm at pH = 4. Absorbance of dye solutions was determined at these wavelengths and dye concentration was calculated by comparing absorbance of sample with standard.

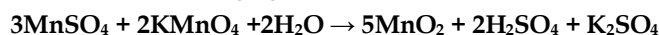
$$C_{\text{sam}} = \frac{C_{\text{std}}}{A_{\text{std}}} \times A_{\text{sam}} \times \text{dilution factor}$$

Where, C_{sam} – dye conc. in sample solution, C_{std} – conc. of dye in standard solution, A_{std} – absorbance of standard solution of the dye, A_{sam} – absorbance of sample of the dye.

3 RESULTS AND DISCUSSION

3.1 Synthesis of MnO₂

Reaction between MnSO₄ and KMnO₄ take place at the neutral pH and room temperature to form MnO₂ which can be represented as follows. This reaction is a basic reaction of Volhard's method for the analysis Mn(II) by using standard KMnO₄ as an oxidizing agent [13].



In this reaction Mn(II) from MnSO₄ is oxidized to MnO₂ while Mn(VII) from KMnO₄ is reduced to MnO₂ i.e. redox reaction take place between Mn(II) and Mn(VII) to form Mn(IV) i.e. MnO₂. MnO₂ is water insoluble and appears as colloidal brown-black colored solid product in solution.

3.2 Properties of MnO₂

Chemical analysis of dried colloidal MnO₂ showed that it contains 99.21% of MnO₂ i.e. synthesized MnO₂ is highly pure. Scanning electron microscopy observation revealed that the amorphous MnO₂ fine-particles were roughly spherical, uniformly distributed, and not highly agglomerated (fig. 1 a) and surface is porous in nature (fig.1 b). It is found that the average partical size of MnO₂ powder is 210 nm.

XRD spectrum (fig. 2) do not showed any characteristic peak indicating that synthesized MnO₂ is non-crystalline in nature.

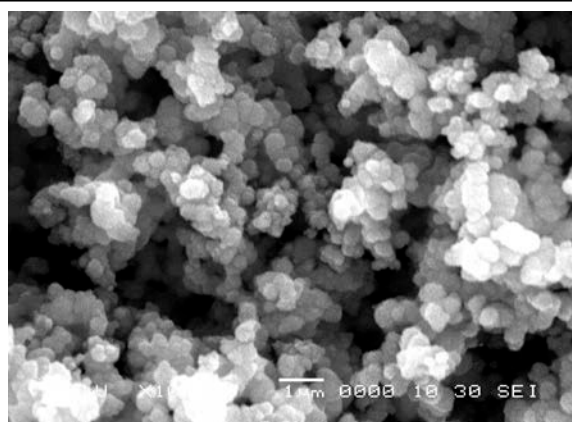


Fig.1(a): SEM photograph of synthesized MnO₂

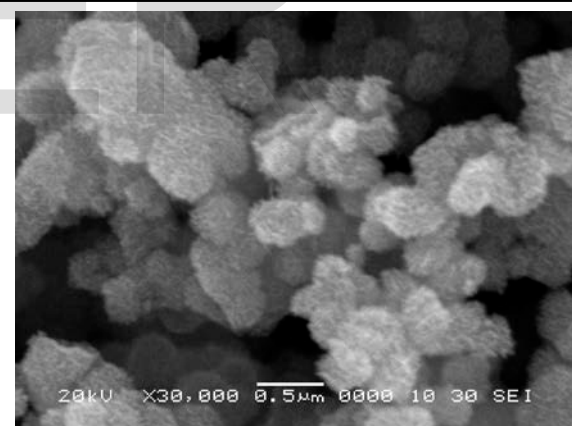


Fig.1(b): SEM photograph of synthesized MnO₂

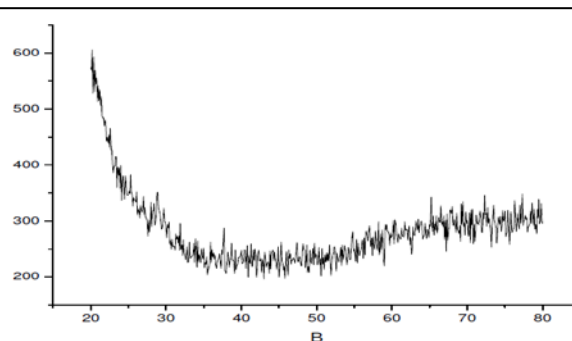


Fig.2 - XRD spectra of synthesized MnO₂

3.3 Primary Experiment

Primary experiment was performed to evaluate ability of the synthesized MnO_2 to degrade / decolorize MO and MR dyes from the aqueous solution. Results of primary experiment showed that on treatment with MnO_2 about 91% MO and 48% MR solution were decolorized indicating that MnO_2 has ability to decolorize these dyes under ambient condition. Decolorization by metal oxide may occur due to the surface adsorption or by catalytic degradation. MnO_2 which was used for dye colorization was treated with 2M CH_3COOH and in the process dye is not released in the CH_3COOH solution, indicating that contact between MnO_2 and dye resulted into degradation of dye. Our observation is also supported by Jiantuan and Jiuhui [3] and Clarke *et. al.* [14]. Therefore, further experiments were carried out to optimize the reaction conditions.

3.4 Effect of pH

This experiment was performed to investigate best pH for the degradation of MO and MR by colloidal MnO_2 as a catalyst. Results depicted in (fig. 3) clearly indicate that rate of degradation of azo dyes is governed by pH of the dye solution. In case MR percent degradation goes on continuously increasing with decrease in pH of the dye solution and below pH 4 appreciable degradation was observed that at pH 5 to 7. In comparison to MR, effect of pH is less marked on degradation of MO and appreciably high degradation of MO was observed at all the pH used in experiment (above 71.52%). Depending on results of this in further experiments different pH are used for both dye, these are 5 for MO and 3 for MR. Clarke *et. al.* [14] also has reported similar results on oxidation of acid orange-7 by manganese oxide a catalyst. They observed appreciable high oxidation of an azo dye acid orange-7 below pH 5. At pH below 5, H^+ ion concentration in solution is sufficiently high to cause protonation of MnO_2 at surface which generate active chemical species like MnOH^{2+} , MnOH , MnO^- etc. In the process electron transfer take place from dye to MnO_2 [3]. High H^+ ion concentration solution also help to form side product and removal of sideproduct from surface of MnO_2 [15].

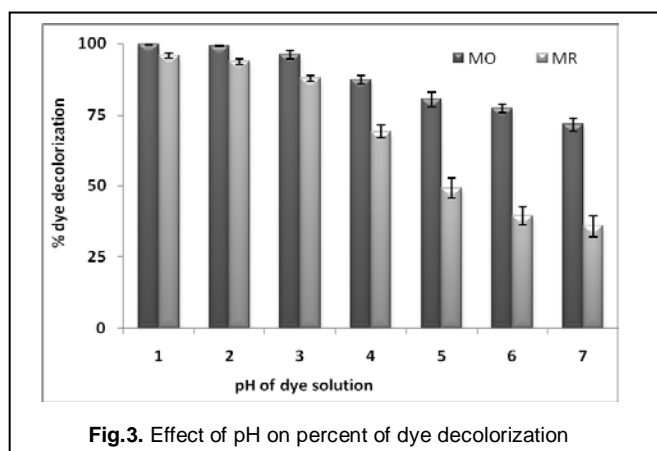


Fig.3. Effect of pH on percent of dye decolorization

3.5 Effect of Catalyst Dose

This experiment was performed to know minimum quan-

tity of MnO_2 that should be used for complete degradation of particular dye. The results depicted in (fig. 4) clearly point out that the quantity of dye degraded goes on increasing with increase in quantity of MnO_2 however percent degradation assume nearly constant value above 200 mg MnO_2 per 100 ml dye solution. As such from 100 to 500 mg quantity of MnO_2 significant difference was not observed in quantity of dye degraded. Thus quantity such as 1mg per ml is sufficient to carry out degradation of dye from water solution within 60 to 90 minutes. It is well known fact that rate of a chemical reaction increases with increase in quantity of catalyst in a reaction and at particular value it assumes constant value. Similar results were observed in our experiment.

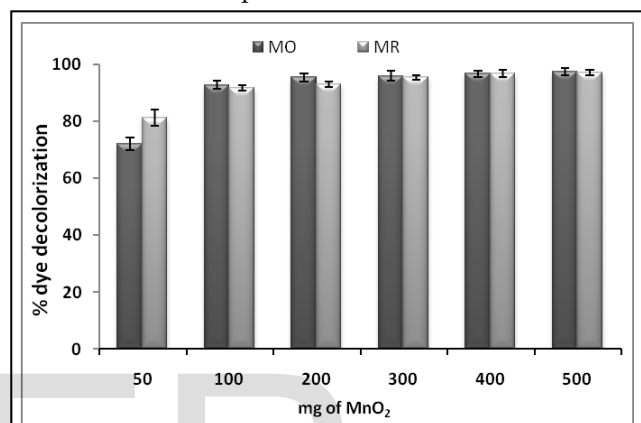


Fig.4. Effect of catalyst dose on percent of dye decolorization

3.6 Kinetics of Dye Degradation

This experiment was performed to investigate time required for complete degradation of the dye from definite volume with fixed quantity of MnO_2 . The results summarized in fig. 5 and 6 point out that for both dyes initial rate of degradation is very high which goes on decreasing logarithmically with time. In case of MO, in first 10 minutes about 76% degradation has taken place while for about 100% degradation 50 minutes were required while for MR about 52% degradation of dye had taken place in first 10 minutes and for complete degradation about 75 minutes were required. Initially high rate of degradation was observed which is due to high initial concentration of dye in the solution.

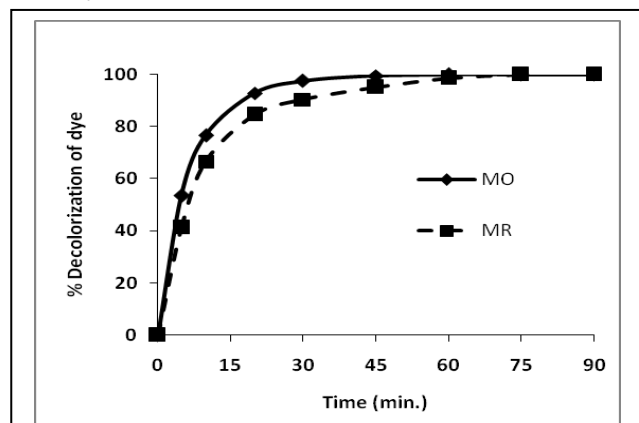


Fig.5. Kinetics of dye decolorization

With time dye concentration goes on decreasing in solution hence rate of reaction also goes on decreasing. Thus, after 30 minutes time of the reaction, rate of change of concentration of the dye with time is very less which results into long time for complete degradation of the dye from solution. Comparison of results of kinetics of degradation of two dyes demonstrates that for 100% degradation MR required significantly higher time than MO. From these observations we can conclude that MO is more prone towards degradation by MnO_2 than MR. The time required for degradation MO and MR is comparable or even low than by other reported [13, 16].

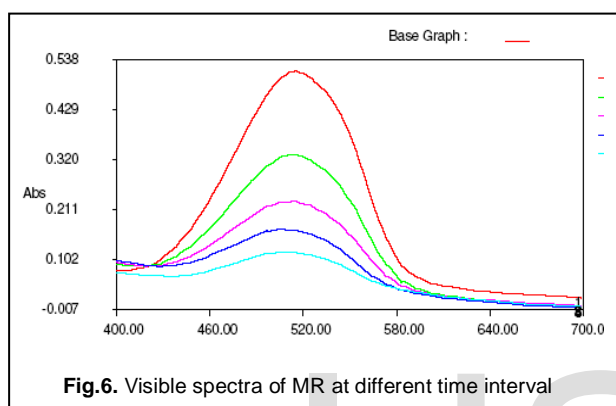


Fig.6. Visible spectra of MR at different time interval

3.7 Effect of Temperature: Temperature is one of the important factors governing rate of a chemical reaction. Results summarized in table-1 show that with increase in temperature rate of degradation of dye goes on increasing but

TABLE -1

Percent decolorization of dyes at different temperatures

Temp (°C)	% Decolorization	
	MR	MO
26	91.72±1.03	98.90±1.49
35	98.17±0.94	100
50	100	100

observed effect is not too distinct at temperature 26, 35 and 50 °C. At 50 °C 100 % degradation was observed for both dyes in less than 45 minutes. MR showed 91.72±1.03% degradation at room temperature while 98.17±0.94% degradation at 35 °C within 60 minutes time. Similar pattern of result was observed for MO at room temperature and at 35 °C. Temperature decreases energy of activation and there by increases rate of degradation reaction of dyes.

4 CONCLUSIONS

Colloidal MnO_2 can be used as heterogeneous catalyst for degradation of the azo dyes and it is possible to remove azo dyes completely from aqueous solution by degradation process. Process is simple and costeffective as catalyst is regenerated and reused. However, further work must be carried out to so that method can be adopted for large scale treatment of effluent containing variety of the azo dyes.

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