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Facile manganese-iron mixed metal oxy-hydroxide nanostructures – synthesis and its catalysis

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Manganese-iron oxide based multi-valance metal (oxy) hydroxide nanostructures were developed by simple green process. Crystal structures and morphologies of prepared samples were characterized by powder X- ray diffraction; scanning electron microscopy attached with energy dispersive X- ray spectroscopy, Fourier transform Infar-red spectroscopic methods. The combined effects of iron and microwave irradiation, temperature on manganese oxide crystal structures were investigated. The catalytic performance of the prepared nanostructures were investigated towards Methylene Blue (MB) dye degradation in presence and absence of oxidant such as hydrogen peroxide. The results displayed that almost all the catalysts exhibited exceptional activity towards dye degradation of MB dye with peroxide. Among them the microwave assisted synthesized metal (oxy) hydroxide – bio char nanostructures displayed higher catalytic activity towards dye degradation.

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Keywords: Manganese (Oxy) hydroxide, Layered structures, Oxygen vacancy, Active oxygen, Dye degradation

1. Introduction

Nanostructured materials have the unique physical features especially size, shape and significant surface morphology which influence their chemical and physical features. They find extensive applications like electrical and optical sensor, photovoltaic and environmental related applications [1]. Remarkably, the researchers manipulating their chemical and physical properties through the well-organized chemical synthesis process.

More than 10000 synthetic dye stuffs are used for the various dying process, and the number increased continuously increased significantly over the years. These spent or unused dyes stuffs from the dying process released from the industries causes water and soil pollution. Numbers of treatment process were proposed either by chemical, physical and biological treatments. In recent years, significant attention has been made to remove of organic and inorganic materials – major pollutants in aquatic and soil media by the researchers. In connection with that considerable efforts have been made on these problems via both experimental and thermotical way. Organic and inorganic based colorants especially synthetic dyes stuffs have increased enormously over the past few decades to the rapid enhancement of human population.

In common, Methylene blue, a cationic organic dye extensively used as colorant towards

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coloring the cotton, silk and wool based textile materials. Which is highly toxic, environmental persist (human, and plants), carcinogenic, mutagenic in nature. In the plant system, this will prevent the photosynthesis process [2-10]. Hence, the decolorization of the dye stuffs has an important towards the practical importance.

Oxidation Process is an effective method for the decolorization of organic colorents from small to large molecular structures. The prime importance of these methods to remove/degrade the carcinogenic colour and the colour providing chemical counter parts. In the recent years, Advances oxidation process with the appropriate catalyst and oxidants to simplify the oxidative decolorization process very efficiently [11-21].

Due to its unique structural features, excellent chemical stability, enhanced surface area, Metal oxides find extensive usage in the energy storage, conversion, environmental remediations. Metal oxides especially, manganese oxides have been reported as an effective catalyst for the advanced oxidation process especially for the dye decolorization /degradation process.

Carbon based nanostructures showed marked interest on the wide range of applications from coating to energy fields. The development new catalyst with enhanced physical and chemical properties is highly essential and by utilization of the excess reactants into useful product is a significant and vital importance in the present scenario. In line with we have made an attempt to develop manganese Oxy hydroxide-carbon nanocompoistes with need like architecture by simple one-pot synthesis followed by calcination process. And the developed catalysts are tested for their efficacy on the degradation of organic dye methylene blue and reduction of 4-nitrophenol in aqueous solution. The detailed results are discussed further.

2. Experimental details

2.1. Materials

In the present work, the chemicals potassium permanganate ($KMnO_4$), ferric chloride ($FeCl_3$), and sucrose ($C_{12}H_{22}O_{11}$) are of analytic grade and procured from Isocheim Chemicals, India. Surfactants received from SD fine chemical India Double-distilled water (DD) were used throughout the experiment to make the solutions.

2.2. Manganese iron (oxy)hydroxide (MnFe) nanostructures

The manganese oxide nanostructures synthesis prepared by earlier reported with some modification, in brief: 20 mL of (3 M) sucrose in aqueous is added into 50 mL of aqueous (0.19 M) $KMnO_4$and 0.19 M $FeCl_3$. nH_2O to result in a hasty, exothermic reaction in which a brown gel is formed (2-5 min.). Water is occasionally drained over the next 2-3 hr as the gel undergoes synergies and drying at 110°C for 24 hr. Further, a part of the sample was subjected to calcination at 200°C for 2 hr labeled a s TMFOx and another part was heated in a microwave oven for 5 minutes with 30 sec regular intervals labeled as MMFOx.

2.3. Characterization

As synthesized materials were characterized by Powder XRD (X-6000, Shimadzu), Scanning Electron Microscope (JSM 6390, JEOL), FTIR (shimadzu, Japan). The prepared catalysts were characterized using powder XRD (Shimadzu 6300, Japan) and Scanning electron microscope (JEOL 630, Japan), Fourier transformed Infra-red spectroscope (Shimadzu, Japan).

The catalytic activity of the prepared catalyst was carried out in a 250 ml glass flask, which contained 100 ml of Methylene blue colorant solution, and known quantity of catalysts. After adding required amount of H_2O_2 aqueous solution, the mixture was permitted the reaction at room temperature with continuous stirring at the speed of 250 rpm. For a specified time interval, about 1 ml of the dye catalyst mixture solution was pipetted out into a volumetric flask and diluted with distilled water to 25 ml proceeding to each analysis. For optical absorption measurements, the diluted solution was centrifuged (5000 rpm) in order to eliminate the catalyst particles. The centrifuged dye solution was then placed into a quartz glass cell (path length 1.0x1.0 cm) and then the absorption spectrum was measured with a ultraviolet–visible (UV–Vis) spectrophotometer. The catalytic decolorization of Methylene blue dye calculated by batch studies, by varying the catalyst, reaction time, and concentration of the dye was characterized by double beam UV-Visible spectrophotometer (Wensar, India).

3. Results and discussion

The Manganese oxide materials have the futuristic characteristic of micro porous and meso-porosity and various layered nano architecture manganese oxide nanomaterials are prepared through a variety of routes. Most of these materials with comparable structural features show a variety of properties and depends on the definite synthetic route. These variances can be ascribed to differences in the particle shape and/or size, the type and quantity of orderliness or defects in the structures. For this purpose, changes in synthetic methodology can result in active materials with ion-exchange, including chemical and electrochemical properties.

Precipitation methods involve redox reactions of $Mn^{7+}$and/or Mn^{2+} precursors are common for the formation of layered MnO_x materials, because molecular Mn^{4+} materials are suitable starting material are occasional. Materials formed by the precipitation method or routes include layered manganese oxides (birnessites) and condensed phase manganese oxide materials such as hausmannite (Mn_3O_4) are very common one and these structures can be inter convertible by suitable post experimental process. These manganese oxide materials, which incorporate catio neither alkali earth metal nor their ion scan occupy between the layers to stabilize the negative charged species on the sheets. Additionally, to maintain by the hydrated water molecules. They can easily experience ion-exchange reactions by replacing the cations as well as protons. In line with that we have made an attempt to developed manganese based mixed (oxy)hydroxides at low temperature.

3.1. Structural characterization

In powder XRD patterns of as prepared Mn-Fe Xerogel, TMFOx and MMFOx are revealed in Figure 1(a-c). The XRD points 2θ at 9˚ and 12.5˚ matches with the birnessite type of layered manganese-iron xerogel with the interlayer spacing of about 4.0 A˚, this is comparatively lower than the pure MnOx. This lower interlayer space presumed to be the mixed valance cation such as Mn and Fe led to disordered architecture i.e., defective nanoarchitectures. And all the three XRD patterns are highly amorphous in nature, it indicates that the as prepared MFOx is highly distorted structure with excellent catalytic activity. Both defective structure, mixed valance, and nano architectures expected to be better catalyst. FT-IR analysis (Figure 2) showed the xerogels holds hydroxyl moiety in the inner and outer layers, up on thermal treatment it was removed subsequently. This hydroxyl moiety presumed to have more positive interaction with dye molecules in aqueous medium, this phenomenon reflects in the adsorption of dye molecules over the catalyst hence, the adsorption of dye is expected to be high in all these catalysts. Two peaks around 630 and 525 cm^{-1} of all the three samples corresponds to the Mn-O and Mn-O-Mn stretching vibrations. And strong absorption peak at 3448 cm^{-1} confirms the presence of -OH stretching vibration of -OH [22].

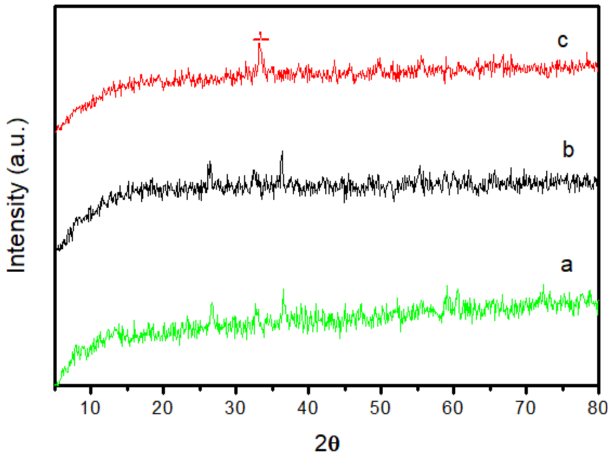

Fig. 1. Power X- ray diffraction Mn-Fe – xerogels (a) as prepared 110°C, (b) Mn-Fe - xerogel heated at 200 ° C resulted TMFOx (c) Mn-Fe - xerogel heated using microwave as nanostructures resulted MMFO.

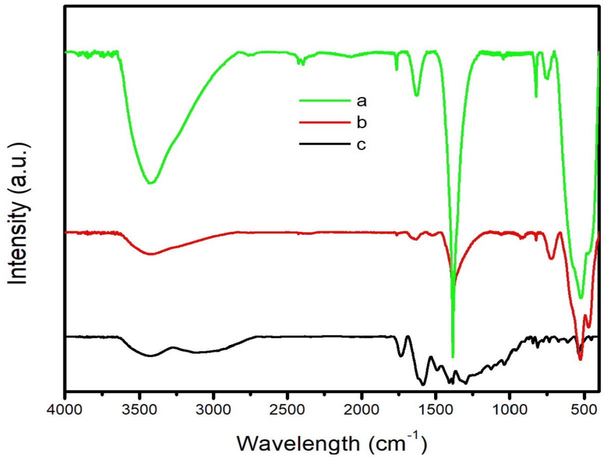

Fig. 2. FT-IR spectrum of Mn-Fe – xerogels (a) as prepared (b) TMFO and (c) MMFO.

3.2. Morphological characterization

The catalyst material developed by various methods initially, the xerogels were formed by simple sol-gel method, which results amorphous nanostructured particles. This would be subject to calcinations by two different process (i) heating at 200°C labeled as M and (ii) subjected to microwave oven for 5 min. with regular interval of 30 sec. yields manganese (oxy)hydroxides with nanorods/strips and nanoparticles (SEM void-infra). As it mostly amorphous in nature hence the XRD does not show any appreciable peaks like crystalline one. On calcinations few peaks observed 2θ at 26° and 37° indicate the formation Mn_3O_4 like nanostructures. Additionally, the xerogels shows a peak around 2θ at 8°-9°, indicates the layered nanostructures with 7 Å interlayer distance.

The scanning electrons microscopic analysis (Figure 3) exhibits the different type of nanoarchitectures were formed over the process. Xerogel exhibits as small nanoparticles with the size ranges from 30-100 nm. Up on calcinations at 400°C, small needles or particles with straps like nanoarchitectures were formed and labeled as TMFO (Figure 4). On the other hand microwave calcinated sample shows a particle remains as nanoarchitectures and labeled as MMFO (Figure 5).

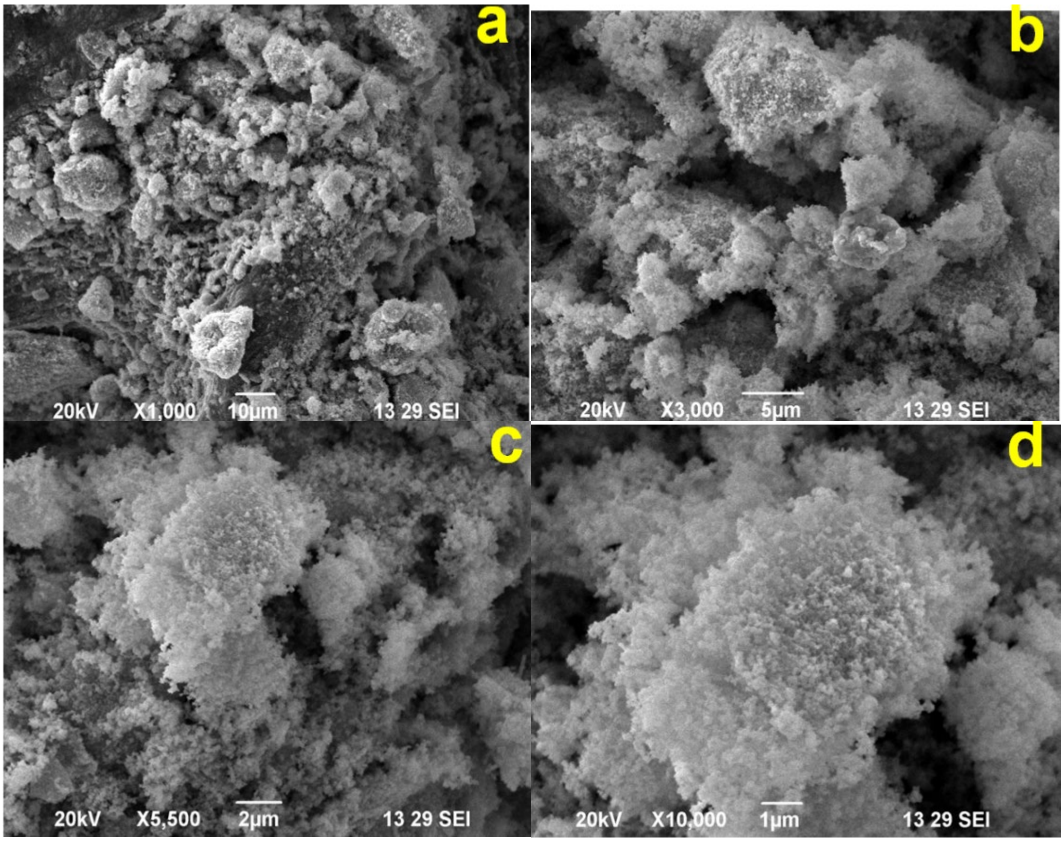

Fig. 3. Scanning electron Micrographs of Manganese (oxy)hydroxide prepared by hydrothermal method as prepared xerogels.

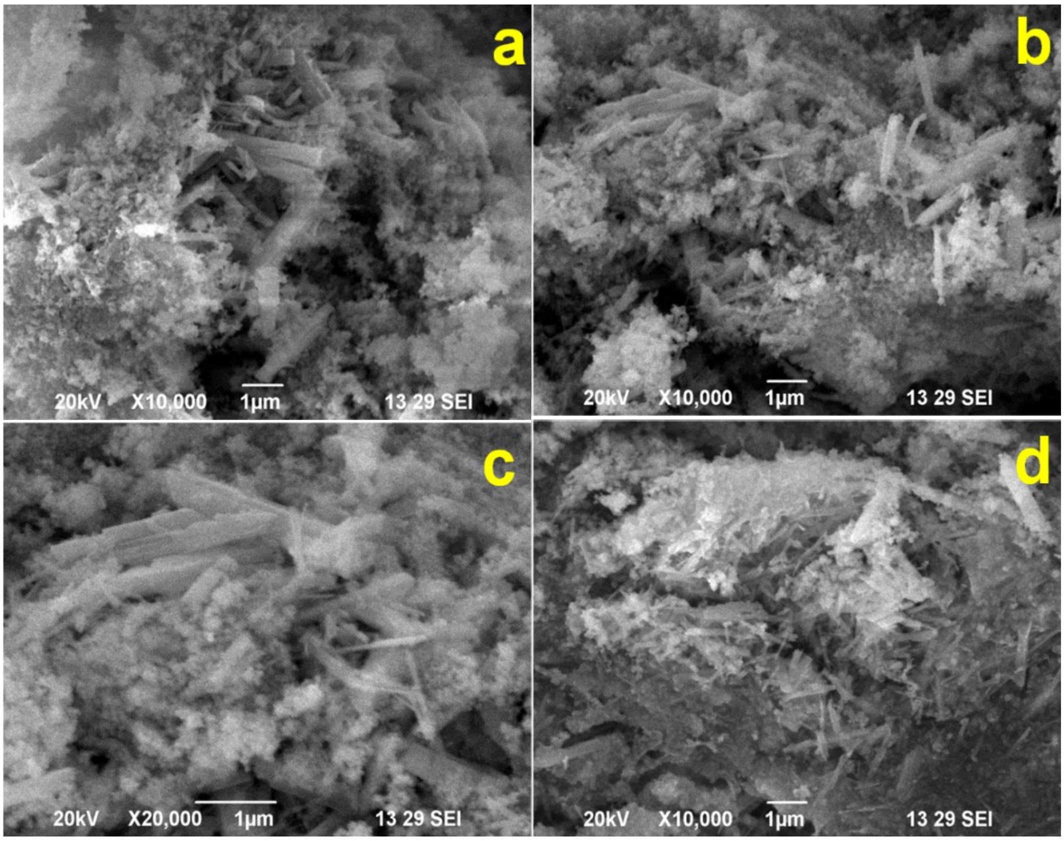

Fig. 4. Scanning electron Micrographs TMFOx nanostructures.

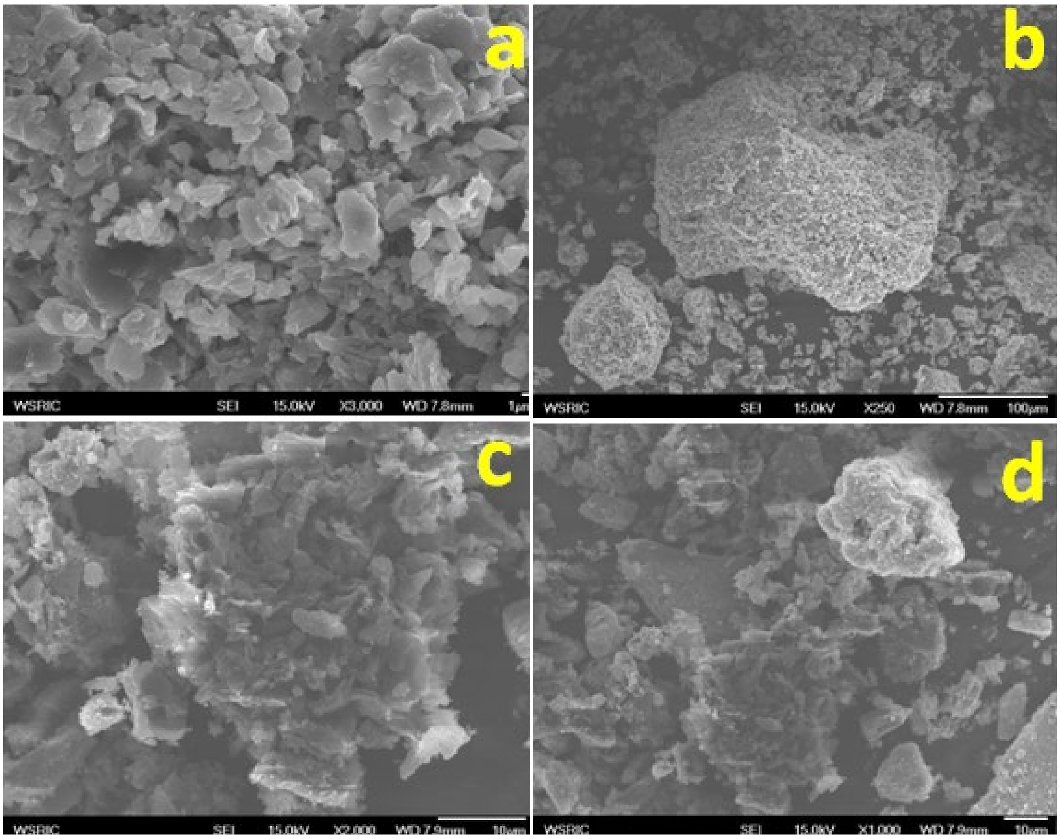

Fig. 5. Scanning electron Micrographs MMFOx nanostructures.

3.3. Catalytic studies

Adsorption is one of the major parameters to access the reaction between the catalyst and dye molecules. Initially the much active surface area will be available hence the adsorption is very high at low concentration of dye solution. On higher concentration, the first layer covered by the dye molecules. So further adsorption will be slow down. About 74-80 % adsorption was observed for the Xerogel, TMFOx and MMFOx catalysts for initial 10 min. And maximum adsorption of 100 % observed for 50 min. at 0.01mMol/L of M dye (Figure 6).

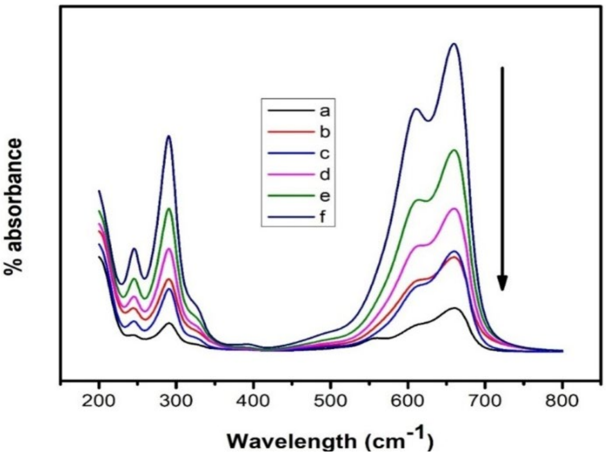

Fig. 6. UV-Vis spectrum for (a) MB dye, (b) MB + 1% H_2O_2, (c) MB + MnO_2 adsorption Xerogel (d) MB + MFOx Xerogel + 1% H_2O_2 (e) MB + TMFOx+ 1% H_2O_2 (f) MB + MMFOx + 1% H_2O_2.

3.3.1. Amount of catalyst

The role of catalyst quantity required for to degrade the MB was calculated at a fixed quantity of MB dye is 250 ml (10-5 M) and various amount of catalyst in aqueous solution showed in Figure 7 was tested. The amount of Xerogel, TMFOx and MMFOx was mixed between 100 and 1000 mg/L, in order to improve the amount of catalyst for the active catalytic decolorization of MB. MMFOx sowed an initial decolorization of 21% which is comparatively higher than the TMFOx (12%), Xerogels (11%). As the quantity of catalysts increases, the decolourization rate of the MB dye progressively increases. This is due to the better adsorption of MB dye on the catalyst was increase propositionally results maximum contact between the active sites and MB dye molecules. The extreme efficiency was achieved at a concentration of 1000 mg/L. At this concentration, the active surface areas on the catalyst were very high and provide better surface area and will be engaged by the MB dye molecules. The other experiments were carried out using the optimal concentration of the catalyst, which is 100 mg/L (Figure 8).

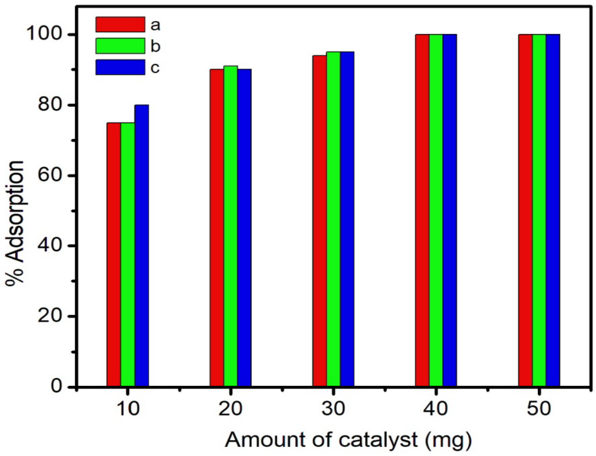

Fig. 7. Adsorption profile of MB dye over the catalyst (a) Xerogel, (b) TMFOx and (c)MMFOx.

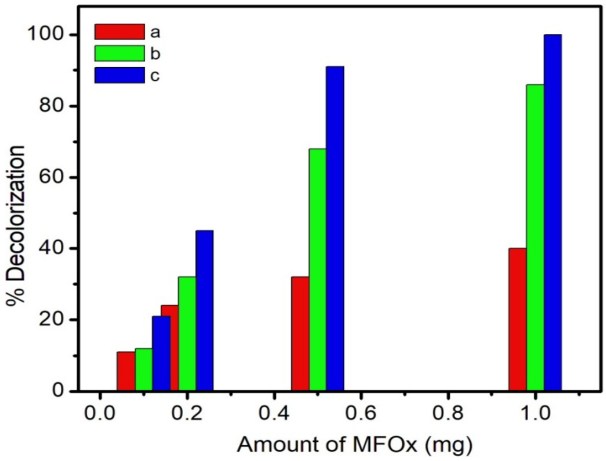

Fig. 8. Adsorption profile of MB dye over the catalyst (a) Xerogel, (b) TMFOx and (c) MMFOx

3.3.2. Reaction time

Similarly, reaction time place important role, the reaction time calculated from 5 to 60 min. and highest degradation observed at 60 min. as the reaction increases the adsorption was enhanced and there by the decolorization was also enhanced. The maximum decolorization was observed at 60 min. because the complete decomposition of peroxide needs this time period.

Hence, for the optimization we have carried out further experiments at 60 min (Figure 9).

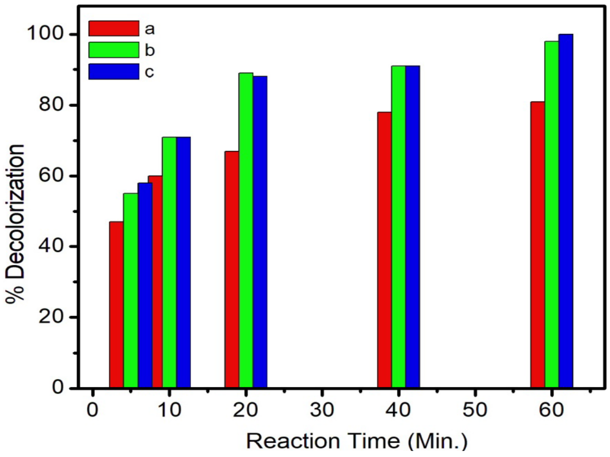

Fig. 9. Effect of reaction time– and their profile of MB dye degradation over the catalyst (a) Xerogel, (b) TMFOx and (c) MMFOx

3.3.3. Effect of concentration of MB dyes

The concentration of Methylene Blue dyes important parameter to assess the degradation effectiveness, in low concentration, 100 % degradation observed, but at higher concentration its reduced, because at high concentration the MB molecules aggregated and formed as dimmers, so breaking of the dye molecules needs much energy, additionally these molecules would not able to reach the reaction surface. The initial dye molecules adsorbed on the manganese-based catalyst active surface area and it will get breakdown, then, further adsorption of dye molecules on the surface is very difficult or it may take much time for the reaction. At 0.5 mMol/L showed maximum of 40, 20 and 20 for MMFOx, TMFOx and xerogels respectively (Figure 10).

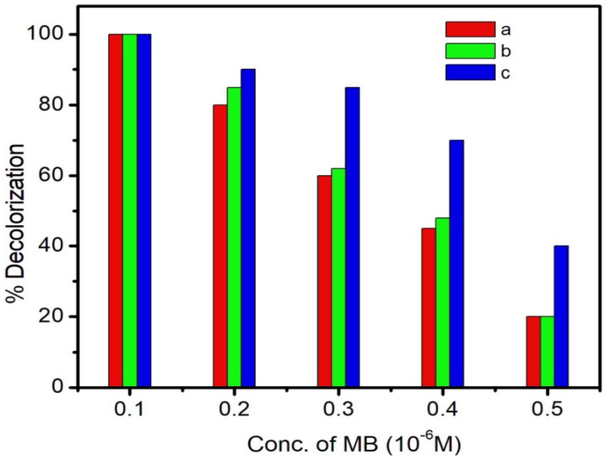

Fig. 10. Effect of concentration of MB dye – and their profile on degradation with the catalyst (a) Xerogel, (b) TMFOx and (c) MMFOx

3.3.4. Effect of surfactants

In the dying process, surfactants were used for the better fixation of dye on to the material. Thus, the dye house effluents contain notable quantity of surfactants, it as the significant interference on the degradation process. Hence, we tested the effect of anionic surfactant – SDS, cationic –CTAB and non-ionic surfactant – Brij 30 were tested towards. The degradation was significantly affect these surfactant. Especially, cationic surfactant such as CTAB shows the maximum interference and degradation efficiency 40 %. Whereas SDS and Brij about 80% and 86 % respectively. This may be accounted by the following reasons: 1. The repulsive interaction between Cationic dye MB and surfactant CTAB results non-adsorption of dye on catalyst lower the degradation efficiency, on the other hand the anionic and non-ionic surfactant have the associative interaction may leads to better degradation (Figure 11).

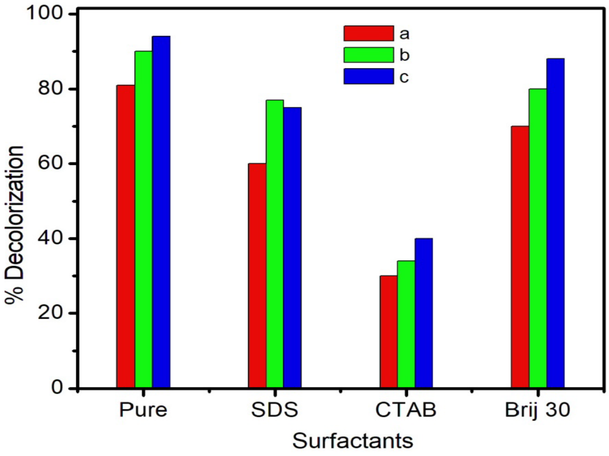

Fig. 11. Effect of Surfactants and their profile on degradation MB dye with the catalyst (a) Xerogel, (b) TMFOx and (c) MMFOx.

3.3.5. Recyclability

Finally, the catalyst efficiency tested by the recycling the catalyst. The catalytic efficiency decreased on further run; this is because of the reaction the catalyst surface may be affected by the oxidant (Figure 12).

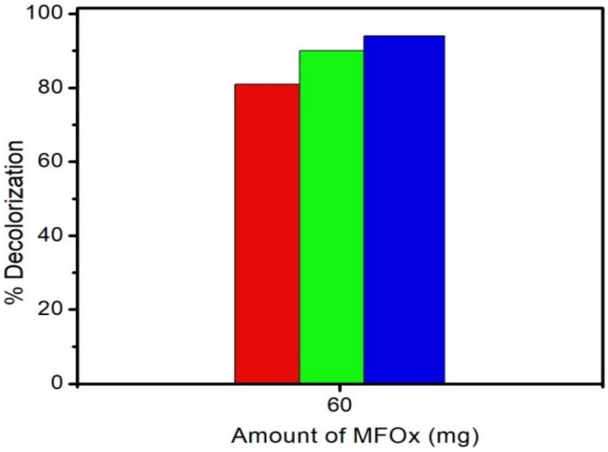

Fig. 12. Effect of surfactants and their profile on degradation MB dye with the catalyst (a) Xerogel, (b) TMFOx and (c) MMFOx.

3.4. Mechanism

The marked consideration has been paid as the hydrogen peroxide (H_2O_2) based oxidant in various industrial processes. Numerous radical species including hydroxyl (•OH), Oxyhydroxyl(•OOH) or peroxide(•O^{2-}) are tangled in the decomposition reaction. But, the mechanisms of decomposition of organic matter by these oxidants are unable to fide. It is extensively identified that $H_2O_2$is not vigorous at low or room atmospheric temperature. Therefore, a number of methods have been reported to trigger it which including increased temperature, metal and nanostructured oxides-based activation. Thus, we have made an attempt at metal (oxy)hydroxide-activated peroxide for the better process to degrade the MB dye (Figure 13).

$$H_2O_2 \longrightarrow 2^{\cdot}OH$$

$$\text{Mn-Ov-Fe}^{n+}\ \text{(Surface)} + H_2O_2 \longrightarrow \text{Mn-Fe}^{(n+1)} + HO^{*} + OH^{-}$$

$$\text{MB dye + active HO•/Oxygen radicals} \longrightarrow \text{Degraded product} + H_2O$$

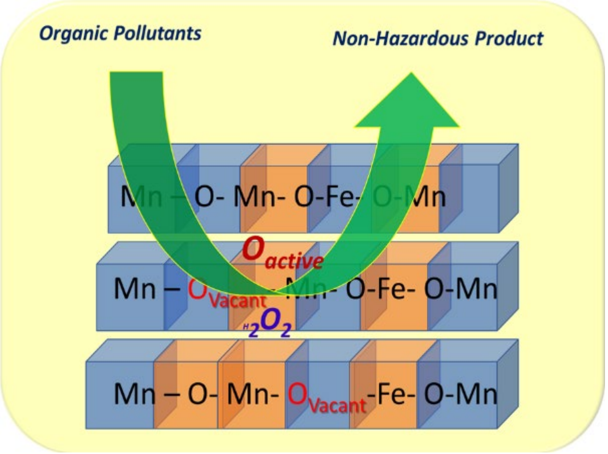

Fig. 13. Schematic representation of MFOx catalyst – active Oxygen generation towards dye degradation.

4. Conclusions

The present work indicates the performance of Manganese (oxy)hydroxide catalyst help to degrade the organic pollutant and as Methylene blue dye as a model system have been tested. Here we have used H_2O_2 as oxidants. By simple preparation method we have developed active nanostructured MFOx catalyst. The XRD result shows it forms like layered nanostructures and SEM results shows long strips of nanostructures. The catalytic studies show the prepared catalyst is highly amorphous and exhibits good catalytic decolorization of MB dye at room temperature. This is due accounted by the following, the direct involvement of active oxygen/hydroxy radical generated on the surface of the catalyst with the help of peroxide help to decolorize the MB dye in effective manner. From these experimental results, low temperature synthesized manganese oxide materials possess high surface defects, these defects will help to develop active oxygen based radical to degrade the organic dyes in room temperature. Furthermore, the reaction kinetics and application of these catalyst towards waste water treatment are underway. The proposed catalysts are economical, facile and ecofriendly.

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