

Wet oxidation of acid brown dye by hydrogen peroxide using heterogeneous catalyst Mn-salen-Y zeolite: A potential catalyst

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Abstract

Catalytic wet hydrogen peroxide oxidation of acid dye has been explored in this study. Manganese(III) complex of *N,N'*-ethylene bis(salicylidene-aminato) (*salenH*₂) has been encapsulated in super cages of zeolite-Y by flexible ligand method. The catalyst has been characterized by FT-IR, XRD, TG/DTA and nitrogen adsorption studies. The effects of various parameters such as pH, catalyst and hydrogen peroxide concentration on the oxidation of dye were studied. The results indicate that after 20 min at 30 °C, 0.175 M H₂O₂ and 3 g/L catalyst, about 90% dye removal was obtained. These studies indicate that manganese-salen complex immobilized on zeolite framework can act as a good heterogeneous catalyst for removal of dye from wastewaters.

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Keywords: Heterogeneous catalysis; Mn(III); Flexible ligand method; Zeolite; Dye removal

1. Introduction

Dyes find potential applications and are omnipresent in many industries like textile, leather, food, paper, etc. The effluent arising from these industries is obviously colored and causes great concern owing to their negative impact on the environment [1,2]. Treatment of dye-loaded effluent has been a very active area of research in recent times. A variety of techniques are being used for the removal of dyes from wastewaters, e.g. adsorption, oxidation, microbiological, photocatalysis, etc. [3–6]. Though activated carbon demonstrates its potential to remove the dyes, the high initial cost of carbon, coupled with problems associated with regeneration/reuse necessitates search for other alternatives. The ability of biological treatment processes for decolorization of industrial effluents has limitations in that it is affected by the concentration, non-biodegradable, toxic and inhibitory nature, alkalinity and elevated temperature of the dye effluents. Owing to these reasons chemical oxidation methods are preferred.

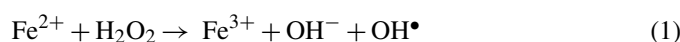
Various advanced oxidation processes (AOP's) have been developed to meet the increasing need of effective wastewater treatment [7]. Elimination of dyes in wastewater by oxidation with molecular O₂ and sunlight is the most environment friendly pollution treatment method. Hydrogen peroxide is a powerful cum environment friendly oxidizing agent since the products of its reduction are H₂O and O₂. H₂O₂ oxidation with UV-light, heat, etc. has been investigated [8,9]. Fenton reagent is an efficient oxidant of various organic substances in aqueous solutions. Fenton reagent has received great attention as means for decolorization of synthetic dyes [10]. However, homogenous Fenton systems have limitations like limited pH range, production of iron-containing waste sludge and catalyst deactivation by some iron complexing agents like phosphates anions [11]. Hence, one of the promising methods to remove dyes effectively is the use of heterogeneous catalysts [12–15].

Heterogeneous catalysis eliminates the need of adding soluble catalytic substances and also the need for treating the resultant sludge. The most attractive properties of zeolites are their well-connected nano-pores and nano-channels, which serve readily as hosts for various molecules. Several studies on synthesis and catalytic activity of encapsulated metal complexes in zeolites have been carried out [16–20]. A photocatalytic system involving iron(II) bipyridine supported on Na-Y zeolite has been

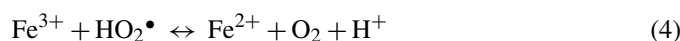
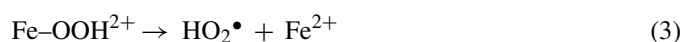
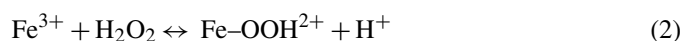
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studied for degradation of malachite green [21]. Degradation of reactive dyes by catalytic wet hydrogen peroxide oxidation using Fe-exchanged Y zeolite as catalyst has also been studied [22,23].

Fenton kind of process is a very promising AOP, wherein wastewater reacts with H_2O_2 in a non-pressurized reactor, at low temperature, in the presence of a catalyst; yielding CO_2 and water or other oxidation products [24]. Oxidation of many organic substance with H_2O_2 is improved by the addition of a catalyst to activate the H_2O_2 molecule, leading to the formation of hydroxyl radical (OH^\bullet). These are the true oxidant species, which exhibits a very high oxidation potential of 2.8 V [25]. The limiting step in these kinds of oxidation reactions is the formation of hydroxyl radicals (OH^\bullet) through the following reactions [24]:



Iron(II) is slowly regenerated through the so called Fenton like reaction between Fe(III) and H_2O_2 [26]:



The OH^\bullet species formed through Eq. (1) will then attack the organic substrates present the wastewater.

In this present work, the characterization of Mn-exchanged Na-Y zeolite and the kinetics and catalytic activity of the same for degradation of acid dye Dermapel brown has been studied.

2. Experimental

2.1. Materials

The zeolite Na-Y purchased from Süd Chemie India Ltd., India, was used. The ligand *N,N'*-bis(salicylaldehyde)-ethylenediamine (salenH_2) was prepared by procedure reported below. The other chemicals used were of AR quality.

2.2. Synthesis of ligand

A solution of 1 mM ethylenediamine in 25 mL methanol was slowly added to a stirred solution of the salicylaldehyde (2 mmol) in 50 mL of methanol. The reaction mixture was then refluxed for 30 min, during which the yellow colored Schiff base ligand precipitated. After cooling the ligand was filtered, washed with cold methanol and dried.

2.3. Preparation of metal exchanged zeolite

3.67 g of manganese(II) acetate was dissolved in 300 mL of warm distilled water. Five grams of Na-Y was added under stirring. The system was heated under reflux for 8 h and cooled. The solid was filtered and washed thoroughly with hot demineralized water till the washings were colorless. The exchange process was

repeated twice more. The solid Mn-Y zeolite obtained after third exchange was dried at $80 \pm 5^\circ\text{C}$ overnight in an air oven.

2.4. Ligand encapsulation (flexible ligand method)

The ligand-encapsulated zeolite was prepared by taking salen in a round bottomed flask immersed in an oil bath at $90 \pm 5^\circ\text{C}$. Mn-Y zeolite was then added (salen:Mn ratio is 3:1). After being stirred at this temperature condition for 24 h, the solid formed was taken out and Soxhlet extracted with methanol for 24 h, followed by diethyl ether and acetonitrile for 8 h, respectively, till all the unreacted salen was removed and the extract was colorless. The brown color material obtained was then dried at 100°C .

2.5. Characterization of catalyst

The FT-IR spectra of the zeolite, solid catalyst and the neat complex were recorded between 400 and 4000 cm^{-1} using Perkin-Elmer Spectrum RX I FT-IR system, using the KBr disk technique. The TG/DTA analyses of the neat metal complex and the catalyst were recorded using NETZSCH STA 409C, thermal analyzer. The X-ray powder diffractograms of the zeolite and solid catalyst were recorded using Shimadzu XD-D1 X-ray diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). Manganese content present in the zeolite was measured using atomic absorption spectroscopy.

2.6. Catalytic activity studies (decomposition of H_2O_2)

0.25 g of catalyst was added to 50 mL of 0.175 M H_2O_2 (30%) at ambient temperature and the reaction mixture was kept stirring. After 2 h of stirring, the catalyst was filtered and a small aliquot of the filtrate was titrated against standard potassium permanganate solution after the addition of 10 mL of 2 M H_2SO_4 and distilled water.

2.7. Preparation of synthetic dye solution

The dye solution was prepared by dissolving the acid dye Dermapel brown obtained from Clariant India Ltd., India, in deionized water to produce a stock solution of 500 mg/L (pH 6.45). This stock solution was diluted in accurate proportions to produce solutions of different initial concentrations.

2.8. Effect of pH and temperature on discoloration

The effect of pH on discoloration was studied using 50 mL of 50 mg/L dye solution taken in stoppered conical flask containing 0.15 g of catalyst and 0.175 M H_2O_2 . The pH of the solution was varied from 2.0 to 8.0 using 0.1N H_2SO_4 and 0.1N NaOH. The solution at the respective pH was agitated for a period of 2 h in a rotary mechanical shaker (70 strokes per min) at room temperature ($30 \pm 1^\circ\text{C}$). For temperature studies, 50 mL of 50 mg/L dye solution was agitated with 0.15 g of catalyst and 0.175 M H_2O_2 for a period 2 h for various temperatures (30, 40, 50 and 60°C).

2.9. Role of H_2O_2 and catalyst

The role of H_2O_2 in the oxidation of dye was studied by varying the amount of H_2O_2 used for the experiment (0.175, 0.350, 0.525, 0.700 and 0.875 M) with 0.15 g of Mn NaY catalyst. The solutions were agitated in a rotary mechanical shaker for a period of 2 h at room temperature. The effect of the catalyst dosage on the dye oxidation was also studied. To 50 mL of 50 mg/L dye solution, different catalyst concentrations varying from 0.2 to 5 g/L were added along with 0.175 M H_2O_2 . The flasks were agitated in rotary mechanical shaker at room temperature for a period of 2 h. The reduction in color was measured at various time intervals ranging from 10 min to 2 h for each trial using Perkin-Elmer Lambda 35 UV–vis spectrophotometer.

2.10. Rate of discoloration

In order to determine the time required for complete removal of color, 50 mL of 100 mg/L dye solution was taken in 100 mL stoppered conical flask containing 0.15 g of the catalyst and 0.175 M H_2O_2 . The contents of the flask were agitated in a rotary mechanical shaker at room temperature ($30 \pm 2^\circ\text{C}$) and the absorbance was measured at various time intervals ranging from 15 min to 5 h for each trial. The dye concentration was estimated by measuring absorbance at 436 nm using Perkin-Elmer Lambda 35 UV–vis spectrophotometer. In order to study the effectivity of the catalyst against various initial concentrations of the dyes, the following experiments were carried out. Fifty milliliters of five different concentrations of dye, viz., 10, 25, 75 and 100 mg/L were taken into five stoppered conical flasks containing 0.15 g of catalyst and 0.175 M H_2O_2 each and the flasks were agitated in rotary mechanical shaker at room temperature for a period of 3 h, after which the concentration of dye remaining was measured.

3. Results and discussion

3.1. Synthesis and characterization of catalysts

Synthesis of Mn complex of salen encapsulated in the super cages of zeolite-Y was carried out by the flexible ligand method. In this method, a flexible ligand able to diffuse freely through the zeolite pores, complexes with a previously exchanged metal ion. The resulting complex becomes too large and rigid to escape out of the cages. Salen ligand offers the desired flexibility hence this method was adopted. Moreover, it has been shown in the case of zeolite encapsulated copper complexes that catalysts obtained by synthesizing the complexes *in situ* in the cavities of zeolites by flexible ligand method contain a higher concentration of complex than those obtained by synthesizing the zeolites around the preformed metal complex [27]. The Mn-exchanged Na-Y catalyst was characterized by various physico-chemical techniques like AAS, IR, XRD, surface area analysis and thermal analysis. The manganese content present in supercages of catalyst is 5.2% (w/w).

3.2. IR spectral studies

The IR spectra of neat complex and the catalyst showed essentially similar bands though the intensity of bands in zeolite matrix is low. Peaks due to the zeolite dominate the spectra of Mn-salen-Y. These include the OH vibrations in the range $3700\text{--}300\text{ cm}^{-1}$. Some of the bands characteristic of the complex could, however, be distinguished. The bands appearing between 1600 and 300 cm^{-1} can be considered as signature of the complex. Vibrational bands due to C=N, C–O and C=C in encapsulated complexes occurred around 1540 , 1360 and 1600 cm^{-1} , broadly similar to those of the neat complex.

3.3. Thermogravimetric analysis

Thermal analysis for neat complex and the catalyst was carried out to study the stability of Mn-salen-Y to heat. The thermal degradation pattern for Mn-salen and Mn-salen-Y are depicted in Fig. 1. The decomposition occurs in two stages, the first step corresponding to the loss of four intra-zeolite water molecules and second step due to the decomposition of the chelating ligand. An endothermic loss of 15.8% corresponding to the loss of intra-zeolite water occurs between 100 and 200°C for Mn-salen-Y. Thus the thermal stability of Mn-salen complex was not

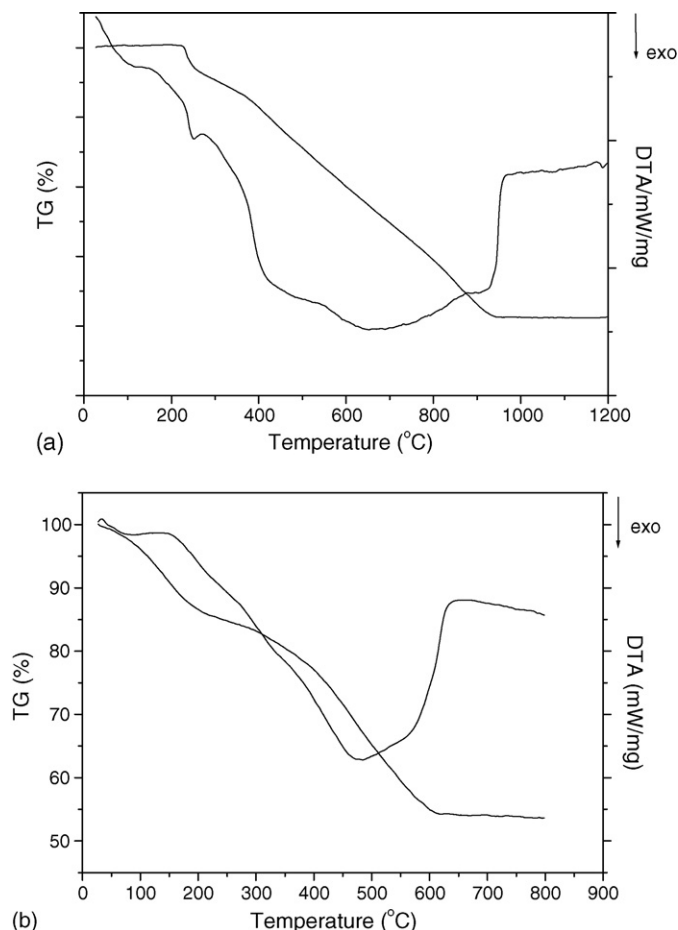


Fig. 1. TG/DTA profiles of (a) neat complex and (b) catalyst.

Table 1
Surface area and pore volume of NaY and Mn(III)-salen-Y

Name	Surface area (m ² /g)	Monolayer volume (cm ³ /g)	Pore specific volume (cm ³ /g)
Na-Y	319	73.16	0.262
Mn-salen-Y	158	36.3	0.120

affected much by the incorporation of the same into the zeolite matrix.

3.4. Surface area and pore volume analysis

The surface area and pore volume of the zeolite and the catalyst are shown in Table 1. The inclusion of Mn(III)-salen complex dramatically reduces the adsorption capacity and the surface area of the zeolite. It has been reported that BET surface area of zeolite Na-X containing Mn-salen complexes are of order 75–135 m²/g [28]. It could be seen from Table 1 that the catalyst has lower surface and pore volume indicating the

presence of Mn(III)-salen complex within the cavities and not on the surface.

3.5. XRD studies

In order to study the changes in the crystallinity of zeolite on incorporation of metal complex, powder XRD studies were carried out. The X-ray powder diffraction patterns of Na-Y and Mn-salen-Y are depicted in Fig. 2a and b, respectively. It can be seen that XRD patterns of both are similar though slight change in the intensity of bands is noticed. This indicates that the framework of the zeolite has not undergone any significant structural changes during encapsulation of Mn-salen.

3.6. Catalytic activity study

Metal complex encapsulated Y-zeolite matrix was tested for its catalytic activity towards the decomposition of H₂O₂. The catalytic activity was observed at different reaction times. The data are presented in Table 2. It is clear from the data that the decomposition of H₂O₂ up to 1 h is relatively slow (4%) with the catalyst. There was above three-fold increase in the percentage of decomposition (14%) after 2 h in comparison to the observed value within 1 h. These results indicate that catalyst [Mn (salen)]-Y requires a longer contact time to improve decomposition of H₂O₂, which in turn would be helpful in improving the oxidation reactions using this as an oxidant.

3.7. Role of H₂O₂ and catalyst

In order to study the catalytic activity of Mn-salen-Y zeolite and the role of H₂O₂ in catalytic oxidation of dye, dye degradation studies with H₂O₂ alone, catalyst alone and both H₂O₂ and catalyst together were carried out. The residual concentrations of dye in the solution after treatment with H₂O₂ alone, catalyst alone, and H₂O₂ with catalyst are given in Fig. 3. It can be seen that system with both H₂O₂ and catalyst gives maximum removal of dye. The residual concentration of dye is 29 mg/L with both H₂O₂ and catalyst whereas it is 42 and 41 mg/L for H₂O₂ alone and catalyst alone, respectively, for an initial concentration of 55 mg/L of dye. This clearly indicates that the activity of H₂O₂ is enhanced in the presence of the catalyst. The presence of catalyst also leads to enhancing the rate of the reaction. This can be seen from the figure, which shows that for the same amount of dye removal, the time taken for the system employing both catalyst and H₂O₂ is less.

Table 2
Percentage decomposition of H₂O₂ by the catalyst after 1 and 2 h of contact time

Time (h)	% H ₂ O ₂ reacted	TOF
1	4	25.1
2	14	87.5

TOF, turn over frequency: moles of substrate converted per mole of metal in solid catalyst per hour.

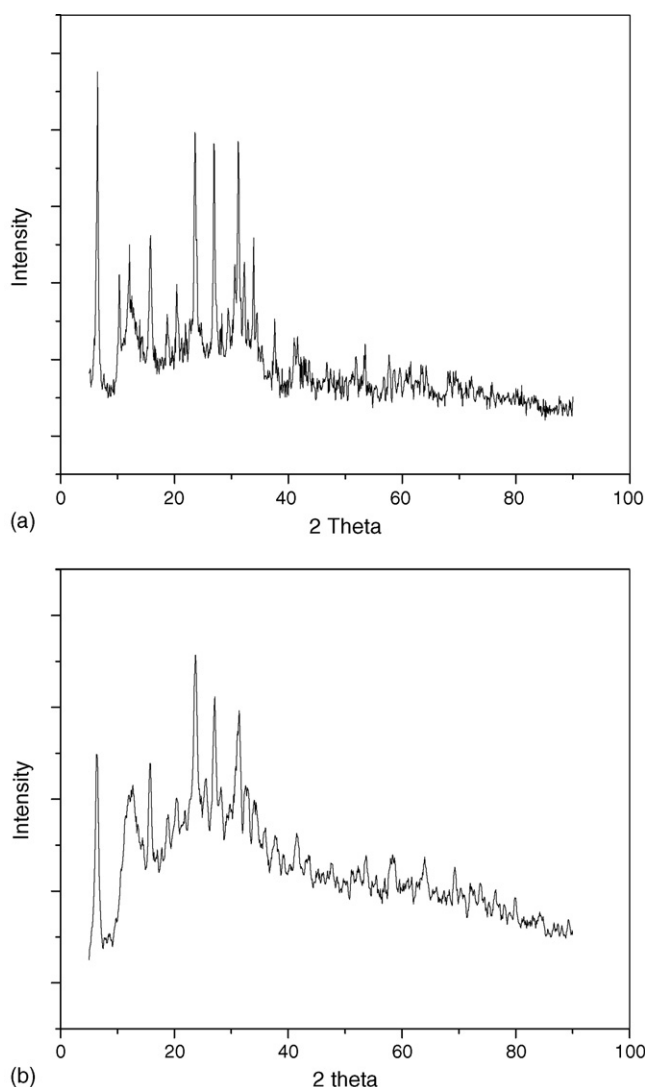


Fig. 2. X-ray powder diffraction spectrum of (a) Na-Y zeolite and (b) catalyst.

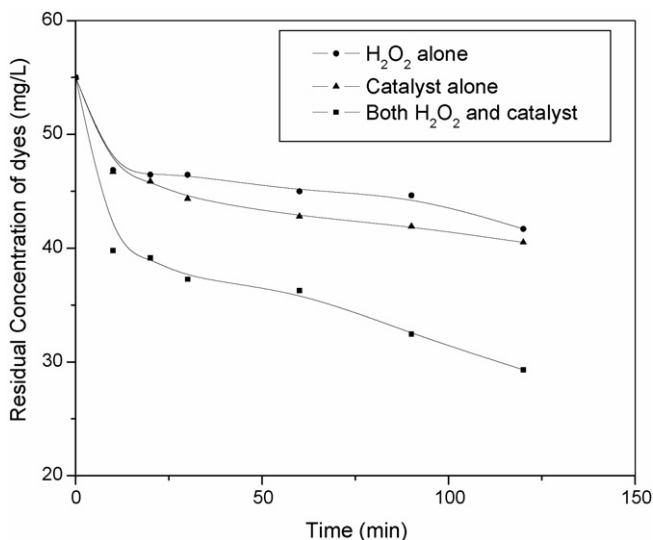


Fig. 3. Role of H₂O₂ and catalyst in the reduction of dye concentration in the effluent. Initial conditions: dye concentration = 55 ppm; temperature = 30 ± 3 °C; pH 8.0.

3.8. Effect of H₂O₂ concentration

The influence of hydrogen peroxide concentration on the oxidation of the dye by Mn-salen-Y as catalyst is presented in Fig. 4. The dependence of the oxidation rate on the initial concentration of hydrogen peroxide was studied by varying its concentration between 0.175 and 0.875 M, while maintaining constant the quantity of catalyst used, dye concentration, pH and temperature. As expected, the increase in H₂O₂ concentration accelerated the dye decolorization at the beginning of the reaction. This can be explained by the effect of OH• radicals produced additionally. However, it can be seen from the figure that after a period of 1 h there was no significant reduction in % dye removal on increasing the concentration of H₂O₂. After a reaction time of 1 h, with a 0.175 and 0.350 M of H₂O₂, color removal of about 78 and 79%, respectively, was obtained. After

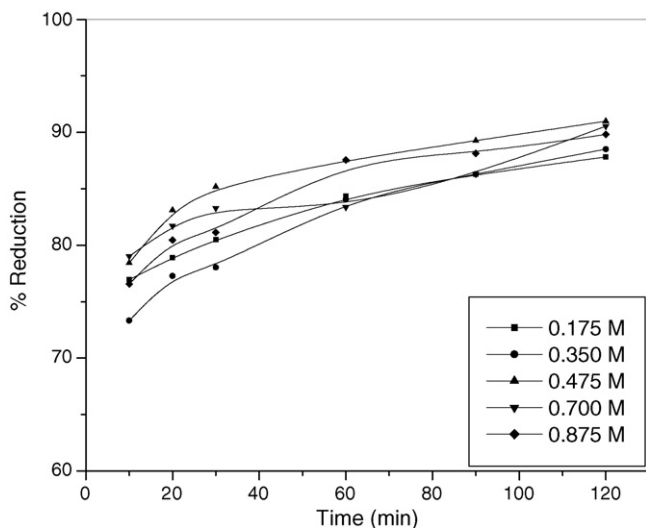
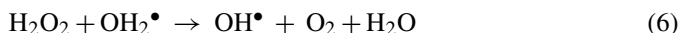
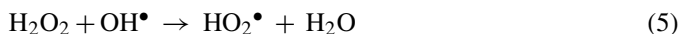


Fig. 4. Effect of H₂O₂ concentration on the oxidation of acid dye. Initial conditions: dye concentration = 55 ppm; temperature = 30 ± 3 °C; pH 8.0.

a period of two hours the % color removal increased to 84–85%. Thus the effective concentration of H₂O₂ was fixed as 0.175 M.

The addition of H₂O₂ is known to increase the rate of dye degradation by allowing an enhancement in the quantum yield of formation of hydroxyl radical. Consequently, the degradation rate is expected to be enhanced. But at high dosage, H₂O₂ is a powerful OH• scavenger.



Thus, the addition of higher concentration of H₂O₂ did not improve much the degradation, could be due to the hydroperoxyl radicals (HO₂•) generated in the presence of a local excess of H₂O₂. Although HO₂• promotes radical chain reactions and is an effective oxidant itself, its oxidation potential is much lower than that of OH•. The hydroperoxyl radicals are much less reactive and do not contribute to the oxidative degradation of organic substrates, which occur only by reaction with OH• [22,29].

3.9. Effect of catalyst concentration

The effect of catalyst concentration on removal of dye was studied by varying the catalyst concentration from 0.2 to 5 g/L and the same is depicted in Fig. 5. It can be seen that with increasing concentration of the catalyst, there is decrease in the residual concentration of dye in the solution indicating increase in the degradation of dye. It can be seen from the figure that above 3 g/L, the removal of dye is not significantly higher. As the concentration of the catalyst was increased, the number of dye molecules adsorbed is increased owing to an increase in the number of zeolite particles. Above certain level, the dye molecules available are not sufficient for adsorption by the increased number of zeolite particles. Hence, the additional catalyst powder is not involved in the catalysis activity and the rate does not

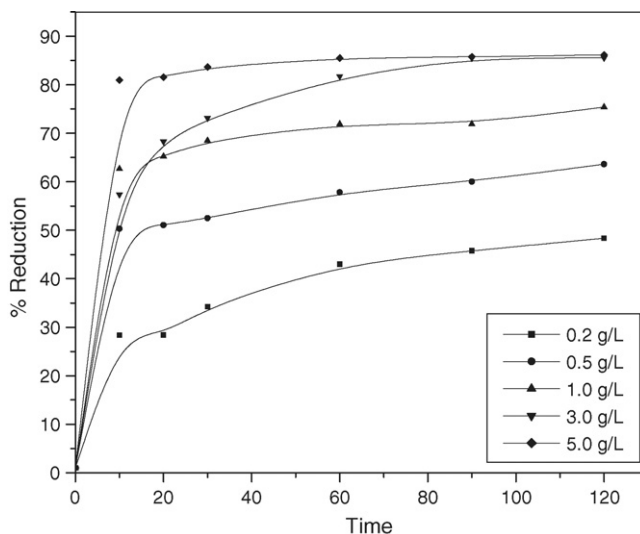


Fig. 5. Effect of catalyst concentration on the oxidation of acid dye. Initial conditions: dye concentration = 55 ppm; temperature = 30 ± 3 °C; pH 2.0.

increase with an increase in the amount of catalyst beyond a certain limit. The aggregation of zeolite particles at high concentration must also be considered, which causes a decrease in the number of the surface active sites available. Further, for the catalyst concentration of 3 and 5 g/L the amount of dye removed is the almost same (about 86%) after 2 h of treatment time. Hence, 3 g/L has been taken as optimum catalyst concentration for further experiments.

3.10. Significance of pH

The influence of pH on the dye oxidation was studied using five solutions with pH values determined initially (2, 3, 4, 5 and 8) and without any modifications or control of the pH during the process. The results obtained for dye removal as a function of the initial pH of the solution at various reaction times are presented in Fig. 6. The maximum conversion of about 90% was achieved after 2 h from the start of the reaction for a pH of 2.0. It can be seen from the figure that there is a decrease in % removal as the pH is increased from 2 to 8. The reason could be that Fenton type reactions are known to work better in acidic pH range. Earlier studies on heterogeneous Fenton system have shown that lower pHs are favored for maximum removal of dyes [22,23]. At higher pH, many transition metal complexes are known to form hydroxo species and such species are less effective in a Fenton type reaction. Thus the optimum pH for other experiments was maintained at 2.0.

3.11. Role of temperature

The influence of temperature on the dye removal using Mn-salen-Y was studied by varying the temperature from 30 to 60 °C. The % reductions in dye for the different temperatures are shown in Table 3. It can be seen from the table that the increase in the % reduction of dye is only marginal on increasing the temperature. Hence, further experiments were carried out at the room temperature (30 ± 1 °C).

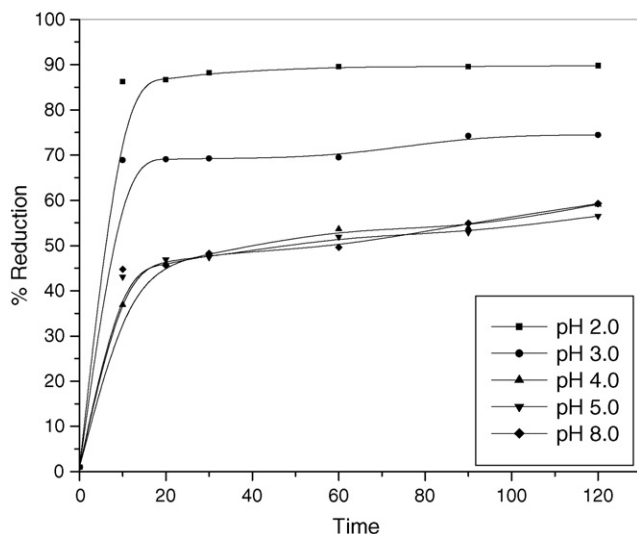


Fig. 6. Effect of pH on the oxidation of acid dye. Initial conditions: dye concentration = 55 ppm; temperature = 30 ± 3 °C; catalyst concentration = 3.0 g/L.

Table 3
Effect of temperature on dye degradation

Temperature (°C)	Concentration of dye (mg/L) ^a	% reduction
30 ± 1	5.75	81.56
40 ± 1	6.73	84.25
50 ± 1	6.85	84.52
60 ± 1	8.02	86.76

^a Initial concentration of dye = 43.46 mg/L.

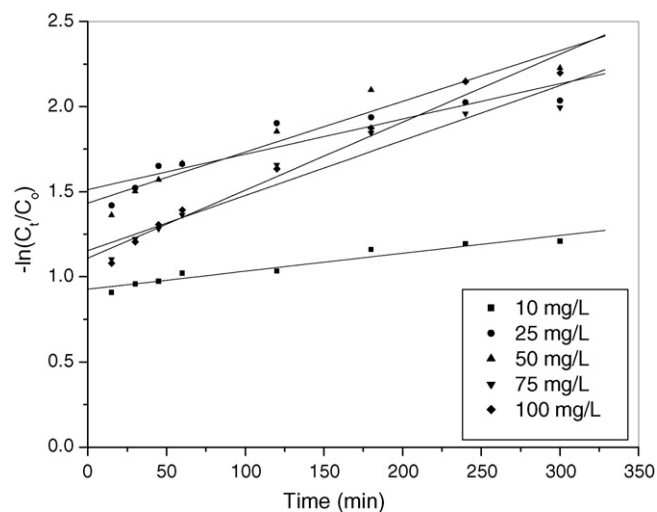


Fig. 7. Pseudo-first order kinetic plot at various initial concentrations. Initial conditions: temperature = 30 ± 3 °C; catalyst concentration = 3.0 g/L; pH 2.0.

3.12. Kinetic studies

Kinetic study is important for any catalytic reaction and helps in identifying the reaction pathway and rate dependence on the limiting reaction systems. The kinetic measurements were carried out under pseudo-first order conditions with respect to the acid dye. The observed rate constant, k_0 , was determined from graphical fit (Fig. 7) to the following equation:

$$\ln C_t = \ln C_0 - k_0 w t \quad (8)$$

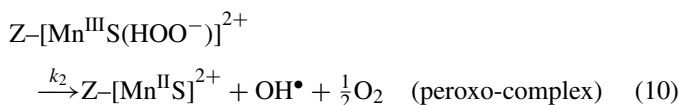
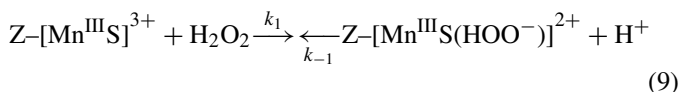
where C_t is the concentration of dye at time = t , C_0 the initial concentration of dye and w is the amount of the catalyst used. The k_1 (Table 4) value per gram of the dry catalyst was determined from the slope of the plot $-\ln(C_t/C_0)$ versus time (t). The straight lines in the plot indicate that the decolorization rate is pseudo-first order with respect to C_0 .

Table 4
Kinetic constants of the first order plot

Concentration of dye (mg/L)	k_1 ($\times 10^{-4} \text{ min}^{-1}$)	R^2
10	3.5	0.935
25	6.9	0.863
50	9.97	0.937
75	10.77	0.938
100	13.3	0.974

3.13. Reaction mechanism

The possible mechanism for the degradation could be explained as follows. In the redox sites of the zeolite, Mn^{3+} is converted into Mn^{2+} by protons of the reaction medium. Then by a Fenton type reaction OH^\bullet is formed by reaction with H_2O_2 that can carry out the electrophilic attack to the aromatic ring of the substrate. This highly active intermediate can be decomposed in the rate-determining step, giving the final oxidation products as follows:



from Eq. (9), the concentration of the peroxo-complex is given by:

$$Z-[Mn^{III}S(HOO^-)]^{2+} = \frac{K_1[Z-[Mn^{III}S]^{3+}][H_2O_2]}{[H^+]} \quad (15)$$

where $K_1 = k_1/k_{-1}$.

Applying steady state approximation for the determination of $[OH^\bullet]$ and $[AB(OH^\bullet)]$:

$$\frac{d[OH^\bullet]}{dt} = k_2[Z-[Mn^{III}S(HOO^-)]^{2+}] - k_3[AB][OH^\bullet] - k_5[Z-[Mn^{II}S]^{2+}][OH^\bullet] = 0 \quad (16)$$

Assuming that

$$Z-[Mn^{III}S(HOO^-)]^{2+} = Z-[Mn^{II}S]^{2+}$$

and by substituting from Eq. (15) in Eq. (16), we get:

$$[OH^\bullet] = \frac{k_2 K_1 [Z-[Mn^{III}S]^{3+}][H_2O_2]}{k_3 [AB][H^+] + k_5 K_1 [Z-[Mn^{II}S]^{2+}][H_2O_2]} \quad (17)$$

and

$$\frac{d[AB(OH^\bullet)]}{dt} = k_3 [AB][OH^\bullet] - k_4 [AB(OH^\bullet)] = 0 \quad (18)$$

Thus by substituting from Eq. (17) in (18), we get:

$$[AB(OH^\bullet)] = \frac{k_2 k_3 K_1 [AB][Z-[Mn^{III}S]^{3+}][H_2O_2]}{k_3 k_4 [AB][H^+] + k_4 k_5 K_1 [Z-[Mn^{II}S]^{2+}][H_2O_2]} \quad (19)$$

The rate-determining step, Eq. (12) expresses the rate equation and is given by:

$$\text{rate} = k_4 [AB(OH^\bullet)] \quad (20)$$

Thus by substitution from Eq. (19) in (20), we get:

$$\text{rate} = \frac{k_2 k_3 K_1 [AB][Z-[Mn^{III}S]^{3+}][H_2O_2]}{k_3 [AB][H^+] + k_5 K_1 [Z-[Mn^{II}S]^{2+}][H_2O_2]} \quad (21)$$

using the initial concentrations of both reactants, $[H_2O_2]_0$ and $[AB]_0$ and since,

$$[H_2O_2]_0 = [H_2O_2]_{\text{free}} + [Z-[Mn^{III}S(OOH^-)]^{2+}] + [OH^\bullet] \quad (22)$$

Thus substituting from Eqs. (15) and (16) and assuming that:

$$k_3 [AB][H^+] \ll k_5 K_1 [Z-[Mn^{III}S]^{3+}][H_2O_2]$$

therefore:

$$[H_2O_2]_{\text{free}} = \frac{[H^+]\{k_5 [H_2O_2]_0 - k_2\}}{k_5 [H^+] + k_5 K_1 [Z-[Mn^{III}S]^{3+}]} \quad (23)$$

Also,

$$[AB]_0 = [AB]_{\text{free}} + [AB(OH^\bullet)] \quad (24)$$

Substituting from Eq. (19) and assuming that:

$$k_3 k_4 [AB][H^+] \ll k_4 k_5 K_1 [Z-[Mn^{III}S]^{3+}][H_2O_2] \quad (25)$$

$$[AB]_{\text{free}} = \frac{[AB]_0 k_4 k_5}{k_4 k_5 + k_2 k_3}$$

$$\text{rate} = \frac{k_2 k_3 k_4 k_5 K_1 [AB]_0 x [Z-[Mn^{III}S]^{3+}][H_2O_2]_0}{k_3 k_4 k_5 [AB]_0 x \{ [H^+] + K_1 [Z-[Mn^{III}S]^{3+}] \} + K_1 k_5 [Z-[Mn^{III}S]^{3+}] x [H_2O_2]_0 \{ K_1 k_5 k_4 + k_2 k_3 \}}$$

From Eqs. (21), (23) and (25), the rate is given by assuming that $k_4 k_5 K_1 \gg k_2 k_3$, therefore, we get:

$$\text{rate} = \frac{k_2 k_3 K_1 [AB]_0 x [Z-[Mn^{III}S]^{3+}][H_2O_2]_0}{k_3 [AB]_0 x \{ [H^+] + K_1 [Z-[Mn^{III}S]^{3+}] \} + K_1^2 k_5 [Z-[Mn^{III}S]^{3+}][H_2O_2]_0} \quad (26)$$

Eq. (26) shows that at lower $[AB]_0$, the first term in the denominator becomes very small compared with the second and can be neglected. Therefore, the rate attaining a first order dependence on the $[AB]_0$. However, with increasing $[AB]_0$, the rate decreases and attains a limiting rate at higher concentration. This equation also predicts that reaction rate has a first order dependence on $[H_2O_2]_0$ at low concentrations. With increase in concentration of H_2O_2 , the rate decreases and attaining a limiting value at high concentrations.

4. Conclusion

It is evident from the above studies that Mn-salen-Y can successfully be employed for the oxidative removal of dyes from

wastewaters. This is a simple and cost effective method for the treatment of dye containing wastewater. Flexible ligand method has been adopted for the incorporation of the metal complex in to the zeolite matrix and the IR studies confirm the same. TG/DTA studies show that the stability of complex is not affected on encapsulation. XRD studies show that crystallinity of the zeolite matrix is unaltered after incorporation of the metal complex. Optimum conditions required for 90% removal is 20 min at 30 °C, with 0.175 M H₂O₂ and 3 g/L catalyst. The advantages of this method include recyclable catalyst and no iron sludge formation unlike the other known homogeneous catalytic methods.

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