

MnO₂ Catalysed Microwave Mediated Removal of Trace Amounts of Indigocarmine Dye from Water

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Abstract: The application of microwave (MW) catalysis using MnO₂ as catalyst for the removal of trace amounts of the dianionic dye Indigocarmine (IC) from water is investigated. Comparison of thermal and MW initiated degradation under identical conditions show that the MW degradation is much faster thus suggesting that the MW effect is not just heating the reaction system. The presence of semiconductor oxide catalysts ZnO or TiO₂ which are known to enhance the degradation in photocatalysis is not effective in the presence of MW. Addition of H₂O₂ inhibits the MW-assisted degradation initially. This is attributed to the absorption of MW by H₂O₂ and its degradation to inactive H₂O and O₂. Further, H₂O₂ consumes some of the reactive ·OH radicals which could have been beneficially used by the IC for its degradation. The microwave radiation may not be affecting the surface characteristics of the semiconductor as in the case of other AOPs even though the lattice oxygen removed from the catalyst plays significant role. This lattice oxygen vacancy is later replenished by dissolved oxygen taking MnO₂ to its original composition. The degradation is maximum under extreme acidic and alkaline conditions in both thermal and MW processes. H₂O₂ formed in the reaction undergoes concurrent formation and decomposition resulting in oscillation in its concentration though the phenomenon is not consistently reproducible. The observations are analysed and a general mechanism is proposed.

Key words- Hydrogen peroxide, indigo carmine, manganese dioxide, microwave

I. INTRODUCTION

Microwave radiation is extensively used in recent years in several domestic, industrial and medical applications such as inorganic and organic synthesis, polymerization, food sterilization, environmental remediation, waste treatment etc. [1- 7]. Due to its capability for molecular level heating, increased selectivity of reaction, lower activation energy and ease of control, MW as well as its combination with other energy sources has been increasingly investigated as a possible tool for wastewater treatment [8-12]. The technique may be useful especially for the removal of non-degradable materials from wastes. The heterogeneous processes occurring in MW assisted catalytic reactions at solid/solid, solid/liquid, solid/gas or liquid/gas interfaces can be beneficially tailored in environmental remediation. MW alone, being a low energy radiation with $E = 1.6 \times 10^{-3}$ eV may not be able to degrade many pollutants. However, in combination with light and H₂O₂, MW has been found highly efficient for the degradation of many pollutants such as dyes, phenolic compounds, pesticides and sulphonated aromatic compounds. Horikoshi et al. [13] demonstrated that MW irradiation can accelerate the photocatalytic degradation of RhB in presence of UV/TiO₂. Similar results were reported in the case of photocatalytic oxidation of ethylene over TiO₂/ZrO₂ [6]. Improvement of UV/H₂O₂ oxidative decomposition of aqueous phenol by MW radiation [14] and carbofuran degradation by MW/H₂O₂ process [10] have been reported.

The limitation of MW is that most of the organic compounds do not absorb electromagnetic energy in the S-band (2.4 GHz) of the MW. Hence identification of materials that absorb considerable MW and then transfer the energy to the reactant is important [12, 15, 16]. In addition to the widely recognized thermal role, MW could also induce organization of the irradiated medium known as “athermal effect”, “nonthermal” or “specific effect” of electromagnetic radiation [17]. The level of coupling with the electric field of MW radiation relies on the dielectric constant of the material. The dielectric constant determines the ability of the material to be polarized by an electric field [17]. Interaction of MW with dipolar molecules or ionic species results in rapid heating [18]. MnO₂ has dielectric constant of approx. 10000 and hence very good coupling with MW radiation is possible [12]. Further, MnO₂ has excellent semiconductivity, porosity and mixed-valent properties which make it a probable catalyst for many applications. Considering these, in the current study, the application of

MnO₂ as an MW catalyst for the degradation of one of the widely used special application dye, i.e. Indigo carmine (IC) is examined.

Indigo Carmine (3,3'-dioxo-1,3,1',3'-tetrahydro-[2,2']-bi-indolylidene-5,5'-disulphonic acid disodium salt) is an important industrial dye used for dyeing of clothes and also for medical diagnostic purposes. It can also help to target biopsies even better since the homogeneously stained or unstained areas can be correlated with intraepithelial neoplasia [19]. The chemical structure of IC is as in Fig. 1.

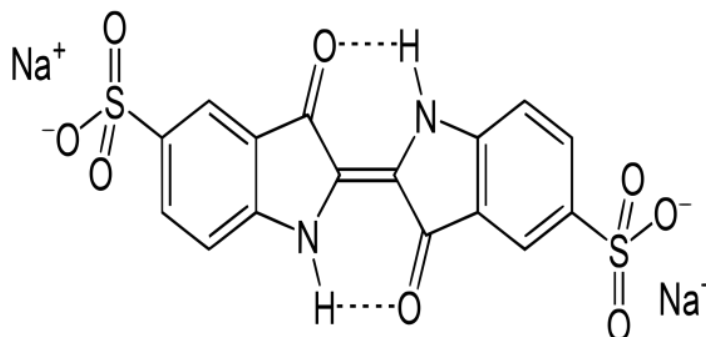


Figure1: Chemical structure of Indigo carmine

The dye is highly toxic, carcinogenic and has the potential to cause permanent injury to eyes. It can also lead to reproductive, developmental disorders and neuro and acute toxicity. Other health effects include possible tumors at the site of application, cardiovascular and respiratory effects and gastrointestinal irritation [20]. Extensive application of the dye will naturally lead to environmental contamination through different routes, in particular water. Many investigations aimed at the removal of the dye from water have been reported [21-25]. Most of these are based on Advanced Oxidation Processes (AOP), especially photocatalysis.

In the present study we are reporting the results of our investigations on the application of Microwave catalysis with MnO₂ as the catalyst for the removal of IC in small concentrations from water. The efficacy of the MW based technique is evaluated by examining the degradation of IC under various reaction conditions and identifying the optimum parameters.

II. MATERIALS AND METHODS

MnO₂ used in the study was supplied by Merck India Limited. The particles were approximately spherical and nonporous with over 99% purity. The surface area of MnO₂ as determined by the BET method is 31 m²/g. Indigo carmine (AnalaRExtra Pure Grade 99.5% purity) from Sisco Research Laboratories Pvt. Ltd (India) was used as such without further purification. Doubly distilled water was used in all the experiments. All other chemicals were of AnalaR Grade or equivalent. The pore volume of MnO₂ was approximately 0.05 cm³/g and the average pore width was 74.2 Å.

The experiments were performed using aqueous solutions of IC of desired concentration. Simple Pyrex glass reactor is used for the experiments. The temperature is noted using digital pyrometer. In the case of experiments with added catalysts, specified quantity of the catalyst is suspended in the solution and kept in suspension by periodic mechanical mixing. A microwave oven of 2450 MHz frequency and variable power up to 500W was used in the experiments. The reactor was placed in the microwave oven as done normally. Up to eight reactors could be placed in the oven at a time. As and when required, an in-house designed jacketed reactor with provision for circulating water was used. Experiments were initiated by supplying the desired power to the system. The reaction temperature was not allowed to go above 40^oC and controlled by regulating coolant water flow/switching off the MW oven periodically. For experiments with added H₂O₂, appropriate quantity of H₂O₂ solution in water was introduced into the IC solution such that the net concentration of both will be as desired. Periodically samples were drawn, centrifuged in the case of experiments with catalysts to remove the suspended materials and analysed for IC using Spectrophotometry at 608 nm. Whenever required, H₂O₂ concentration is determined by standard iodometry. Conventional Heating (CH) experiments were conducted in a water bath instead of the microwave oven under otherwise identical conditions. The removal efficiency (%) was calculated by applying the following equation.

$$\text{Removal efficiency} = [(C_0 - C)/C_0] \times 100 \quad (1)$$

Where C_0 is the initial IC content and C is the content retained in solution at any point in time.

Adsorption studies were performed as follows [26, 27]:

A fixed amount (0.1 g) of the catalyst was added to 100 ml of IC solution in a 250 ml flask and the pH was adjusted as required. The suspension was agitated continuously at constant temperature of $29 \pm 1^\circ\text{C}$ for 2hrs to achieve equilibrium. This was then centrifuged at 3000 rpm for 10 min. After centrifugation the concentration of IC in the supernatant was determined colourimetrically. The adsorbate uptake was calculated from the relation

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where C_0 is the initial adsorbate concentration (mg/L), C_e is the equilibrium adsorbate concentration in solution (mg/L), V is the volume of the solution in Liter, W is the mass of the adsorbent in gram and q_e is the amount adsorbed in mg per gram of the adsorbent.

III. RESULTS AND DISCUSSION

Preliminary investigations on the use of microwave irradiation in environmental remediation were made using various types of catalytic materials for the degradation of small concentration of IC in water. Of the various semiconductor oxides tested, MnO_2 was found to be the most efficient catalyst in MW. Typical results are shown in Fig.2.

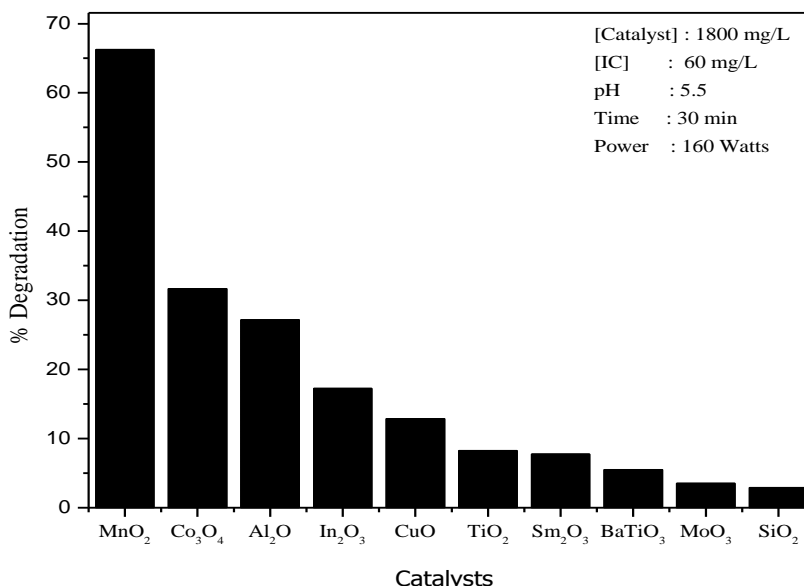


Figure2: MW assisted degradation of IC in presence of various catalysts

As can be seen, MnO_2 is at least 8 times more active than TiO_2 . Hence the MnO_2 catalysed MW degradation of the dye is investigated in detail. Since MW irradiation leads to rise in temperature of the reaction system, the degradation is compared with the results under identical conditions using conventional heating (CH) as well as normal room temperature (RT). See Fig.3.

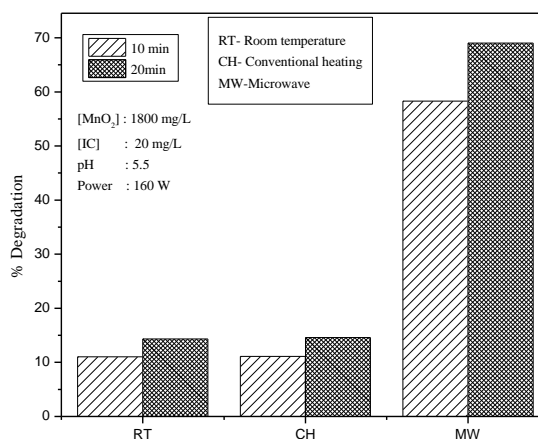


Figure3: Comparative degradation of IC in presence of MnO₂ under various conditions

At catalyst loading of 0.18 g/L, even at room temperature with no irradiation the concentration decreases by about 11% in 10 minutes time which is probably due to adsorption. Under CH conditions also, in presence of MnO₂ the concentration falls by only 11%. Hence the degradation of IC under thermal condition alone is not significant. Under similar conditions, the degradation is about 60% in presence of MW irradiation in 10 minutes and 70% in 20 minutes, clearly demonstrating the role of MW irradiation in the degradation of IC in presence of MnO₂. In the absence of catalyst, the decrease in concentration is negligible at comparable temperature of 40°C.

The effect of various reaction parameters on the degradation of IC under MW irradiation is investigated in detail.

3.1. Effect of MnO₂ dosage

The effect of MnO₂ dosage on the degradation is as in Fig.4.

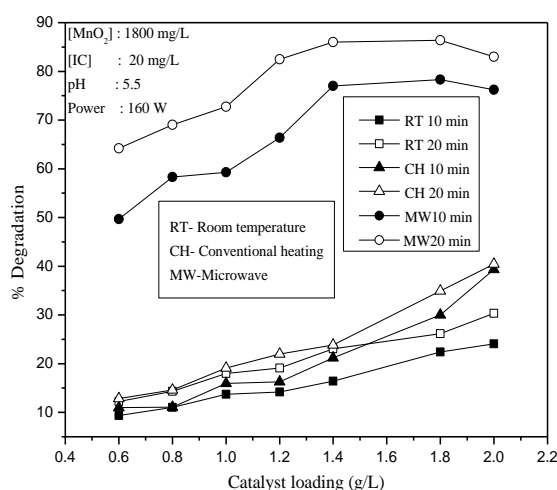


Figure4: Effect of catalyst dosage on the degradation of IC under MW, CH and RT

As expected, the degradation increases with increase in loading both under CH and MW conditions. In the case of CH the degradation continues to rise gradually even at the dosage of 2 g/L studied here. The slow decrease in the concentration of IC even at room temperature is due to the adsorption of the dye on the catalyst. The adsorption as measured at different concentrations at room temperature is very small and does not change

much with concentration in the range 10-100 mg/L. However in the case of MW experiments the degradation levels off at 1.4-1.8g/L.

Naturally, at higher loadings there will be more number of adsorption sites and hence better adsorption of the dye leading to more effective MW activity and degradation. However, at very high loadings, there may be aggregation of catalyst particles causing decrease in the number of available active surface sites and reduced adsorption of the substrate on the surface. The particles cannot be fully and effectively suspended beyond a particular loading in a particular reactor which also leads to suboptimal penetration of radiation. However, the optimum catalyst loading will also depend on the size, shape and geometry of the reaction assembly. Hence, for each reactor configuration the optimization has to be made separately.

Since the optimum loading of MnO₂ under MW is 1.8g/L, all further experiments were carried out with this dosage.

3.2. Effect of concentration of IC

The percentage degradation of IC in MW/MnO₂ systems decreases with increase in concentration as shown in Fig.5.

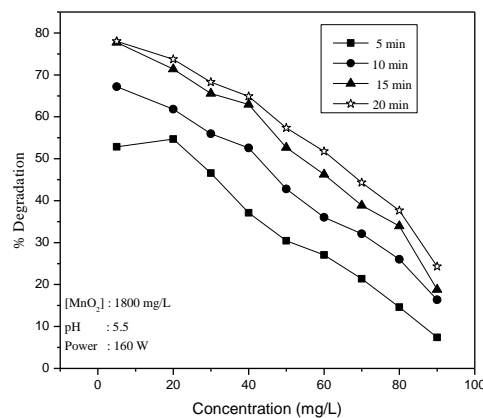


Figure5: Percentage degradation Vs concentration of IC at different irradiation times

The trend remains more or less the same after different durations of irradiation. The rate of degradation as a function of concentration at various times of irradiation is computed and shown in Fig.6.

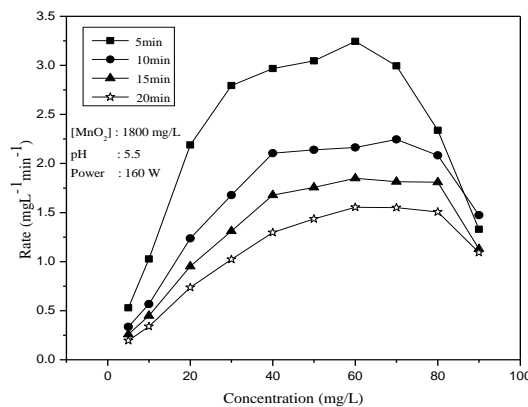


Figure6: Rate of degradation of IC at various concentrations

The rate increases with increase in concentration from 5 to 40 mg/L and almost levels off in the range 40-70 mg/L and decreases again. This is similar to most of the AOP systems which are shown to follow pseudo first order kinetics at lower concentrations.

The influence of initial concentration of the substrate on the AOP degradation rate of most organic compounds is explained based on pseudo-first order kinetics which is rationalized in terms of the Langmuir-Hinshelwood model, modified to accommodate reactions occurring at solid-liquid interface [28,29]. The simplest way to represent the degradation, assuming that there is no competition with reaction by-products/intermediates is

$$r_0 = -dC/dt = k_rKC_0 / (1+KC_0) \quad (3)$$

where r_0 is the rate of disappearance ($\text{mg L}^{-1} \text{min}^{-1}$) and C_0 is the initial concentration (mg L^{-1}) of reactant. K is the equilibrium adsorption coefficient of the reactant and k_r is the optimum reaction rate constant. Equation 3 can be rewritten as

$$1/r_0 = 1/k_r + 1/k_rK * 1/C_0 \quad (4)$$

Plot of $1/r_0$ against $1/C_0$ yields straight line in the concentration range 5-40 mg/L confirming first order kinetics and L-H mechanism (Fig.7).

At higher concentrations the rate remains almost the same irrespective of the concentration and attains zero order kinetics. It is also to be noted that the rate of reaction decreases with time of irradiation. The concentration of IC remaining in the system decreases as the reaction progresses and correspondingly the rate of degradation also decreases.

3.3. Effect of MW power

Increase in MW power enhanced the degradation of IC as shown in Fig. 8.

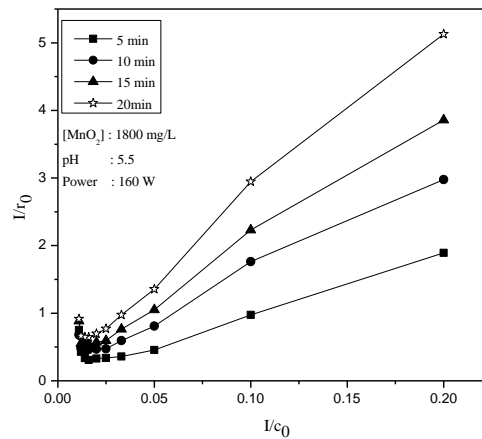


Figure7: Reciprocal plot of $1/r_0$ Vs $1/C_0$ for various concentrations of IC

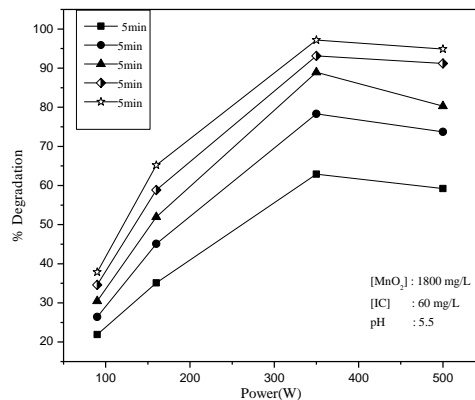


Figure8: Effect of MW power on the degradation of IC in presence of MnO₂

When the power increased ~4 times from 90W to 350 W, keeping all other parameters constant, the degradation almost tripled from ~ 22% to ~ 63% in 5 minutes time. The degradation remained more or less same at 350 and 500 W indicating an optimum power for the degradation under the reaction conditions. However, since the degradation is quite fast at higher MW, to avoid the over-volatilizing of water during the reaction, all further experiments were carried out at 160W and for 10 and 20 minutes at which, the rate of degradation is proceeding at reasonable rates and can be followed more correctly and consistently.

The increase in MW power is known to increase the temperature and hence the degradation at higher power can be partially attributed to this. The lack of correlation between power and degradation at higher input power can be attributed to the difference in the effect of temperature on various intermediates formed during the degradation of the pollutant [13]. At higher power, more intermediates such as oxalic acid, acetic acid, nitrobenzene, malic acid etc may be getting accumulated in the system [21, 30] and the effect of MW may be relatively more on them than the IC. MW which is a kind of electromagnetic wave, with very small wavelength causes about 2.45 billion times of vibrations /translations/rotations of water molecules [31]. These kinds of molecular movements can contribute to increasing the temperature and increasing the rate of degradation, the rates being different for different molecules.

3.4. Effect of Temperature

The effect of temperature in presence of MW on the degradation of organics is a matter of contention often. Our studies show that in the presence of MW, the degradation is not due to the heat generated by it, even though the thermal contribution cannot be fully ruled out. For e.g. in the current case, under CH conditions of ~37°C, for an initial concentration of 20 mg/L of IC, the degradation is ~20% in 20 minutes while under identical conditions but in presence of MW the degradation is over 4 times more i.e. ~85% during the same period (Fig. 4). That the effect of temperature is not the major factor in the MW catalytic degradation of pollutants is further proven from the experiments under controlled temperature conditions in presence of MW. The results are given in Fig. 9.

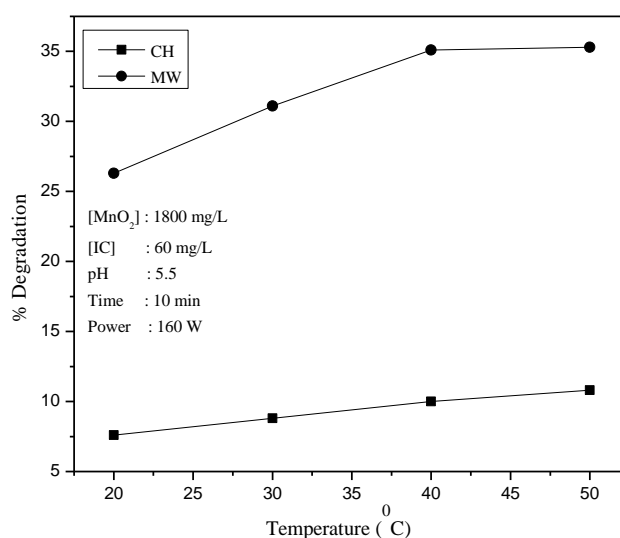


Figure 9: Effect of temperature on the degradation of IC in presence of MW radiation

As the figure shows, even at a low temperature of 20°C, the degradation in presence of MW irradiation is 26% in 10 minutes while it is only 7.5% in case of CH. The degradation increases with increase in temperature in presence of MW. However, just as in the case of optimum MW power as seen in figure 8, in presence of MW there is an optimum temperature beyond which the degradation is stable. In the case of CH the degradation increases slowly with temperature and is more or less stabilized in the range 40-50°C. Hence it may be concluded that temperature does affect the degradation of IC in presence of MW, while the effect is less pronounced in the absence of MW.

3.5. Effect of pH

The effect of pH on the degradation of IC in presence of MW/MnO₂, CH/MnO₂ and RT/MnO₂ under otherwise identical conditions is shown in Fig. 10.

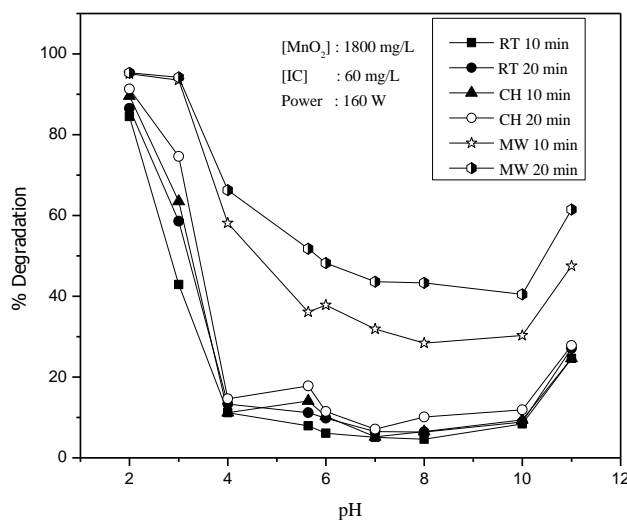


Figure 10: Effect of pH on the MW degradation of IC

At all pH, the degradation follows the order MW/MnO₂ > CH/MnO₂ > RT/MnO₂. The degradation remains more or less steady at their respective values under all three conditions in the pH range of 5-10. The degradation is high at pH < 4 and > pH 10 in all cases. The drastic shift in degradation occurred below pH 4 which can be explained based on the point of zero charge (PZC) of ~ 4.7 of MnO₂ [32]. Below this pH value the surface is positively charged and hence its oxidizing ability can be sharply enhanced. IC is a dianionic dye in aqueous solution and it can keep the dianionic configuration in the pH range 3-11 [24]. At low pH electrostatic interaction between the positive catalyst surface and the dianions can lead to strong interaction and subsequent reaction. Heterogeneous degradation is known to be initiated with the formation of precursor complex between the target contaminants and surface bound Mn [33]. Electrons are transferred from the organic compound to the surface bound Mn(IV) on the MnO₂ surface. This results in the oxidative degradation of the pollutant and Mn(II) is reductively dissolved from MnO₂ into bulk solution. Thus MnO₂ can also play the role of an oxidant. Dissolved O₂ in solution can oxidize the Mn(II) to Mn(IV) oxide again. In this respect MnO₂ plays the role of a catalyst and dissolved O₂ acts as the oxidant. It is the solution pH beyond the PZC that promotes the re-adsorption of free Mn(II) ions in solution back onto MnO₂ surface which is responsible for the catalytic oxidation. At the natural pH of 5.6 of the reaction system, MnO₂/CH is ~2 times more efficient than MnO₂/RT while MW/MnO₂ is ~ 4.5 times more active than RT/MnO₂. The alleviation of pH dependence of MnO₂ assisted degradation of Methylene blue by MW [32] is not seen in the present context. High degradation under extreme pH of 2 shows that it is due to pH induced degradation with little contribution from MW or CH. However, MW and CH play an accelerating role once the reaction is initiated. The dramatic increase in the degradation of IC at around pH 2 has been reported during the photocatalytic oxidation of the dye on Mn supported TiO₂ [24]. Since the IC keeps its anionic configuration upto around pH 11 only the neutral species of the hydrophilic IC can accumulate on the surface or at least come closer to the MnO₂ around this pH. It may be inferred that at higher pH, when there are more OH ions present in the system, formation of more reactive ·OH radicals is possible and this can interact with the IC in close proximity to the surface and cause higher degradation.

However, the pH effect is very complex and needs to be investigated in detail.

3.6. Effect of added H₂O₂

In many AOPs the reaction is accelerated by extra ·OH radicals. Hence the effect of addition of H₂O₂ which can form OH radicals under MW irradiation as in (5) below on the degradation of IC is examined.



However in the present context, addition of H₂O₂ decreased the degradation of IC initially (Fig.11).

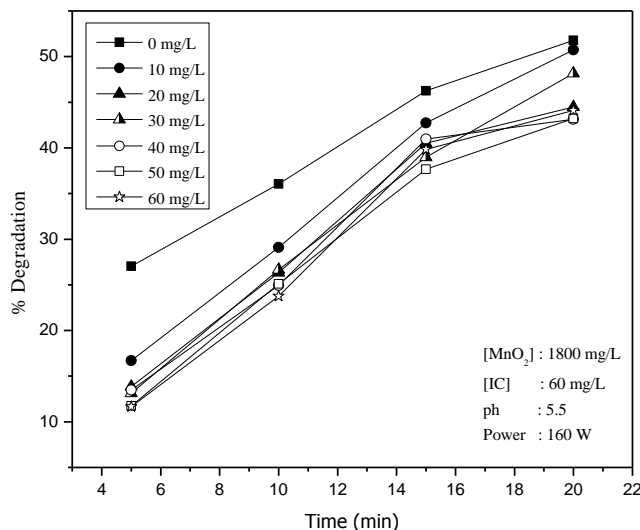
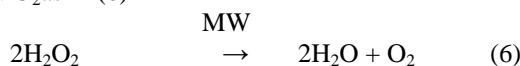


Figure 11: Effect of added H₂O₂ on the degradation of IC

In the presence of MW radiation, H₂O₂ is known to absorb MW energy and undergo decomposition to H₂O and O₂ as in (6)



This naturally results in decrease in the MW available for the catalyst and the substrate as well as reduction in the availability of reactive OH radicals which lead to decrease in the degradation of IC. It is also known that H₂O₂ is formed insitu in the system though its concentration does not increase with time and undergoes periodic oscillation as shown in Fig.12.

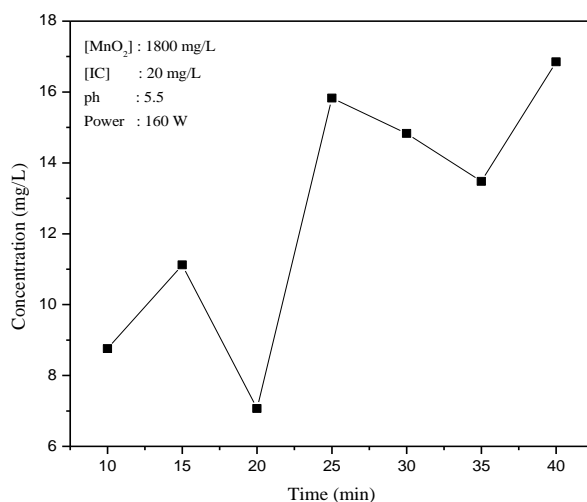
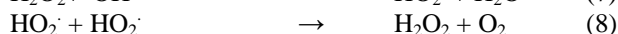
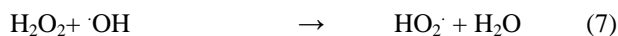


Figure 12: Oscillation in the concentration of H₂O₂ formed during the MW degradation of IC

Similar results are reported in the case of sono, photo and sonophotocatalytic degradation of organic pollutants in water [34-36]. However, the actual quantity of H₂O₂ formed in the system is not reproducible in

repeated experiments and instances of complete absence of H₂O₂ are also observed. This inconsistency may be due to the strong adsorption and/or decomposition of H₂O₂ in the presence of MnO₂. In addition to reactions (5) and (6), the concurrent decomposition of H₂O₂ takes place as follows:



The HO₂· thus formed is less reactive compared to ·OH radicals resulting in decreased degradation of the substrate. Thus H₂O₂ serves simultaneously as producer and scavenger of ·OH radicals. Part of the OH radicals formed from the decomposition of H₂O₂ will be used for the degradation of IC and the other part will be interacting with H₂O₂ itself and degrade it. Thus the net OH radicals available for degrading the dye are reduced resulting in decreased degradation. This concurrent formation and decomposition of H₂O₂ as well as various other complex free radical interactions together with the partial absorption of MW by H₂O₂ result in decreased degradation.

3.7 General mechanism

MnO₂ is a strong MW absorbent which can significantly absorb and transfer MW energy. This could create large amounts of 'hot spots' which could enhance the degradation of molecules [37]. Electrophilic O₂ ions such as O₂⁻, O⁻ and O²⁻ which are derived from lattice oxygen of MnO₂ show high activity in catalytic reaction [38] and could participate in the degradation of IC. The vacancies of lattice oxygen are later replenished by molecular oxygen dissolved in solution [39]. The reaction is very slow in presence of MW only without catalyst, probably because the energy of the MW photons is quite low (10⁵eV) compared to chemical bonds. Hence MW alone cannot initiate a degradation reaction while in presence of a catalyst like MnO₂, it can initiate and accelerate the reaction. The degradation is more in the case of MW/MnO₂ compared to CH/MnO₂ suggesting that it is not only the thermal effect that is responsible for the degradation, though its contribution cannot be ruled out.

Various Reactive Oxygen Species (ROS) such as H₂O₂, HO₂·, ·OH etc formed from the lattice, surface and dissolved oxygen as explained earlier, can interact with IC leading to its degradation and eventual mineralization as in the case of many AOPs



The study clearly shows that MnO₂ is one of the most efficient MW catalysts for the removal of organic pollutants in trace amounts from water.

IV. CONCLUSION

Trace amounts of the toxic pollutant dye IC in water can be degraded and eventually mineralized by MnO₂ in presence of MW irradiation. The degradation is much faster compared to identical thermal conditions suggesting that the MW effect is not just heating the reaction system. The degradation follows variable kinetics with pseudo first order at lower concentration range and zero order at higher concentration. The degradation is pH dependent with enhanced degradation at extreme acidic and alkaline pH. Addition of H₂O₂ inhibits the MW assisted degradation which is attributed to the absorption of MW by H₂O₂ and its degradation to inactive H₂O and O₂. Further, H₂O₂ consumes some of the ·OH radicals which could have been beneficially used by the IC for its degradation. H₂O₂ formed in the reaction undergoes concurrent formation and decomposition resulting in oscillation in its concentration as in the case of photo and sonocatalysis though the phenomenon is not observed consistently. The microwave radiation may not be affecting the surface characteristics of MnO₂ as in the case of other AOPs even though the lattice oxygen removed from the catalyst plays significant role. This lattice oxygen vacancy is later replenished by dissolved oxygen taking MnO₂ to its original composition.

V. Acknowledgements

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