

Microwave Assisted Catalytic Degradation of Traces of RhodamineB in Water in Presence of H₂O₂

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Abstract: The degradation of trace amounts of the cationic dye RhodamineB (RhB) pollutant in water in the presence and absence of catalysts investigated under microwave (MW) irradiation. The degradation is much faster compared to identical thermal conditions thus suggesting that the MW effect is not just heating the reaction system. The presence of semiconductor oxide catalyst ZnO which is known to enhance the degradation of many organic chemical pollutants photocatalytically enhances the degradation in presence of MW as well. Addition of H₂O₂ enhances the MW-assisted degradation significantly in the presence as well as absence of catalyst. The increased efficiency can be attributed to increased formation of reactive free radicals and their interaction with the dye. The MW radiation may not be affecting the surface characteristics of the semiconductor as in the case of other AOPs. The effect of different parameters, viz. catalyst dosage, concentration of the dye, pH, MW power and H₂O₂ concentration on the degradation rate is evaluated and optimum parameters for the mineralization of the pollutant are identified. The degradation is favored under extreme acidic and alkaline conditions in both thermal and MW processes. There is considerable synergy in the MW/ZnO/H₂O₂ process compared to the respective individual processes.

Key words-Hydrogen peroxide, microwave radiation, rhodamine B, zinc oxide.

1. INTRODUCTION

Advanced Oxidation Processes (AOP) such as photocatalysis, sonocatalysis, fenton process, photofenton process and their combinations which are primarily based on the formation of highly reactive ·OH radicals have been proven effective for the oxidative destruction of recalcitrant organic compounds such as dyes, pesticides, phenols etc and the reduction of several heavy metals [1-6]. However these techniques, except in the case of photocatalysis in few instances, have still not gained acceptance as adequately efficient and effective stand-alone technologies for the commercial level decontamination of wastewater. Attempts to enhance the efficiency of the AOPs by adding oxidants, cations, anions, dyes etc to the reaction system and modification of catalyst characteristics by doping, supporting and coatings have also been reported [7-11].

Rhodamine B is a commonly used xanthene dye containing 4 N-ethyl groups on either side of the xanthene ring. It is used in textile industry, biological stains and dye laser materials. It is highly soluble in water and its use in food and cosmetic application is prohibited due to potential toxic and carcinogenic effects. Hence its absolute removal from water is important. In this context AOPs need to be investigated as viable candidates since many of the conventional and modern techniques are unable to remove the last traces of the pollutant from water. Earlier we have reported the application of photocatalysis for the mineralization of Rhodamine B in water in presence of sunlight using Pt/TiO₂ as catalyst [12]. Recently, microwave (MW) irradiation has been tested increasingly for the treatment of contaminated water due to its advantages including molecular level heating, lower activation energy and increased selectivity [13,14].

However MW alone, being a low energy radiation with $E = 1.6 \times 10^{-3} \text{ eV}$ may not be able to degrade many pollutants. When combined with light and H₂O₂, MW has been found to be highly efficient for the degradation of many pollutants such as dyes, phenolic compounds, pesticides and sulphonated aromatic compounds. Horikoshi et al [15] 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 [16]. Improvement of oxidative UV/H₂O₂ decomposition of aqueous phenol and H₂O₂ assisted degradation of carbofuran by MW radiation [17, 18] have also been reported. In the present study we are reporting the application of ZnO/H₂O₂/MW as an efficient tertiary process for the removal of Rhodamine B in traces from water. The efficacy of the MW method is evaluated by examining the degradation of Rhodamine B under various reaction conditions and identifying the optimum parameters. The structure of Rhodamine B is as shown in Fig.1.

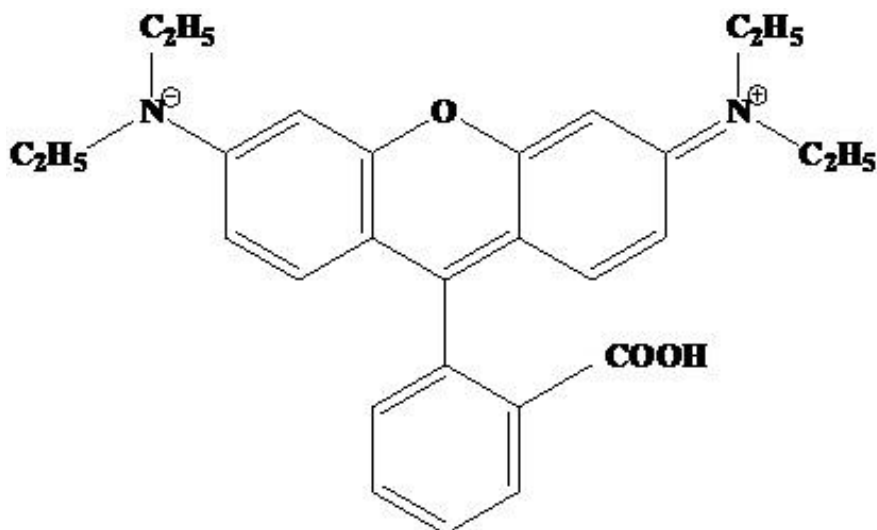


Figure 1: Structure of Rhodamine B

II. MATERIALS AND METHODS

ZnO 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 ZnO, as determined by the BET method is 12 m²/g. Rhodamine B (AnalaR Grade 99.5% purity) from Qualigen (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 average particle size of ZnO was approximately 10x10⁻² μm unless mentioned otherwise. Typical SEM image of ZnO is shown in Fig.2.

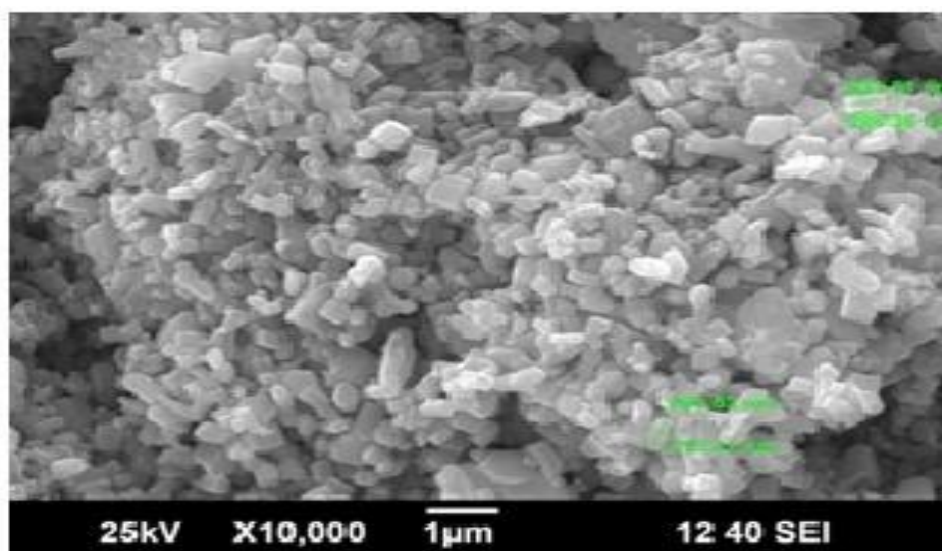


Figure 2: Typical SEM image of ZnO

The experiments were performed using aqueous solutions of RhB of the desired concentration. A specially designed Pyrex jacketed glass reactor is used for the experiments. The jacket is used for circulating water at different flow rates to control the temperature. 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 power up to 800W was used in the experiments. The reactor was introduced into the microwave oven by making an opening at the top. Experiments were initiated by supplying the desired power to the system. The reaction temperature was not allowed to go above 65°C and controlled by regulating the water flow rate. For experiments with added H₂O₂, appropriate quantity of H₂O₂ solution in water was introduced into the Rhodamine B 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 RhB using Spectrophotometry at 554 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.

Adsorption studies were performed as follows [19, 20]:

A fixed amount (0.1 g) of the catalyst was added to 50 ml of RhB solution in a 250 ml flask and the pH was adjusted as required. The suspension was agitated continuously at constant temperature of 29 ± 1°C for 2 hrs to achieve equilibrium. This was then centrifuged at 3000 rpm for 10 min. After centrifugation the concentration of RhB in the supernatant was determined colorimetrically.

The adsorbate uptake was calculated from the relation

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C₀ 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 degradation of RhB were conducted with RhB solution alone, RhB with catalyst ZnO, RhB with H₂O₂ and RhB with ZnO and H₂O₂ in the presence as well as absence of MW as control experiments. In the case of MW experiments at various temperatures, identical experiments were conducted in parallel under CH conditions to isolate the MW effect from thermal effect. The results of these control experiments are given in Table 1. No degradation occurred in the absence of H₂O₂ or even in the presence of MW at room temperature. Reasonable amount of degradation occurred under conventional thermal heating. No degradation occurred in the presence of catalyst at room temperature in presence of MW except for the adsorption.

The results show that at normal room temperature, MW causes only negligible degradation of RhB even in the presence of the catalyst unlike in the case of sono, photo or sonophotocatalysis [20]. At the same time CH in the absence of catalyst results in approximately 0.7% degradation at 65°C while MW radiation under identical conditions result in ~ 2 % degradation. Conventional heating in presence of ZnO catalyst results in 1.4% degradation while MW treatment in presence of ZnO under identical conditions results in 1.7%. Presence of H₂O₂ enhances the degradation under thermal as well as MW conditions both in presence and absence of catalyst. Combination of MW irradiation and presence of H₂O₂ yields maximum degradation of approx 24 %. Comparison of results under MW and CH under otherwise identical conditions shows that the effect of MW is not just simple heating. At the same time significant enhancement in presence of added H₂O₂ shows that the reactive oxidant as well as the reactive free radicals such as ·OH formed from it plays important role like in the case of other AOPs. MW is not effective at room temperature after 4 hr of MW irradiation. The results show that under identical conditions (which are not optimized for individual parameters), the degradation by MW/ZnO/H₂O₂ is at least 15 times faster than MW/ZnO alone and at least 3 times faster than MW/H₂O₂ technique. Similarly MW/ZnO/H₂O₂ is 3 times faster than CH/ZnO/H₂O₂. This clearly shows that the irradiation source MW, catalyst ZnO and oxidant H₂O₂ together play a synergistic role in degradation of RhB. Hence all further experiments were carried out with either MW/ZnO or MW/ZnO/H₂O₂ systems.

Table 1: Degradation of Rhodamine B in water under various conditions
 [Rh B]: 10 mg/L, Time: 2 hr, [ZnO]: 0.1 mg/L, [H₂O₂]: 10 mg/L, pH: ~ 6.0
 MW Frequency:2450MHz, MW power: 800 W

Sl. No	Reaction Condition	Temp °C	Catalyst	H ₂ O ₂	% Decrease in RhB concentration
1	MW	29	None	Nil	0.0
2	MW	29	ZnO	Nil	0.5
3	MW	29	None	Yes	2.4
4	MW	29	ZnO	Yes	2.3
5	MW	65	None	Nil	2.0
6	MW	65	ZnO	Nil	1.7
7	MW	65	None	Yes	7.5
8	MW	65	ZnO	Yes	24.3
9	CH (RT)	29	None	Nil	0.0
10	CH (RT)	29	ZnO	Nil	0.5
11	CH (RT)	29	None	Yes	0.5
12	CH (RT)	29	ZnO	Yes	2.7
13	CH	65	None	Nil	0.7
14	CH	65	ZnO	Nil	1.4
15	CH	65	None	Yes	4.9
16	CH	65	ZnO	Yes	7.2
17	No MW/CH	29 ⁰ C	None	Yes	0.0
18	No MW/CH	29 ⁰ C	ZnO	Yes	0.5

MW = Microwave CH = Conventional Heating RT = Room Temperature

3.1. Effect of MW power:

Increase in MW power enhanced the degradation as shown in Fig.3. When the power increased from 100W to 800W, keeping all other parameters constant, the degradation almost doubled from 4% to 8% in 10 minutes irradiation. The degradation increased slowly above 450W indicating an approximate optimum for the effective MW power in the range of 450-800 W.

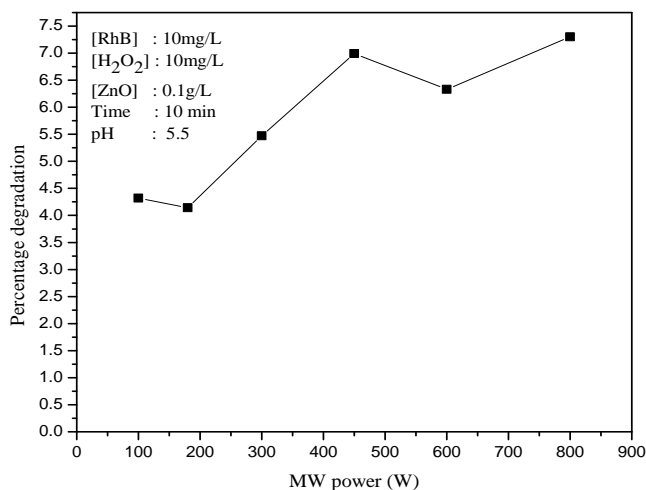


Figure 3: Effect of MW power on the degradation of RhB

The increase in MW power increases the temperature and hence the degradation at higher power can be

partially attributed to this. However, the effect is not thermal alone as seen from the results in presence of CH. The maximum temperature attained by the reaction system which was subjected to slow controlled cooling to avoid overshoot of temperature at various MW power in presence of ZnO as well as in ZnO/H₂O₂ are as in Table 2.

Table 2: Maximum temperature attained at various MW power

Power (W)	Temperature (°C)
100	36
180	41
300	46
450	48
600	54
800	65

As can be seen from Fig.3, there is no strict direct correlation between the degradation of RhB and MW power. According to Horikoshi et al [15] this is due to the difference in the effect of temperature on various intermediates formed during the degradation of the pollutant. MW is relatively more effective in degrading the RhB than degrading the intermediates formed in the process. 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 [21]. These kinds of molecular movements can contribute to increasing the temperature and increasing the rate of degradation, the rates being different for different molecules. The kinetics of photocatalytic degradation of RhB is also shown to be temperature dependent, with the rate increasing with increase in temperature. This is explained as due to the increased adsorption of RhB on the surface [22].

The increase in temperature of the reaction solution/suspension due to MW is also explained based on the violent rotation and migration of the polar molecules resulting in friction. The violent motion can lead the molecules to higher excited state through an increase of collision numbers between reactants thereby resulting in acceleration of the rate of decomposition [23].

3.2. Effect of catalyst dosage:

The effect of varying catalyst loading on the degradation of RhB in presence of MW and H₂O₂ is plotted in Fig.4. When the dosage increased from 0.04 to 0.16 g/L, the degradation increased from 4.5 to 10.5%. Thereafter the degradation decreases indicating 0.1 g/L as the optimum loading under the reaction conditions.

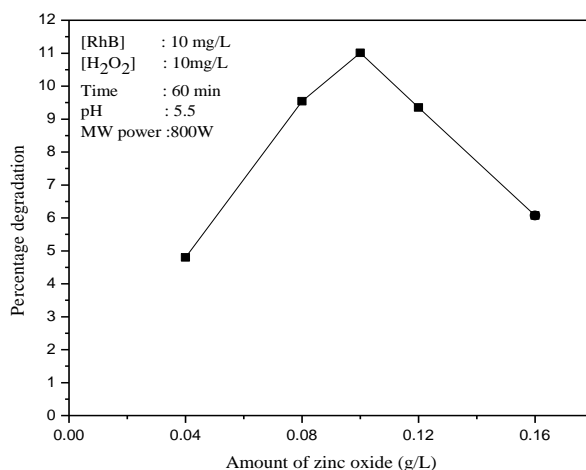


Figure 4: Effect of catalyst dosage on the MW degradation of RhB

Naturally, at higher loadings there will be more number of adsorption sites and hence better adsorption of the dyemolecules leading to more effective MW activity and degradation. However, at very high loadings beyond the optimum, there may be the 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.

3.3. Effect of RhB concentration:

The percentage degradation of RhB in MW/ZnO/H₂O₂ systems decreases with increase in concentration as shown in Fig.5. This is similar to most of the AOP systems which are shown to follow pseudo first order kinetics.

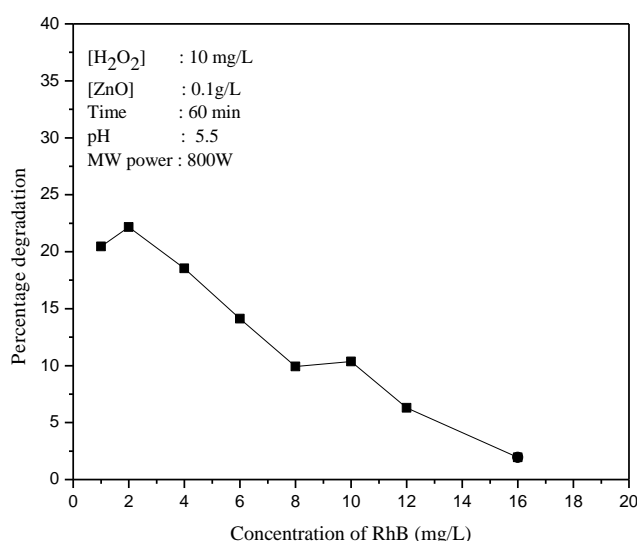


Figure 5: Effect of concentration of RhB on its degradation

The effect of initial concentration of substrate on the rate of degradation is shown in Table 3.

Table 3: Effect of concentration of RhB on the rate of degradation
[ZnO]: 0.1 g/L, [H₂O₂]: 10 mg/L, time: 1 hr, pH: 5.6, MW power: 800W

Conc. of dye (mg/L)	Rate of degradation mg/L hr ⁻¹
1	0.21
2	0.45
4	0.78
6	0.80
8	0.80
10	0.90
12	0.72
16	0.40

As seen in the table, the rate increases initially upto 4 mg/L following pseudo first order kinetics and stabilises thereafter. This zero order kinetics at higher concentration is possibly because at this concentration range, the substrate molecules are sufficient to interact with the available catalyst sites, get activated and react

with H₂O₂ and free radicals there from. Hence further increase does not cause additional interaction or degradation as long as the catalyst dosage and radiation are kept the same. At very high concentration, the dye molecules are excessive in comparison to the active centres available. Further, with the dye molecules overlapping on the surface in multiple layers, the activation capability of the surface is reduced. Since the degradation is mainly caused by the H₂O₂, any hindrance to the interaction and activation of H₂O₂ to form ·OH radicals will cause decrease in degradation.

3.4. Effect of varying H₂O₂ concentration:

The effect of concentration of H₂O₂ on the degradation of the dye appears rather complex. In the lower concentration range of 3-14 mg/L, the rate increases slowly. Marginal increase in H₂O₂ does not enhance the rate further and the degradation stabilized for a while (Fig.6a). When the concentration is increased to relatively higher range of 50 -500 mg/L, the rate increases again steeply in the beginning and slowly thereafter (Fig.6b).

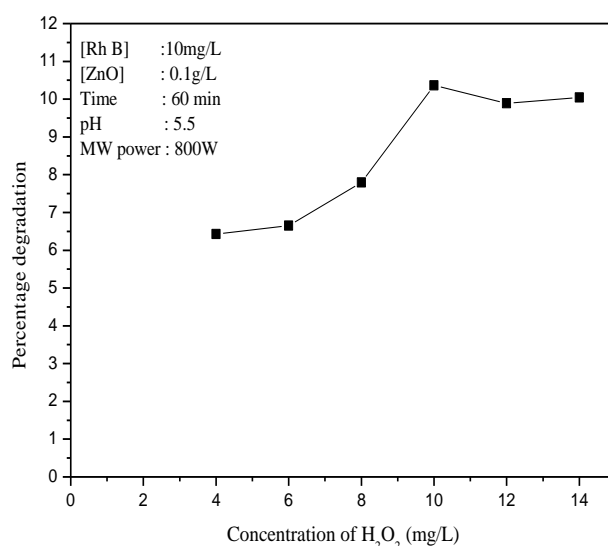


Figure 6a: Effect of lower concentrations of H₂O₂ on the MW degradation of RhB

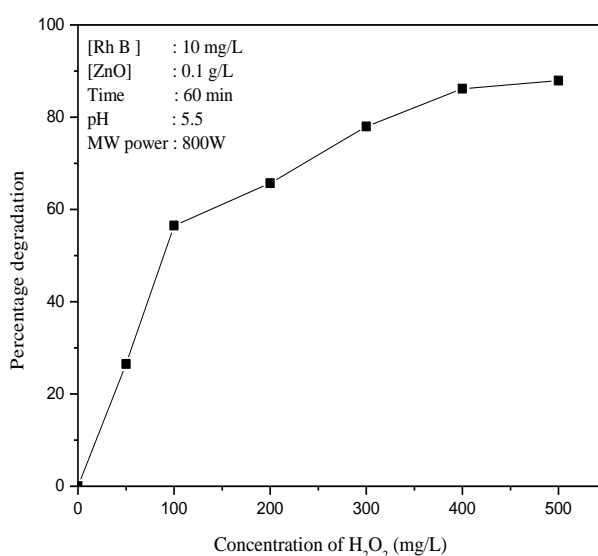


Figure 6b: Effect of higher concentrations of H₂O₂ on the MW degradation of RhB

The degradation stabilizes close to 90% at 400 mg/L of H₂O₂ probably because the relative concentration of the dye is less at this stage and hence the frequency of interaction between the substrate molecules and the reactive free radicals is lower. The importance of H₂O₂ in the degradation is further verified by adding comparable concentrations of H₂O₂ into a reaction in progress. As can be seen in Fig.7, the reaction is accelerated significantly by the in-between addition of H₂O₂ initially after 1 hr and later after 2 hr.

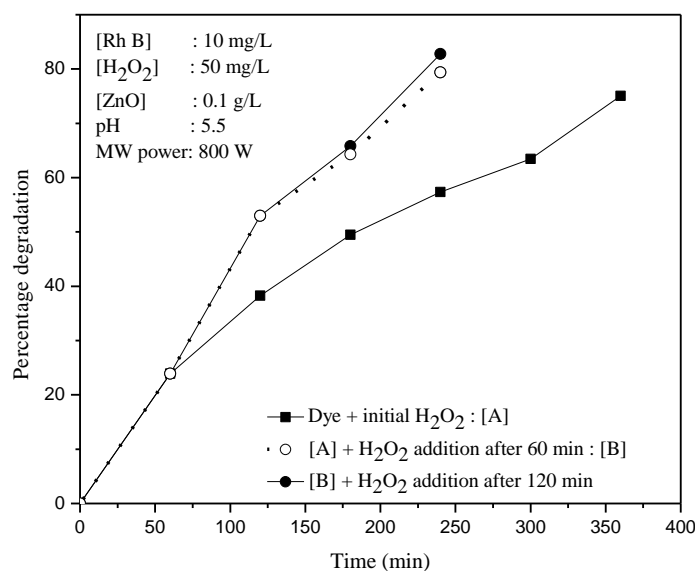


Figure 7: Effect of in-between addition of H₂O₂ on the MW degradation of RhB

The effect is less after the second extra addition of H₂O₂. This may probably be because the concentration of substrate available in the system is significantly less and the H₂O₂ already present is sufficient to carry the reaction forward. Any increase in H₂O₂ at this stage will only block the surface sites and inhibit or stabilize the degradation of the dye. The extra H₂O₂ will also interact with the 'OH radicals as follows resulting in the formation of less active HO₂' radicals.



The enhancement in the MW assisted degradation of RhB in presence of H₂O₂ may be due to the formation of reactive 'OH radicals by the decomposition of the former. The H₂O₂ decomposition is enhanced considerably by ZnO. The 'OH radicals react rapidly and nonselectively with aromatic molecules primarily by addition – elimination reaction to form corresponding hydroxyl compounds or by hydrogen abstraction. For e.g.; hydrocarbons are oxidised by hydrogen abstraction to alcohols, carbonyl compounds or carboxylic acids [24] which can eventually mineralize to CO₂ and water [25].

3.5. Effect of pH:

The effect of pH on the MW and CH degradation of RhB under different conditions is shown in Fig.8a and b respectively. The degradation remains more or less steady in the pH range of 5-9 in both cases. The degradation is quite high at pH < 4 and > pH 9 in presence of MW as well as CH. Even at room temperature, in the absence of MW and CH, the trend remains similar even though the degradation of RhB is quite small. At the same time the degradation remains more or less the same at all pH in the absence of H₂O₂ in presence of both MW and CH indicating that the pH effect is more on the processes involving H₂O₂. 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 cause higher degradation. Under extreme acidic condition when ZnO surface is +vely charged, the dye will be in cationic form and hence not adsorbed to the surface. Hence the enhanced degradation may be due to the activation of H₂O₂ and generation of reactive 'OH radicals which is facilitated by the MW and

CH conditions. However, the pH effect, as in the case of many AOPs, is very complex and needs to be investigated in detail.

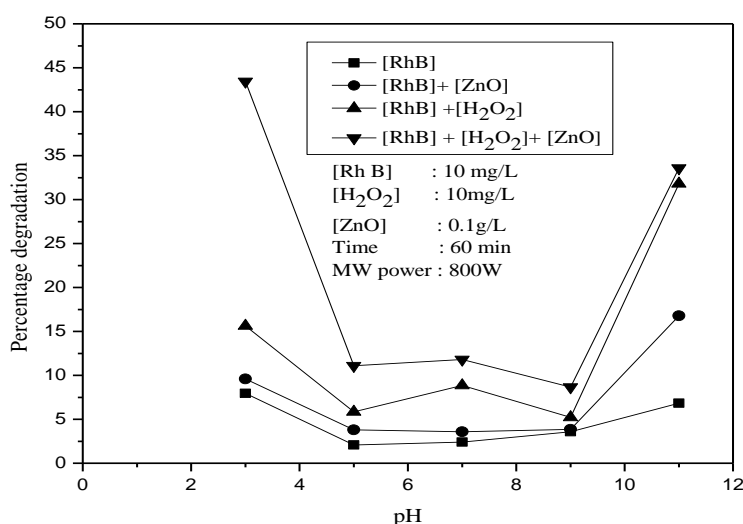


Figure 8a: Effect of pH on the MW degradation of RhB

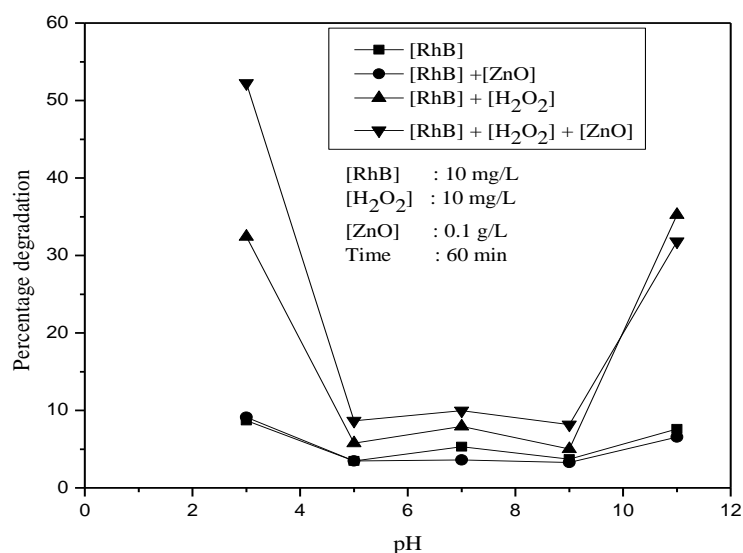
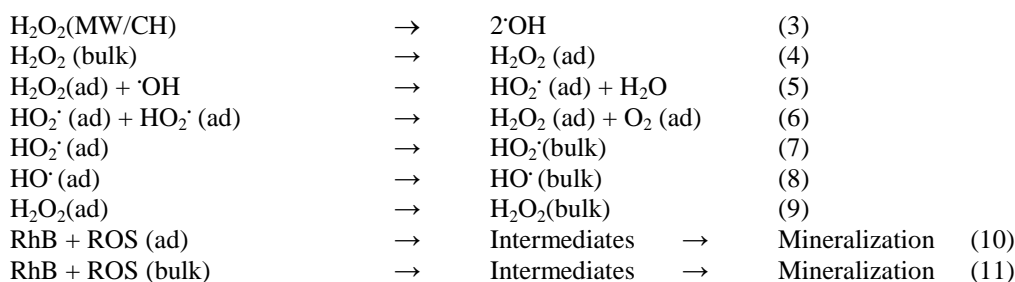


Figure 8b: Effect of pH on the CH degradation of RhB

3.6. General mechanism:

The question of whether MW initiated degradation of organic molecules is effected by the radiation itself or the MW-generated heat or both was always a subject of intense investigations and discussions. The current study shows that it is not the thermal effect alone that is responsible for the degradation, though its contribution cannot be ruled out. Horikoshi et al [15] suggests that the heat released has little effect on the degradation. Comparison of CH and MW treatment under identical conditions shows that the degradation is significantly more under MW conditions thus suggesting that the radiation has an important role to play. However, under extreme acidic and alkaline conditions, the thermal effect also becomes important in presence of H₂O₂. Enhancement in the degradation in presence of H₂O₂ clearly shows that oxidizing agents and/or the free

radicals derived from them are involved in the reaction leading to the degradation and eventual mineralisation of RhB. Various reactions possibly taking place on the surface as well as in the bulk may include the following steps:



Combination of the process with other AOPs such as photocatalysis is known to enhance the degradation considerably due to the aggressive roles played by electrons and holes generated by irradiation of semiconductor oxides. H₂O₂ plays a unique role of both electron and hole scavenger thereby preventing the recombination of surface electrons and holes.

IV. CONCLUSION

Rhodamine B (RhB) pollutant in water in trace amounts can be effectively degraded in the presence as well as absence of catalyst under microwave (MW) irradiation. The MW degradation is much faster compared to identical thermal conditions suggesting that the MW effect is not just heating the reaction system. Addition of H₂O₂ enhances the MW-assisted degradation significantly. The increased efficiency can be attributed to increased formation of reactive free radicals and their interaction with the dye. The microwave radiation may not be affecting the surface characteristics of the semiconductor as in the case of other AOPs. The reactions are investigated in detail and optimum parameters for the mineralization of the pollutant have been identified. The degradation is maximum under extreme acidic and alkaline conditions in both thermal and MW processes. There is considerable synergy in the MW/ZnO/H₂O₂ process compared to the respective individual processes. Possible causes for the observations are analyzed and a general mechanism is proposed.

V. Acknowledgements

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