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Purification of water contaminated with traces of Rhodamine B dye by microwave-assisted, oxidant-induced and zinc oxide catalyzed advanced oxidation process

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ABSTRACT

Microwave (MW)-activated H_2O_2 and persulfate (PS)-induced ZnO-catalyzed purification of water contaminated with the cationic dye Rhodamine B (RhB) is investigated. The degradation is much faster compared with that under identical conventional heating (CH) conditions thus suggesting that the MW effect is not just thermal. PS is more efficient for the oxidation and eventual mineralization of RhB compared with H_2O_2. Combination of H_2O_2 and PS does not have either synergic effect or even additive effect thereby demonstrating the mutual destruction of the oxidants in the presence of one another at least to a limited extent. The enhanced MW degradation in the presence of oxidants is attributed to increased formation of reactive free radicals and their interaction with the dye. ZnO, which enhances the degradation of many organic chemical pollutants under advanced oxidation process (AOP) conditions, inhibits the degradation in the presence of MW/PS and CH/PS. The activation energy of the degradation is reduced by MW in comparison with CH under identical reaction conditions. The effect of different reaction parameters, namely, oxidant dosage, concentration of the dye, pH, MW power, dosage of catalyst, temperature, and reaction volume on the degradation/mineralization rate is evaluated and optimum conditions are determined. The identity of many of the intermediates formed during the degradation is confirmed by LC/MS.

Keywords: Peroxydisulfate; Microwave radiation; Zinc oxide; Rhodamine B; Hydrogen peroxide

1. Introduction

Advanced oxidation processes (AOP) have been widely investigated in recent years as promising environment-friendly technologies for the removal of toxic and hazardous pollutants such as dyes, pesticides, and phenols and even heavy metals from water [1–6]. The AOPs include, but are not limited to, photocatalysis, sonocatalysis, electrocatalysis, wet air oxidation, Fenton process, photo-Fenton process and their combinations. These are primarily based on the formation of highly reactive ·OH radicals. However, except in the case of photocatalysis, in few instances, these processes have gained only limited acceptance so far, as viable and effective methods for the large-scale decontamination of wastewater. Attempts to enhance the efficiency of the individual AOPs by (i) their combination, (ii) addition of oxidants, cations, anions, dyes, etc. to the reaction system and (iii) modification of the surface and absorption characteristics of the catalyst by doping, supporting and coatings have also been reported [7–12].

Recently, microwave (MW) irradiation has been tested increasingly for the treatment of contaminated water due to its advantages such as molecular level heating, lowering of activation energy and increased selectivity [13,14].

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However, being a low energy radiation with energy in the range of 1.24 meV to 1.24 μeV (frequency 300 GHz to 300 MHz), MW alone may not be able to degrade many pollutants. When combined with light and oxidants such as H_2O_2, MW has been found to be highly efficient for the degradation/mineralization of pollutants [15–25].

Many of the organic chemical pollutants are potentially carcinogenic/hazardous and hence their absolute removal from water is important. In this context, AOPs such as MW-based processes are relevant since many of the conventional and even modern techniques are unable to remove the last traces of the pollutant from water. Rhodamine B {RhB, chemical class: xanthenes, molecular formula $C_{28}H_{31}N_2O_3Cl$, molecular weight: 479.01 g/mol, IUPAC name: *N*-[9-(ortho-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-ylidine] diethylammonium chloride} is a refractory dye pollutant containing four *N*-ethyl groups on either side of the xanthene ring. It is widely used in textile and food industry and is reported to be carcinogenic. Other major health hazards are reproductive and developmental toxicity, neurotoxicity and chronic toxicity towards humans and animals [26]. Hence, removal of even the last traces of RhB from water is important from the health, safety and environmental angle.

Earlier we have reported the application of solar photocatalysis for the mineralization of RhB in water using ZnO as catalyst [12]. In this paper, application of MW as the source of activation for the removal of traces of RhB from water is investigated under different conditions. Role of two well-known oxidants, that is, H_2O_2 and peroxydisulfate (PS) as well as a typical semiconductor oxide catalyst ZnO on the degradation of the dye is evaluated individually and in combination and optimum reaction conditions are identified.

2. Materials and methods

2.1. Materials

RhB (AnalaR Grade, >99.5% purity) from Sigma-Aldrich (India) and PS (~99%) and H_2O_2 (30.0% w/v) from Qualigen (India) were used without any further purification. ZnO (>99% purity, Brunauer, Emmett and Teller (BET) surface area ~12 m^2/g) used in the study was supplied by Merck India Lt. The particles were approximately spherical and non-porous. The average particle size was ~100 nm unless indicated otherwise. X-ray diffractogram (XRD, Bruker D2 Phaser), transmission electron microscopy (Jeol/JEM 2100, Source LaB6) and scanning electron microscopy (JEOL Model JSM-6390 LV) images confirmed the identity of ZnO. Doubly distilled water was used in all the experiments. All other chemicals were of AnalaR Grade or equivalent.

2.2. Experimental setup

A specially designed jacketed Pyrex glass reactor was used for the experiments. The jacket is used for circulating hot or cold water at appropriate flow rates to control the temperature of the reaction medium. In the case of experiments with added catalysts, specified quantity of the catalyst is suspended in the solution and kept as evenly distributed suspension by periodic mechanical mixing. A MW oven of 2,450 MHz frequency and power up to 800 W, modified by making an opening at the top for introducing the reactor, was used in the experiments. All experiments, except those in the case of UV irradiation, were conducted in the absence of light.

Experiments were performed using aqueous solutions of RhB of the desired concentration and by applying the desired MW power to the system. The reaction temperature was measured by using a pyrometer and was not allowed to rise above 67°C (unless indicated otherwise) by regulating the water flow rate in the jacket. 'For experiments with added water-soluble components, appropriate quantity of the respective aqueous solution was introduced into the RhB solution such that the net concentration of the dye and the additive will be as desired'. In the case of ZnO, which is insoluble in water, the solid powder was precisely weighed and added to the reaction solution. A schematic diagram of the experimental setup is shown in Fig. 1.

Conventional heating (CH) experiments for comparison were conducted at the same temperature as of MW experiments. A heated water bath was used in place of the MW oven under identical conditions. Room temperature (RT) experiments were carried out under identical conditions but without the use of MW or water bath.

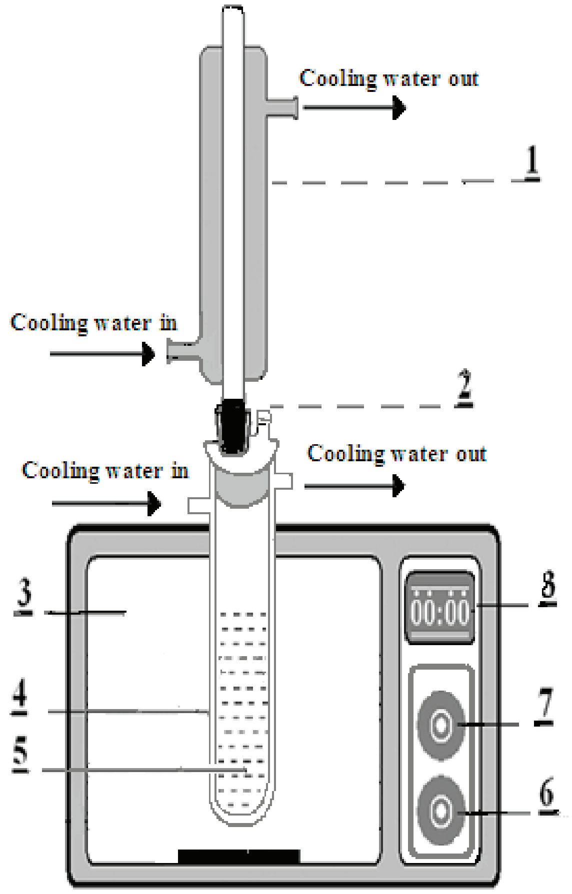

Fig. 1. Schematic representation of the reactor assembly; (1) condenser, (2) thermometer pocket/sampling port, (3) microwave oven cavity, (4) reactor, (5) reaction solution/suspension, (6) power adjuster, (7) timer and (8) time display.

2.3. Analytical methods

Samples were drawn periodically, centrifuged in the case of experiments with catalyst to remove the suspended materials and analyzed for remaining RhB using UV–Vis Spectrophotometry at 554 nm. H_2O_2 concentration is determined by standard iodometry.

2.4. Adsorption measurements

Adsorption measurements were made by the standard procedure [27,28]. A fixed amount (0.1 g) of ZnO was suspended in 100 mL of the dye solution in a 250 mL reaction flask. The pH was adjusted as required. The suspension was agitated continuously at constant temperature of 29°C ± 1°C for 2 h to achieve equilibrium. It was then kept undisturbed for 2 h followed by centrifugation at 3,000 rpm for 10 min. After centrifugation, the concentration of the dye in the supernatant was determined by UV–Vis spectroscopy as mentioned earlier. The suspension kept overnight before centrifuging did not make any significant difference in the concentration of RhB in the supernatant indicating that the 2 h period is adequate to complete the adsorption.

The adsorption was calculated from the relation:

$$q_e = (C_0 - C_e)V/W \tag{1}$$

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 (L), W is the mass of the adsorbent (g) and q_e is the amount adsorbed (mg/g of the adsorbent).

2.5. Detection of hydroxyl radicals

The formation of ·OH radicals in the reaction system during the MW irradiation was tested by the photoluminescence (PL) technique using terephthalic acid (TPA) as the probe molecule [29]. The ·OH, if formed in situ in the system, will react with TPA and form 2-hydroxy terephthalic acid (HTPA), which is a fluorescent molecule. The intensity of its PL will be proportional to the quantum of ·OH present in the system. In this method, the reaction solution of optimized concentration is mixed with aqueous solution of TPA (2×10^{-4} M) and NaOH (2×10^{-3} M) and irradiated by MW. The PL spectrum of the product HTPA is recorded periodically in the range of 400–450 nm. The PL intensity at 425 nm corresponds to the concentration of HTPA and hence of the ·OH radicals formed in the system. Shimadzu model RF-5301PC fluorescence spectrophotometer was used for recording the spectrum.

3. Results and discussion

Preliminary investigations on the degradation of RhB in water were conducted under various conditions in the presence and in the absence of ZnO and two typical oxidants, H_2O_2 and PS; that is, (i) RhB solution alone, (ii) RhB + ZnO, (iii) RhB + H_2O_2, (iv) RhB + ZnO + H_2O_2, (v) RhB + $S_2O_8^{2-}$, (vi) RhB + ZnO + $S_2O_8^{2-}$, (vii) RhB + $S_2O_8^{2-}$ + H_2O_2 and (viii) RhB + H_2O_2 + $S_2O_8^{2-}$ + ZnO. MW and CH were used as the energy sources. In most cases, the ambient temperature was 29°C ± 1°C. In cases where the ambient temperature was different, it was adjusted to 29°C ± 1°C by heating or cooling, as required, by circulating water at the required temperature from a thermostat through the jacket of the reactor. For every MW experiment, corresponding CH experiment was conducted in parallel under identical conditions in order to isolate the MW effect from simple thermal effect. The results of the preliminary study at two temperatures under various reaction conditions are presented in Table 1.

No significant degradation of RhB occurred in the absence of PS even in the presence of MW or H_2O_2 at RT. Small amount of the dye was slowly getting degraded at RT in the presence PS. Moderate degradation occurred at ~65°C under CH in the presence of H_2O_2 and PS, the latter being more efficient. The presence of H_2O_2 at RT does not have any effect under MW and CH. However, the degradation increases significantly in the presence of H_2O_2 at higher temperature under MW irradiation. No noticeable degradation of RhB occurred in the presence of ZnO alone under CH or MW at both temperatures, except for the minor adsorption of ~2%. The results clearly show that ZnO, which has been proven to be an effective catalyst under other AOPs, that is, sono-, photo- and sonophotocatalysis [28], is not effective under MW irradiation. Hence, MW by itself is not an effective source for the activation of semiconductor oxides. It is also possible that the mechanism of MW activation may be different from that of light or sound. The degradation in the presence of H_2O_2 and PS at RT is practically unaffected by ZnO and the slight enhancement may be due to adsorption. However, at higher temperature, ZnO enhances the H_2O_2-mediated MW degradation of RhB significantly from 7.5% to 24.5%, that is, by ~225%. The enhancement in the presence of ZnO from 4.9% to 7.2% at higher temperature under CH can be attributed to adsorption only. In the case of MW at higher temperature, the degradation of 24.5% in the simultaneous presence of ZnO and H_2O_2 is synergic, in comparison with their individual presence (1.7% and 7.5%, respectively) while it is simply additive under CH.

In the case of the stronger oxidant PS, the degradation is inhibited in the presence of ZnO, by ~18% and ~32% under MW and CH, respectively. Combining both PS and H_2O_2 does not provide any synergic or even additive effect on the degradation. In fact, the combination is only as active as PS alone under both CH and MW. Addition of ZnO inhibits the combination (PS + H_2O_2)-mediated degradation under both CH and MW. In this case, the extent of inhibition is comparable with that in the case of 'PS-only' showing that in the simultaneous presence of PS and H_2O_2, the former is the driving force for the degradation of RhB. The results thus show that the mechanism of the effect of ZnO on the PS/H_2O_2-mediated degradation of RhB is different under MW and CH.

3.1. Effect of varying concentration of PS and RhB

The gradual increase in the percentage degradation of RhB with increase in concentration of PS under MW and CH is shown in Figs. 2(A) and (B), respectively.

In both cases, the percentage degradation increases with increase in PS concentration, fairly steeply in the beginning and slowly stabilizing later. Complete degradation of RhB (10 mg/L) is achieved in ~3 h in the presence of 50 mg/L of PS under MW. Under identical conditions, the degradation

Table 1
Degradation of Rhodamine B in water under various conditions

S. no.	Reaction condition	Temperature (°C)	% Degradation of RhB
Microwave irradiation (MW)			
1.	RhB	29	~0.0
2.	RhB + ZnO	29	~2.0
3	RhB + H_2O_2	29	~0.0
4	RhB + ZnO + H_2O_2	29	~2.0
5	RhB + PS	29	~3.0
6	RhB + ZnO + PS	29	~5.0
7	RhB + PS + H_2O_2	29	~5.5
8	RhB + PS + ZnO + H_2O_2	29	~5.0
9	RhB	65	2.0
10	RhB + ZnO	65	1.7
11	RhB + H_2O_2	65	7.5
12	RhB + ZnO + H_2O_2	65	24.5
13	RhB + PS	65	24.5
14	RhB + ZnO + PS	65	20.5
15	RhB + PS + H_2O_2	65	25.5
16	RhB + PS + ZnO + H_2O_2	65	21.5
Conventional heating (CH)[a]			
17	RhB only	29	~0.0
18	RhB + ZnO	29	~1.5
19	RhB + H_2O_2	29	~0.5
20	RhB + ZnO + H_2O_2	29	~2.7
21	RhB + PS	29	~2.5
22	RhB + ZnO + PS	29	~3.0
23	RhB + PS + H_2O_2	29	~3.0
24	RhB + PS + ZnO + H_2O_2	29	~2.5
25	RhB	65	0.7
26	RhB + ZnO	65	2.4
27	RhB + H_2O_2	65	4.9
28	RhB + ZnO + H_2O_2	65	7.2
29	RhB + PS	65	11.0
30	RhB + ZnO + PS	65	7.5
31	RhB + PS + H_2O_2	65	10.5
32	RhB + PS + ZnO + H_2O_2	65	6.0

[Rh B]: 10 mg/L, time: 1 h, [ZnO]: 0.1 mg/L, [H_2O_2]: 10 mg/L, [PS]: 10 mg/L. MW frequency: 2,450 MHz, MW power: 800 W, pH: ~4.5.
[a] For CH at 29°C, mild heating or cooling as required.

is only ~65% in the case of CH, thus reconfirming that the role of MW is not simply thermal. Since PS at the concentration of 50 mg/L is highly efficient under the reaction conditions, all further studies were made using this concentration. Obviously, the quantitative requirement of PS will be different for different concentrations of the dye and under different reaction conditions including reactor size and geometry.

The apparent rate constant *k* of the degradation of RhB (10 mg/L) at varying concentration of PS (5–50 mg/L) is computed assuming pseudo-first-order kinetics as in the case of many AOPs and the results are given in Table 2.

The increase in the rate of degradation of RhB with increase in concentration of PS slows down at higher concentration of the latter under both MW and CH. When the concentration of PS is increased from 5 to 10 mg/L, that is, 100%, *k* also increased by 100% under MW. However, when the concentration of PS is increased further from 20 to 40 mg/L (100% increase), *k* increased by only ~25%. Under CH, the increase in *k* under similar conditions is 66.7% and 36.5%, respectively. The rate of increase of *k* slows down and may eventually stabilize or even decrease under both MW and CH. Progressive dip in the percentage increase in *k* is less under CH compared with MW. Asgari et al. [30] also reported similar observations in the case of MW/PS degradation of pentachlorophenol in aqueous solution. They conducted the experiments at alkaline pH, RT and higher concentrations of both the substrate and PS. Other experimental conditions and procedures were more or less identical.

Relatively higher concentration of PS with respect to RhB is needed probably to compensate for the strong scavenging of reactive sulfate radical by various unproductive reactions (see section 4) which do not lead to the degradation of RhB.

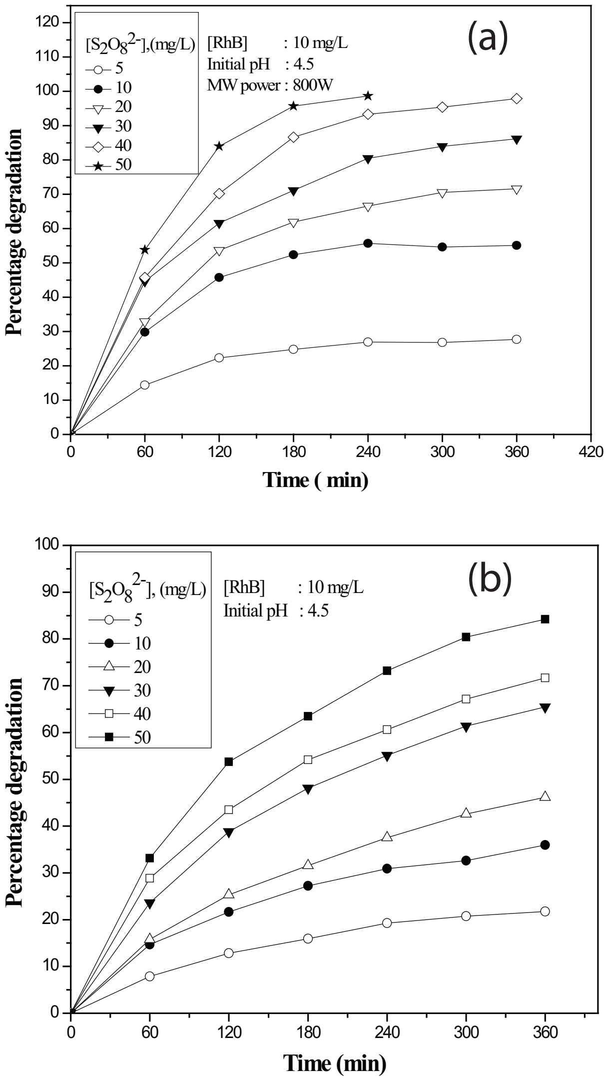

Fig. 2. Effect of $S_2O_8^{2-}$ concentration on the degradation of RhB. (A) Under MW irradiation and (B) under conventional heating.

The gradual increase in the rate of degradation of RhB with concentration of PS (Fig. 3(M)) can be due to increased availability of the latter per RhB molecule.

Once the decolorization of the dye forming various relatively stable intermediates is complete, the PS remaining in the system will be used by those intermediates for their slow degradation and eventual mineralization. The adequacy of the concentration of PS in the reaction system is tested by increasing the PS in between the reaction at two different time intervals (2 h, 4 h) and the results are shown in Fig. 3(N). In this case, the concentration of RhB is kept higher at 20 mg/L to ensure the availability of substrate for the excess PS. In-between addition of PS enhanced the degradation at both stages. Hence, it may be inferred that the insufficient availability of adequate PS may be one of the reasons for the gradual slowdown in the degradation of RhB with time. Decreasing concentration of RhB and increasing competition from the in situ formed intermediates for the PS for further degradation and eventual mineralization may also contribute to the decreased rate as the reaction advances. The formation of stable organic acids such as oxalic acid (OA), succinic acid, maleic anhydride/acid, and adipic acid during the photocatalytic degradation of RhB has been reported [18,31,32].

In order to identify at least some of the probable intermediates during the MW irradiation of RhB/PS, the reaction is carried out at a higher concentration of the dye (100 mg/L) and corresponding proportion of PS under the standardized conditions. The products at ~50% degradation of RhB were analyzed using LC/MS. Major transient and stable intermediates identified are listed in Table 3.

Since detailed investigation of the products/intermediates of the degradation at different stages of MW irradiation was not made, it is possible that all the intermediates are not identified. There may be more transient intermediates at different stages of the degradation. Some of the intermediates identified here may be the result of simple structural rearrangement under MW irradiation. Some intermediates formed in the early stages of reaction might have been transformed into other products or even mineralized. There may be more intermediates at later stages of the reaction formed either from RhB itself or from the other intermediates already formed. The characteristics and the fate of multitude of intermediates

Table 2
Pseudo-first-order rate constant for RhB degradation at varying PS concentrations

Source of activation	Temperature (°C)	[RhB] (mg/L)	[PS] (mg/L)	Rate constant (*k*) ($\times10^{-2}$ h^{-1})	% Increase in *k*
MW	65	10	5	7.5	–
	65	10	10	15.0	100
	65	10	20	20.0	33.3
	65	10	40	25.0	25.0
	65	10	50	28.5	14.0
CH	65	10	5	4.5	–
	65	10	10	7.5	66.7
	65	10	20	11.0	46.5
	65	10	40	15.0	36.5
	65	10	50	18.0	20.0

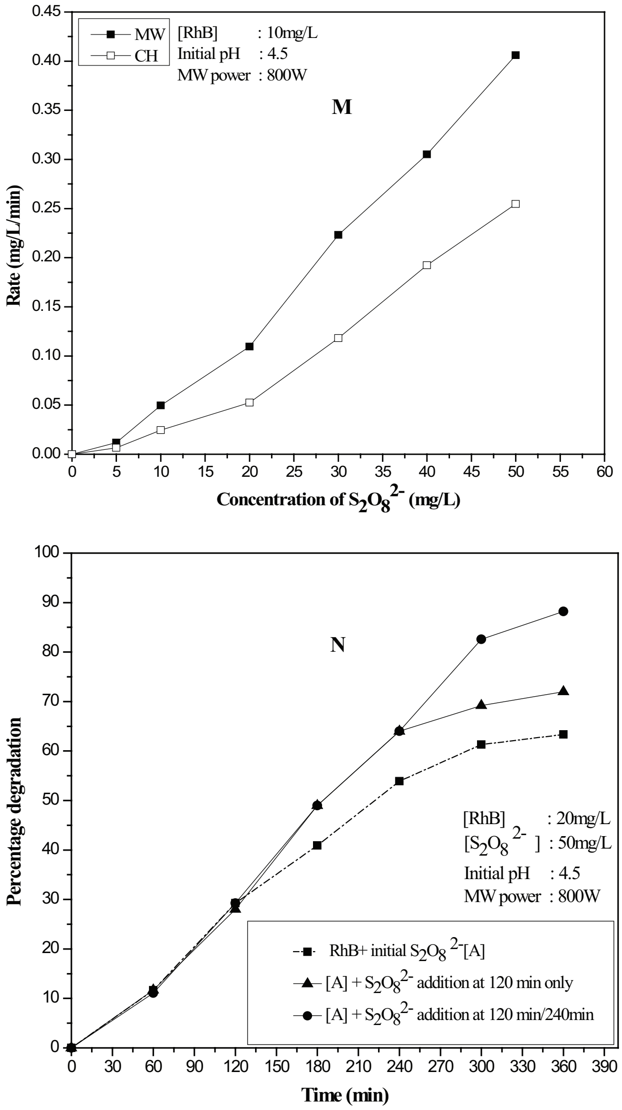

Fig. 3. (M) Effect of concentration of $S_2O_8^{2-}$ on the rate of degradation of RhB. (N) Effect of in-between addition of $S_2O_8^{2-}$ on MW degradation of RhB.

merit further detailed investigation, which is beyond the scope of the current study.

The formation of stable organic acids, that is, succinic acid, oxalic acid, malonic acid, 3-hydroxy benzoic acid, 2,5-dihydroxy benzoic acid and hydroxypentanedioic acid was detected. Decrease in the pH of the reaction system from 4.5 before MW irradiation to 4.2 after the decolorization also confirms the formation of acids. They are relatively more stable and hence cannot be mineralized easily as explained in section 3.7.

The effect of varying the relative concentration of PS and RhB on the degradation of the latter is tested further by varying the concentration of RhB and keeping the concentration of PS constant. The results are similar to those in the experiments described earlier, that is, as long as the relative concentration of PS is sufficiently more in the system, the degradation of RhB will continue. Once the relative concentration of PS is less, the degradation of RhB slows down and gets stabilized.

Table 3
Major components/intermediates identified by LC/MS during the MW/PS degradation of RhB

S. No	Retention time (min)	Mass to charge ratio (m/z)	Assignment
1	4.47	331.7	Rhodamine 110
2	4.63	148	Phthalic anhydride
3	4.99	359.5	*N*-ethylrhodamine
4	5.39	387	*N*-ethyl-*N′*-ethyl rhodamine
5	5.39	387	*N*,*N*-diethyl rhodamine
6	5.52	138	3-Hydroxybenzoic acid
7	5.82	415	*N*,*N*-diethyl-*N′*-ethyl-rhodamine
8	5.82	117.06	Succinic acid
9	5.82	91.05	Oxalic acid
10	6.07	443	Rhodamine B
11	6.19	154	2,5-Dihydroxybenzoic acid
12	6.61	359	*N*-ethylrhodamine
13	6.69	104	Malonic acid
14	7.03	149	Hydroxypentanedioic acid

Thus, at a higher constant concentration of PS (50 mg/L), the rate of degradation of RhB increases steadily with increase in its concentration in the lower concentration range of 5 to 20 mg/L. However, at higher concentration of RhB (>20 mg/L), the rate of degradation is stabilized or even decreases due to the inadequacy of PS to effectively interact with the abundant dye molecules. Similar trend is observed in the case of CH also. In the case of MW, it is also possible that higher concentration of the dye (in the range studied here) may be a constraint for the effective penetration/utilization of the radiation by the reaction system.

The logarithmic plot for the concentration range of 10 to 20 mg/L of RhB (Fig. 4) confirmed the pseudo-first-order kinetics.

The importance of the relative concentration of PS and RhB is further verified by periodic addition of PS, when it is in limited supply (as seen from the decreasing/stabilized rate of degradation of RhB), to the MW/RhB/PS system. The results are shown in Fig. 5.

After the steep decrease up to 300 min, when the RhB concentration is more or less stabilized, addition of more PS (after 390 and 540 min of irradiation), leads to accelerated degradation and hence steep decrease in the concentration of the dye. This reconfirms that the stabilization in the degradation of RhB with time is due to inadequacy of PS in the system. When the amount of PS in the system is adequate, efficient degradation of even the in-between added RhB continues even after 630 min.

Since the rate of degradation of RhB continues to increase with increase in its concentration in the range 5–20 mg/L and higher concentration leads to extended reaction times and inconsistent kinetics, 10 mg/L is chosen as the convenient concentration for further investigations.

3.2. Effect of MW power and reaction volume

The effect of varying MW power on the degradation of RhB in the presence of PS is tested. The degradation increases slowly with power in the range 100–450 W (not shown here). Thereafter the increase is very steep. However, due to experimental constraints, the effect is not tested above 800 W. Variation in the MW power has been shown to influence the degradation of water pollutants in the presence and in the absence of oxidants [15,24]. The increase in MW power can increase the temperature of the reaction system and hence, the degradation at higher power is often attributed to this [17]. However, in this study, the temperature of the reaction medium is always maintained constant by circulating cooling water in the reactor jacket. Hence, the enhanced rate of degradation with increase in MW power cannot be attributed to increase in temperature.

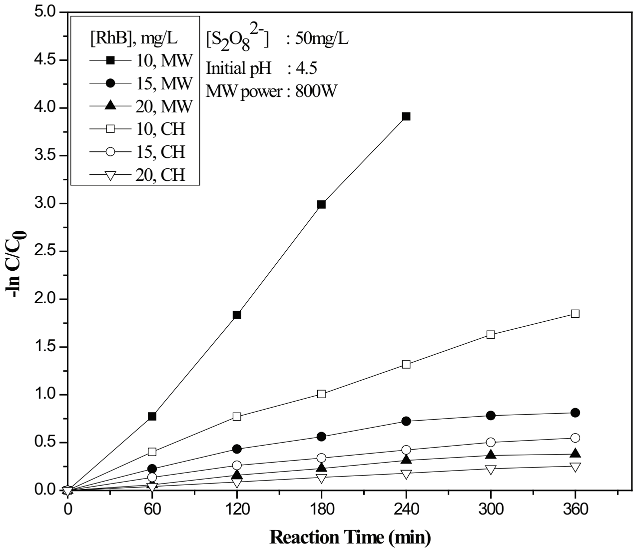

Fig. 4. Logarithmic plot for the degradation of RhB under MW irradiation and conventional heating (CH).

The effect of reaction volume on the degradation of RhB was investigated in the range of 20–100 mL at two distinct MW power, that is, 300 and 800 W. It was observed that the rate of degradation increases with increase in volume up to 70 mL and levels off thereafter in both the cases as shown in Fig. 6.

The absorption of MW energy increases with increase in volume. Hence, higher volume is not a constraint for efficient degradation of the pollutant at least up to a critical stage, which is important for the eventual commercial application of the process. However, the optimum may vary with the size and geometry of the reactor as well as with other reaction parameters. Enhancement in the absorption of MW and rate of reaction with increase in volume of the reactant has been reported earlier also [33]. Optimum power, irradiation time and volume along with other reaction parameters can be identified for each reactor to achieve efficient degradation.

MW is electromagnetic radiation in the frequency range of 0.3–300 GHz. Low energy MW irradiation (E = 0.4–40 J mol^{-1}, ν = 1–100 GHz) is responsible for dielectric heating causing thermally initiated reactions. Laboratory MW reactors like the one used here operate in the range of 2.45 GHz (±100 MHz). In combination with oxidants such as H_2O_2 (E = 1.8 eV) and/or PS (E = 2.1 eV), MW is observed to be efficient for the degradation of organic pollutants. These oxidants have the ability to absorb and utilize MW energy and generate more powerful reactive species such as ·OH (E = 2.8 eV) and SO_4^{-}· (E = 2.6 eV) [20–25]. In both instances, electron transfer, hydrogen abstraction or addition mechanisms are possible for the degradation of the substrate. However, increase in MW power need not enhance the degradation in all cases. There are reported instances where no further increase in absorption of MW or degradation of substrate happens at higher MW power beyond an optimum [24]. Characteristics of the organic compound and the oxidant are also important in the efficient utilization of the MW power.

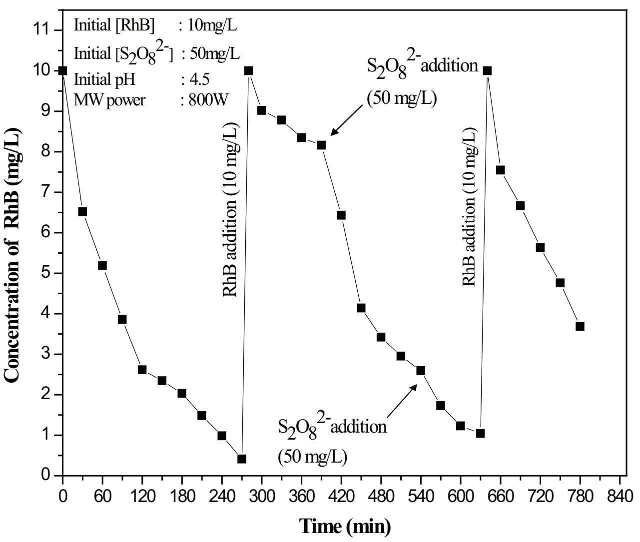

Fig. 5. Effect of in-between addition of RhB/$S_2O_8^{2-}$ on MW degradation of RhB.

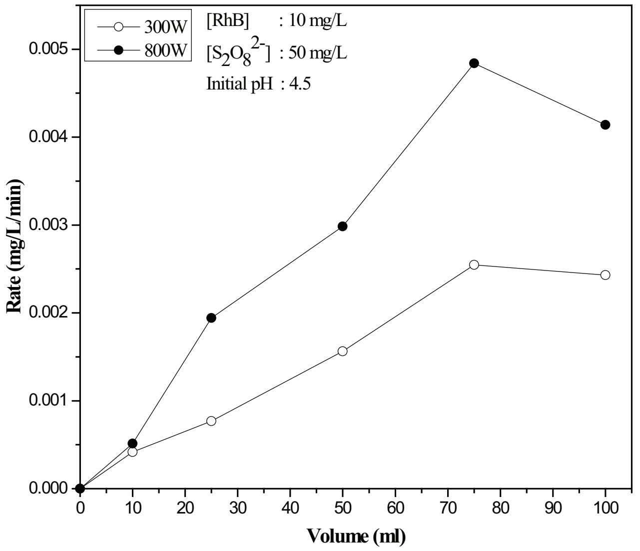

Fig. 6. Effect of MW power on rate of RhB degradation at different volumes.

The enhancement in the degradation of organics under MW irradiation, in comparison with CH, is often attributed to 'specific' or 'non-thermal' effect [16,17,23] that increases with increase in MW power. The effect includes (i) absorption of MW energy by the molecules that results in micro-stirring and consequently increased mixing and better interaction between the reactive species and (ii) continuous and violent vibration, migration and rotation of the reactant molecules induced by MW, leading to faster increase of solution temperature due to friction, better activation by increased collision, more efficient interaction and consequently accelerated rate of degradation [34]. The ability of the reaction system to convert MW energy into thermal energy depends on its dielectric constant. Since the energy of MW is lower compared with chemical bonds, no breaking/making of bonds is possible by simple absorption of the radiation. This is confirmed by the observation that there is no degradation of RhB even after 2 h of simple MW irradiation at RT. Similarly, the non-thermal effect of MW alone does not result in the formation of extra reactive free radicals from the oxidants PS or H_2O_2. This is evident from the absence of any significant degradation of RhB in the presence of these oxidants under MW irradiation at RT. Once the reaction is initiated at higher temperature, it can be accelerated by the 'non-thermal' factors.

Thermal heating of a reaction medium leads to increase in temperature and induces an increment of kinetic energy in the molecule. This accelerates the rate of collision of molecules. However, only very few of these collisions have enough energy and appropriate orientation to result in bond making/breaking and formation of new molecules. Simple heating results in an isotropic excitation of molecules and hence the collisions are less efficient. Anisotropic excitation caused by suitable activation tools such as MW results in the modification of the kinetic energy distribution of molecules (even at identical temperatures of the reaction medium and same average value of the energy distribution attained by CH) and consequently more efficient collision and enhanced reaction rate. The non-thermal effect of MW irradiation can also be explained at least partially based on this premise [35].

3.3. Effect of temperature

The effect of temperature on the degradation of RhB under both MW/PS and CH/PS is investigated by carrying out experiments at different temperatures (from 35°C ± 1°C to 75°C ± 2°C) under identical conditions and the activation energy for the processes is calculated. The rate of degradation increases with increase in temperature in both cases. The PS-induced degradation of organics under many AOPs involves two distinct steps: (i) formation of reactive $SO_4^{-}\cdot$ and $\cdot OH$ radicals and their interaction with the substrate and (ii) mineralization of the substrate either directly in single step or alternatively through a number of intermediates and competitive steps. Accordingly, the total activation energy of the current process (apparent activation energy E_a) will be the sum of the activation energies of the two independent processes, that is,

$$E_a\text{ (total)} = E_a1\text{ (free radical formation)} + E_a2\text{ (free radical reactions with RhB)} \quad (2)$$

The possible sites of interaction of the reactive free radicals with RhB are the C–H bonds, –COOH functional groups, aromatic rings and –N< [36]. The decolorization of the dye is primarily due to loss of aromaticity. Hence, for calculating the activation energy of the process, the possibility of competitive reactions is ruled out [37].

The apparent activation energy E_a of the degradation of RhB under MW/PS and CH/PS is calculated assuming pseudo–first-order kinetics using Arrhenius equation:

$$\ln k = (-E_a/kT) + \ln A \quad (3)$$

where k is the rate constant, T is the temperature of reaction in Kelvin and A is the Arrhenius factor.

The E_a calculated from the Arrhenius plot of ln$k$ vs. $1/T$ is 49.7 kJ/mol for the decolorization under CH conditions while it is 31.5 kJ/mol under MW conditions. The apparent activation energy under CH conditions is higher compared with the reported values of 40.7 and 40 kJ/mol for RhB degradation under UV/H_2O_2 and UV/MW, respectively [36,37]. These values are higher than that reported by Byrappa et al. [38] for UV/TiO_2 degradation of RhB (32.3 kJ/mol) that is comparable with the E_a value of 31.5 kJ/mol obtained for the MW/PS degradation in the current study. The lower activation energy in the case of MW irradiation implies that the 'non-thermal' effect of MW serves to reduce the activation energy that is at least partially responsible for the enhanced degradation. The relative enhancement of degradation by MW over CH is less at higher temperatures suggesting that even the latter is capable of providing adequate energy to drive the degradation under high temperature conditions.

MW irradiation of RhB/UV/H_2O_2 system is reported to result in enhanced degradation of the dye and reduced treatment time [17]. According to Ferrari et al. [36], this enhancement is not caused by decrease in activation energy implying that the potential energy of reactants, products and the reaction intermediates are not altered by MW irradiation. This is in contrast with the obtained results in which the MW irradiation of the system reduces the activation energy significantly. Ferrari et al. [36] conducted the experiments at very low MW power of less than 100 W. Further, in those experiments, the thermal effects of MW were removed using cooling water circulation. Earlier results have shown that the potential of MW cannot be fully exploited by separating the thermal effect and the 'non-thermal' effect from one another [15,24]. The current study proves that MW enhances the thermal degradation of RhB in the presence of PS, at least partially, by reducing the activation energy.

3.4. Effect of pH

The effect of pH on the PS-induced degradation of RhB under MW, CH and RT is experimentally determined and the results are shown in Fig. 7.

The trend remains more or less the same under all conditions with maximum degradation at pH 3, decreasing till neutral pH and slightly increasing and stabilizing thereafter in the alkaline pH. The decrease is steeper under CH and MW. The higher degradation of RhB under MW/PS compared with CH/PS is maintained at all pH. The dye solution as such remains practically unaffected at all pH indicating

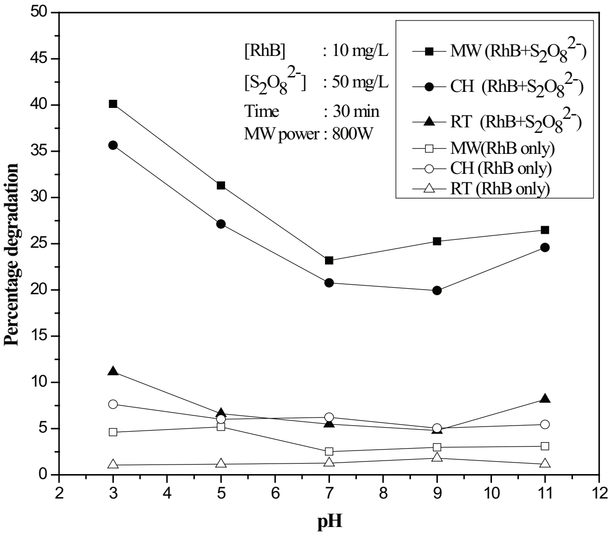

Fig. 7. Effect of pH on the degradation of RhB.

that the pH has significant effect on the degradation of RhB only in presence of the oxidant PS and under CH or MW. The influence of pH is less significant even in the presence of the strong oxidant PS in the absence of CH or MW.

The standard pH of the PS/RhB system under optimized conditions is 4.5. Degradation below pH 3 is not tested because of the inconveniences associated with extreme acidic conditions, especially for commercial application. The similarity in the qualitative trend of pH effect under RT, CH and MW shows that the mechanism of interaction or the nature of the reactions occurring at respective pH leading to the degradation of RhB in the presence of PS are the same. MW or CH simply accelerates the process. The observation is similar to the results reported by Gu et al. [39], on the degradation of trichloroethylene (TCE) in which PS-initiated degradation decreases as pH is raised from 3 to 11.

The pH of the reaction system decreases with time in the case of PS-induced degradation. This may be explained based on the generation of hydrogen ion during the process of sulfate radical (formed from PS as in reactions 20, 21 and 26) consumption at high temperature as follows:

$$SO_4^{-}\cdot + H_2O \rightarrow \cdot OH + SO_4^{2-} + H^+ \quad (4)$$

Under alkaline conditions, the OH^- ions may act as scavengers of the reactive SO_4–· radicals to give hydroxyl radicals which are also strong oxidants.

$$SO_4{-}\cdot + OH{-} \rightarrow \cdot OH + SO_4^{2-} \quad (5)$$

This may be the reason for the moderate degradation and eventual stabilization even under the alkaline pH conditions.

At acidic pH, $SO_4^{-}\cdot$ is more numerous and stable. As pH increases, the concentration of the radicals can decrease also due to their interaction with water as in reaction (4). However, correspondingly, the ·OH radicals increase and hence the pH effect is not severe over a wide range. Another reason for the moderate degradation under alkaline pH, despite the decrease in SO_4–· concentration due to reaction (5), is the more effective absorption and transmission of MW in this pH range [40,41]. At the same time, the radicals $SO_4^{-}\cdot$ and ·OH can interact with each other resulting in mutual deactivation [42]. Hence, the increasing rate of degradation cannot be sustained for long and it gets stabilized.

Thus, it may be seen that the total radical concentration as well as the relative concentration of the two reactive free radicals is pH-dependent. The physicochemical characteristics of the substrates at different pH also will influence their interaction with the two reactive radical species. This may be the reason for the contradicting reports on pH effect in the case of PS-induced degradation of different substrates [42,43].

3.5. Effect of added H_2O_2

The effect of added H_2O_2 on the MW degradation of RhB is found to be dependent on its relative concentration in the system. Under the standardized conditions as discussed earlier, the rate of degradation of RhB increases slowly, with increase in the concentration of added H_2O_2 in the range of 3–10 mg/L. Thereafter small incremental increase in H_2O_2 does not enhance the rate further and the degradation is stabilized for a while. However, when the concentration of H_2O_2 is increased to higher range of 50–500 mg/L, the rate of degradation of RhB increases again steeply in the beginning and slowly thereafter.

The enhancement in the MW-assisted degradation of RhB in presence of H_2O_2 can be due to the formation of reactive ·OH radicals by the decomposition of the latter as follows:

$$H_2O_2 + MW \rightarrow 2\cdot OH \quad (6)$$

The ·OH radicals react rapidly and non-selectively with aromatic molecules primarily by addition–elimination reaction to form corresponding hydroxyl compounds or by hydrogen abstraction. These intermediates can eventually get mineralized to CO_2 and water [44]. At moderately higher concentration of H_2O_2, the reactive ·OH radicals will interact more with it and less with the substrate leading to decreased rate of degradation. This interaction results in the formation of relatively less active $HO_2\cdot$ radicals (redox potential: 1.7 eV) as in reaction (7):

$$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2\cdot \quad (7)$$

The $HO_2\cdot$ and ·OH radicals can form H_2O_2 again as in reactions (8) and (9):

$$2\,HO_2\cdot \rightarrow H_2O_2 + O_2 \quad (8)$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \quad (9)$$

However, when the relative concentration of H_2O_2 is much higher, the comparative rate of formation of ·OH is more and the rate of degradation of RhB also is enhanced significantly. It is also possible that, at higher concentration, H_2O_2 absorbs more energy from the MW radiation and undergoes decomposition to H_2O and O_2 [20,23].

$$2H_2O_2 + MW \rightarrow 2H_2O + O_2 \quad (10)$$

Thus, H_2O_2 could simultaneously be a free radical producer and consumer. Hence, some of the ·OH-generated in situ will react with the RhB and degrade it while another part will react with the abundantly available H_2O_2 and decompose it as shown above. Due to this conflicting role, the effect of H_2O_2 on the degradation of RhB is not consistent or quantitatively reproducible.

3.6. Effect of combination of PS with H_2O_2 and ZnO

ZnO has been reported to be an efficient photocatalyst for the degradation of a number of pollutants [12]. Hence, the effect of its presence on the MW and CH-initiated degradation of RhB under various conditions is experimentally verified with the objective of possible combination of MW/CH and light. H_2O_2 also can enhance the degradation, depending on the concentration. The effect of addition of ZnO and H_2O_2 under MW and CH conditions is shown in Figs. 8(A) and (B), respectively.

While H_2O_2 is moderately effective as an oxidant of the dye, the effect is not seen additively in the presence of PS. In fact, the degradation of RhB under MW/PS is same as MW/PS/H_2O_2. This may be due to the deactivation of the reactive $SO_4^{-}\cdot$ by H_2O_2 (reaction 11) beyond a critical concentration of either so that the net concentration of the oxidants remain more or less the same.

$$SO_4^{-}\cdot + H_2O_2 \rightarrow SO_4^{2-} + H^+ + .O_2H \tag{11}$$

At higher concentrations, it is also possible that the reactive free radicals ·OH and $SO_4^{-}\cdot$ interact with each other more frequently resulting in unproductive chain termination. However, under CH conditions, H_2O_2 actually inhibits the PS-promoted degradation (Fig. 8(B)). This might probably be because under CH, unlike under MW, the rate of formation of $SO_4^{-}\cdot$ is not adequate to compensate for the deactivation caused by the interaction of H_2O_2/·OH and $SO_4^{-}\cdot$. Further, the added H_2O_2 may also quench the ·OH formed in the system by reaction (7) cited earlier. These detrimental effects are not compensated by commensurate formation of equally reactive free radicals under CH. Hence, the net effect of more H_2O_2 in the presence of PS is either negligible or slight inhibition.

The slight degradation of the dye alone (in the absence of any additive) in the presence of MW is moderately enhanced in the presence of ZnO. Similarly, the MW/H_2O_2 degradation of the dye is also enhanced by ZnO. The enhancement is attributed to the higher amount of ·OH free radicals generated from H_2O_2 in the presence of MW/ZnO. Under identical conditions, after 120 min, the degradation of RhB by MW/ZnO/H_2O_2 is ~7 times faster than MW/ZnO or MW/H_2O_2. Similarly, MW/ZnO/H_2O_2 is ~4 times faster than CH/ZnO/H_2O_2. This clearly shows that the irradiation source MW, catalyst ZnO and oxidant H_2O_2 together play a synergistic role in the degradation of RhB. However, the highest amount of degradation achieved in the presence of MW/PS as well as MW/PS/H_2O_2 is inhibited by ZnO. The presence of ZnO promotes formation of ·OH radicals from H_2O_2, which enhance the degradation. At the same time, in the presence of PS, the ·OH radicals interact more with the $SO_4^{-}\cdot$ resulting in the destruction of both by chain termination. This leads to decrease in the degradation. The trend remains the same under CH as well.

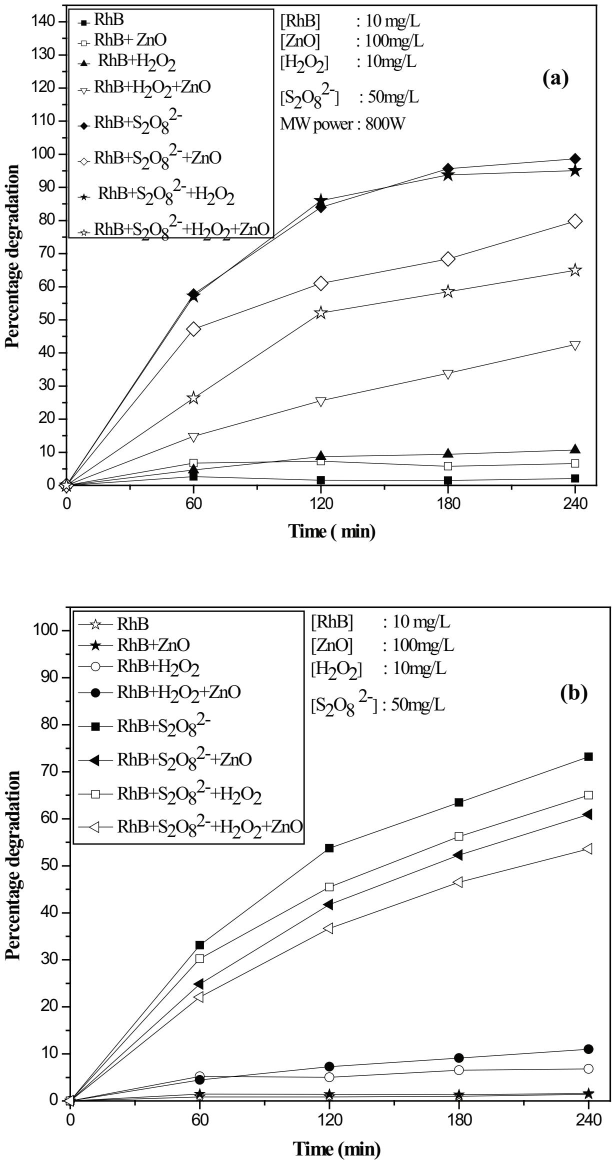

Fig. 8. Degradation of RhB using different combination of additives. (A) Under MW irradiation and (B) under conventional heating.

Another reason for the inhibition of MW/PS promoted degradation of RhB by ZnO may be the physicochemical effects of suspended particles which retard the availability of MW for the PS to generate reactive $SO_4^{-}\cdot$. This is similar to the observation by Saien et al. [45] of the effect of TiO_2 on UV/PS-induced degradation of triton. If the effect is due to reduction in the availability of MW radiation to the target sites, it must happen in the presence of other solids also. Experiments with MnO_2, Al_2O_3, SiO_2 and TiO_2 under identical conditions as in the case of ZnO showed that the PS/MW degradation of RhB is inhibited in this case as well (Fig. 9).

However, the inhibition is relatively less in the presence of MW-active solids SiO_2, Al_2O_3 and MnO_2. The inhibition is in the order, $ZnO > TiO_2 > SiO_2 > Al_2O_3 > MnO_2$. Earlier studies on the relative MW activity of various oxides for the degradation of trace organic pollutants in water showed that the activity is in the order ZnO < SiO_2 < TiO_2 < Al_2O_3 < MnO_2 which was largely correlated with the dielectric constant of the oxide [24]. Hence, the inhibition to the MW/PS degradation of RhB by ZnO or other oxides can be attributed, at least partially, to the reduction in the availability of MW radiation to PS. Highly MW-active solids such as MnO_2 will induce facile degradation of RhB in parallel. Hence, in their presence, the net inhibition of the PS-induced degradation is less. This is further confirmed by the observation that the more the MW activity of the solid, the less its efficiency for inhibition of the PS-promoted degradation. In the case of H_2O_2/ZnO, the net availability of MW is sufficient to initiate the decomposition of H_2O_2 and form reactive ·OH radicals, which is catalyzed by ZnO. Hence, ZnO enhances the degradation of RhB in the case of the MW/ H_2O_2 system.

Various reactions involving H_2O_2 taking place on the surface (in presence of ZnO) as well as in the bulk are as follows:

$$H_2O_2\ (\text{MW/CH}) \rightarrow 2{\cdot}OH \tag{12}$$

$$H_2O_2\ (\text{bulk}) \rightarrow H_2O_2\ (\text{ad}) \tag{13}$$

$$H_2O_2\ (\text{ad}) + {\cdot}OH \rightarrow HO_2{\cdot}\ (\text{ad}) + H_2O \tag{14}$$

$$HO_2{\cdot}\ (\text{ad}) + HO_2{\cdot}\ (\text{ad}) \rightarrow H_2O_2\ (\text{ad}) + O_2\ (\text{ad}) \tag{15}$$

$$HO_2{\cdot}\ (\text{ad}) \rightarrow HO_2{\cdot}\ (\text{bulk}) \tag{16}$$

$$HO{\cdot}\ (\text{ad}) \rightarrow HO{\cdot}\ (\text{bulk}) \tag{17}$$

$$H_2O_2\ (\text{ad}) \rightarrow H_2O_2\ (\text{bulk}) \tag{18}$$

$$\text{RhB} + \text{ROS (ad)/ROS (bulk)} \rightarrow \text{Intermediates} \rightarrow \text{Mineralization} \tag{19}$$

where ad. refers to adsorption on the surface of ZnO and ROS refers to reactive oxygen species such as ·OH, $HO_2{\cdot}$, and H_2O_2.

However, the surface as well as the bulk processes need not be additive and may be even competitive as seen by the 'practically no effect' or slight decrease in the degradation of RhB in the simultaneous presence of PS and ZnO. Combination of the MW process with other AOPs such as photocatalysis can enhance the degradation due to the aggressive roles played by electrons and holes generated by irradiation of semiconductor oxides. In this respect, investigations on the role of ZnO in MW/PS degradation/mineralization of pollutants are particularly important. In such combination processes, H_2O_2 may play the unique role as both electron and hole scavenger thereby preventing the recombination of surface electrons and holes and thus enhance the degradation.

Experiments on the effect of ZnO dosage in the range 0.002 to 0.01 mg on the degradation of RhB shows that there is no linear correlation between the effect and the quantity of ZnO in the narrow range studied here. This may be due to the complexity of various physicochemical processes occurring concurrently, as explained above. Addition of ZnO in between the ongoing degradation of RhB in the presence of PS/MW, H_2O_2/MW and (PS + H_2O_2)/MW also shows that the degradation is enhanced in the case of MW/H_2O_2 while it is inhibited in the case of MW/PS (Fig. 10). The net inhibitive effect of addition of ZnO in the case of MW/(PS+ H_2O_2), is less compared with that in the case of MW/PS thereby reconfirming the enhancing role (of ZnO) in the presence of H_2O_2.

The inhibiting effect of 'addition of ZnO in the beginning' on the degradation of RhB is more under MW/PS/H_2O_2, than that under MW/PS (Fig. 8(A)). This is quantitatively different from the effect of the 'in-between addition' of ZnO under the above two conditions (Fig. 10) which may be attributed to the complexity of the reaction system consisting of too many highly reactive free radicals in the bulk as well as on the surface. The possibility of adsorption of PS

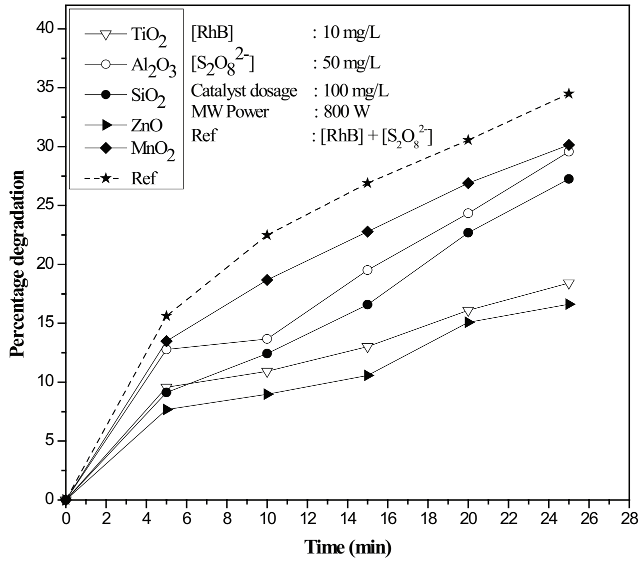

Fig. 9. Effect of different suspended oxides on MW/$S_2O_8^{2-}$ degradation of RhB.

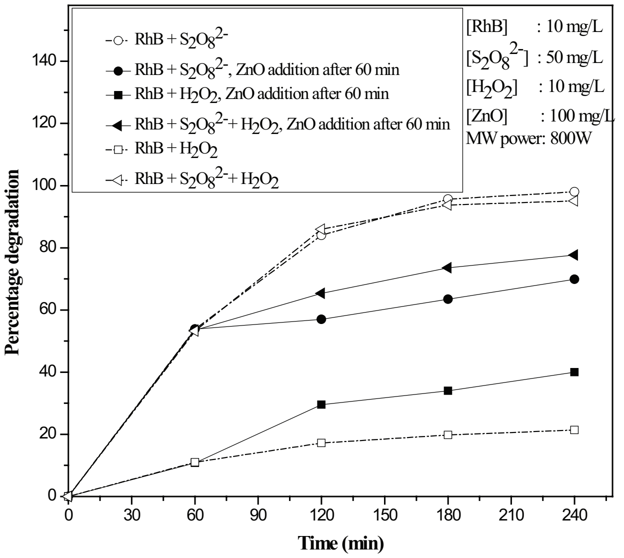

Fig. 10. Effect of in-between addition of ZnO on MW degradation of RhB.

on ZnO and consequent reduction in the concentration of the former, as the cause of inhibition of MW/PS degradation of RhB is tested experimentally. It is observed that adsorption or decomposition of PS is practically negligible in the presence of ZnO. Other factors such as modification of the active net volume of the reaction system and its dielectric properties by the suspended solid, modification in the physical characteristics and composition of the reaction system, creation/deactivation of different types of transient reactive species by ZnO, multiple interactions between the ROS on the surface as well as in the bulk may also contribute to the ZnO effect and complicate the system. This needs further in-depth investigation.

3.7. Effect on the COD

Estimation of chemical oxygen demand (COD) of the MW/PS and CH/PS reaction system at various intervals shows that the degradation/decolorization does not lead to instant mineralization. However, once the solution is decolorized and the MW irradiation is continued, slow mineralization takes place. In the case of CH, the mineralization is negligible even on prolonged heating after the decolorization. This shows that initially the dye is degrading/decolorizing fast to relatively more stable colorless intermediates which mineralize to CO_2 and water only slowly. Even extended exposure of the reaction system to MW irradiation is not powerful enough to mineralize these intermediates as seen from the stable COD (Fig. 11).

However, exposure of the decolorized solution containing PS to UV light for relatively shorter period mineralizes the dye/intermediates as seen from the almost complete disappearance of COD. ZnO which inhibits the degradation of RhB/MW accelerates the UV irradiation–induced mineralization and COD removal. This confirms the potential of combining photocatalysis and MW irradiation for faster mineralization of water pollutants.

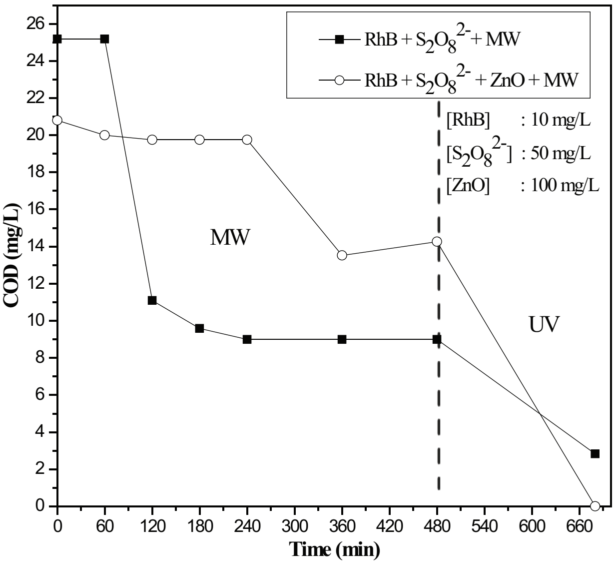

Fig. 11. Variation of COD with time during the MW/$S_2O_8^{2-}$ degradation of RhB: effect of ZnO and UV irradiation.

4. General mechanism

MW-initiated degradation of organic molecules is effected by the radiation itself and/or the MW-generated heat. According to Horikoshi and Serpone [16] the heat released has little effect on the degradation. However, the current study shows that the contribution of thermal effect is important and it is enhanced by the MW radiation. Enhancement of the degradation in the presence of oxidants clearly shows that oxidizing agents and/or the free radicals derived from them are involved in the reaction leading to the degradation and eventual mineralization of RhB.

PS-promoted degradation of organics takes place primarily by the interaction of the reactive $SO_4^{-}\cdot$ formed in situ. As the concentration of PS increases, more reactive $SO_4^{-}\cdot$ radicals are formed under CH as well as MW and a series of chain reactions follow as in Eqs. (20)–(27) [37].

$$S_2O_8^{2-} + MW \rightarrow 2SO_4^{-}\cdot \tag{20}$$

$SO_4^{-}\cdot$ radical is a stronger oxidant (oxidation potential 2.5–3.1 eV) than $S_2O_8^{2-}$ (2.01 eV).

$$S_2O_8^{2-} + R \rightarrow 2SO_4^{-}\cdot + \text{intermediates} \tag{21}$$

R: organic substrate

$$SO_4^{-}\cdot + H_2O \rightarrow HSO_4^{-}\cdot + \cdot OH \tag{22}$$

$$SO_4^{-}\cdot/\cdot OH + R \rightarrow \text{intermediates} \rightarrow \text{products} \tag{23}$$

$$SO_4^{-}\cdot + e \rightarrow SO_4^{2-} \tag{24}$$

$$2\cdot OH \rightarrow H_2O_2 \tag{25}$$

$\cdot OH$ can also interact with $S_2O_8^{2-}$ as follows:

$$S_2O_8^{2-} + \cdot OH \rightarrow HSO_4^{-} + SO_4^{-}\cdot + 0.5O_2 \tag{26}$$

$$HSO_4^{-} \leftrightarrow H^{+} + SO_4^{2-} \tag{27}$$

The formation of ·OH radicals is confirmed by the PL technique as described under section 2.5. No PL was observed in the absence of MW and PS thereby confirming the role of these two components in the formation of ·OH. The formation of ·OH in various AOPs has been demonstrated earlier also [29,46,47].

Both $SO_4^{-}\cdot$ and ·OH are highly reactive radical species, capable of readily interacting with and degrading the RhB. However, the formation of ·OH radicals by the MW activation is slow as seen from the PL measurements. Hence, the degradation is mostly by the interaction with $SO_4^{-}\cdot$ radicals. Trapping of the ·OH by PS resulting in $SO_4^{-}\cdot$ (reaction 26) may not affect the rate significantly since both free radicals have comparable redox potential. The comparative oxidation potential of various reactive species likely to be present in MW/PS system is shown in Table 4 [32].

At higher concentrations of PS, the $SO_4^{-}\cdot$ can interact with the former as follows [48,49]:

Table 4
Oxidation potential of likely reactive species in MW/PS system

Species	Oxidation potential (eV)
$S_2O_8^{2-}$	+2.1
SO_4^-	+2.6
H_2O_2	+1.8
·OH	+2.8
HSO_5^-	+1.4
O_2-	−0.2
HO_2	+1.7

$$SO_4^{-\cdot} + S_2O_8^{2-} \rightarrow SO_4^{2-\cdot} + S_2O_8^{-\cdot} \quad (28)$$

$k = 6.1 \times 10^5\ M^{-1}\,s^{-1}$

$SO_4^{-\cdot}$ can also get deactivated forming PS as follows:

$$SO_4^{-\cdot} + SO_4^{-\cdot} \rightarrow S_2O_8^{2-} \quad (29)$$

$k = 4.0 \times 10^8\ M^{-1}\,s^{-1}$

Thus, the reactive $SO_4^{-\cdot}$ is transformed into less reactive $S_2O_8^{-\cdot}$ radicals or PS itself.

Hence, the degradation slows down with reaction time.

The higher effectiveness of MW over CH under identical conditions is primarily attributed to the 'non-thermal effect' as explained in section 3.2. The reactive free radical formation is also enhanced because of higher temperatures produced in shorter times and the molecular level heating [34]. Lowering of the activation energy by MW, as demonstrated in section 3.3, is another reason for the higher efficiency of MW radiation.

PS is a strong two electron oxidant (2.01 eV), comparable with O_3 (2.07 eV) and H_2O_2 (1.78 V). However, at ambient temperature, oxidation by PS is slow. MW serves as a powerful activation tool for PS by producing reactive oxidant $SO_4^{-\cdot}$ radicals (2.6 eV) which can degrade organic pollutants. The formation of $SO_4^{-\cdot}$ with one unpaired electron and ·OH radicals from PS by thermal reaction was explained earlier.

The initial rate of degradation of RhB under MW/PS is ~10 times more than that under MW/H_2O_2. However, under CH/PS, the degradation is only ~6 times more compared with CH/H_2O_2. MW/PS/ZnO is ~2.5 times more active compared with MW/H_2O_2/ZnO. These results support the earlier report [30] that MW activates PS more than H_2O_2. The combination of H_2O_2 and PS does not provide any additive or synergic effect, probably because the 'H_2O_2 effect' which is primarily due to the formation of ·OH radicals is already in action in the presence of PS which also generates ·OH, as already explained.

5. Conclusion

Water contaminated with trace amounts of Rhodamine B pollutant can be effectively purified by oxidants such as PS and/or H_2O_2 under MW irradiation. The MW-initiated decontamination is considerably faster compared with CH under identical conditions suggesting that the MW effect is not just thermal. The enhancement is primarily due to 'non-thermal' effects of MW and reduction in the activation energy of the degradation. The relative enhancement of the degradation by MW over CH is more in the presence of PS compared with H_2O_2. The combination of H_2O_2 and PS does not produce any additive effect and the degradation is more or less the same as in the presence of PS alone. Semiconductor oxide ZnO, which functions as a catalyst in many AOPs, inhibits the degradation under MW/PS while it enhances the degradation under MW/H_2O_2. However, under combined MW and UV light irradiation, ZnO serves as a photocatalyst and enhances the mineralization of RhB. The rate of degradation depends on the type of oxidant, concentration of various components, temperature, MW power, pH, etc. The reactions are investigated in detail and optimum parameters for the mineralization of the pollutant are determined. Major transient intermediates are also identified. The observations are critically analyzed and a general mechanism is proposed.

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