

## Solar fenton process: An inexpensive green technology for the decontamination of wastewater from toxic chemical pollutants

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**Abstract:** The classic fenton reaction involving use of simple ferrous salt and  $H_2O_2$  under ambient conditions as well as under sunlight irradiation is investigated as a potential AOP for the removal of toxic dye pollutant RhB from water. The ratio of  $Fe^{2+}$  ion and  $H_2O_2$  is optimized. Interestingly the optimum is quite different under normal Fenton process and solar Fenton process. The requirement of relative amount of  $Fe^{2+}$  is more under normal Fenton while the relative amount of  $H_2O_2$  is more under solar Fenton process. The  $Fe^{2+}$  which gets transformed into  $Fe^{3+}$  during the process is converted back into  $Fe^{2+}$  during the process itself. Thus by the intermittent addition of extra  $H_2O_2$  to compensate for the consumption in the process, the  $Fe^{2+}$  can be recycled any number of times. Thus the disadvantages of fenton sludge formation as the possible reason for its poor acceptance as an environment-friendly technology is overcome here by careful design of the component ratio. Typical oxidant such as persulphate enhances the degradation moderately. Various dissolved anions in water do not have any significant influence on the efficiency of the process. The process offers the potential for the inexpensive environment-friendly decontamination of polluted wastewater, using sunlight as the source of energy.

**Keywords:** Fenton reagent; Solar energy; Rhodamine B, Persulphate, Anions

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### I. Introduction

Advanced Oxidation Processes (AOP) have generated considerable interest in recent years, individually as well as in combination, as energy-efficient, environment-friendly technique for the destruction of toxic organic pollutants in water [1-8]. The techniques include photocatalysis, sonocatalysis, electrocatalysis, wet air oxidation, fenton process, photo-fenton process and their combinations which are primarily based on the formation of highly reactive  $\cdot OH$  radicals. Major advantages of these AOP include relatively mild reaction conditions and their proven ability to degrade several toxic refractory pollutants. The  $\cdot OH$  radicals are highly reactive species which (oxidation potential 2.8V) can attack most part of an organic molecule with rate constants usually in the range of  $10^6$ - $10^9$   $L\ mol^{-1}s^{-1}$  [9]. Hydroxyl radical is the second strongest oxidant next only to fluorine ( $E = 3.03V$ ) and it reacts at least  $10^6$ - $10^8$  times faster than  $O_3$  for the degradation of many organic compounds [10].

AOPs are broadly classified into homogeneous and heterogeneous types according to the reactive phase. Homogeneous type AOPs include Fenton based processes such as Fenton ( $H_2O_2 + Fe^{2+}$ ), Fenton like processes ( $Fe^{2+} + H_2O_2 + m^{n+}$ ), Sono-, photo-, electro-fenton, their combinations such as Sono-photo-, Sono-electro-, Sono-photo-electro- fenton etc. Other homogeneous processes include  $O_3$ ,  $H_2O_2$ ,  $O_3$ -UV,  $H_2O_2$ -UV and  $O_3$ - $H_2O_2$ -UV etc [11,12]. All processes involving suspended catalysts belong to the category of heterogeneous AOPs. However these processes, except probably heterogeneous photocatalysis, have gained only limited acceptance so far, as viable and effective methods for the large scale decontamination of wastewater due to complexity of the process, cost, operational constraints etc. Of late, AOPs based on ionizing radiations, microwaves and pulsed plasma techniques are also being investigated widely. However, economic viability of these processes is still to be proven. In this respect, the simple inexpensive classic fenton reaction has attracted renewed interest [13,14]. In this paper, results of our investigations on improvement of the Fenton and

Fenton like processes and their application as a possible candidate for the removal of hazardous organics from wastewater is examined using the dye Rhodamine B (RhB) as the candidate pollutant. The Fenton process as such without any external activation and sunlight induced Fenton process (solar Fenton) are investigated in detail and compared.

Rhodamine B [RhB], a xanthenes dye {molecular formula  $C_{28}H_{31}N_2O_3Cl$ , molecular weight: 479.01g/mole, IUPAC name: N-[9-(ortho-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-ylidene]diethylammonium chloride} is a refractory dye pollutant widely used in textile and food industry. RhB is toxic for animals and humans and is reported to be carcinogenic. Hence removal of the last traces of RhB from water is important from the safety and environmental angle. The structure of Rhodamine B is as shown in figure 1.

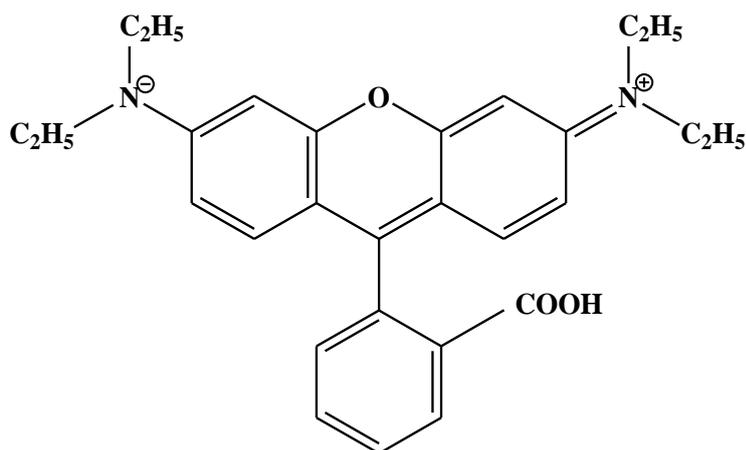


Fig 1. Structure of Rhodamine B

## II. Materials and methods

RhB (>99.6%) and ZnO (>99.5%) used in the study were from Sigma Aldrich India and used as such.  $H_2O_2$  (30.0% w/v) and  $FeSO_4 \cdot 7H_2O$  (FS) from Qualigen (India) were also used as such without further purification. ZnO is characterized by adsorption, surface area ( $12 \text{ m}^2/\text{g}$ ), particle size distribution, Scanning Electron microscopy (SEM, instrument: JEOL Model JSM-6390 LV), X-ray diffractogram (XRD, instrument: Bruker D2 Phaser) etc. Typical SEM and XRD images are shown in Figures 2A and B. Pore size analysis using Micrometrics Tristar surface area and porosity analyser showed that more than 70% of the pores in ZnO were  $< 250 \text{ \AA}$ . The average pore width is  $123 \text{ \AA}$  and size distribution is approximately;  $< 250 \text{ \AA}$  (70.1%),  $250\text{-}500 \text{ \AA}$  (11.3%) and  $> 500 \text{ \AA}$  (17.8%). The particle size was analysed using Malvern Mastersizer 3000. The average particle size is  $3.2 \text{ \mu m}$ .

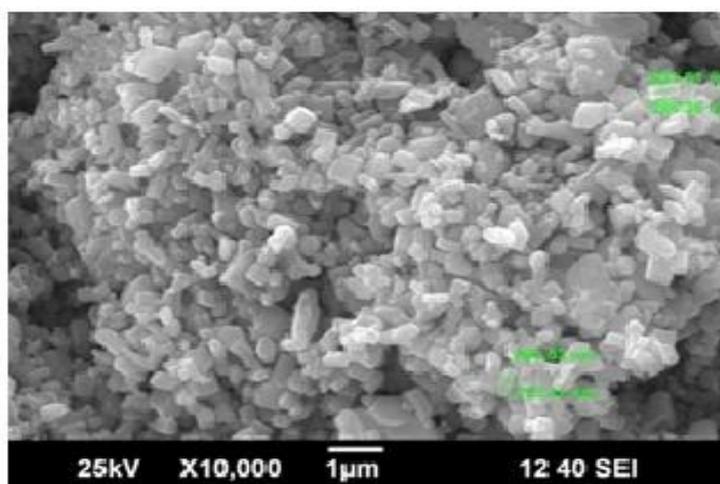
Adsorption studies were performed as follows [15]:

A fixed amount (0.1 g) of the adsorbent was added to 100 ml of the dye solution in a 250 ml reaction flask and the pH was adjusted as required. The suspension was agitated continuously at constant temperature of  $29 \pm 1^\circ\text{C}$  for 2 hrs to achieve equilibrium. The suspension was kept undisturbed for 2 hr and was then centrifuged at 3000 rpm for 10 min. After centrifugation the concentration of RhB in the supernatant was determined colorimetrically. Keeping the suspension overnight before centrifuging did not make any significant difference indicating that the 2 hr period is adequate to complete the adsorption. The adsorbate uptake was calculated from the relation

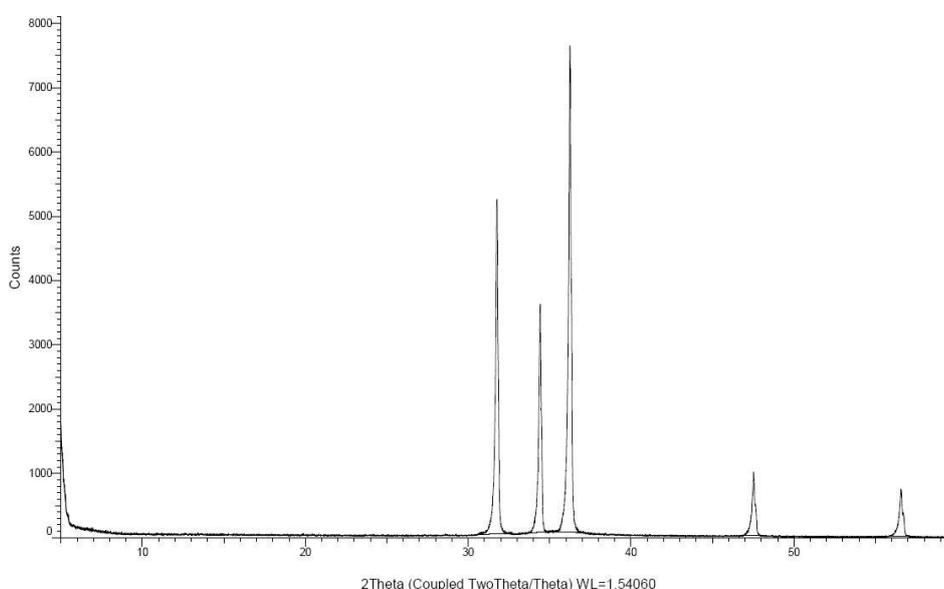
$$q_e = (C_0 - C_e)V/W \quad (1)$$

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 in Litre,  $W$  is the mass of the adsorbent in gram and  $q_e$  is the amount adsorbed in mg per gram of the adsorbent.

In a typical experiment without external activation, the dye solution of required concentration is mixed with appropriate combinations of FS and  $H_2O_2$  (HP) in a 250 ml closed pyrex glass reactor and wrapped with black paper to avoid photochemical reactions, if any. The degradation is monitored by analyzing for the RhB remaining in the system by using UV-VIS spectrophotometry at 554 nm. Solar experiments were performed by placing the system on the roof top of our laboratory at Kochi, Kerala, India ( $9^{\circ} 57' 51''$  N,  $76^{\circ} 16' 59''$  E) during sunny days in August-November 2015. The experiments are performed under varying reaction conditions and optimum parameters for the degradation of the dye were identified.



**Figure 2A.;** Typical SEM image of ZnO



**Figure 2 B :** Typical XRD image of ZnO

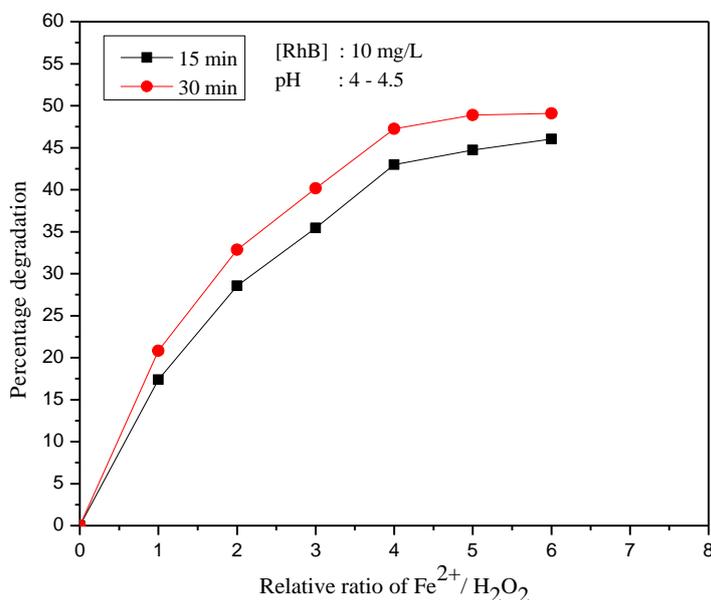
### **III. Results and discussions**

Preliminary investigations showed that Fenton process is effective for the degradation and decolorisation of RhB. It is also observed that the efficiency of the process depends on the relative concentration of FS and HP. Hence detailed investigations were made on optimizing the ratio of these two critical components for RhB degradation under normal as well as solar conditions. The RhB concentration is kept constant at 10 mg/L. The quantity of FeS and HP is optimized by keeping one component constant and varying the other. The % degradation of RhB is measured at varying the concentrations of FeS and HP and it has been confirmed that in the case of normal fenton (NF) the rate increases with increase in concentration of FS and the optimum ratio of FeS/HP is identified as 4:1 (Figure 3a). However under solar fenton experiments (SF) the optimum ratio is in the reverse order with FeS/HP in the ratio 1:3 (Figure 3b). At the respective optimized ratio, the optimum quantity of the fenton reagent (FR) for the degradation of fixed amount of RhB is determined for both NF and SF from a series of experiments. The results are presented in 4a and b which show that the rate of degradation increases with increase in quantity of FR with gradual slowdown at later stages, probably because the concentration of the dye has become too low for effective utilization of the higher availability of FR.

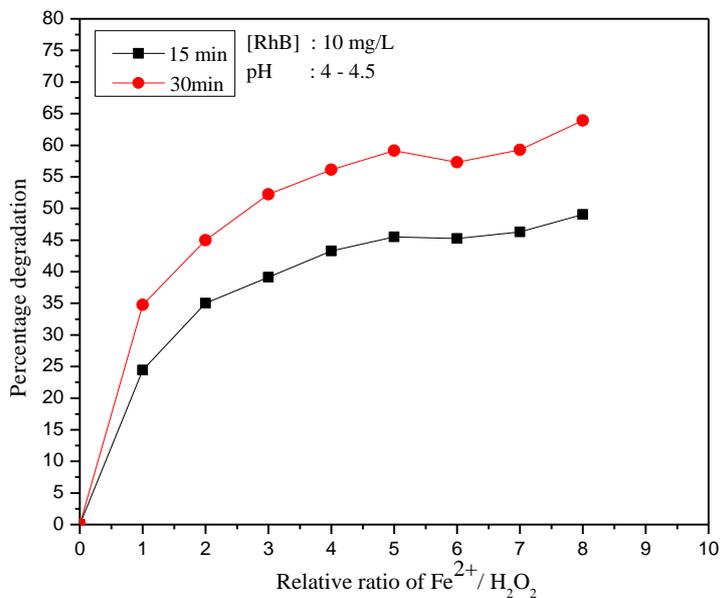
Based on the data, the quantity of FR at the pre-optimized ratio of components for subsequent experiments is identified as follows:

NF: FeS=20 mg/L, HP = 5 mg/L

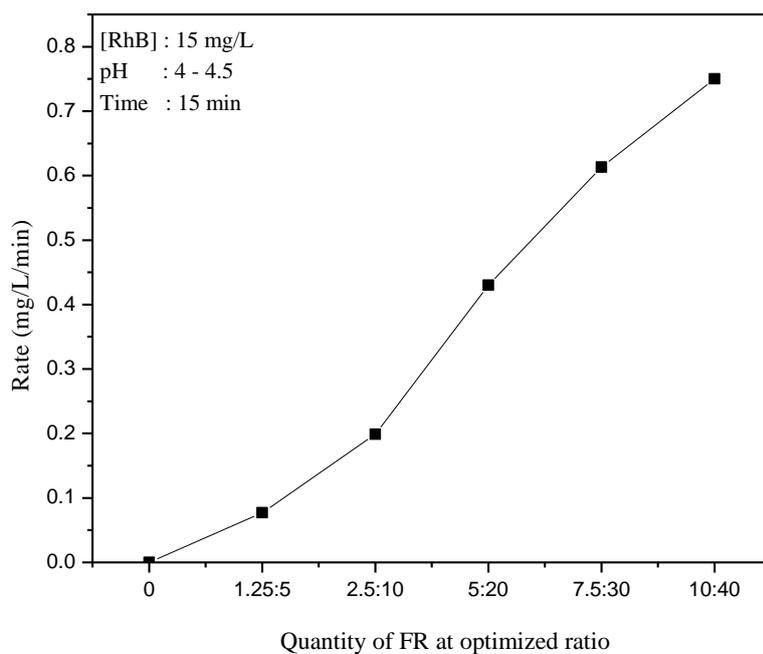
SF: FeS = 2.5 mg/L, HP = 7.5 mg/L



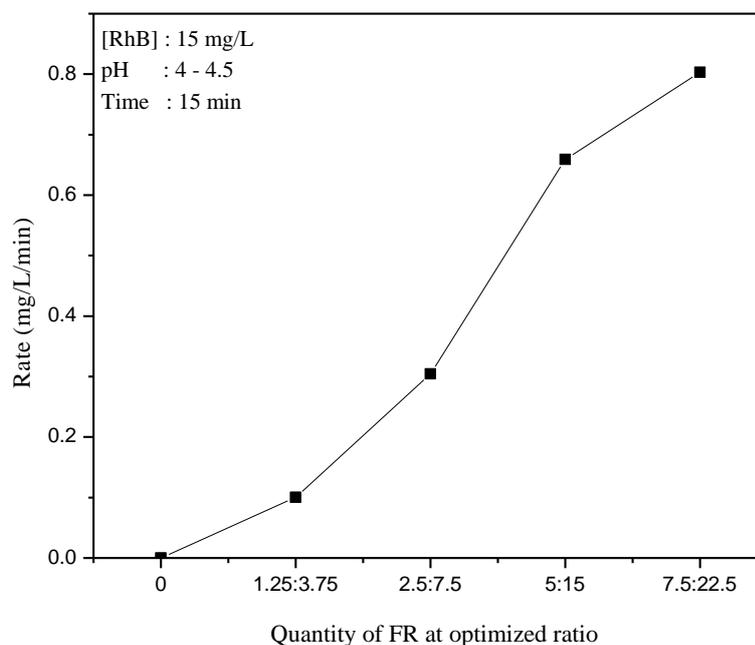
**Figure 3 a :** Effect of  $Fe^{2+}/H_2O_2$  ratio in NF on the efficiency of RhB degradation



**Figure 3 b :** Effect of Fe<sup>2+</sup>/ H<sub>2</sub>O<sub>2</sub> ratio in SF on the efficiency of RhB degradation



**Figure 4 a :** Effect of quantity of FR on the rate of RhB degradation under NF



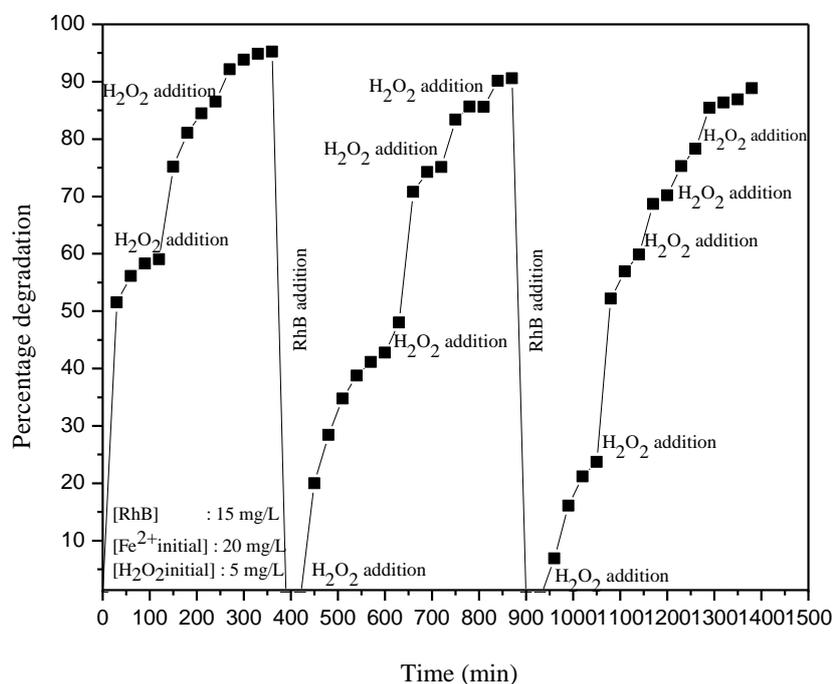
**Figure 4 b** : Effect of quantity of FR on the rate of RhB degradation under SF

The data further shows that SF, even at lower amounts of FeS and HP is many times more efficient for the degradation of RhB compared to NF. However, the parameters may vary under another set of reaction conditions, reactor geometry, size etc and hence every time the conditions are changed, the optimum also needs to be reworked.

Fenton processes are reported to be very sensitive to reaction conditions, especially the relative availability of the FR and the substrate. Accordingly, the rate of degradation at various concentrations of the dye is experimentally determined both under NF and SF conditions. As expected, when there is sufficient quantity of FR in the system, the dye degrades fast. However, with increase in concentration of dye beyond a particular optimum the rate of degradation stabilises and even slows down gradually (figure 3). Accordingly 15 mg/L of RhB is chosen for further investigations.

One of the advantages of FR is that moderate excess in quantity over the stoichiometrically required amount does not inhibit the degradation of the pollutant and the reagent can be utilized quantitatively. This possibility is tested by adding the FR/H<sub>2</sub>O<sub>2</sub>/FeS into a reaction system in which the degradation of the pollutant was fully completed or leveled off due to the inadequacy of the reagent. Fig 5 shows the effect of in-between addition of H<sub>2</sub>O<sub>2</sub> to the NF system. In this case the optimized ratio of FeS/HP has excess FeS and hence the leveling off may be due to the exhaustion of H<sub>2</sub>O<sub>2</sub>. Thus addition of H<sub>2</sub>O<sub>2</sub> after 150 minutes when the degradation of RhB has leveled off at around 60% kick-starts the degradation again. It levels off again at ~ 95% after 300 minutes, this time possibly due to the non availability of both the dye and H<sub>2</sub>O<sub>2</sub>. At this stage, more RhB is added. However, the degradation does not proceed, probably due to the non availability of H<sub>2</sub>O<sub>2</sub>. At this stage more H<sub>2</sub>O<sub>2</sub> is added and the degradation takes place at a fast pace. By periodic addition of H<sub>2</sub>O<sub>2</sub> the stabilised degradation can be restated any number of times as seen from the graph. This clearly shows that the FeS present in the system does not get poisoned or deactivated and can be recycled any number of times by the addition of required

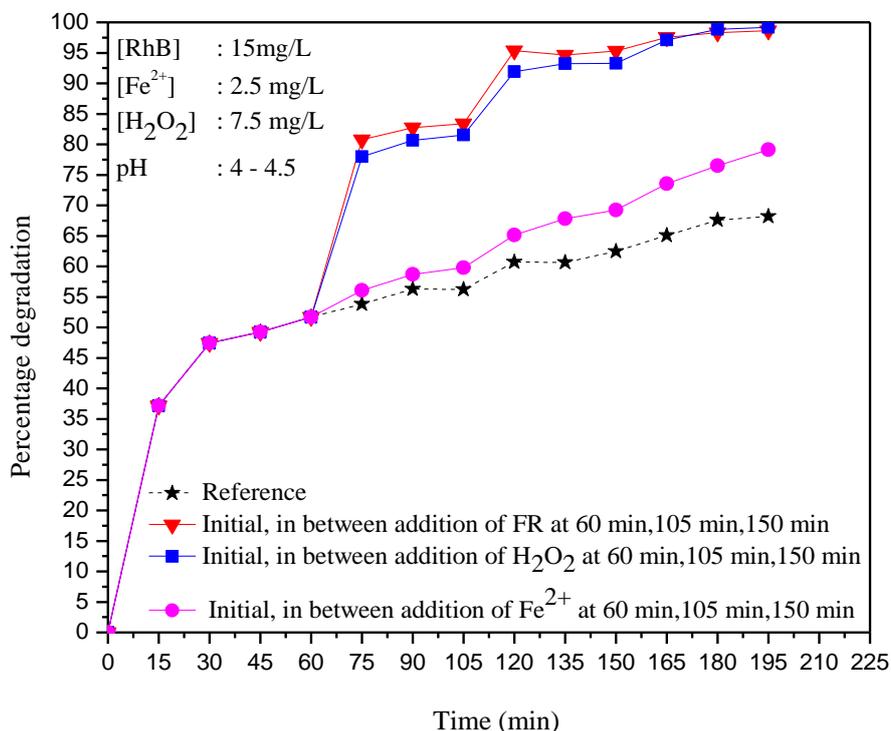
amounts of  $H_2O_2$ . This will also eliminate the accumulation of Fe sludge which is often blamed as a disadvantage of using FR in wastewater treatment.



**Figure 5 :** Recycling of  $Fe^{2+}$  by in between addition of  $H_2O_2$

Similar study was made in the case of SF also. In this case the optimum ratio of FeS/HP has excess of  $H_2O_2$ . The results of the in between addition of the components of FR and FR itself are shown in Figure 6. Once again it can be seen that in between addition of FeS, when the degradation of RhB has stabilised at ~ 50% enhances the degradation only marginally thereby confirming that even under light irradiation, FeS does not get deactivated and the leveling off is not due to the non-availability of FeS. This is further confirmed from the in between addition of  $H_2O_2$  and FR. In both cases, addition of extra reagent at every level-off point (60 min., ~50% degradation, 105 min., ~80% degradation) enhances the degradation significantly.

The effect of progressive addition of  $H_2O_2$  becomes less and less with each addition. In addition to the participation in the degradation self decomposition of the  $H_2O_2$  is also taking place in parallel. Hence the  $H_2O_2$  in the system is inadequate, even though it is based on the optimized composition. This also shows that moderate excess over the optimized level of  $H_2O_2$  is desirable to ensure continued degradation. This



**Figure 6 :** Effect of in between addition of Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/FR on RhB degradation

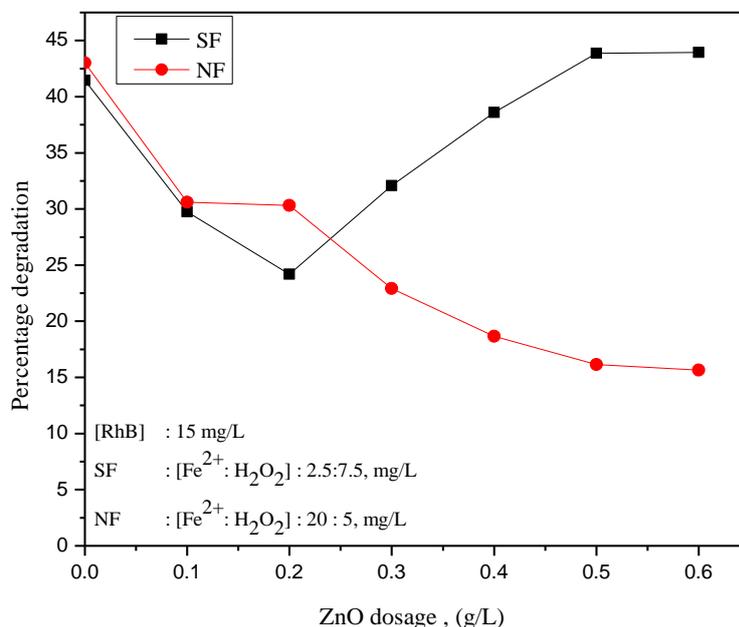
Is further confirmed by the in between addition of FR. In this case addition after 45 minutes enhanced the degradation significantly and stabilised. At that point extra addition of FR enhanced the degradation moderately. Further addition did not increase. At this stage almost 90% of the dye is already degraded. Hence the insignificant effect is due to the relatively lower availability of the dye to effectively utilize the available FR. This also shows that in the case of FR, excess of reagent is always recommended to effect good degradation of the target substrate, due to the self decomposition of H<sub>2</sub>O<sub>2</sub> and blocking of Fe<sup>2+</sup> by the reactants/intermediates. The relative efficiency of Fenton process under normal and solar conditions is shown in Table 2

**Table 2.** Relative efficiency of normal Fenton and Solar Fenton for the degradation of Rh B

% Degradation	Normal Fenton			Solar Fenton		
	[FeS]	[H <sub>2</sub> O <sub>2</sub> ]	Time (min)	[FeS]	[H <sub>2</sub> O <sub>2</sub> ]	Time (min)
50	20	5	45	2.5	7.5	45
80	20	15	105	2.5	15	105
95	20	20	180	2.5	22.5	150

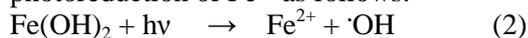
### 1.1. Effect of ZnO, Photocatalytic Fenton process

It has been shown that semiconductors like ZnO and TiO<sub>2</sub> enhance the photocatalytic degradation of many water pollutants. ZnO is relatively more efficient for harnessing solar energy, in view of its better absorption characteristics in the visible range of solar spectrum. In this context, the possibility of combining FR with ZnO is examined under both normal and solar conditions. The results are shown in Figure 7.



**Figure 7 :** Effect of catalyst dosage on RhB degradation under NF and SF

Contrary to the expectation, ZnO inhibits the degradation initially under both NF and SF conditions. This might be probably due to the initial adsorption/catalytic decomposition of H<sub>2</sub>O<sub>2</sub> which reduces the availability for the generation of reactive ·OH radicals. In the case of NF, in the absence of any high energy source of activation, the suspended solids may block the free interaction of FR with the target molecules. The substrate as well as the components of FR may get shielded by the ZnO particles which also may lead to the inhibition. However, in presence of sunlight, due to the photochemical and photocatalytic effects of ZnO, the trend is different. In this case, after the initial inhibition, the degradation increases with increase in concentration of ZnO, indicating the enhancement effect of the combination, i.e. solar photocatalytic fenton process over the fenton process. In presence of light, the Fe<sup>3+</sup> ions produced from the FR are regenerated into Fe<sup>2+</sup> by photoreduction of Fe<sup>3+</sup> as follows:



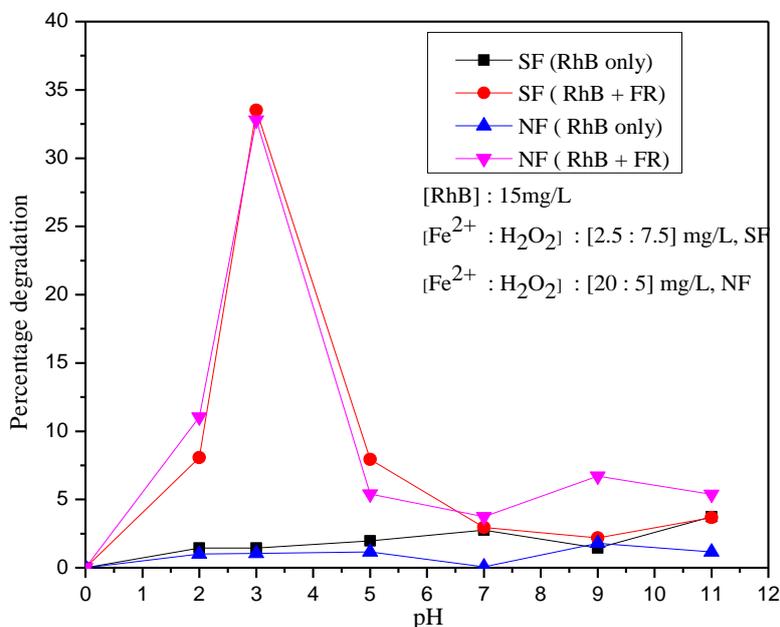
It is also possible that at least a part of H<sub>2</sub>O<sub>2</sub> may get directly photolysed to ·OH which can facilitate the degradation.



However under Fenton conditions, the iron complexes will strongly absorb the radiation and hence the above reaction can contribute only to a limited extent.

### 3.2. Effect of pH

Another important parameter in FR process is pH, especially due to the speciation factors of  $\text{Fe}^{2+}$  and HP. Hence the effect of pH is critically examined and the results plotted in figure 8. The optimum pH was found to be 3. This is in agreement with all FR related reactions irrespective of the target substrate. Thereafter it slows down, at higher pH which is attributed to the presence of relatively inactive iron oxohydroxides and formation of ferric hydroxide precipitate [16,17]. Consequently, the free iron ions are reduced and less hydroxyl radicals are generated. Further the oxidation potential of hydroxyl radicals decrease with increase in pH. The oxidation potential of the redox couple  $\text{OH}/\text{H}_2\text{O}_2$  is  $\sim 2.59$  vs NHE at pH 0 and 1.64 V vs NHE at pH 14. Further, the auto-decomposition of  $\text{H}_2\text{O}_2$  is accelerated at higher pH. The decrease in degradation below pH 3 may be due to the presence of iron complex  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  which reacts more slowly with  $\text{H}_2\text{O}_2$  to generate reactive species [18,19]. It is also possible that the peroxides get solvated in the presence of high concentration of  $\text{H}^+$  ions to form stable oxonium ion  $[\text{H}_3\text{O}_2]^+$ . These ions make  $\text{H}_2\text{O}_2$  more stable and reduce its reactivity with ferrous ions [20,21]. Thus it is clear that proper maintenance of the pH is important in FR driven degradation of pollutants.



**Figure 8 :** Effect of pH on Fenton oxidation of RhB under NF and SF

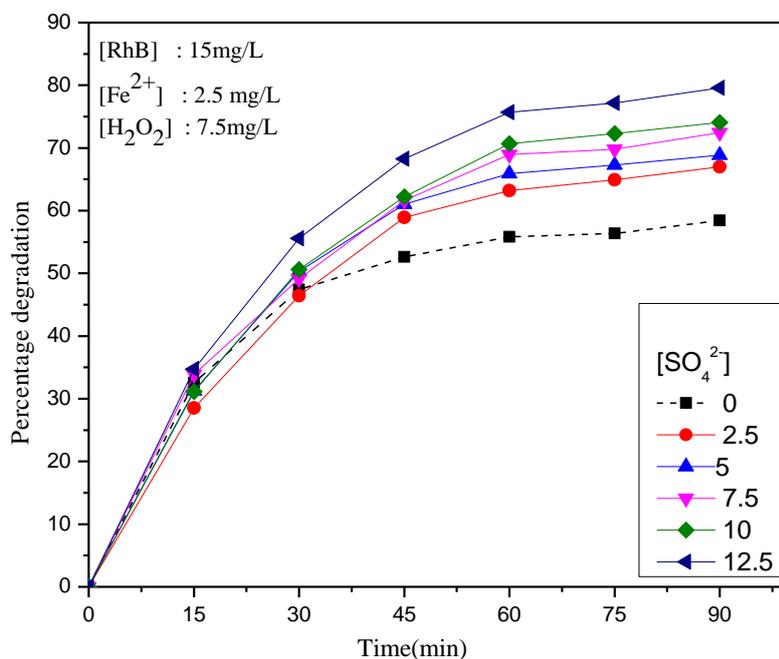
The degradation stabilized at  $\sim 45\%$ . At this stage more  $\text{Fe}^{2+}$  is added at three different time intervals, i.e. 45, 90, and 135 minutes. The degradation increased only marginally indicating that inadequate concentration of the  $\text{Fe}^{2+}$  is not the main reason for the stabilization. At the same time addition of  $\text{H}_2\text{O}_2$  increases the degradation considerably. Hence the stabilization is due to the nonavailability of adequate  $\text{H}_2\text{O}_2$ . However further addition of  $\text{H}_2\text{O}_2$  after 90 minute had only moderate effect and addition after 135 minutes had no effect. Hence it is evident that in addition to the participation in the degradation self decomposition of the  $\text{H}_2\text{O}_2$  is also taking place in parallel. Hence the  $\text{H}_2\text{O}_2$  in the system is inadequate, even though it is based on the optimized composition. This also shows that moderate excess over the optimized level of  $\text{H}_2\text{O}_2$  is desirable to ensure continued degradation. This is further confirmed by the in between addition of FR. In this case addition after 45 minutes enhanced the degradation significantly and stabilised. At that point extra addition of FR

enhanced the degradation moderately. Further addition did not increase. At this stage almost 90% of the dye is already degraded. Hence the insignificant effect is due to the relatively lower availability of the dye to effectively utilize the available FR. This also shows that in the case of FR, excess of reagent is always recommended to effect good degradation of the target substrate, due to the self decomposition of  $H_2O_2$  and blocking of  $Fe^{2+}$  by the reactants/intermediates.

### 3.3 Effect of persulphate

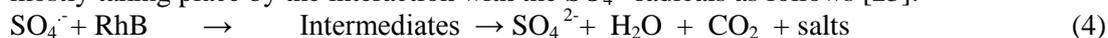
Persulphates are proven to be strong oxidants in AOPs due to the formation of highly reactive  $SO_4^{\cdot-}$  radical anions. The probability of enhancing the efficiency of FR by the addition of persulphates is tested at various concentrations for various reaction times. The results show that persulphates have practically no effect. This might be due to the inherent inability of persulphates to form reactive radicals in the absence of proper activation by thermal, photochemical, sono or other techniques. This is further confirmed from the solar fenton experiments. The results are shown in Figure 9.

The enhancement in the degradation of organics in presence of persulphate (PS) can be attributed to the formation of highly reactive  $SO_4^{\cdot-}$  from PS. With increase in concentration of PS more reactive  $SO_4^{\cdot-}$  radicals may be formed under the oxidizing environment. These radicals can interact with RhB and result in degradation/mineralization [22]. The formation of  $\cdot OH$  radicals also is possible in presence of high energy activation sources such as UV light or ultrasound. However, in the current instance of solar fenton

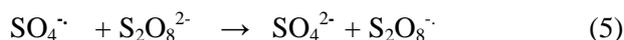


**Figure 9 :** Effect of persulphate on RhB degradation under SF

process, the formation of  $\cdot OH$  radicals by this route is not very dominant. Hence the degradation is mostly taking place by the interaction with the  $SO_4^{\cdot-}$  radicals as follows [23]:



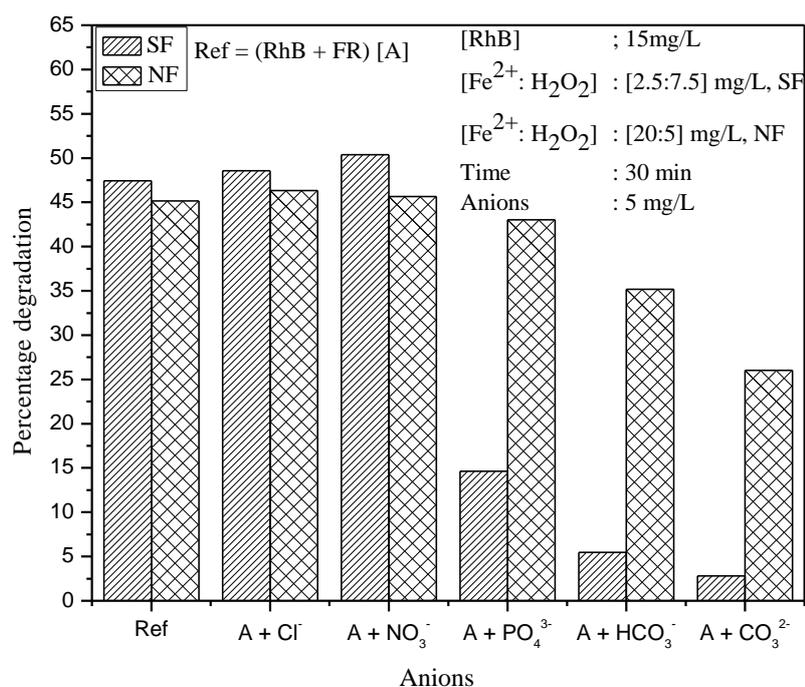
At higher concentrations of PS,  $SO_4^{\cdot-}$  can interact with the former and transform the same to less reactive  $S_2O_8^{\cdot-}$  as follows:



Hence the rate of degradation slows down at higher concentration of PS and with reaction time.

### 3.4. Effect of Anions

Natural water contains a variety of anions/salts. They can influence the efficiency of many AOPs designed to remove the pollutants. In this respect the effect of few common anions, ie  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$  on the FR initiated degradation under natural as well as solar irradiation conditions was evaluated. The results are shown in figures 10



**Figure.10** : Effect of Anions in NF and SF for RhB degradation

There is no consistency in the effect of anions and they behave differently at random. For e.g.,  $\text{Cl}^-$  and  $\text{NO}_3^-$  ions slightly enhance the degradation initially at lower concentrations of the anion.  $\text{PO}_4^{3-}$  and  $\text{CO}_3^{2-}$  inhibit initially. However, the effect is concentration and time dependent and at higher concentration, all anions become inhibitors. This extremely complex behavior of anions requires extensive investigation. Such unpredictable behavior of anions is well documented in literature, though the reasons are not consistent.

### 3.5. Mineralization process

One of the disadvantages of many AOPs is that the degradation often stops after one or two stages forming stable intermediates which effectively do not make water fully reusable. For this purpose, the intermediates also have to be degraded and eventually mineralized into harmless products such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and salts. In order to evaluate the mineralization efficiency, the chemical oxygen demand (COD) of the reaction solution is determined at various stages of reaction. The results show that the degradation stops with intermediates under normal Fenton reaction while it slowly decreases further under solar Fenton and eventually disappears. It is also observed that by simply

combining with UV irradiation, the mineralization is completed in just 2 hr after the COD has stabilized under solar Fenton.

#### IV. General Mechanism

The mechanism of the FR degradation of RhB may be summarized as follows:

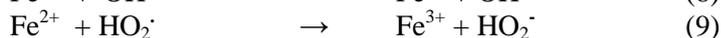
First step is the oxidation of ferrous to ferric ions and decomposition of  $\text{H}_2\text{O}_2$  into  $\cdot\text{OH}$  radicals



The ferric ions can be reduced by excess  $\text{H}_2\text{O}_2$  to form  $\text{Fe}^{2+}$  ions again and more radicals.



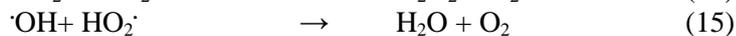
Other possible reactions are:



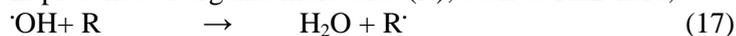
The  $\text{Fe}^{3+}$  can get reduced by reaction with excess  $\text{H}_2\text{O}_2$  to form  $\text{Fe}^{2+}$  again as in



The highly reactive free radicals may get self scavenged or by interaction with other radicals or  $\text{H}_2\text{O}_2$



In presence of organic molecules (R), such as RhB here;



Thus at room temperature and pressure itself, a series of reactive free radicals are generated and these can interact with the dye in a variety of ways to produce intermediates and eventually mineralize the pollutant. Activation of the system by high energy sources such as UV light is expected to enhance the rate significantly.

#### V. Conclusion

The classic fenton reaction involving use of simple ferrous salt and  $\text{H}_2\text{O}_2$  under ambient conditions as well as under sunlight irradiation is investigated as a potential AOP for the removal of toxic dye pollutant RhB from water. The ratio of  $\text{Fe}^{2+}$  ion and  $\text{H}_2\text{O}_2$  is optimized. Interestingly the optimum is quite different under normal Fenton process and solar Fenton process. The requirement of relative amount of  $\text{Fe}^{2+}$  is more under normal Fenton while the relative amount of  $\text{H}_2\text{O}_2$  is more under solar Fenton process. The  $\text{Fe}^{2+}$  which gets transformed into  $\text{Fe}^{3+}$  during the process is converted back into  $\text{Fe}^{2+}$  during the process itself. Thus by the intermittent addition of extra  $\text{H}_2\text{O}_2$  to compensate for the consumption in the process, the  $\text{Fe}^{2+}$  can be recycled any number of times. Thus the disadvantages of fenton sludge formation as the possible reason for its poor acceptance as an environment-friendly technology is overcome here by careful design of the component ratio. Typical oxidant such as persulphate enhances the degradation moderately. Various dissolved anions in water do not have any significant influence on the efficiency of the process. The process offers the potential for the inexpensive environment-friendly decontamination of polluted wastewater, using sunlight as the source of energy.

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