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Investigations on Classic Fenton Reaction As A Simple Inexpensive Technique for The Removal of Toxic Chemical Pollutants From Water

KEYWORDS: Fenton reagent; Rhodamine B; Zinc oxide; Persulphate; Anion effect

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ABSTRACT *The classic Fenton reaction involving the interaction between Fe2+ and H2O2 generating reactive .OH radicals is investigated as a potential tool for the removal of toxic dye pollutant rhodamine B from water. The efficiency of the process depends on reaction parameters such as pH, concentration of the reagent, relative ratio of Fe2+ and H2O2, concentration of pollutants etc. Anions such as CO32-, HCO3-, Cl- ,PO43- and NO3- influence the rate of degradation differently varying from inhibition to moderate enhancement. Persulphate, which is a strong oxidant in many advanced oxidation processes does not have any effect on the Fenton process while semiconductor oxide ZnO inhibits the degradation. An important finding of the study is that the Fe2+ of the Fenton reagent can be recycled many times by replenishing the consumed H2O2. This will address one of the major drawbacks of the Fenton process, i.e. accumulation of Fe2+ /Fe3+ from the used reagent in the environment.*

Introduction

Advanced Oxidation Processes (AOP) have been widely investigated in recent years as viable, environment-friendly and economical techniques for the removal of toxic and hazardous wastes such as dyes, pesticides, phenols etc. and the reduction of several heavy metals from water. 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 ·OH radicals [1-8]. According to the reactive phase, AOPs are classified also into homogeneous and heterogeneous types. Examples of homogeneous type AOPs include Fenton based processes such as classic Fenton (H_2O_2 + Fe^{2+}), Fenton like processes (Fe^{2+} + H_2O_2 + $metal^{n+}$), sono-, photo-, electro-Fenton, processes based on O_3, H_2O_2, O_3-UV, H_2O_2-UV and O_3-H_2O_2-UV etc. All processes involving suspended catalysts belong to the category of heterogeneous AOPs. However these processes 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. In this respect, the simple inexpensive classic Fenton process and its variations become important [8,9].

Classical Fenton process uses a combination of ferrous iron and H_2O_2 in which the former gets oxidized to ferric iron concurrently generating reactive ·OH radicals. These radicals attack the organic pollutant and lead to mineralization through a number of intermediates. Combination of Fenton reaction with other AOPs is being investigated widely to enhance the efficiency and economy of the mineralization process. These include photo-fenton, sono-fenton, microwave- fenton, photoelectro-fenton etc. [9-11]. The current study forms part of our series of investigations on Fenton reaction and various combination AOPs as possible environment-friendly, economical remediation measures for water contaminated with chemical and bacterial pollutants [12,13].

Rhodamine B [RhB], a xanthene 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-ylidine] 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 shown in Fig. 1.

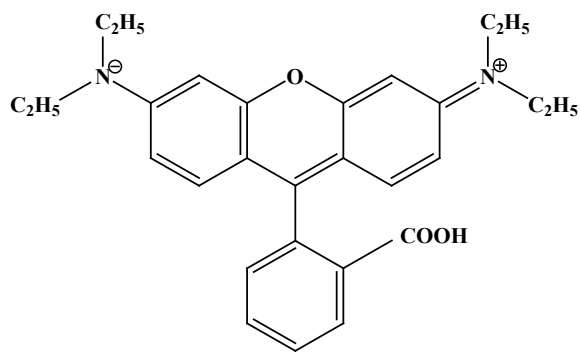

Fig 1. Structure of Rhodamine B

Materials and Methods

RhB (>99.6%) and ZnO (>99.5%) used in the study were from Sigma Aldrich India. H_2O_2 (30.0% w/v) and $FeSO_4.7H_2O$ (FS) from Qualigen (India) were used as such without further purification. Various other chemicals used were also of AnalaR grade or equivalent, unless indicated otherwise.

In a typical experiment, the dye solution of required concentration is mixed with appropriate combinations of FS and H_2O_2 in a 250 ml closed pyrex glass reactor and wrapped with black paper to avoid photochemical reactions, if any. The reaction system is mixed continuously using magnetic stirrer. The reaction volume is maintained at 50 ml, unless indicated otherwise. The degradation is monitored by analyzing the RhB remaining in the system by using UV-VIS spectrophotometry at 554 nm. H_2O_2 is analysed by standard iodometry.

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Results and Discussion

Optimization of Fe^{2+}/H_2O_2 ratio

Preliminary studies showed that the efficiency of the Fenton process depends on the relative concentration of FS and H_2O_2. Hence detailed investigations were made on optimizing the ratio of these critical components for RhB degradation. The RhB concentration is kept constant at 10 mg/L. The efficiency of degradation at varying ratios of FS and H_2O_2 is evaluated. The results are shown in Fig.2.

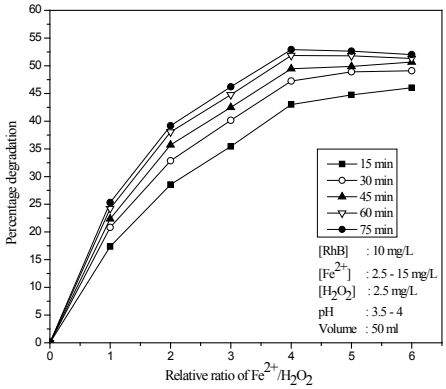

Fig 2. Effect of Fe2+/H2O2 ratio on the efficiency of Fenton degradation of RhB at different times

The rate of degradation increases with increase in concentration of FS and the optimum ratio of FS/ H_2O_2 (mg/L) is identified as 4:1. Interestingly, this observation is not in agreement with many previous reports according to which the ideal relative concentration of H_2O_2 is more in Fenton processes. This variation may be due to the characteristics of the substrate.

Effect of quantity of Fenton reagent

The effect of quantity of the Fenton reagent (FR), at the optimized ratio of FS/ H_2O_2 (4:1) as above, on the degradation of RhB is verified from a series of experiments. The results showed (Fig.3) that the degradation increases with increase in quantity of FR with no well-defined optimum, i.e. the more the FR, the more the degradation.

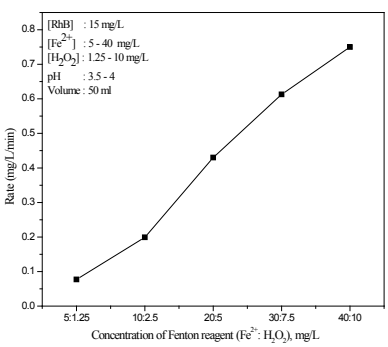

Fig 3. Effect of concentration of Fenton reagent on the rate of degradation of RhB

Eventually the rate slows down, 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 concentration of FR at the selected ratio of components is chosen as; FS= 20mg/L and H_2O_2 = 5mg/L (volume of reaction medium = 50 ml) for convenience. However, these optimized parameters may vary under another set of reaction conditions, reactor geometry, size etc. Hence every time when the reaction conditions are changed, the optimum also needs to be reworked.

Effect of concentration of RhB

Fenton processes are reported to be very sensitive to reaction conditions. Accordingly, the rate of degradation at various concentrations of the dye is experimentally determined. As expected, when there is sufficient quantity of FR in the system, the dye degrades fast; the rate of degradation increases with increase in concentration of the substrate. However, beyond a particular optimum concentration, the rate of degradation stabilises and even slows down gradually (Fig.4). Accordingly 15 mg/L of RhB is chosen as the optimum for further investigations.

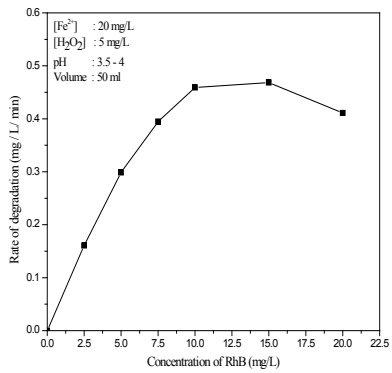

Fig 4. Effect of concentration of RhB on its degradation

Effect of ZnO on the degradation

Earlier studies have shown that ZnO and TiO_2 mediated photocatalysis is efficient for the degradation and mineralization of a variety of pollutants [14-17]. Of these two widely investigated semiconductor oxides, ZnO has been proven to be more active for solar energy harvesting due to its better absorption characteristics in the visible range of solar spectrum [16-19]. Hence the possibility of enhancing the efficiency of the Fenton process for RhB degradation by combining it with semiconductor photocatalysis is tested by introducing ZnO into the system. In the absence of any light irradiation, ZnO inhibits the degradation. The effect of increasing dosage of ZnO on the degradation of RhB is presented in Fig.5.

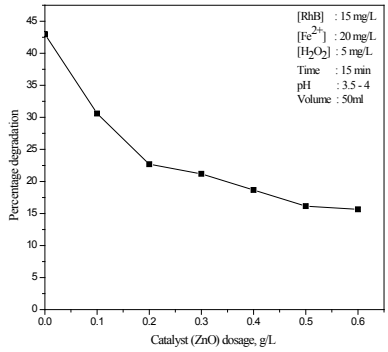

Fig 5. Effect of ZnO dosage on the Fenton degradation of RhB

The adsorption of H_2O_2 on ZnO and consequent decrease in the concentration of the former as the cause of the inhibition is ruled out since the adsorption has been observed to be negligible. Hence, the suspended ZnO particles may be inhibiting effective interaction between Fe^{2+} and H_2O_2 thereby reducing the rate of formation of reactive ·OH radicals. The substrate also may get shielded from interaction with the reactive free radicals by the ZnO particles which also may lead to the inhibition.

However, in presence of sunlight, under photo-fenton con-

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ditions, the inhibition by ZnO slows down gradually and eventually the degradation becomes comparable to solar Fenton process. Ultimately the degradation in this case, i.e. ZnO+FR+sunlight, becomes comparable to simple photocatalysis in presence of ZnO, i.e. ZnO+sunlight, with no synergic or even additive effect (Fig. 6). Hence solar fenton, solar photocatalysis and solar photocatalytic fenton all become comparable.

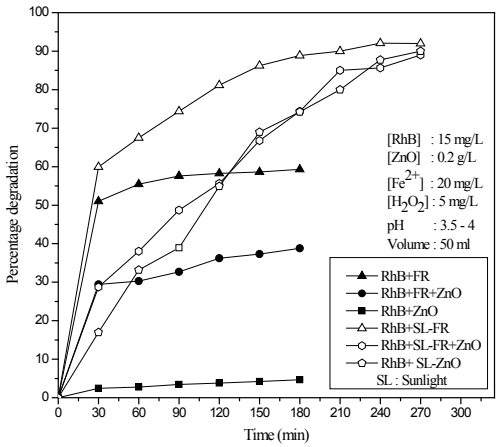

Fig 6. Effect of ZnO on the efficiency of the Fenton process for the removal of RhB under different conditions

Further studies on the identification of suitable combination AOPs for the removal of chemical pollutants from water are in progress.

Effect of pH

Another parameter important in FR processes is pH, especially due to the speciation factors of Fe^{2+} and H_2O_2. Hence the effect of pH is critically examined. The results are plotted in Fig. 7.

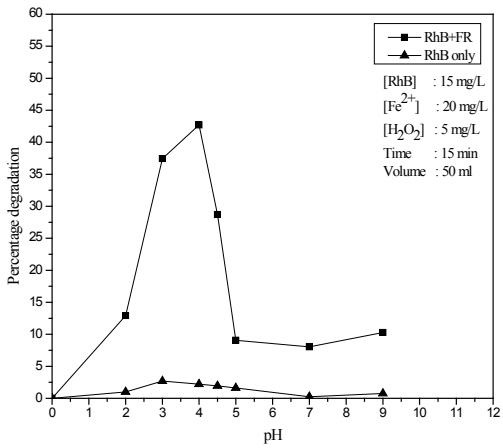

Fig 7. Effect of pH on the degradation of RhB in presence and absence of Fenton reagent (FR)

The optimum pH for the degradation of RhB was found to be ~ 4. This is in agreement with most of the FR-related reactions irrespective of the target substrate. The degradation falls steeply above pH 4, reaches around 10% (from~ 45%) at pH 5 and remains stable at higher pH. The stabilization can be attributed to the presence of relatively inactive iron oxohydroxides and formation of ferric hydroxide precipitate [17]. Consequently, the free iron ions are reduced and less hydroxyl radicals are generated. Further the oxidation potential of hydroxyl radicals decreases with increase in pH. The oxidation potential of the redox couple $\cdot OH/H_2O_2$ is ~ 2.59 vs NHE at pH 0 and 1.64 V vs NHE at pH 14. The auto-decomposition of H_2O_2 is accelerated at higher pH. The decrease in degradation below pH 4 may be due to the presence of iron complex $Fe(H_2O)_6^{2+}$ which reacts more slowly with H_2O_2 to generate reactive species. It is also possible that the peroxides get solvated in the presence of high concentration of H^+ ions to form stable oxonium ion $[H_3O_2]^+$. These ions make H_2O_2 more stable and reduce its reactivity with ferrous ions. Thus it is clear that proper maintenance of the pH is important in FR- driven degradation of pollutants.

Effect of periodic replenishment of FR/Fe^{2+}/ H_2O_2

The eventual stabilization of the degradation of RhB with time of reaction may be due to the inadequate availability of the FR or any of the components at the required level or the interference of reaction intermediates or their combination. The possibility of inadequate availability of the constituents of the FR is verified by in-between addition of them individually as well as the FR itself (at the optimized ratio) into the reaction system. The quantity of individual component added after each time interval is H_2O_2 = 5 mg/L, Fe^{2+} = 20 mg/L and FR = (20 + 5) mg/L. The results are shown in Fig. 8.

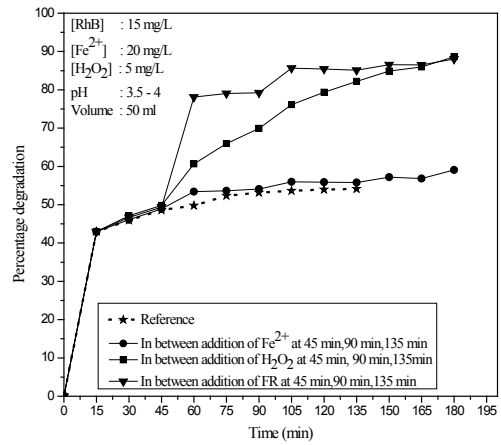

Fig 8. Effect of in-between addition of Fe2+/ H2O2/FR on the Fenton degradation of RhB

The degradation is initially stabilized at ~ 45%. At this stage more of FR (at the optimized ratio), Fe^{2+} and H_2O_2 are added individually at three different time intervals, i.e. 45, 90, and 135 minutes. The degradation increased only marginally when Fe^{2+} is added indicating that consumption or inadequate concentration of the ferrous ion is not the main reason for the stabilization of the degradation. At the same time addition of H_2O_2 at the first stabilization stage increases the degradation considerably. Hence the stabilization is at least partly due to the poor availability of adequate H_2O_2. However further addition of H_2O_2 after 90 minutes had only moderate effect and addition after 135 minutes had no effect. Hence it is evident that too much excess of H_2O_2 over what is optimised for the FR is not of much use for enhanced degradation of the pollutant. This also shows that moderate excess over the optimized (based on initial rate) level of H_2O_2 is desirable to ensure continued degradation. The need for replenishing the components of FR is further confirmed by the in between addition of FR. In this case addition after 45 minutes enhanced the degradation significantly and then stabilised. At that point extra addition of FR enhanced the degradation moderately. Further addition did not increase the degradation. At this stage ~ 90% of the dye is already

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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, moderate excess of reagent over what is optimized based on the initial rate of reaction is always recommended to effect total degradation of the target substrate. This is necessitated partially due to the self- decomposition of H_2O_2 as well as blocking/trapping of Fe^{2+} by complexation and/or other chemical interaction with the reactants/intermediates.

Effect of additives

Persulphates ($S_2O_8^{2-}$) are proven to be strong oxidants in AOPs due to the formation of highly reactive $SO_4^{\cdot-}$ radical anions [7,12,16]. Hence the probability of enhancing the efficiency of FR by the addition of persulphate is tested at various concentrations for various reaction times. The results showed that persulphates have practically no effect on the FR- induced degradation. This might be due to the inherent inability of persulphates to form reactive radicals in the absence of proper activation by thermal, photo, sono, MW or other techniques.

The presence of chemical contaminants such as salts/anions/cations is known to influence the efficiency of AOPs for the mineralization of pollutants in water [1,4]. In this context, the effect of few common anions which are likely to be present in many natural water sources on the efficiency of the Fenton process is examined. The results are presented in Fig. 9.

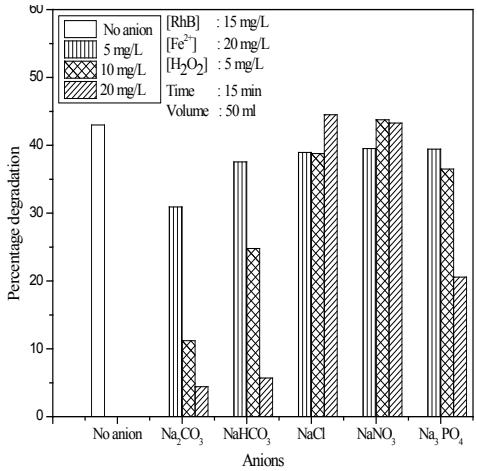

Fig 9. Effect of anions at different concentrations on Fenton degradation of RhB

As the figure shows different anions influence the FR initiated degradation differently. For e.g., CO_3^{2-}, PO_4^{3-} and HCO_3^- ions inhibit the degradation, the inhibition increasing with increase in the concentration of the anion. Cl^- and NO_3^- have practically no effect or slightly enhance the degradation at higher concentration of the anion. The change in the effect of anions from enhancement to inhibition or vice versa, with time of reaction, observed earlier in our laboratory in the case of certain anions in sono or photocatalysis is not seen here. Thus the inhibitors remain inhibitors and enhancers remain enhancers even after extended time of reaction.

Since SO_4^{2-} is already present from the $FeSO_4$, further test of the effect of this anion is not done. The basic reason for the inhibition by the anion may be the scavenging of the reactive ·OH radicals formed insitu during the Fenton reaction by the anions. The radical anions formed in the process are also moderately active for the degradation. Their concentration will increase steadily unlike the ·OH radicals which decrease progressively by recombination and deactivation. Hence, reasonable rate of degradation will continue even in presence of the ·OH radical-scavenging anions. Another reason for the anion effect in the case of Fenton reaction is the variation in pH in presence of the anions. Even mild variation in the pH, especially from the optimum of ~ 4 affects the Fenton process strongly. The variation in the pH in presence of anions is shown in Fig. 10.

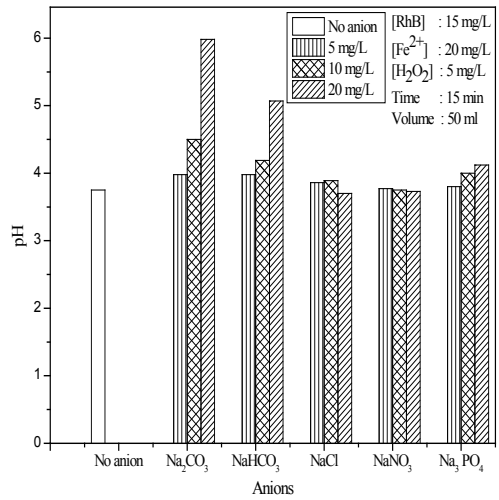

Fig 10. Variation in pH of RhB/FR system in presence of anions at different concentrations

By comparing these results with the data on pH effect presented in Fig.7, it may be observed that the inhibition by the anions CO_3^{2-} and HCO_3^- can be attributed at least partially to the change in pH. Cl^- and NO_3^- ions do not affect the pH in the concentration range studied here. The degradation of RhB also is not affected much thereby confirming the correlation between pH and anion effect. The inhibition by PO_4^{3-} cannot be attributed to its effect on the pH. In this case, the inhibition in the formation of ·OH radicals and also their trapping by the PO_4^{3-} ions may be responsible for the slowdown in the degradation of the substrate.

Effect of volume of reactants

Since Fenton reaction is a relatively simple facile process which proceeds smoothly as long as there is sufficient concentration of the reagents and the substrate, the scaling up of the process is expected to be relatively easy with the size of the reactor being the only constraint. In order to verify the influence of reactor size, the effect of volume of the reaction system on the rate of degradation of RhB is tested under optimized reaction parameters in the same reactor. The results shown in Fig.11 confirm the expected outcome, i.e. the rate of degradation increases smoothly with increase in volume as long as the ingredients are available in required quantities.

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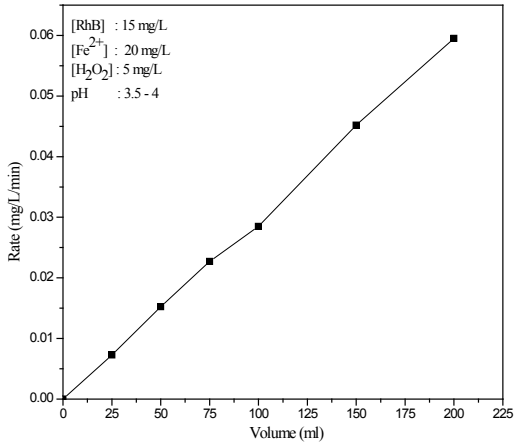

Fig 11. Effect of volume of the reaction system on the Fenton degradation of RhB

Recycling of Fe^{2+}

The rate of degradation of RhB increases with increase in concentration of Fe^{2+} as explained earlier. However, beyond a critical optimum, extra ferrous iron has no effect on the rate of degradation as seen in Fig. 8. Similar observations were reported by other workers too [20,21].

One of the criticisms against the use of Fenton process for water purification is the undesirable loading of dissolved Fe^{2+} in the effluent water. Hence the possibility of recycling the Fe^{2+} is tested by periodically replenishing the consumed H_2O_2 in the Fenton reagent and using the same for water treatment. When degradation of the pollutant has leveled off, more H_2O_2 is added to the system and the rate of degradation took off instantly as shown in Fig. 12.

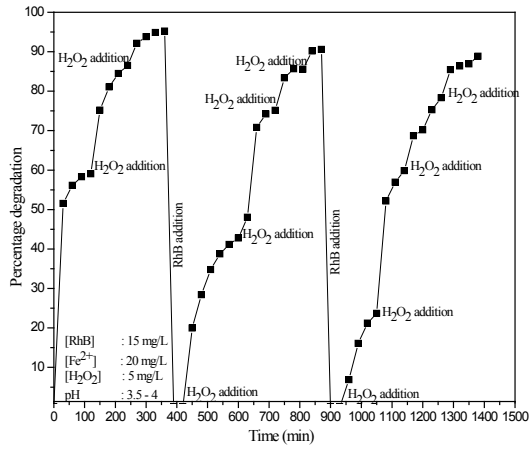

Fig 12. Recycling of Fe2+ and continuous operation of the Fenton process by replenishing H2O2 periodically

When the degradation of RhB is complete, fresh RhB solution is added to the system to economically utilize the remaining Fe^{2+}/ H_2O_2. The degradation is continuously monitored and when stabilized more H_2O_2 is added again. The cycle could be repeated many times thereby confirming the possibility of recycling Fe^{2+} and reducing its excessive loading in the discharged water. Thus one of the major criticisms against the use of FR for water treatment is addressed.

3.10. Effect on COD

The real test of any AOP for the removal of toxic pollutants from water is its efficiency to mineralize the pollutant into harmless products such as CO_2 and water and minimize the chemical oxygen demand (COD). The COD of the RhB-contaminated water is tested at different times during the Fenton treatment. The results are plotted in Fig. 13.

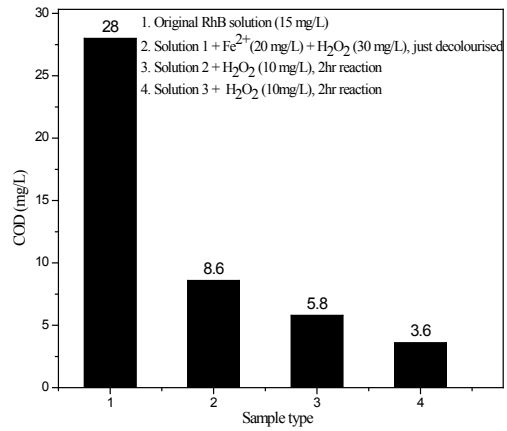

Fig 13. Progressive COD removal from aqueous solution of RhB by Fenton process

As seen in the figure, the COD decreases steeply on decolorization indicating that at least some of the intermediates formed during the decolorization are not stable and get mineralized fast. Continuation of the Fenton treatment by ensuring adequate supply of H_2O_2 results in complete mineralization. Hence it may be confirmed that Fenton process is an efficient inexpensive method for the complete removal of RhB pollutant from water.

General Mechanism

The first step in the Fenton reaction is the oxidation of ferrous to ferric ions and decomposition of H_2O_2 into ·OH radicals as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \quad (1)$$

The Fe^{3+} is reduced by excess H_2O_2 to regenerate Fe^{2+} and more free radicals as in reaction (2)

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \quad (2)$$

Other possible reactions are:

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \quad (3)$$

$$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^- \quad (4)$$

$$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + O_2 + H^+ \quad (5)$$

The highly reactive free radicals may get deactivated by self-scavenging, interaction with other radicals and/or H_2O_2

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

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

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (8)$$

$$\cdot OH + HO_2^{\cdot} \rightarrow H_2O + O_2 \quad (9)$$

In the absence of any organic substrate to be oxidized, H_2O_2 self-decomposes as in reaction (10).

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

In presence of organic molecules (R), such as RhB in the current instance, the degradation can take place as in reactions (11) – (13) or dimerization occurs as in (14). Eventually mineralization takes place as in (15).

$\cdot OH + R \rightarrow H_2O + R^{\cdot} \rightarrow$ (Partial mineralization + Colorless intermediates) (11)

$R^{\cdot} + Fe^{2+} \rightarrow R^{-} + Fe^{3+}$ (12)

$R^{\cdot} + Fe^{3+} \rightarrow R^{+} + Fe^{2+}$ (13)

$R^{\cdot} + R^{\cdot} \rightarrow RR$ (14)

$R^{\cdot}$ or R^{-} or R^{+} or RR + $\cdot OH$, $HO_2^{\cdot}$, H_2O_2 etc. $\rightarrow$ intermediates $\rightarrow \rightarrow \rightarrow CO_2 + H_2O$ + salts (mineralization) (15)

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. Preliminary studies in our laboratory show that the activation of the system by external energy sources such as UV light, ultrasound, microwave etc. and their combinations can enhance the Fenton degradation significantly. Further studies are in progress.

Conclusion

The study shows that the classic Fenton reaction involving use of simple ferrous salt and H_2O_2 under ambient conditions can be revisited and used as an effective advanced oxidation technique for the removal of traces of toxic pollutants from water. Many naturally occurring contaminants in water which are reported to adversely affect the mineralization of pollutants in many AOPs do not influence the Fenton reaction. The disadvantages of the Fenton sludge formation from accumulated Fe^{2+}/Fe^{3+} can be overcome by recycling the same with periodic replenishment of the consumed H_2O_2. The volume of the reactants is not a constraint as long as the necessary ingredients are available in the required ratio. These factors together with the relative simplicity of the process make Fenton reaction a promising candidate for economic and efficient wastewater treatment.

Acknowledgement

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