
Mechanism and kinetic model of the oxidative degradation of Rhodamine B dye in aqueous solution by ultrasound-assisted Fenton's process

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Abstract: A plausible mechanism for sono-Fenton reaction has been proposed and a kinetic model was developed with verification by experimental data. Degradation of Rhodamine B dye using sono-Fenton process has been investigated. Effects of initial pH, initial dye concentration, dosage of FeSO₄, H₂O₂ and ultrasonic power density were studied. Optimum values were: pH = 3, H₂O₂ = 2.74×10^{-2} mol/dm³, FeSO₄ = 3.60×10^{-4} mol/dm³. Maximum 99.57% decolourisation and 69.41% COD reduction were obtained in 30 minutes. Sono-Fenton process was more efficient than dark-Fenton or sonolysis under the same conditions. Decolourisation rate increased with increase in initial dye concentration up to 7.30×10^{-4} mol/dm³ after which it decreased. Similarly, the maximum decolourisation rate was obtained at 2.74×10^{-2} mol/dm³ of H₂O₂. Decolourisation increased with increasing FeSO₄ dosage and ultrasonic power density. Initial rate was influenced by initial dye concentration, ultrasonic power density and the initial dosage of H₂O₂ and FeSO₄.

Keywords: kinetics; mechanism; sono-Fenton's process; Rhodamine B dye; wastewater; ultrasonic cavitation; decolourisation; COD removal.

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1 Introduction

Decontamination of coloured wastewater from textile and dye industries is a critical issue as it contains non-biodegradable dyes with high COD as well as suspended solids with other chemicals (Basturk and Karatas, 2014; Mohan, 2016). These coloured pollutants hinder the penetration of sunlight into water bodies and damage aquatic life by decreasing the oxygenation capacity of surface water (Özdemir et al., 2011). Advanced oxidation processes (AOPs) are comparatively more efficient than the conventional techniques for the degradation of recalcitrant pollutants such as some dyes (Bagal and Gogate, 2014; Harichandran and Prasad, 2016; Merouani et al., 2010; Zhang et al., 2009). Fenton process is an AOP which is based on the production of hydroxyl radicals ($\bullet OH$) by catalytic decomposition of hydrogen peroxide (H_2O_2) in presence of ferrous ions (Fe^{2+}) under acidic conditions, as shown in equation (1) (Nidheesh et al., 2013; Özdemir et al., 2011; Zhang et al., 2019).



In presence of light or ultrasound, rate of generation of $\bullet OH$ is enhanced (Ma et al., 2012). Though photo-Fenton process performs extremely well, it is not suitable for treatment of dark or turbid wastewater (Dutta et al., 2014; Maezono et al., 2011) due to poor penetration of light into the liquid. In such cases ultrasound-assisted Fenton process can be a viable alternative. In this technique ultrasound is applied to a liquid for propagation of pressure waves through the medium. During the alternate rarefaction and compression, bubbles form, grow and collapse violently. This phenomenon is called acoustic cavitation (Ince and Güyer, 2004; Özdemir et al., 2011; Wang et al., 2008) and it can be easily generated at a frequency of 20–40 kHz. During acoustic cavitation in water, free hydroxyl radicals ($\bullet OH$) are produced with generation of high local temperature (5,000 K) and pressure (101.325×10^6 Pa) (Dükkancı et al., 2014; Merouani et al., 2010; Miklos et al., 2018; Özdemir et al., 2011). A simple mechanism for radical formation and depletion during water sonication is shown below (Behnajady et al., 2008).



Reports on sonochemical degradation of various recalcitrant aqueous pollutants have been documented (Li et al., 2013; Merouani et al., 2010; Özdemir et al., 2011; Siddique et al., 2014; Weng et al., 2013). But most of them report the experiments and observations and a few of them reported only a lumped kinetic parameter as the rate constant (Basturk and Karatas, 2014; Harichandran and Prasad, 2016; Siddique et al., 2014). Available literatures on sono-Fenton degradation of organic pollutant in wastewater seldom propose possible mechanism or kinetic model for the process. The present study aims at proposing a suitable mechanism, developing the rate equation based on the proposed mechanism and validating the proposed kinetic model by experimental results. Rhodamine B (RhB), a xanthene dye was used as a model pollutant for studying the efficacy of the sono-Fenton process. Influences of varying process parameters like initial pH of the solution, initial dye concentration, initial FeSO_4 dosing, initial H_2O_2 dosing, and ultrasonic power density have also been studied to establish the relation of the parameters with the reaction rate.

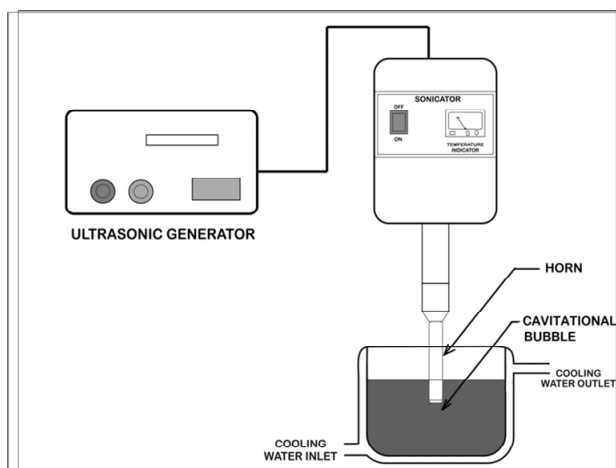
2 Methods

2.1 Materials

Rhodamine B (RhB) (C.I. no. 45170, $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$, mol wt. 479.01), was procured from Loba Chemie, Mumbai, India. Hydrogen peroxide (H_2O_2 , 30% w/w) was purchased from Merck Specialities Private Limited, India. Crystalline ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was obtained from Sisco Research Laboratories Pvt Ltd., India. Sodium hydroxide (NaOH) and sulphuric acid (H_2SO_4) of analytical grade were purchased from Merck (Germany). Sodium bisulphite (NaHSO_3) was from Loba Chemie. The chemicals were used without further purification. The stock RhB solution of $2.0875 \times 10^{-3} \text{ mol/dm}^3$ was prepared by dissolving the RhB powder in distilled water and then kept in a dark place. Freshly prepared distilled water was used for preparation of all solutions.

2.2 Experimental procedure

Sono-Fenton experiments ($\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{ultrasound}$) were performed using a probe-type sonicator (Trans-O-Sonic, Model: D-120/P) having $30 \pm 3 \text{ kHz}$ frequency and a rated power 120 W. The tip of the probe was $1.5 \times 10^{-2} \text{ m}$ in diameter and was dipped $2 \times 10^{-2} \text{ m}$ into the reaction mixture (Figure 1). 0.25 dm^3 dye solution was taken in a borosil glass reactor and the probe of the sonicator was dipped into it. Required volumes of 0.5% FeSO_4 solution and H_2O_2 (30% w/w) solution were added. The reactor was provided with a water circulating jacket to prevent heating of reaction mixture. pH of the mixture was measured using a calibrated pH metre. The pH was adjusted by adding either 0.1 (N) sulphuric acid or sodium hydroxide. During reaction, $1 \times 10^{-3} \text{ dm}^3$ samples were withdrawn at fixed time intervals. $1 \times 10^{-5} \text{ dm}^3$ of 5.00 (N) sodium bisulphite (NaHSO_3) solution was added to each withdrawn sample to quench residual H_2O_2 . The samples were analysed spectrophotometrically for residual colour concentration.

Figure 1 Schematic representation of experimental set-up

2.3 Determination of acoustic power dissipation

In sonochemical reactions, it is generally accepted that electrical energy is first converted to mechanical energy that in turn converts to acoustic cavitation energy. The ultrasonic power dissipated in the solution was estimated using a calorimetric process (Plattes et al., 2017).

The power dissipated was calculated from the following equation:

$$P = mC_p \frac{dT}{dt} \quad (6)$$

where m is the mass of 0.25 dm³ water (kg), C_p is the heat capacity of water (4.18 kJ/kgK) and dT/dt is the temperature gradient over time. The results have been tabulated in Table 1.

Table 1 Actual power dissipation and the corresponding efficiency of ultrasonic probe

Area of dissipation (m ²)	9.42×10^{-4}
Actual power dissipated in the given volume P(W)	20.9
Efficiency (%) $\eta = \frac{P}{120} \times 100$	17.42

Note: Power rating: 120 W.

2.4 Analytical methods

The wavelength of maximum absorbance (λ_{\max}) of RhB was determined as 554 nm using a UV-V is spectrophotometer (Hitachi U 4100) with 1×10^{-2} m optical path. Concentrations of the residual dye in the synthetic wastewater were calculated from dye absorbance values at λ_{\max} using a calibration curve. COD of the initial and treated samples was determined by standard open reflux method as described in APHA handbook (Eaton et al., 2005).

3 Results and discussion

3.1 Reaction mechanism and rate equation

The following steps are proposed for the pathway of sono-Fenton oxidative degradation reaction. Initial rate method was used to avoid interference by reaction intermediates and products that can occur at a later stage:

Hydroxyl radical attack on *RhB* dye is described by equation (7):



Hydroperoxyl radical ($\bullet OOH$) is also an oxidising species, though it is less powerful than hydroxyl radical.



Pyrolysis due to ultrasound may cause degradation of *RhB* dye, though to a small extent (Oturán and Aaron, 2014; Özdemir et al., 2011). Equation (9) shows the pyrolysis reaction:



In all equations, rate constants k 's are given over the arrows and ultrasound is indicated with I_s .

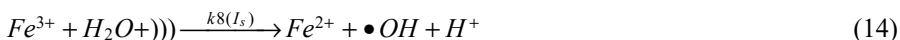
H_2O_2 may be sonolysed to generate hydroxyl radicals, since ultrasound imparts external energy (Bagal and Gogate, 2014; Nidheesh et al., 2013).



The following steps are the steps of classical Fenton's reaction whereby $\bullet OH$ radicals are generated (Ma, 2012).



Due to the presence of ultrasound, following reactions also happen (Ma, 2012).



Here the rate constants k_3 , k_4 , k_7 , and k_8 are considered to be influenced by the power density of probe sonicator (I_s), i.e., $k_3 = k_3(I_s)$, $k_4 = k_4(I_s)$ and so on (Dutta et al., 2014). Initial rate can be expressed as:

$$r_i = -\frac{d}{dt}[RhB] \quad (15)$$

where concentration of *RhB* dye is given by $[RhB]$. Initial rate is calculated by calculating the initial gradient of a time-concentration curve for decolourisation.

•OH free-radicals are generated by elementary reaction routes represented by equations (10), (11) and (14) whereas they are consumed in the dye degradation reaction represented by equation (7). So the net rate for •OH free radical generation is:

$$\begin{aligned} \frac{d}{dt}[\bullet OH] = & k_4(I_s)[H_2O_2]_i + k_5[Fe^{2+}]_i[H_2O_2]_i \\ & + k_8(I_s)[Fe^{3+}][H_2O] - k_1[RhB]_i[\bullet OH] \end{aligned} \quad (16)$$

Similarly the other reactive intermediates namely $[Fe^{3+}]$, $[\bullet OOH]$ and $[Fe - OOH^{2+}]$ have their own pathway of formation and decay as represented by the proposed mechanism. According to the well-known theory of non-elementary reactions, concentrations of all the reactive intermediates are assumed to be constant (pseudo-steady state assumption) (Dutta et al., 2014). Therefore,

$$\frac{d}{dt}[\bullet OH] = \frac{d}{dt}[Fe^{3+}] = \frac{d}{dt}[\bullet OOH] = \frac{d}{dt}[Fe - OOH^{2+}] = 0 \quad (17)$$

This leads to the following expression of initial rate:

$$r_i = k_3(I_s)[RhB]_i + k_4(I_s)[H_2O_2]_i + 2k_5[Fe^{2+}]_i[H_2O_2]_i \quad (18)$$

Since only one process parameter was varied at a time keeping the other parameters unchanged, the above equation will reduce to the following equations for each of the parameters:

When $[Fe^{2+}]_i$, $[H_2O_2]_i$ and power density (I_s) of probe sonicator are constant:

$$r_i = k_3(I_s)[RhB]_i + M \quad (19)$$

where $M = k_4(I_s)[H_2O_2]_i + 2k_5[Fe^{2+}]_i[H_2O_2]_i$.

Similarly when $[RhB]_i$, $[Fe^{2+}]_i$ and power density (I_s) of probe sonicator are constant then:

$$r_i = N[H_2O_2]_i + k'_3 \quad (20)$$

where $N = k_4(I_s) + 2k_5[Fe^{2+}]_i$ and $k'_3 = k_3(I_s)[RhB]_i$.

Similarly when $[RhB]_i$, $[Fe^{2+}]_i$ and $[H_2O_2]_i$ are constant then:

$$r_i = X(I_s) + k'_5 \quad (21)$$

where $X(I_s) = k_3(I_s)[RhB]_i + k_4(I_s)[H_2O_2]_i$ and $k'_5 = 2k_5[Fe^{2+}]_i[H_2O_2]_i$.

Now when $[RhB]_i$, power density (I_s) and $[H_2O_2]_i$ are constant then:

$$r_i = R[Fe^{2+}]_i + S \quad (22)$$

where $R = 2k_5[H_2O_2]_i$ and $S = k_3(I_s)[RhB]_i + k_4(I_s)[H_2O_2]_i$.

It is evident from the proposed pathway that the initial rate of reaction depends on initial concentration of RhB, initial $FeSO_4$ dosing, initial H_2O_2 dosing and ultrasonic power density. A cooling jacket was provided to prevent rise in temperature by acoustic cavitation. So the input ultrasonic power density has been considered as the influencing parameter. Though pH is an important parameter, Fenton reaction is in general most

effective in the pH range of 3–4. We varied the other parameters keeping the pH in this effective range for kinetic study.

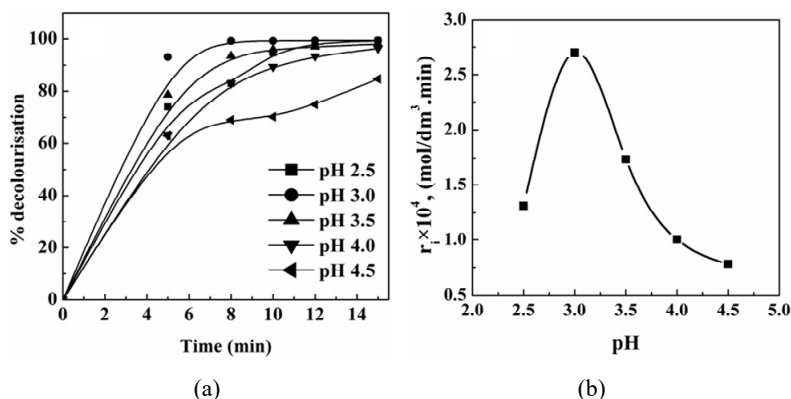
3.2 Influences of varying process parameters

Since it was observed that both the initial rates and the extents of degradation are influenced by the variation of the mentioned process parameters, it is pertinent to study the nature or trend of such influences.

3.2.1 Effect of pH

pH is an important process parameter for the oxidation of pollutants (here RhB) as it controls the concentration of Fe^{2+} in the solution and the generation of $\bullet\text{OH}$ by Fenton's reagent (Basturk and Karatas, 2014; Özdemir et al., 2011). In the present study, degradation experiments with RhB were performed in the range of pH 2.5 to pH 4.5. The maximum decolourisation of RhB was achieved at pH 3. At this pH the recombination of free radicals is hindered (Bagal and Gogate, 2014). This enhances the rate of $\bullet\text{OH}$ radical generation that favours the oxidation of pollutants. As shown in Figure 2(a), an increase in pH from 3 onwards caused a decline in the degradation of RhB. At pH more than 4, formation of Fe(II) complexes and precipitation of ferric oxy-hydroxides occur which inhibit the regeneration of Fe^{2+} ion in the solution. All these effects decrease the rate of degradation of the pollutants (Bagal and Gogate, 2014; Harichandran and Prasad, 2016). At lower pH (pH-2.5), complexes like iron (II) hydroxide $[\text{Fe(II)} (\text{OH})^{2+}]$ are formed, which react slowly with hydrogen peroxide. Hence production of reactive hydroxyl radicals decreases, thereby reducing the degradation efficiency (Özdemir et al., 2011). These facts are manifested in Figure 2(b). We have studied the influence of other parameters on the kinetics keeping pH at this optimum value of 3.

Figure 2 (a) The effect of initial pH on the decolourisation of RhB (b) Variation in initial rate with initial pH

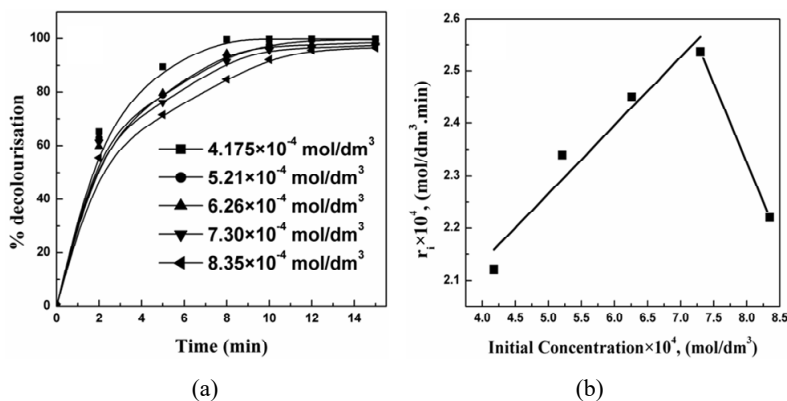


Notes: $[\text{RhB}] = 4.175 \times 10^{-4} \text{ mol/dm}^3$, $[\text{H}_2\text{O}_2] = 3.92 \times 10^{-2} \text{ mol/dm}^3$,
 $[\text{FeSO}_4] = 5.76 \times 10^{-4} \text{ mol/dm}^3$ and power density = 83.6 W/dm^3 .

3.2.2 Effect of initial dye concentration

The effect of the initial concentration of RhB on decolourisation efficiency was investigated with the RhB concentration ranging from 4.175×10^{-4} mol/dm³ to 8.35×10^{-4} mol/dm³. Figure 3(a) shows that percentage decolourisation decreases with increase in RhB concentration. This may be because when the concentration is high, the effect of cavitation is not enough for all the pollutant molecules under the given conditions (Bagal and Gogate, 2014; Harichandran and Prasad, 2016). The quantity of •OH radical produced is insufficient to degrade the large numbers of pollutant molecules and hence the decolourisation is less. However, as Figure 3(b) shows, initial rate of decolourisation increases monotonously within the concentration range of 4.175×10^{-4} mol/dm³ to 7.30×10^{-4} mol/dm³. This can be explained by the fact that RhB molecules, being non-volatile, are mainly present in the bulk of the liquid medium, while the •OH radicals formed by acoustic cavitation are mostly aggregated on the surface of the cavitation bubble. The diffusivity of •OH radical through the liquid medium being low, very few •OH radicals reach the bulk to attack the molecules. But as the initial concentration of the solution is increased, the concentration of dye molecules around the bubble surface increases considerably, leading to a greater probability of attack on the dye molecules by •OH radicals (Merouani et al., 2010). The linearly increasing portion of Figure 3(b) has been considered for the calculation of rate constant from the proposed kinetic model. This observation corroborates with equation (19) in the set of rate equations. On increasing the dye concentration beyond 7.3×10^{-4} mol/dm³, it has been observed that the rate of decolourisation decreases linearly. This may be attributed to the fact that at higher dye concentrations, there is increased (•OH) radical scavenging leading to a decrease in the effective free radical concentration (Merouani et al., 2010).

Figure 3 (a) The effect of initial dye concentration on the decolourisation of RhB (b) Variation in initial rate with initial RhB concentration



Notes: $[\text{H}_2\text{O}_2] = 3.92 \times 10^{-2}$ mol/dm³, $[\text{FeSO}_4] = 5.76 \times 10^{-4}$ mol/dm³ at pH 3.0 and power density = 83.6 W/dm³.

3.2.3 Effect of FeSO_4 dosage

The optimisation of FeSO_4 dosing is necessary as overdose of iron would produce too many ferrous ions, which may scavenge hydroxyl radicals resulting in reduced degradation efficiency (Basturk and Karatas, 2014; Özdemir et al., 2011). Moreover, if the amount of $\text{Fe}(\text{OH})_3$ sludge increases, cost of treatment of such sludge will also increase (Bagal and Gogate, 2014). Decolourisation of RhB at different FeSO_4 dosages has been investigated with FeSO_4 dosing ranging from 0 mol/dm³ to 5.76×10^{-4} mol/dm³. The results are shown in Figure 4(a). The increase in FeSO_4 concentration enhances the degradation efficiency of RhB in the mentioned range because of:

- 1 the catalytic decomposition of H_2O_2
- 2 increased rate of generation of $\bullet\text{OH}$ radical in Fenton's [$\text{Fe}(\text{II})/\text{H}_2\text{O}_2$] and Fenton-like [$\text{Fe}(\text{III})/\text{H}_2\text{O}_2$] processes according to the following equations (Merouani et al., 2010):



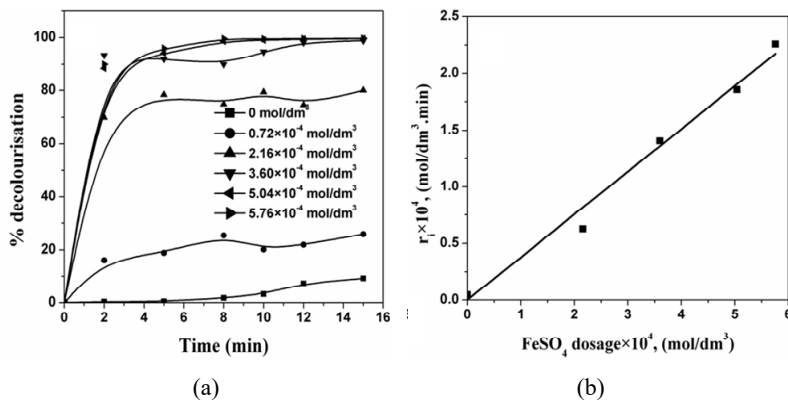
As seen in Figure 4(a), removal efficiency of RhB increases from 25.87% to 99.70% at 15 minutes of reaction time by increasing the FeSO_4 concentration from 7.20×10^{-5} mol/dm³ to 5.76×10^{-4} mol/dm³ for sono-Fenton process. Only 9.2% decolourisation of RhB was achieved without adding FeSO_4 solution. It is also evident that for 15 minutes of reaction time, increasing the dosage of FeSO_4 from 3.60×10^{-4} mol/dm³ to 5.76×10^{-4} mol/dm³ does not significantly raise the decolourisation percentage. Hence 3.60×10^{-4} mol/dm³ of FeSO_4 was taken as the optimum dosage from the point of view of process economics. Figure 4(b) shows that the initial reaction rate increases monotonically with FeSO_4 dosage in a straight line. This observation validates equation (22) in the set of the rate equations.

3.2.4 Effect of H_2O_2 dosage

Dosage of H_2O_2 , the oxidant generator, is the most important process parameter for the sono-Fenton process. Effect of H_2O_2 dosage on the decolourisation efficiency of RhB has been studied at the optimum pH of 3 with H_2O_2 concentration varying between 0 mol/dm³ and 3.92×10^{-2} mol/dm³. In absence of H_2O_2 the decolourisation of RhB was negligible as evident from Figure 5(a). The production of $\bullet\text{OH}$ radicals in the bulk liquid is insignificant in presence of ultrasound alone. It was observed that the decolourisation efficiency of RhB increased from 4.97% to 98.93% by increasing the amount of H_2O_2 from 0 mol/dm³ to 2.74×10^{-2} mol/dm³. Figure 5(b) shows that the initial reaction rate increased linearly with H_2O_2 up to 2.74×10^{-2} mol/dm³ and then at 3.92×10^{-2} mol/dm³, it decreased slightly due to $\bullet\text{OH}$ radical scavenging by excess H_2O_2 itself (Dutta et al.,

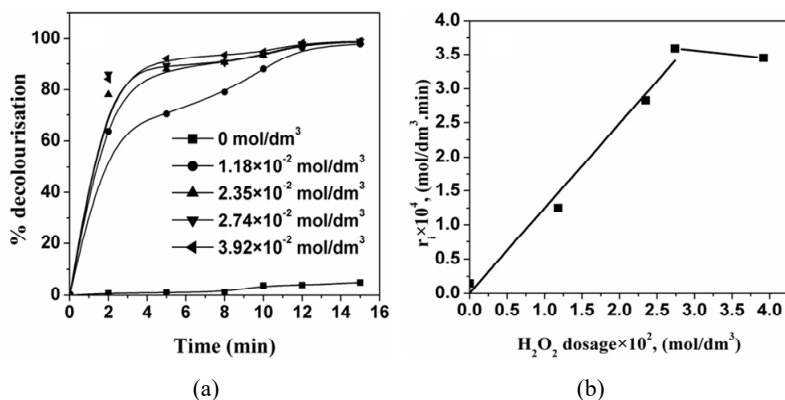
2014). As before, the kinetic model was considered valid within the linearly increasing portion of Figure 5(b).

Figure 4 (a) The effect of FeSO_4 dosing on the decolourisation of RhB (b) Variation in initial rate with increasing FeSO_4 dosing



Notes: $[\text{RhB}] = 4.175 \times 10^{-4}$ mol/dm³, $[\text{H}_2\text{O}_2] = 3.92 \times 10^{-2}$ mol/dm³ at pH 3.0 and power density = 83.6 W/dm³.

Figure 5 (a) The effect of H_2O_2 dosing on the decolourisation of RhB (b) Variation in initial rate with increasing H_2O_2 dosing



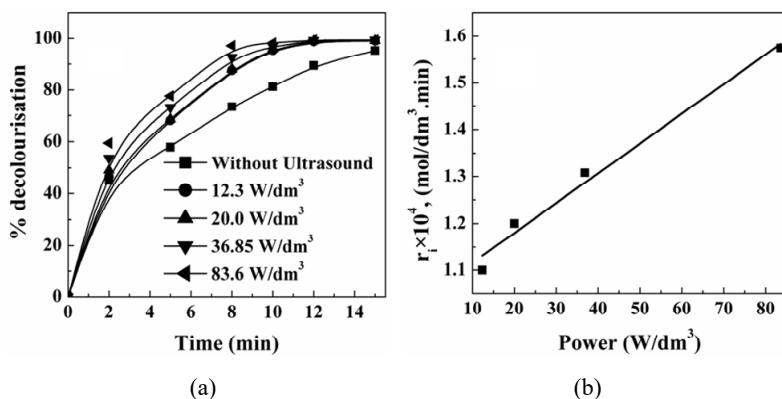
Notes: $[\text{RhB}] = 4.175 \times 10^{-4}$ mol/dm³, $[\text{FeSO}_4] = 3.60 \times 10^{-4}$ mol/dm³ at pH 3.0 and power density = 83.6 W/dm³.

3.2.5 Effect of ultrasonic power density

The influence of acoustic power density was studied by varying the power density from 12.35 W/dm³ to 83.6 W/dm³ considering the volume of the reaction mixture as 0.25 dm³. A blank experiment without ultrasound was also conducted for comparison. It was observed that the decolourisation of RhB increases with increasing power density. Increase in ultrasound density may have increased the rates of reactions represented by equations (9)–(10) and equations (13)–(14). Additionally increase in ultrasonic power may cause increased turbulence generated by implosion of cavitation bubbles and

micro-jetting (Siddique et al., 2014; Zhang et al., 2009). All these factors cause increased production of $\bullet\text{OH}$ radicals. Figure 6(a) shows that the decolourisation efficiency of RhB increases from 95.19% to 99.48% by increasing the ultrasonic power density from 0 W/dm^3 to 83.6 W/dm^3 after 15 minutes of reaction. However, the difference of the final decolourisation efficiency under different powers was not perceptible. This showed that ultrasonic irradiation would only affect the generation rate of hydroxyl radicals. Figure 6(b) illustrates that the initial reaction rate also increases with increasing ultrasonic power density. Equation (21) in the set of rate equations matches with this observation.

Figure 6 (a) The effect of ultrasonic power density on the decolourisation of RhB
(b) Variation in initial rate with increasing ultrasonic power density

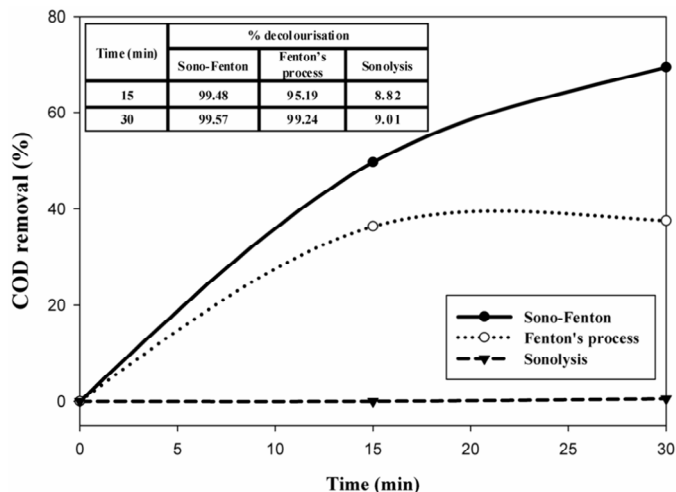


Notes: $[\text{RhB}] = 4.175 \times 10^{-4} \text{ mol/dm}^3$, $[\text{H}_2\text{O}_2] = 2.74 \times 10^{-2} \text{ mol/dm}^3$ and $[\text{FeSO}_4] = 3.60 \times 10^{-4} \text{ mol/dm}^3$ at pH 3.0.

3.2.6 Chemical oxygen demand (COD) analysis

Mineralisation of RhB was investigated in terms of COD removal (Figure 7). The degradation of $4.175 \times 10^{-4} \text{ mol/dm}^3$ of RhB has been carried out at pH 3 keeping the H_2O_2 concentration at $2.74 \times 10^{-2} \text{ mol/dm}^3$ and FeSO_4 dosing fixed at $3.60 \times 10^{-4} \text{ mol/dm}^3$. $30 \pm 3 \text{ kHz}$ ultrasonic frequency was used for sonication. It is evident from Figure 7 that COD removal by sonolysis alone was negligible while 49.76% and 36.39% COD were removed at 15 minutes of reaction by sono-Fenton and Fenton process respectively while the corresponding decolourisations were 99.48% and 95.19%. This is due to the fact that the intermediate products such as carboxylic acids are not susceptible to oxidation resulting in a very slow oxidation rate. Hence COD removal requires much higher residence time than decolourisation which involves only chromophore fragmentation (Zhang et al., 2009). In sono-Fenton process, because of the cyclic regeneration of the hydroxyl radicals shown earlier, the amount of hydroxyl radicals remains sufficient for further degradation of the dye molecule, which is not possible in Fenton's process. Hence sono-Fenton process is comparatively more effective for mineralisation than Fenton process.

Figure 7 Comparative study of COD reduction of RhB solution by ultrasonic-assisted Fenton's process, Fenton's process and ultrasound only



Notes: $[\text{RhB}] = 4.175 \times 10^{-4} \text{ mol/dm}^3$, $[\text{H}_2\text{O}_2] = 2.74 \times 10^{-2} \text{ mol/dm}^3$,
 $[\text{FeSO}_4] = 3.60 \times 10^{-4} \text{ mol/dm}^3$ and $\text{pH} = 3.0$ power density = 83.6 W/dm^3 .

3.2.7 Treatment of real-life industrial wastewater by sono-Fenton process

Dye pollutants are generally present in the wastewater emanating from textile, thread or jute-dyeing industries. These wastewaters contain many inorganic ions in addition to the organic contaminants. AOPs are generally meant for degradation of recalcitrant organic pollutants and are influenced by the presence of inorganic ions in the water. For example, chloride ion (Cl^-) significantly affect the COD removal rate by inhibiting the Fenton's oxidation reaction where these (Cl^-) ions prevent the regeneration of Fe(II) from Fe(III) (Deng and Zhao, 2015; Sánchez et al., 2011).

Hence different protocols including suitable pretreatments may be necessary for such wastewater to be treated by sono-Fenton process. The process would vary with the analysis of the particular wastewater.

3.2.8 Validation of the proposed model with experimental data

The overall rate equation, equation (18), shows that the initial rate is influenced by several process parameters. However one parameter was varied at a time keeping the others constant to get equations (19)–(22). Plots of the initial rates against the respective process parameters led to determination of the values of respective rate constants from the slopes and intercepts as envisaged in the equations (19)–(22).

A comprehensive summary of the results are given in Table 2.

The values of the rate constants obtained from equations (19), (20) and (22) are as follows:

$$k_3(I_s) = 0.13 \text{ min}^{-1} = 2.17 \times 10^{-3} \text{ s}^{-1}$$

$$k_4(I_s) = 8.36 \times 10^{-3} \text{ min}^{-1} = 1.39 \times 10^{-4} \text{ s}^{-1}$$

$$k_5 = 5.06 \frac{dm^3}{mol \cdot min} = 0.084 \frac{dm^3}{mol \cdot s}$$

There is no literature that explores the mechanism of sono-Fenton degradation of RhB in the way it has been reported in the present work; hence the rate constant values could not be compared with published data. However, Dutta et al. (2014) have carried out similar work on modified photo-Fenton degradation of Trypan Blue and the rate constants reported were of similar orders of magnitude.

Table 2 Data fitting for various model equations

Equation no.	Figure no.	Slope	Intercept (mol/dm ³ .min)	R ²
(19)	3(b)	0.13 min ⁻¹	2 × 10 ⁻⁴	0.95
(20)	5(b)	0.012 min ⁻¹	7.89 × 10 ⁻⁷	0.9851
(21)	6(b)	6.338 × 10 ⁻⁷ mol/W.min	1 × 10 ⁻⁴	0.984
(22)	4(b)	0.366 min ⁻¹	5 × 10 ⁻⁶	0.981

The rate constants $k_3(I_s)$ and $k_4(I_s)$ were determined at power density = 83.6 W/dm³. From the values of the rate constants, it can be inferred that Fenton's reaction is dominant over all other reaction as the value of k_5 obtained is the highest. The rate constant for the sonolysis reaction $k_3(I_s)$ is very low as the degradation of RhB mainly occurs by oxidative agents produced in the solution and to a very limited extent by pyrolysis in and around the cavitation bubble. RhB dye is not volatile and can dissolve in water; thus it is very difficult for RhB to penetrate into the gas bubbles. For this reason, degradation by oxidative agents (mainly •OH radicals) in the bulk solution is considered as the principal mechanism for the removal of dyes. Hydrogen peroxide decomposition by ultrasound is also very slow as evident from the low rate constant $k_4(I_s)$.

Figure 8 Parity diagram showing experimental and predicted initial rates under varying dosage of RhB, H₂O₂, FeSO₄ and ultrasonic power density

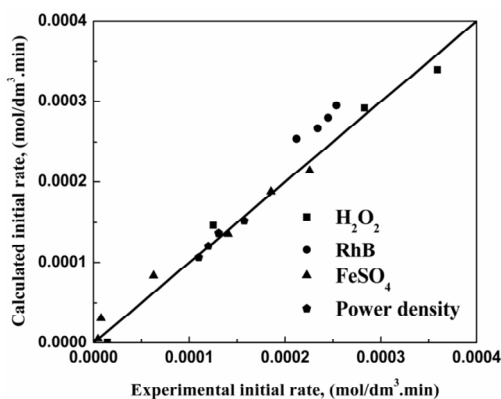


Figure 8 shows the combined parity diagram between predicted and experimental values of initial rate for variations in initial concentrations of RhB, FeSO₄, H₂O₂ and ultrasonic power density respectively. The experimental and predicted values of initial rates agree pretty well and the model is valid within the experimental range of parameter values.

4 Conclusions

In presence of ultrasound, efficiency of Fenton oxidation increases significantly. Possible steps for ultrasound-assisted Fenton degradation of RhB dye have been proposed and a kinetic model has been developed based on the same. The model predicts linear variation of initial reaction rate with initial concentrations of RhB, FeSO₄ and H₂O₂ as well as with ultrasonic power per unit volume. Experimental results of the degradation of RhB dye by sono-Fenton process obtained by varying the mentioned process parameters were used to validate the proposed model. Reaction rates predicted from the model were very close to actual experimental values of the reaction rates. Degradation of dye pollutant was estimated by COD analysis. While the chromophores that impart colour were removed by sono-Fenton process, some colourless intermediates or products with certain COD were also produced. Hence there was a gap between the percentages of decolourisation and mineralisation.

The data obtained from these batch kinetic studies can be utilised to design a stirred-tank type continuous flow reactor for possible industrial scale treatment of RhB dye containing wastewater.

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