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Degradation of *Trypan Blue* in wastewater by sunlight-assisted modified photo-Fenton reaction

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ABSTRACT

Homogeneous Fenton reaction (Fe^{2+}/H_2O_2) is one of the most important advanced oxidation processes to generate $^{\cdot}OH$ free radicals for degradation of organic pollutants in wastewater. Degradation of an azo dye (*Trypan Blue*) by solar photo-Fenton process has been investigated in this work using a batch reactor under sunlight. Instead of acidic pH used in conventional Fenton reaction, neutral pH is used here to modify the same. Effects of the changes in process parameters, including dosage of ferrous sulphate and hydrogen peroxide as well as pH have been examined. Percent degradation was observed to increase with increasing H_2O_2 dosing up to a particular critical value. Increase in $FeSO_4$ dose and acidic medium increased degradation. Complete decolourization was achieved after 2 h when 500 mL of 5.2×10^{-4} mol L^{-1} dye aqueous solution at pH 7 was oxidized with 2.8×10^{-4} mol L^{-1} of ferrous sulphate and 0.03 mol L^{-1} of H_2O_2 under sunlight of average intensity 281 W m^{-2}. Mineralization of dye pollutant was monitored by COD measurement. Additionally, FTIR analysis also supported degradation. A kinetic model was developed and validated with experimental data.

Keywords: Wastewater; Sunlight; Photo-Fenton reaction; Neutral pH; Azo dye; Rate equation

1. Introduction

Dye is a specific pollutant causing visible pollution. Industries like textile finishing, dye manufacturing, pulp and paper, kraft bleaching and tannery are sources of colour pollution. Discharge of coloured effluent, even if it is less toxic than a colourless hazardous pollutant, is more objectionable to a common man. Therefore, colour must be removed before discharging the wastewater into hydrological systems.

Colour is generally imparted in wastewater by phenolic compounds and organic or inorganic colourants. The maximum contribution is by organic dyes and dye intermediates. These dyes may be classified into sulphur, mordant, reactive, azo, cationic, dispersed, acid or vat dyes. Most of these dyes are difficult to remove from wastewater due to their complex

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chemical structure and refractory nature. Nearly 1 million metric tons of dyes are annually produced in the world of which azo dyes contribute about 70% by weight. Azo dyes constitute the largest class of synthetic organic dyes used in industry [1]. More than 2000 azo dyes are known and over half of the commercial dyestuff is azo dye. Azo dyes as well as their precursors and degradation products are often carcinogenic and mutagenic [2].

The traditional technologies applied for the treatment of wastewaters with dye are coagulation/flocculation, membrane separation or activated carbon adsorption. However, these methods merely transfer dyes from the liquid to the solid phase causing secondary pollution and requires further treatment [3]. Advanced oxidation processes (AOP) generate the second most powerful oxidant, that is $OH^{\cdot}$ free radical to oxidize the organic pollutants ultimately to carbon dioxide and water [3,4]. AOPs involving UV radiation, Fe^{2+} ion, H_2O_2, O_3 and different combinations thereof are hence regarded as the alternative techniques for the degradation of dyes and many other organic pollutants in wastewater [5–8]. Fenton reaction with Fe^{2+} and H_2O_2 is one such AOP [1,9–13] that can be further enhanced with the help of visible or UV light [14].

A few reports are available on the photo-fenton oxidation of dye pollutants using UV [15] or solar radiation [16]. Neamtu et al. [17] evaluated the degradation of two azo reactive dyes, CI Reactive Yellow 84 (RY84) and CI Reactive Red 120 (RR120), by photo-Fenton and Fenton-like oxidation. They have used both UV and solar light for enhancing Fenton reaction. Efficacy of Cu(II) and Fe(III) as well as of Fe(II) as a component of Fenton's reagent was also examined in this study. Molar ratio of H_2O_2 to iron was 20:1 and pH was maintained at 3. Based on the degradation after 15 min, they observed that solar photo-Fenton reaction was more effective than its UV-light-assisted counterpart. Their work also includes the determination of an optimum initial concentration of H_2O_2. End products of the reaction were identified as well. Torrades et al. [18] studied degradation of different commercial reactive dyes such as Procion Red H-E7B, Red Cibecron FN-R and a standard Trichromatic system by using solar light-assisted photo-Fenton reaction. They used 100 mg L^{-1} of dye solutions, 100 mg L^{-1} of H_2O_2 and 10 mg L^{-1} Fe^{2+} at 40°C temperature and pH 3. Compared to UV radiation, the rate of degradation was faster with solar energy. Zheng et al. [16] have investigated the Fenton and photo-Fenton degradation of Eosin Y dye under sunlight and artificial UV light. Ninety-six per cent of the dye was reported to be removed within 90 min in solar photo-Fenton oxidation under an acidic pH of 3.5, whereas the initial concentrations of Fe^{2+} and H_2O_2 were at 10 and 600 mg L^{-1}, respectively. Additionally, they have added oxalic acid to enhance the efficiency of solar photo-Fenton process. Reviews on Fenton and photo-Fenton reactions also elucidated degradation of compounds other than dyes [19,20]. Rodriguez et al. [21] have studied the sunlight-assisted photo-Fenton treatment of phenol in surface water. They have also scaled up the small batch process to a pilot-scale *compound parabolic collector* (*CPC*) solar reactor. The pH of the solution was below 3, initial concentrations of phenol, H_2O_2 and Fe^{3+} were 1.4, 21.99 and 1.07 mmol L^{-1}, respectively. They found that intrinsic kinetic parameters to be independent of the radiation source as well as the reactor geometry. Total mineralization was achieved within 20 min. Intensity of sunlight was about 45 W m^{-2}. Three types of reactors were used—a solarbox with a reflecting surface of 0.054 m^2 provided with a 1,500 W Xenon lamp, a parabolic concentrator photoreactor with a parabolic reflector of 0.174 m^2 and a pilot-scale CPC with a collector surface of 5.93 m^2. Samet et al. [22] had evaluated the dark Fenton and solar photo-Fenton oxidation of 4-chloroguaiacol in simulated wastewater from pulp and paper industries. Intensity of sunlight was reported to be 150 W m^{-2} and pH was maintained at 3. Initial concentrations of both Fe^{2+} and H_2O_2 were 16 mmol L^{-1}. The reactor (1 L capacity) was a continuous tubular reactor made of quartz. The rate of circulation was 0.2 L min^{-1}. Eighty-eight per cent of the pollutant was observed to oxidize within 72 min. In general, from the reviewed literatures it becomes evident that in a tropical country with abundant sunlight, a solar photo-Fenton oxidation of pollutants would be economically and ecologically attractive.

Though there are several reports on photo-Fenton treatment of wastewater in acidic medium, reports on the work carried out in neutral medium are not many. The *novelty* of this work lies in the near-neutral pH of the reaction mixture. Since the classical Fenton reaction is generally performed at pH 3, the present process may be termed as a *modified* Fenton reaction. A mechanism and rate model have been proposed, which are very much novel for solar energy enhanced photo-Fenton reaction at neutral pH.

The objective of the present research is to explore the efficacy of solar energy enhanced oxidative degradation of *Trypan Blue* dye using photo-Fenton reaction at neutral pH. Generally, photo-Fenton reactions are carried out at $pH \leq 3$. However, we did not want to impart an additional acidity to the wastewater that needs neutralization before discharging to surface water. Moreover, there will be an increase in the cost due to the acid-resistant equipment and the process of acidification and neutralization; hence, we have carried out the reactions at near-neutral pH. When natural water is exposed to sunlight, it was evident that there are some photo-Fenton reactions at circumneutral pH [23,24]. The process parameters studied were pH and initial concentrations of substrate i.e. H_2O_2 and $FeSO_4$. A kinetic rate model was proposed and validated by the experimental data.

2. Materials and methods

2.1. Materials

Trypan Blue (Direct Blue 14, C.I. No. 23850) is an azo-dye manufactured by Loba Chemie, Mumbai, India with molecular weight of 960.80 and its chemical structure is illustrated in Fig. 1.

Hydrogen peroxide (H_2O_2, 50% v/v) was from Merck Specialities Private Limited, India. Crystalline ferrous sulphate ($FeSO_4{\cdot}7H_2O$) was from Sisco Research Laboratories Pvt. Ltd, India. Different volumes of 0.5% $FeSO_4$ solution and 50% H_2O_2 solution were used for reaction. The pH of the dye solution was adjusted by adding either 0.1 (N) solutions of sulphuric acid (H_2SO_4) or sodium hydroxide (NaOH). Sodium bi-sulphite ($NaHSO_3$) was from Loba Chemie. 5.00 (N) $NaHSO_3$ solution has been used to stop the Fenton reaction at desired point. All solutions were prepared with freshly prepared double distilled water having pH 6.9 and conductivity in the range 4–6 μS cm^{-1}.

2.2. Analytical methods

Residual dye present in the solution was monitored by a Shimadzu 160A UV–vis spectrophotometer at $\lambda_{max} = 590$ nm with 1 cm optical path against a standard calibration curve. Chemical oxygen demand (COD) was determined by standard open reflux method as described in APHA handbook [25]. pH was measured using a calibrated pHtestr 20 instrument. Intensity of solar radiation was measured using a Metravi 1332 digital lux meter. Average intensity of sunlight during the experiments was around 70 klux (281 W m^{-2}). The data in the photometric unit (klux) has been converted to the radiometric unit (W m^{-2}) using the empirical conversion factors provided by Thimijan and Heins [26]. FTIR analysis for identification of the degradation products was carried out in a Jasco-6300 instrument using KBr pellet.

2.3. Experimental procedure

The batch reactor was a stainless steel box provided with a cooling water jacket and a quartz sheet as the top-lid to allow sunlight into it. The reactor was mounted on a magnetic stirrer for complete mixing of the reactants. Fig. 2 shows the schematic of the experimental set-up.

Five hundred millilitre of dye solution of specific concentration was taken into the reactor. The liquid level in the reactor was 2.3 cm only so that the sunlight could easily penetrate. The reaction mixture was vigorously stirred for uniform mixing; hence, the species generated by irradiation were distributed throughout the volume. Required volumes of 0.5% $FeSO_4$ solution and H_2O_2 (50% v/v) solutions were added and the reaction mixture was exposed to sunlight with continuous stirring. pH of the solution was constantly monitored. Since the amounts of H_2O_2 and $FeSO_4$ solutions added were very small, there was no change in pH during the experiment. Aliquots of samples (about 10 mL) were withdrawn at different time intervals; the reaction was stopped using 3.0 μL of 5 (N) $NaHSO_3$ solution and the residual dye was analysed spectrophotometrically as described in the previous section. All the experiments were carried out within the time span between 12 noon and 2 pm during April–May in eastern part of India in order to maintain a constant solar intensity condition. The intensity was measured as described above.

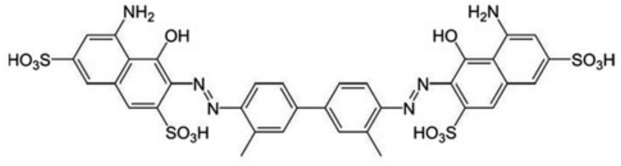

Fig. 1. Chemical structure of Trypan Blue dye.

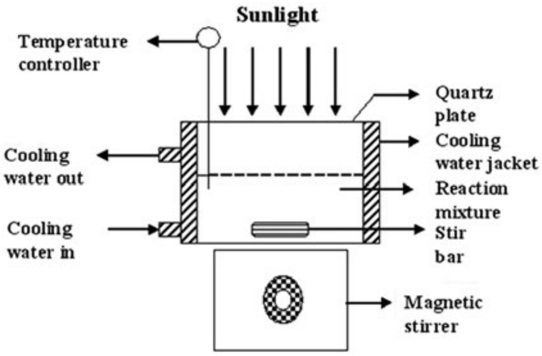

Fig. 2. Schematic representation of experimental set-up.

3. Results and discussion

3.1. Influence of initial concentration of hydrogen peroxide

Initial dosing of H_2O_2 was varied within the range of 0–0.058 mol L^{-1} keeping other experimental conditions unchanged. Other experimental conditions, such as initial concentration of dye (5.71×10^{-4} mol L^{-1}), initial concentration of $FeSO_4$ (2.8×10^{-4} mol L^{-1}) and pH (7.00) were kept unchanged. Time–concentration profiles for the degradation of dye with various H_2O_2-dosing are given in Fig. 3(a). For initial concentrations of H_2O_2 of 0, 0.014, 0.020, 0.024, 0.03, 0.044 and 0.058 mol L^{-1}, removal of colour after 120 min were 0, 89.16, 97.39, 97.85 and 100%, respectively. Corresponding COD reductions were observed to be 0, 31.65, 36.26, 42.4, 51.62, 53.15 and 50.08%. With the increase in H_2O_2-dosing, initial reaction rate of dye increased up to a particular dosing of 0.03 mol L^{-1}, further increase in the dosing of H_2O_2 resulted in the decrease of the rate of degradation (Fig. 3(b)). This may be attributed to the hydroxyl radical scavenging effect of H_2O_2 at higher concentration of the later [27].

3.2. Influence of initial ferrous sulphate concentration

Initial dosing of $FeSO_4$, the component of the Fenton's reagent other than H_2O_2, was varied in the range of 0–3.6×10^{-4} mol L^{-1}. $FeSO_4$ is the catalyst that enhances generation of $OH^{\cdot}$ free radicals from H_2O_2. Without $FeSO_4$, only H_2O_2 could decolourize 39.94% of the initial dye. It shows that H_2O_2 being an oxidizing agent can remove colour, but $FeSO_4$ catalyzes the oxidation reaction and enhances the rate of oxidative degradation. When light is present, requirement of $FeSO_4$ is small. However, without H_2O_2, only $FeSO_4$ could not degrade the azo dye. Fig. 4(a) shows the time–concentration data for dye decolourization at different initial concentrations of $FeSO_4$. With 2.8×10^{-4} mol L^{-1} of $FeSO_4$, percent removal of dye was 100%, whereas the respective COD was found to reduce by 51.6%. With 3.6×10^{-4} mol L^{-1} of $FeSO_4$, percent removal of dye was 100% with 53.15% of COD removal.

Some authors [17] have reported an optimum dose of Fe^{2+}, above which the degradation decreased due to competition of Fe^{2+} with $OH^{\cdot}$ radical and also due to colour resurgence by Fe^{2+}. In our case, we obtained a continuous increase in degradation with increase in Fe^{2+} dosing in the experimental range. This is due to the very small concentration of Fe^{2+} used.

3.3. Influence of pH

In most of the available literature, it has been shown that the Fenton reaction is generally favoured in acidic medium and pH has a significant influence on the rate dye decolorization. The pH was regulated by adding H_2SO_4 or NaOH to the aqueous solution of dye. Fig. 5(a) shows the time–concentration profiles for the degradation reaction at various initial pH of the reaction mixture. Fig. 5(b) indicates the trend of the initial rate with variation of initial pH. Though the rate of degradation is more in case of acidic pH, addition of acid imparts secondary pollution to the treated water. Even if neutralization is done before discharging the same to surface water body, it increases the total dissolved solid in water. Moreover, for performing the reaction in acidic medium in the industrial scale, one has to use suitable material or lining in the reactor, which would increase the fixed cost of the process.

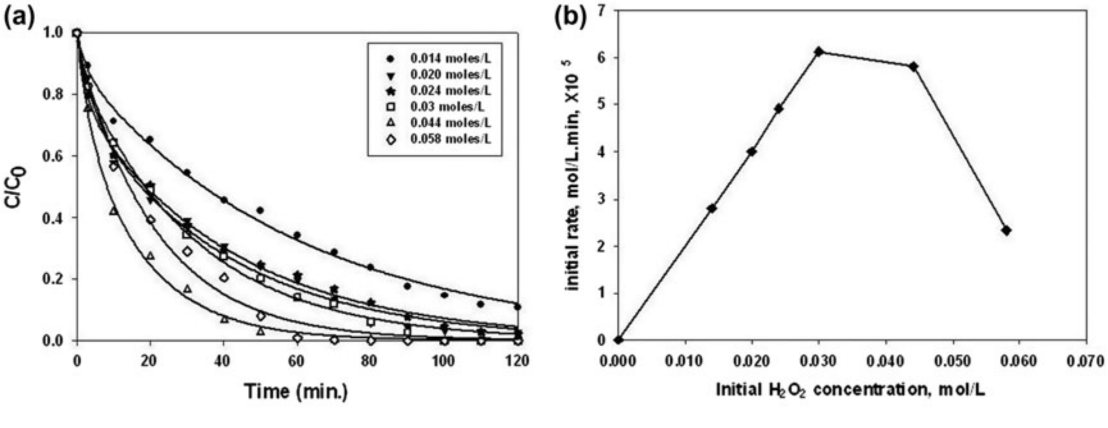

Fig. 3. (a) Effect of different initial concentrations of H_2O_2 on decolorization of dye. (b) Variation in initial rate with increasing concentration of H_2O_2. (Experimental conditions: initial concentration of dye 5.2×10^{-4} mol L^{-1}, $FeSO_4$ 2.8×10^{-4} mol L^{-1}, pH 7.00, sunlight 70 klux (281 W m^{-2}) and temperature 30°C.)

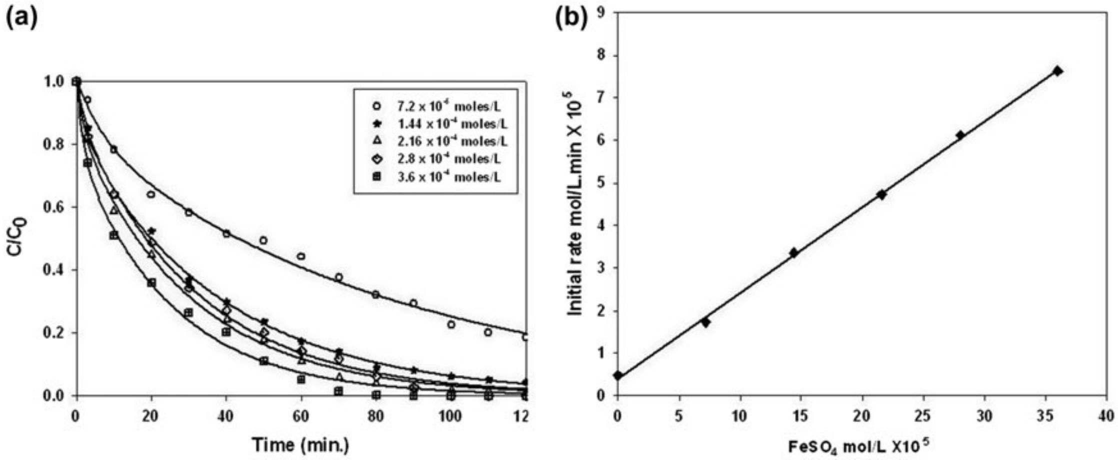

Fig. 4. (a) Effect of different initial concentrations of $FeSO_4$ on decolorization of dye. (b) Variation in initial rate with increasing concentration of $FeSO_4$. (Experimental conditions: initial concentration of dye 5.2×10^{-4} mol L^{-1}, H_2O_2 0.03 mol L^{-1}, pH 7.00, sunlight 70 klux (281 W m^{-2}) and temperature 30℃.)

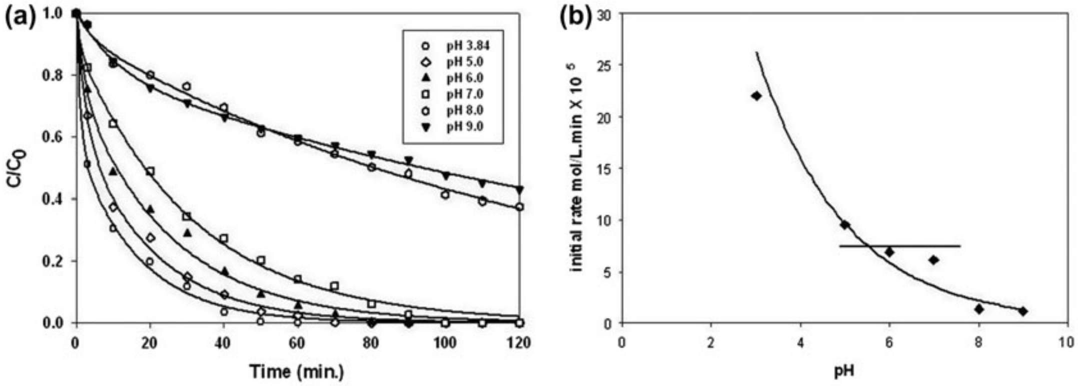

Fig. 5. (a) Effect of different initial pH on decolourisation of dye. (b) Variation of initial rate with pH [Experimental conditions: initial concentration of dye 5.2×10^{-4} mol L^{-1}, $FeSO_4$ 2.8×10^{-4} mol L^{-1}, H_2O_2 0.03 mol L^{-1}, sunlight 70 klux (281 W m^{-2}) and temperature 30℃.].

Therefore, we have conducted the photo-Fenton degradation of dye pollutant in near-neutral pH. It may also be noted from the figures that neither the percent degradation after 2 h nor the initial rate varies much with variation of pH from 5 to 7 (indicated by the horizontal line in Fig. 5(b). Suprateanu and Zaharia [28] observed nearly no change in degradation of Acid Red G dye with the change in pH. Souad and Al-Sayed [29] studied the photocatalytic activity of titanium dioxide (TiO_2) and gold (Au)-modified TiO_2 (Au/TiO_2), supported in polymethylmethacrylate thin film. They have also observed that the best degradation was at pH 2. However, the mechanism of heterogeneous photocatalysis is different from that of the homogeneous photo-Fenton reaction. Within 2 h we have obtained complete decolorization. On the other hand, in alkaline medium both the initial rate and the percent degraded after 2 h were too low to perform the reaction. Reports are there for coagulation/precipitation of Fe^{3+} complex at higher pH; in our case, the dose of iron was too low to be precipitated.

The decrease in degradation in an alkaline medium may be explained by the fact that in an alkaline medium, the following reaction is favoured:

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{1}$$

The conjugate base anion of hydrogen peroxide generates $HO_2^{\bullet}$ followed by $HO^{\bullet}$ radicals. Because $HO_2^{\bullet}$ radicals are less reactive than $HO^{\bullet}$, increasing $HO_2^{\bullet}$does not significantly contribute to the dye destruction [30].

3.4. Effect of initial concentration of dye

As expected, being limited by the availability of $OH^{\cdot}$ free radical, the percent degradation decreased from 100 to 69 with 18% increase in initial concentration of dye solution from 4.6×10^{-4} to 8.3×10^{-4} mol L^{-1} (Fig. 6(a)). Moreover, increased concentration of dye solution inhibited sunlight to enter the bulk of solution and hence the generation of $OH^{\cdot}$ free radical was also less. However, the initial rate remained almost independent of the initial concentration within the range of experimental concentration (4.9×10^{-4}–5.7×10^{-4} mol L^{-1}). This indicates that within this particular range, the initial rate is independent of the initial concentration of dye solution (Fig. 6(b)). Therefore, we have performed experiments of varying other parameters keeping the initial solution concentration within this range.

3.5. Chemical oxygen demand

Chemical oxygen demand is an indicator of the presence of oxidizable organic compounds in wastewater. In this work, we find that the solar energy-assisted photo-Fenton oxidation of Trypan Blue dye reduced 51.6% of the original COD in the simulated wastewater that was imparted due to the presence of 5.2×10^{-4} mol L^{-1} of dye in the baseline experiment. The molar ratio of Dye: $FeSO_4$:H_2O_2 in the mentioned baseline experiment was 1:0.55:59.14 at pH 7. The temperature was maintained at 30˚C and the intensity of sunlight was 70.00 klux (281 W m^{-2}). Removal of COD was less (51%) compared to the removal of colour (100%) in the baseline experiment. This was due to the formation of colourless, though oxidizable intermediates or products during the photo-Fenton oxidation process.

3.6. Rate equation and kinetics

A few researchers [23,24,31] suggested that at near-neutral pH, the Fenton reaction proceeds via ferryl species [Fe(IV)]. Barbusinski [24] suggested a shift of mechanism from free radical to ionic route. However, in presence of light, the generation of $OH^{\cdot}$ free radical either from H_2O_2 or from iron species cannot be completely ruled out. Grčić et al. [32] have studied the solar photo-Fenton degradation of Reactive Black dye with zerovalent iron (ZVI). They have immobilized the solid catalyst into two novel reactors. Two routes of mechanism and rate equation were proposed by them while discussing the reaction pathway in details. In one of the proposed mechanisms they considered heterogeneous catalysis, whereas for the other the homogeneous reaction was considered with the leached Fe(II) from immobilized solid ZVI. However, their system was different and they have conducted the experiments in strong acidic medium to facilitate Fe(II) leaching. They did not consider Fe(IV) species. Hence, we propose the following steps and mechanism for the solar photo-Fenton reaction at neutral pH. It is a comparatively slower path. We have used the initial rate (at $t = 0$) technique [33] to eliminate the interference of the intermediates that may occur later during the experiment for a long time.

$$Fe^{2+} + H_2O_2 \xrightarrow{k1} Fe^{4+} + 2OH^- \tag{2}$$

$$Fe^{4+} + H_2O_2 \xrightarrow{k2} Fe^{3+} + OH^- + OH^{\cdot} \tag{3}$$

$$Fe^{3+} + H_2O \xrightarrow[hv]{k_3(Is)} Fe^{2+} + OH^{\cdot} + H^+ \tag{4}$$

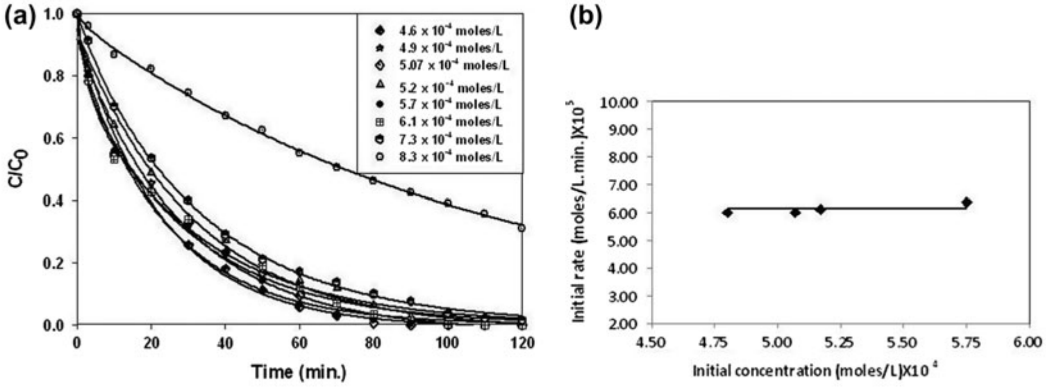

Fig. 6. (a) Effect of different initial concentrations of dye on degradation. (b) Initial rate vs. initial concentration. (Experimental conditions: $FeSO_4$ 2.8×10^{-4} mol L^{-1}, H_2O_2 0.03 mol L^{-1}, pH 7.00, sunlight 70 klux (281 W m^{-2}) and temperature 30˚C.)

$$H_2O_2 \xrightarrow[hv]{k_4(Is)} OH^{\cdot} + OH^{\cdot} \qquad (5)$$

$$\text{Dye} + OH^{\cdot} \xrightarrow{k_5} \text{products} \qquad (6)$$

Here the rate constants k_3 and k_4 are considered to be dependent on the light intensity (I_S), i.e. $k_3 = k_3(I_S)$ and $k_4 = k_4(I_S)$. Now rate of degradation is the rate of hydroxyl free radical attack to dye. Hence, the initial rate:

$$r_i = -\frac{d}{dt}(\text{Dye}) = k_5[\text{Dye}][OH^{\cdot}] \qquad (7)$$

Again, $OH^{\cdot}$ is generated by elementary reaction routes represented by Eqs. (3–5) whereas it was consumed in the actual dye degradation reaction, represented by Eq. (6). So the net rate is:

$$\frac{d}{dt}[OH^{\cdot}] = k_2[Fe^{4+}][H_2O_2]_i + k_3(I_s)[Fe^{3+}][H_2O] + k_4(I_s)[H_2O_2]_i - k_5[\text{Dye}]_i[OH^{\cdot}] \qquad (8)$$

Similarly the other reactive intermediates, namely Fe^{4+} and Fe^{3+} have their own pathways 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 pseudo-steady [34]. Therefore,

$$\frac{d}{dt}[OH^{\cdot}] = \frac{d}{dt}\left[Fe^{+3}\right] = \frac{d}{dt}\left[Fe^{+4}\right] = 0 \qquad (9)$$

That leads to the following expression of initial rate:

$$r_i = k_5[\text{Dye}]_i[OH^{\cdot}] = 2k_1[Fe^{2+}]_i[H_2O_2]_i + 2k_4(I_s)[H_2O_2]_i$$
$$\Rightarrow r_i = 2[H_2O_2]_i\{k_1[Fe^{2+}]_i + k_4(I_s)\} \qquad (10)$$

For a fixed dosing of Fe^{2+} ion and fixed intensity of solar radiation and varying H_2O_2 dosing:

$$r_i = K'[H_2O_2]_i \qquad (11)$$

Similarly, for a constant H_2O_2 dosing and constant intensity of solar radiation, the initial rate varies with the initial concentration of Fe^{2+} as follows:

$$r_i = K''[Fe^{2+}]_i + B \qquad (12)$$

where $k'' = 2\{k_1[Fe^{2+}]_i + k_4(I_s)$ $k'' = 2k_1[H_2O_2]_i$ and $B = 2k_4(I_s)[H_2O_2]_i$

It is interesting to note that the initial rate is independent of the initial concentration of dye solution and it is as per our proposition under Section 3.4 before. The initial rate of reaction depends upon the initial concentrations of H_2O_2 and Fe^{2+} as well as on the intensity of sunlight. Keeping the other two parameters constant, initial rate can be predicted either by varying initial concentration of H_2O_2 or by varying initial concentration of Fe^{2+}.

A plot of initial rate vs. initial concentration of H_2O_2 gives the value of K' (from Eq. 11). Similarly, a plot of initial rate vs. initial concentration of $FeSO_4$ (Fig. 4(b)) gives the value of K' and B from its slope and intercept, respectively (from Eq. 12). k_1 was determined from both the equations. Hence, the mean values of the rate constants can be calculated as follows:

$$k_1 = 2.97\,\text{mol}^{-1}\,\text{L min}$$

$$k_4(I_S) = 6.67 \times 10^{-5}\text{min}^{-1} \text{ at } I_S = 281\text{W m}^{-2}$$

The above values of k_1 and k_4 are less than those reported in most of the literature. This may be attributed to the initial pH of the reaction mixture, since it was observed that initial rates vary by orders of magnitude with the variation of pH [23,24]. A parity diagram was constructed with experimental and predicted initial rates (Fig. 7). It was observed that the two agree reasonably well.

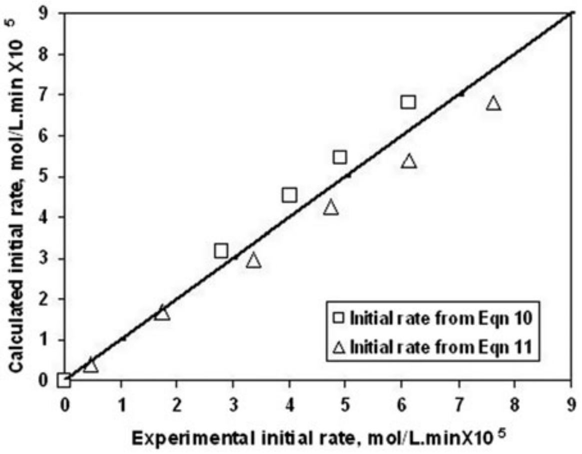

Fig. 7. Parity diagram showing experimental and predicted initial rates.

Table 1
Strong FTIR peaks for degradation of Trypan Blue dye

Before reaction		After reaction	
Wave number (cm^{-1})	%T	Wave number (cm^{-1})	%T
1,236.15	81.5449	1,089.58	75.2725
1,255.43	94.1580	1,236.15	84.8412
1,288.22	93.6007	1,253.50	92.7469
1,384.64	92.8719	1,288.22	92.3717
1,425.14	93.3592	1,375.96	93.0595
1,467.56	92.4654	1,466.60	93.4790
1,640.16	80.3058	1,641.13	77.0986
1,987.29	95.5745	1,948.72	98.4862
2,005.61	95.8316	1,960.29	98.6065
2,038.39	95.2814	1,977.64	98.8077
2,050.92	95.2188	2,127.10	96.5149
2,092.39	94.8513	2,171.45	95.3328
2,123.24	94.6544	2,412.51	93.3945
2,161.81	94.0631	2,858.95	95.1113
2,209.06	93.7133	2,920.66	91.5158
2,399.98	92.6674	3,333.36	61.2966
2,920.66	88.5564	3,940.82	101.611
2,987.2	89.2513		
3,844.4	100.215		

3.7. Degradation products and intermediates

Kalsoom et al. [35] proposed a mechanism of oxidative breakdown of *Trypan Blue* azo dye with soybean peroxidase. According to their scheme, degradation products and intermediates contained $–NH_2$, –OH, –COOH and $–SO_3H$ groups attached to aromatic rings. In our work, a FTIR spectrum of the dye before and after photo-Fenton reaction has been taken. A set of strong bands ranging between 2,000 and 2,090 cm^{-1} that were present initially before reaction disappeared after reaction. This indicates breaking of azo (–N=N–) and diazo links [36]. Since Trypan Blue dye has azo groups as chromophores, breakage of azo group reduces colours. A set of new peaks appeared within 1,940–1,980 cm^{-1}. These peaks are characteristic of allene structure (>C=C=C<) and these compounds may have formed as intermediate/product during the photo-Fenton degradation though further investigation is required for the exact mechanistic path. This unsaturation has its chemical oxygen demand; hence, when 100% of the colour is removed, removal of COD was only 51%. However, more rigorous analysis with sophisticated instruments like GC-MS/NMR is required for prediction of reaction path or mechanism.

4. Conclusion

Solar energy-assisted photo-Fenton oxidation has been found to be pretty effective for the removal of *Trypan Blue* dye from wastewater in a set of experiments conducted under batch mode. Complete decolorization was observed within 2 h even though the experiments were conducted at pH 7. However, reduction of COD was about 51% due to the formation of oxidizable intermediates/products. The process, marked by near-neutral pH would save the cost of post-treatment neutralization of the treated wastewater and the TDS-load of the same. A kinetic rate model has been proposed and validated by the experimental data. The initial rate was observed to increase with increase in the initial H_2O_2-dosing up to an optimum value and remained independent of the initial concentration of the substrate within experimental range. Increase in the initial dosing of $FeSO_4$ increased the initial rate.

The data obtained from the batch process may be utilized to design a plug-flow type continuous or semi-batch reactor for possible industrial use.

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