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Use of Photo-Fenton reagent for photocatalytic degradation of reactive orange 13 in aqueous solution

Anil Kumar Swarnkar, Bhupendra Kumar Sharma

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Anil Kumar Swarnkar
Department of chemistry,
Mewar University, Gangrar,
Chittorgarh (Rajasthan),
India.

Bhupendra Kumar Sharma
Department of chemistry,
S.G.G. Government College.
Banswara -327001, India.

Correspondence:
Bhupendra Kumar Sharma
Department of chemistry,
S.G.G. Government College.
Banswara -327001.

Abstract

In textile industries, advanced oxidation processes (AOPs) are widely used for degrading and removing color from dye baths which allow wastewater reuse. Degradation of Reactive Orange 13 by Photo-Fenton reagent has been investigated under irradiation of visible light in aqueous solution. The parameters that influence degradation such as concentration of Reactive Orange 13, $FeSO_4$, H_2O_2, light intensity and pH of the experimental solution were studied. The optimum condition for the photocatalytic degradation of dye was established. The decolorization rate fitted to pseudo- first order kinetics with respect of dye concentration.

Keywords: Photocatalytic Degradation, Reactive Orange 13, Photo-Fenton.

1. Introduction

In textile industry the process of dyeing results in the production of large amounts of wastewater exhibiting intense coloration that has to be eliminated before release into natural water streams [1]. Wastewaters from textile industries contain different types of synthetic dyes, which are mostly toxic, mutagenic and carcinogenic. Moreover, they are very stable to light, temperature and microbial attack [2]. Discharging of these wastewaters into receiving streams not only affects the aesthetic aspects but also interferes with transmission of sunlight into streams and therefore reduces photosynthetic activity [3, 4].

Advanced oxidation processes are those groups of technologies that lead to hydroxyl radical ($\cdot OH$) generation as the primary oxidant (second highest powerful oxidant after the fluorine). These radicals are produced by means of oxidizing agent such as H_2O_2 and O_3, ultraviolet irradiation, ultrasound, and homogeneous or heterogeneous catalysts.

Common AOPs which are widely used are H_2O_2/ UV [5], TiO_2/UV [6], Ozonation [7], O_3/UV [8], Fenton reagent [9], UV- Fenton [10] process electron beam irradiation [11], Sonolysis [12], wet-air oxidation [13] and various combination of these methods [14]. Photocatalytic degradation has been proved to be a promising method for the treatment of wastewater contaminated with organic and inorganic pollutants [15-18]. Fenton and Fenton type processes have proven to yield very good results either for complete mineralization of azo dyes or for their transformation into less complex structures that are more easily biodegradable. It can be used to degrade many pesticides [19], harmful chemicals [20-21] and dyes [22-24]. It has been shown that Photo-Fenton reagent cleaves the conjugated bonds of azo-dyes chromophores, leading to color removal and enhancing the biodegradability of the treated wastewater. It has the advantages of coagulation and catalytic oxidation, as well as being able to generate oxygen in water.

Reactive Orange 13 mainly used for dyeing cellulosic fibers, such as cotton and rayon, but are also used for silk, wool, nylon, and leather [25]. The major environmental problem associated with the use of the reactive dyes is their loss in the dyeing process [26]. So it causes great potential of pollution of water environment. Therefore, it is planned to undertake the title investigation. The objective of the present study is to evaluate the dependence factors for the color removal rate such as concentration of Dye (RO13), photocatalyst (Fenton reagent), H_2O_2, light intensity and pH of the experimental solutions.

2. Materials and method

2.1Chemicals

For the present studies the commercial azo dye Reactive Orange 13 was used. Photocatalyst $FeSO_4$ (Merck, 99% purity) and H_2O_2 (Merck, 30% purity) were used for photocatalytic degradation. For the photobleaching process, $1x10^{-3}$M stock solution of dye Reactive Orange 13 was prepared in double distilled water and diluted as required. The desired pH of the solution was adjusted by the addition of previously standardized sulphuric acid and sodium hydroxide solutions.

2.2 Procedure and Analysis

The reaction mixture was prepared by taking 1.0 mL of Reactive Orange 13 dye solution ($1x10^{-3}$ M), 1.0 ml of $FeSO_4$ ($1x10^{-3}$ M) and 1.0 ml of H_2O_2 (30%) in a beaker at pH 3.0. The total volume of the reaction mixture was made 30 ml by adding double distilled water. To carry out the photobleaching, the reaction mixture was irradiated under light source (200W Tungsten lamp). Water filter was used to cut off thermal radiation. The pH of the solution was measured by pH meter (Systronics, 335). The progress of the reaction was observed at definite time intervals by measuring absorbance using spectrophotometer (Systronic Double Beam Spectrophotometer 2203) at **493.1 nm.** The rate of decrease of color with time was continuously monitored. After complete mineralization, the presence of NO_2^-, NO_3^-, SO_4^{2-} ions and evolution of CO_2 were tested by standard procedure.

3. Results and Discussion

Control experiments (in absence of photocatalyst, light) confirm the necessity of photocatalyst, light to follow the photocatalytic path for the photobleaching of dye. The photocatalytic degradation of Reactive Orange 13 was observed at 493.1 nm. The optimum conditions for the photobleaching of dye were [Dye] = 4.0 $x10^{-5}$ M, [$FeSO_4$] = 3.66 $x10^{-5}$ M, H_2O_2 = 1.0 mL and pH = 3.0. The result of photocatalytic bleaching of Reactive Orange 13 is presented in Table- 1. It was observed that absorbance (Abs.) decreases with the increase in time of irradiation indicating that the dye is degraded on irradiation. A graph between 2 + log O.D. and time has been plotted. The linearity of the plot indicates that the photocatalytic bleaching of Reactive Orange 13 follows a first order kinetics. The rate constant of this photobleaching process was determined using the expression **Rate Constant (k) = 2.303 x Slope**.

[Reactive Orange 13]=4.0 $\times 10^{-5}$ M;
pH = 3.0;
[Fe^{2+}] = 3.66 $\times 10^{-5}$ M;
H_2O_2 = 1.0 mL;
λ_{max}= 493.1 nm;
Light Intensity =60 $mWcm^{-2}$;

Table 1: Typical Run of Photocatalytic degradation of Reactive Orange 13

Time (minutes)	O.D	2 + log O.D.
0	0.639	1.8055
2	0.509	1.7067
4	0.409	1.6117
6	0.317	1.5010
8	0.273	1.4361
10	0.211	1.3242

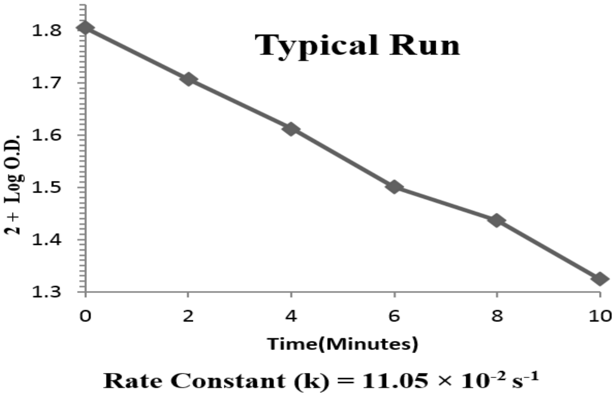

Fig 1: Typical Run of Photocatalytic degradation of Reactive Orange 13

3.1 Effect of pH Variation on Photodegradation of Dye

To study the effect of pH on photodegradation experiments are conducted for **[Reactive Orange 13] = 4.0 × 10^{-5} M,** in presence of **[Fe^{2+}] = 3.66 × 10^{-5} M** and 1.0 ml H_2O_2 at different initial pH values (2.5-3.3). The values of k are given in Table2:

[Reactive Orange 13] = 4.0 × 10^{-5} M;
[Fe^{2+}] = 3.66 × 10^{-5} M;
H_2O_2 = 1.0 mL;
Light Intensity = 60 $mWcm^{-2}$;
λ_{max}= 493.1 nm

Table 2: Effect of pH Variation

pH	$k \times 10^{-2} s^{-1}$
2.5	7.13
2.6	7.67
2.7	8.06
2.8	8.80
2.9	9.90
3.0	11.05
3.1	9.21
3.2	8.06
3.3	7.59

Fenton oxidation is known as a highly pH dependent process since pH plays an important role in the mechanism of OH production in the Fenton's reaction. At high pH (pH > 3.3) the generation of $\cdot OH$ gets slower because of the formation of the ferrichydroxo complexes. On the other hand at very low pH values (<2.5) hydrogen ions act as OH radical-scavengers. The reaction is slowed down due to the formation of complex species $[Fe(H_2O)_6]^{2+}$, which reacts more slowly with peroxide compared to that of $[Fe(OH)(H_2O)_5]^{2+}$.

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

$$Fe^{3+} + H_2O + hv \rightarrow \cdot OH + H^+ + Fe^{2+} \qquad \ldots(2)$$

Thus, it may be concluded that step (i) dominates over step (ii) in the pH range below 3.0. However, retardation of the reaction above pH 3.0 suggests the dominance of step (ii) over step (i).

In addition, the peroxide gets solvated in the presence of high concentration of H^+ ions to form stable oxonium ion $[H_3O_2]^+$. An oxonium ion makes peroxide electrophilic to enhance its stability and presumably substantially reduces the reactivity with Fe^{2+} ion. Maximum color removal efficiencies were obtained at pH 3.0, for the dye in case of photo-Fenton processes.

3.2 Dye Concentration Variation

The effect of initial dyes concentration on the decolorization degree at the optimum pH, Fenton reagent concentration and H_2O_2 dosage, were studied in photo-Fenton processes see. As an example, Dyes concentrations were varied from 2.66 x10^{-5} M, to 4.66 x 10^{-5} M for Reactive Orange 13. The results are given in Table-3. The rate of photochemical degradation was found to increase with increase in the concentration of RO13 up to 4.0×10^{-5} M. On further increasing its concentration, a sudden decrease in the rate of degradation was observed. This may be explained on the basis that on initially increasing the concentration of RO13, more molecules of RO13, are available for degradation. However on increasing the concentration above 4.0×10^{-5} M, the reaction rate was found to decrease. It may be attributed to the fact that as the concentration of RO13 was increased, it started acting like a filter for the incident light, where its large concentration will not permit the desired light intensity to react the dye molecule in the bulk of the solution and thus a decrease in the rate of photochemical bleaching of Reactive Orange 13 has observed. At the optimum conditions for the dye, the best dye concentration was 4.0 x 10^{-5} M.

pH = 3.0;
$[Fe^{2+}] = 3.66 \times 10^{-5}$ M;
H_2O_2 = 1.0 mL;
Light Intensity = 60 mWcm^{-2};
λ_{max}= 493.1 nm;

Table 3: Effect of Reactive Orange 13 Concentration

[Dye] $\times10^{-5}$M	k$\times10^{-2}$ s^{-1}
2.66	5.98
3.0	7.83
3.33	8.98
3.66	10.59
4.0	11.05
4.33	9.67
4.66	8.29

3.3 Effect of Fe^{2+} Ion Concentration

Dye degradation efficiency by Photo-Fenton process is influenced by the concentration of Fe^{2+} ions which catalyze hydrogen peroxide decomposition resulting in ·OH radical production and consequently the degradation of organic molecule. The effect of concentration of Fe^{2+} on the rate of photochemical degradation of Reactive Orange 13 was observed by keeping all other factors constant. The results are given in Table - 3. Initially on increasing ferrous salt concentration, degradation rate of organic compound increases, to certain level while a reverse trend was observed beyond this limit. This may be explained on the basis that on increasing the Fe^{2+} ions in the reaction mixture is accompanied by enhanced generation of ·OH radicals, consequently increasing the rate of photodegradation. After the optimal Fe^{2+} ions addition, the higher concentration of Fe^{2+} resulted in a brown turbidity due to recombination of ·OH radicals and here Fe^{2+} ions act as a scavenger, therefore, the rate decreases.

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^-$ …(3)
$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^-$ …(4)

[Reactive Orange 13] = 4.0×10^{-5} M;
pH = 3.0;
H_2O_2 = 1.0 mL;
Light Intensity = 60 mWcm^{-2};
λ_{max}= 493.1 nm

Table 3: Effect of $FeSO_4$ Concentration

$[FeSO_4]\times10^{-5}$M	k$\times10^{-2}$s^{-1}
1.66	6.44
2.0	6.98
2.33	7.36
2.66	8.34
3.0	9.44
3.33	10.12
3.66	11.05
4.0	9.18
4.33	8.75

3.4 Effect of H_2O_2 Concentration

Concentration of H_2O_2 plays a more crucial role in the overall efficiency of the degradation processes. Usually it has been observed that the percentage degradation of the Reactive Orange 13 increases with an increase in the dosage of H_2O_2, but excess quantities are not recommended.

It was observed that the rate of reaction increases on increasing the amount of H_2O_2 up to 1.0 mL. Thereafter, the rate of degradation decreases on with the increase in the amount of the H_2O_2. This can be explained on the basis that at optimum amount of H_2O_2, more hydroxyl radicals are produced by Fe^{2+} ions which degrade more dye molecules. On further increasing the amount of H_2O_2, the rate of reaction was found to decrease because of the fact that as the amount of H_2O_2 increased along its optimum condition (1.0 mL) the rate of the reaction [Eq. (5) and Eq.(6)] become fast and ·OH radicals are consumed rapidly due to more availability of H_2O_2 molecule. The peroxide radical are utilized and H^+ ions are produced. The production of H^+ ions is confirmed by a slight decrease in pH of the reaction mixture at the end of reaction. As a consequence, the rate of photodegradation decreases.

$Fe^{3+} + H_2O_2 + hv \rightarrow Fe^{2+} + {}^{\cdot}OOH + H^+$ ..... (5)
$H_2O_2 + {}^{\cdot}OH \xrightarrow{\quad} H_2O + {}^{\cdot}OOH$ …. (6)

This may be due to recombination of hydroxyl radicals and also hydroxyl radicals react with H_2O_2 contributing to the ·OH radicals scavenging capacity.

[Reactive Orange 13] = 4.0×10^{-5} M;
pH = 3.0;
$[Fe^{2+}] = 3.66 \times 10^{-5}$ M;
Light Intensity = 60 mWcm^{-2}; λ_{max}= 493.1 nm

Table 5: Effect of H_2O_2 Amount Variation

H_2O_2(ml)	k$\times10^{-2}$s^{-1}
0.5	6.90
0.6	7.29
0.7	8.59
0.8	10.13
0.9	10.53
1.0	11.05
1.1	10.11
1.2	9.21
1.3	8.52

3.5 Effect of Light Intensity

The effect of light intensity on the photodegradation of Reactive Orange 13 was also observed. The results obtained are given in Table - 6. A linear plot was obtained between the rate constant and light intensity, which indicates that an increase in the light intensity increase the rate of reaction because an increase in the intensity of light will increase the number of photons striking catalyst particles per unit time per square cm. As a result, more photons reacts with Fe^{+3} ions and there is an increase in the number of active species, the hydroxyl radicals and corresponding increases in the rate of reaction.

$Fe^{3+} + H_2O + hv \rightarrow {}^{\cdot}OH + H^+ + Fe^{2+}$ …(7)

[Reactive Orange 13] = 4.0×10^{-5} M;
pH = 3.0;
[Fe^{2+}] = 3.66×10^{-5}M;
H_2O_2 = 1.0 mL;
λ_{max}= 493.1 nm

Table 5: Effect of Light Intensity

Light Intensity ($mWcm^{-2}$)	$k \times 10^{-2} s^{-1}$
10	6.79
20	7.77
30	8.58
40	9.21
50	10.23
60	11.05

4. Mechanism

In presence of Fe^{2+}, the peroxide breaks down to ·OH and OH^-, according to the following reaction

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^-$ …. (8)
$Fe^{3+} + H_2O_2 + hv \rightarrow {}^{\cdot}OOH + H^+ + Fe^{2+}$ …. (9)
$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + {}^{\cdot}OH + H^+$ … (10)
${}^{\cdot}OH + H_2O_2 \rightarrow H_2O + {}^{\cdot}OOH$ (Highly Unstable) … (11)
$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^-$ … (12)
$Fe^{3+} + {}^{\cdot}OOH \rightarrow O_2 + Fe^{2+} + H^+$ … (13)
Consumption of ·OH radicals
$H_2O_2 + {}^{\cdot}OH \rightarrow {}^{\cdot}OOH + H_2O$ … (14)
${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2$ … (15)
${}^{\cdot}OH$ + Dye → Colourless Degraded end Product … (16)

The participation of the ·OH radicals as an active oxidizing species was confirmed using the hydroxyl radical scavenger 2-Propanol, Which reduced rate of Photo-degradation.

After continuous irradiation, the complete mineralization of dye occurred via converting into end products. The end products are simple molecules or ions and less harmful to the environment.

Reactive Dyes (S) + ·OH $\longrightarrow$ End Products ($CO_2 + H^+ + H_2O + NO_2^- + NO_3^- + SO_4^{-2}$)

The end products were detected in the reaction mixture by chemical test. Nitrate ions were detected and confirmed by a chemical test using H_2SO_4 and $FeSO_4$. A positive test for presence of nitrite ions is indicated by a dark brown solution, arising from the iron nitric oxide complex. Sulphate ions are precipitated as $BaSO_4$. CO_2 was confirmed by introducing the gas to freshly prepared limewater. The lime water turns milky indicates its presence.

5. Conclusion

Photodegradation efficiency of dye was negligible when photolysis was carried out in the absence of H_2O_2 and UV light. Photo-Fenton reaction increased the production of ·OH radicals and led to 67% mineralization of the dye in 10 minutes. The experimental data demonstrated that photo-Fenton process is promising techniques for the degradation of Reactive Orange 13 dye from aqueous solution. This process is environmental friendly due to generation of biodegradable end products.

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