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PHOTODEGRADATION OF ACID VIOLET 90 IN AQUEOUS SOLUTION BY PHOTO-FENTON REAGENT

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ABSTRACT

Advanced oxidation processes (AOPs) are widely used for the removal of recalcitrant organic constituents from textile industrial and municipal wastewater. Degradation of Acid Violet 90 by Photo-Fenton reagent has been investigated under irradiation of visible light in aqueous solution. A detailed investigation of photo-degradation of Acid Violet 90 using H_2O_2/Fe^{2+} was carried out. It was found that dye degradation is dependent on concentration of Acid Violet 90, $FeSO_4$, H_2O_2 and pH of the experimental solution. The optimum condition for the photodegradation of dye was established. The kinetics of degradation of dye in the dilute solution follows first order kinetics.

Key words: Photo-degradation, Acid violet 90, Photo-Fenton.

INTRODUCTION

Photocatalytic degradation has been proved to be a promising method for the treatment of wastewater contaminated with organic and inorganic pollutants. Degradation of organic pollutants like dyes in industrial wastewater has become increasingly important during the last decade in the field of advanced oxidation processes (AOPs)[1–5]. AOPs are attractive because they hold out the promise of completely mineralizing the target pollutant. AOPs essentially involve the generation of $^{\bullet}OH$, a powerful and non-selective oxidizing agent that can be produced by different combinations of ozone, hydrogen peroxide, UV radiation and titanium dioxide and also by the combination of hydrogen peroxide with ferrous ion in the Fenton's reagent, for the destruction of hazardous pollutants in air and water. The rate of degradation of the organic pollutants by Fenton reaction increases in the presence of an irradiation source.

In recent years, acid dyes have commonly been used in textile industries due to their

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advantages such as better dyeing processing conditions and bright colors. One of the major factors determining the release of acid dye into environment is its degree of fixation on the fiber. Acid dyes in dyeing wastewater have been identified as recalcitrant compounds since they contain high alkalinity, high concentration of organic materials and strong color in comparison with other dyes. Conventional oxidation treatments have found difficulty to oxidize dyestuffs and complex structure of organic compounds. Advanced oxidation processes (AOPs) have provided innovative, cost-effective catalyzed chemical oxidation for treating pollutants in low or high concentration from contaminated soil, sludge and water. AOPs are based on the generation of hydroxyl radical ($^{\bullet}OH$) which has a high oxidation potential (2.8 V) that completely convert organic contaminant into CO_2, H_2O and inorganic ions or biodegradable compounds. Common AOPs which are widely used are (H_2O_2/UV)[6], (TiO_2/UV)[7], Ozonation[8], (O_3/UV)[9], Fenton reagent[10] or UV-Fenton[11] process etc. Fenton and Fenton type processes have been 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[12], harmful chemicals[13-15] and dyes[16,17]. It has the advantages of coagulation and catalytic oxidation, as well as being able to generate oxygen in water.

Acid violet 90 (AV90) is widely used in textile industries, but it causes great potential of water pollution. As a precaution a proper treatment of waste water is necessary before discharge. Therefore, it was planned to undertake the present investigation for the evaluation of various dependent factors for the color removal rate such as concentration of dye (AV90), photocatalyst (Fenton reagent), H_2O_2 and pH of the experimental solutions.

EXPERIMENTAL

Materials

For the present studies, the commercial azo dye Acid violet 90 was used. $FeSO_4$ (Merck, 99% purity) and H_2O_2 (Merck, 6% purity) were used for degradation. For the photobleaching process, 2.5×10^{-3} M stock solution of dye Acid violet 90 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. All laboratory reagents were of analytical grade.

Procedure and analysis

The reaction mixture was prepared by taking 1.5 mL of Acid violet 90 dye solution (2.5×10^{-3} M), 1.0 mL of $FeSO_4$ (1×10^{-3} M), 1.0 mL of H_2O_2 (6%) in a beaker. The total volume of the reaction mixture was made 30 mL by adding double distilled water. The concentration of different ingredients in the reaction mixture was [Dye] = 12.50 x 10^{-5} M, [$FeSO_4$] = 3.33 x 10^{-5} M, H_2O_2 = 1.0 mL and pH = 3.0. To carry out the photobleaching, the reaction mixture was irradiated under light source (200W Tungsten lamp). Water filters were used to cut off thermal radiation. The pH of the solution was measured by pH meter (Systronics, 106). The progress of the reaction was observed at definite time intervals by measuring absorbance using spectrophotometer (Systronic Double Beam Spectrophotometer 2203) at 540 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.

RESULTS AND DISCUSSION

Control experiments (in absence of Fenton reagent, light) confirm the necessity of Fenton reagent and light to follow the photobleaching of dye by photo-Fenton reaction. The degradation of Acid violet 90 was observed at 540 nm. The optimum conditions for the photobleaching of dye were [Dye] = 12.50 x 10^{-5} M, [$FeSO_4$] = 3.33 x 10^{-5} M, H_2O_2 = 1.0 mL and pH = 3.0. The result for photodegradation of Acid violet 90 is presented in Table 1. It was observed that absorbance (Abs.) O. D. 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 bleaching of Acid violet 90 follows a first order kinetics. The rate constant of this photobleaching process was found. $k = 11.27 \times 10^{-2}$ sec^{-1}.

Table 1: Typical run of photo-degradation of acid violet 90

pH = 3.0
H_2O_2 = 1.0 mL

[Acid violet 90] = 12.50×10^{-5} M
[Fe^{2+}] = 3.33×10^{-5} M
Light intensity = 70 $mWcm^{-2}$

Time (seconds)	O.D.	2 + log O.D.
0	0.422	1.6254
30	0.403	1.6054
60	0.380	1.5798
90	0.360	1.5564
120	0.337	1.5277
150	0.324	1.5106
180	0.301	1.4786

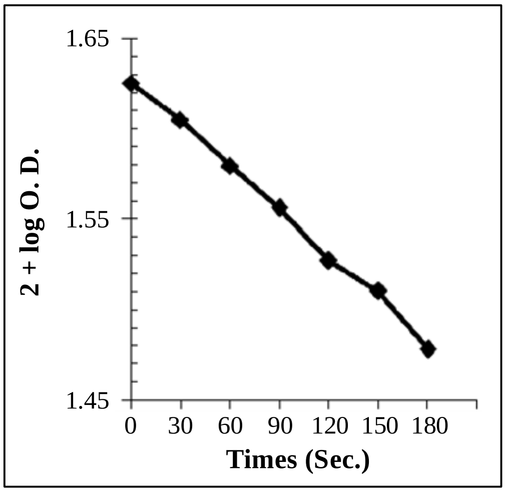

Fig. 1: Typical run for photodegradation of acid violet 90

The effect of variation in various reaction parameters have been studied e.g. pH, concentration of the dye, concentration of $FeSO_4$ and concentration of H_2O_2.

Effect of pH

Fenton oxidation is known as a highly pH dependent process, since pH plays an important role in the mechanism of $^{\bullet}OH$ production in the Fenton's reaction. At high pH (pH > 3.5), the generation of $^{\bullet}OH$ radicals get slower because of the formation of the ferric hydroxo complex. On the other hand, at very low pH (< 2.5), hydrogen ions act as $^{\bullet}OH$ radical scavengers. The reaction is slow down due to the formation of complex species $[Fe(H_2O)_6]^{2+}$, which reacts more slowly with peroxide compared to that of $[Fe(OH)(H_2O)_5]^{2+}$.

Table 2: Effect of pH variation

[Acid violet 90] = 12.50×10^{-5} M　　$[Fe^{2+}] = 3.33 \times 10^{-5}$ M

H_2O_2 = 1.0 mL　　Light intensity = 70 $mWcm^{-2}$

pH	$k \times 10^{-2}$ (s^{-1})
2.5	6.46
2.6	6.73
2.7	7.98
2.8	8.02

Cont…

pH	**$k \times 10^{-2}$ (s^{-1})**
2.9	8.45
3.0	**11.27**
3.1	8.11
3.2	7.90
3.3	7.55
3.4	4.14
3.5	3.76

Effect of dye concentration

Effect of variation of dye concentration on rate of reaction was also studied by taking different concentration of Acid violet 90 solution. The results are given in Table 3.

Table 3: Effect of dye concentration variation

$[Fe^{2+}] = 3.33 \times 10^{-5}$ M pH = 3.0
H_2O_2 = 1.0 mL Light intensity = 70 mWcm^{-2}

[Dye] × 10^{-5} M	**$k \times 10^{-2}$ (s^{-1})**
4.16	5.64
8.33	7.90
12.50	**11.27**
16.66	8.10
20.83	7.55
25.00	4.62
29.16	3.35

The rate of photochemical degradation was found increasing with increase in the concentration of AV 90 upto 12.50 × 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 increasing the concentration of AV 90, more molecules of AV 90, are available for degradation. However on increasing the concentration above 12.50 × 10^{-5} M, the reaction rate was found to decrease. It may be attributed to the fact that as the concentration of AV 90 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 with dye molecules in the bulk of the solution and thus a decrease in the rate of photochemical bleaching of Acid violet 90 has been observed.

Effect of ferrous sulphate concentration

The effect of concentration of Fe^{2+} on the rate of photochemical degradation of Acid violet 90 was observed by keeping all other factors constant. The results are given in Table 4. It is clear that the rate of photodegradation increases on increasing concentration of Fe^{2+} ions upto 3.33×10^{-5} M, 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 accompained by enhanced generation of $^{\bullet}OH$ radicals, consequently increasing the rate of photodegradation. After the optimal Fe^{2+} ions addition, the higher dose of Fe^{2+} resulted in a brown turbidity that causes the recombination of $^{\bullet}OH$ radicals and Fe^{2+} reacts with $^{\bullet}OH$ as a scavenger. Therefore, on further increase, the rate decreases.

Table 4: Effect of ferrous ion concentration

[Acid violet 90] = 12.50×10^{-5} M pH = 3.0
H_2O_2 = 1.0 mL Light intensity = 70 $mWcm^{-2}$

[$FeSO_4$] × 10^{-5} M	**k × 10^{-2} (s^{-1})**
1.66	7.55
3.33	**11.27**
5.00	7.90
6.66	6.70
8.33	6.52
10.00	4.46

Effect of hydrogen peroxide amount

The effect of amount of hydrogen peroxide on photodegradation of Acid violet 90 was also studied. The results are presented in Table 5. It was observed that the rate of reaction increases on increasing the amount of H_2O_2 upto 1.0 mL. Thereafter, the rate of degradation decreases on increasing the amount of the H_2O_2 above 1.0 mL. This can be explained on the basis that at optimum concentration 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. It is because of the fact that as the amount of H_2O_2 was increased along its optimum condition (1.0 mL) the rate of the reaction

[Eq. (2) and Eq. (4) of mechanism] become fast and $^{\bullet}OH$ radicals are consumed rapidly due to more availability of H_2O_2 molecule. The peroxide radicals formed 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.

Table 5: Effect of H_2O_2 amount

[Acid violet 90] = 12.50×10^{-5} M [Fe^{2+}] = 3.33×10^{-5} M
pH = 3.0 Light intensity = 70 $mWcm^{-2}$

H_2O_2 (mL)	**$k \times 10^{-2}$ (s^{-1})**
0.5	5.60
1.0	**11.27**
1.5	8.40
2.0	7.70
2.5	6.40
3.0	4.64

Effect of light intensity

The effect of light intensity on the photodegradation of Acid violet 90 was also observed. The results obtained are given in Table 6.

Table 6: Effect of light intensity variation

[Acid violet 90] = 12.50×10^{-5} M [Fe^{2+}] = 3.33×10^{-5} M
pH = 3.0 H_2O_2 = 1.0 mL

Light intensity ($mWcm^{-2}$)	**$k \times 10^{-2}$ (s^{-1})**
10	3.97
20	4.40
30	6.66
40	7.50
50	7.98
60	8.40
70	**11.27**

A linear plot was obtained between the rate constant and light intensity, which indicates that an increase in the light intensity increases 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.

Mechanism

The mechanism of Fenton oxidation is based on the generation of $^{\bullet}OH$ radicals by the catalytic decomposition of H_2O_2 in acidic media. In presence of Fe^{2+}, the peroxide breaks down to $^{\bullet}OH$ and OH^-, according to the following reaction

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad ...(1)$$

$$Fe^{3+} + H_2O_2 + hv \longrightarrow {}^{\bullet}OOH + H^+ + Fe^{2+} \qquad ...(2)$$

$$Fe^{3+} + H_2O + hv \longrightarrow Fe^{2+} + {}^{\bullet}OH + H^+ \qquad ...(3)$$

$${}^{\cdot}OH + H_2O_2 \longrightarrow H_2O + {}^{\bullet}OOH \qquad ...(4)$$

$$Fe^{2+} + {}^{\bullet}OH \longrightarrow Fe^{3+} + OH^- \qquad ...(5)$$

$$Fe^{3+} + {}^{\bullet}OOH \longrightarrow O_2 + Fe^{2+} + H^+ \qquad …(6)$$

Consumption of $^{\bullet}OH$ radicals

$$H_2O_2 + {}^{\bullet}OH \longrightarrow {}^{\bullet}OOH + H_2O \qquad ...(7)$$

$${}^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2 \qquad …(8)$$

$${}^{\bullet}OH + \text{Dye} \longrightarrow \text{Colourless degraded end product} \qquad …(9)$$

$$\text{End product} = CO_2 + H^+ + NO_2^- + NO_3^- + H_2O + SO_4^{2-}$$

$^{\bullet}OOH$ radicals are highly unstable in water and undergo facile disproportionation rather than reacting slowly with the dye molecules. The participation of the $^{\bullet}OH$ radical as an active oxidizing species was confirmed using the hydroxyl radical scavenger 2-propanol, which drastically reduced rate of degradation. The hydroxyl radical attacks on dye molecule and abstracts a hydrogen atom or adds itself to double bond. After continuous irradiation, the complete mineralization of dye occurred. The end products are simple molecules or ions and less harmful to the environment. The main advantage of using photo-Fenton reagent is the regeneration of the consumed Fe^{2+} ions on illumination.

CONCLUSION

The experimental data demonstrated that photo-Fenton process is promising technique for the degradation of Acid violet 90 dye from aqueous solution. The use of Photo-Fenton reaction increased the production of $^{\bullet}OH$ radicals and led to 29% mineralization of the dye in 180 seconds.

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