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The decolorization and mineralization of azo dye Reactive Yellow 86 in aqueous solution by Photo-Fenton Reagent

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ABSTRACT

At present work, aqueous solutions of azo dye Reactive yellow 86 (RY86) were treated with Fenton reagent. The efficiency of treatment was evaluated by color alteration and mineralization of the dye. A detailed investigation of photodegradation of Reactive Yellow 86 using H_2O_2/Fe^{2+} has been carried out. The reduction of color was determined by UV-VIS spectrophotometer and the results showed that the dye rapidly lost the color while the doses were increased. Results indicate that dye degradation is dependent on concentration of Dye (RY86), photocatalyst (Fenton reagent), H_2O_2 and pH of the experimental solutions. The optimum conditions for the photobleaching of dye had been established. The kinetics of degradation of the dye in the dilute aqueous solutions follows first order kinetics. The results indicated that the treatment of the dye by Photo-Fenton reagent was efficient at optimum conditions.

Keywords- Reactive yellow 86, Photo- Fenton, Photobleaching, mineralization.

INTRODUCTION

Textile effluent is notoriously known to have a strong color, large amount of suspended solids, broadly fluctuating pH, high temperature, high chemical oxygen demand (COD), high biological oxygen demand (BOD) and presence of metal ions[1,2]. Synthetic textile dyes can be structurally different and a very low concentration of dyes in effluent is highly visible and undesirable. Furthermore, their discharge into surface water leads to aesthetic problems and

obstructs light penetration and oxygen transfer into bodies of water, hence affecting aquatic life [3].

In recent years, reactive dyes have been commonly used due to their advantages such as better dyeing processing conditions and bright colors. One of the major factors determining the release of a dye into environment is its degree of fixation on the fiber. Reactive 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 ($\cdot\text{OH}$) 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 $\text{H}_2\text{O}_2/\text{UV}$ [4], TiO_2/UV [5], Ozonation [6], O_3/UV [7], Fenton reagent [8] or UV- Fenton [9] process etc.

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 [10], harmful chemicals [11, 12] and dyes [13, 14]. It has the advantages of coagulation and catalytic oxidation, as well as being able to generate oxygen in water.

Reactive Yellow 86 (RY86) is widely used in textile industries. As, it causes great potential of pollution of water environment, a proper treatment is necessary before discharge into the 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 (RY86), photocatalyst (Fenton reagent), H_2O_2 and pH of the experimental solutions.

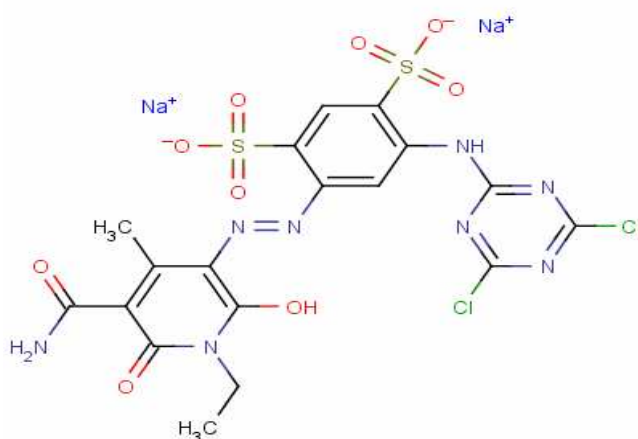


Fig - I : Structure of Reactive Yellow-86
Molecular formula – $\text{C}_{19}\text{H}_{14}\text{Cl}_2\text{N}_8\text{Na}_2\text{S}_2\text{O}_9$ Molecular weight = 862.27

MATERIALS AND METHODS

Materials

For the present studies the commercial azo dye Reactive Yellow 86 (Fig: I) was used. Photocatalyst FeSO₄ (Merck, 99% purity) and H₂O₂ (Merck, 30% purity) were used for photocatalytic degradation. For the photobleaching process, 1x10⁻³M stock solution of dye Reactive Yellow 86 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 3 ml of Reactive Yellow 86 dye solution (1x10⁻³ M), 3 ml of FeSO₄ (1x10⁻³ M), 0.6 ml of H₂O₂ (30%) in a round bottom flask. The total volume of the reaction mixture was made 100 ml by adding double distilled water. The concentration of different ingredients in the reaction mixture was [Dye] = 3x10⁻⁵ M, [FeSO₄] = 3x10⁻⁵ M, [H₂O₂] = 5.87 x10⁻² M.

To carry out the photobleaching, the reaction mixture was irradiated under light source (2 x 200 W Tungsten lamps). 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 (Schimadzu, UV-1700, Pharmaspec) at 419 nm. The rate of decrease of color with time was continuously monitored. After complete mineralization, the presence of NO₂⁻, NO₃⁻, SO₄²⁻ ions and evolution of CO₂ were tested by standard procedure.

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 Yellow 86 was observed at 419 nm. The optimum conditions for the photobleaching of dye were [Dye] = 3x10⁻⁵ M, [FeSO₄] = 3x10⁻⁵ M, [H₂O₂] = 5.87 x10⁻² M and pH=3. The result of photocatalytic bleaching of Reactive Yellow 86 is graphically presented in Fig.II.

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 Abs. and time has been plotted. The linearity of the plot indicates that the photocatalytic bleaching of Reactive Yellow 86 follows a first order kinetics. The rate constant of this photobleaching process was determined using the expression.

$$\begin{aligned} \text{Rate (k)} &= 2.303 \times \text{Slope} \\ &= 8.82 \times 10^{-5} \text{ sec}^{-1} \end{aligned}$$

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

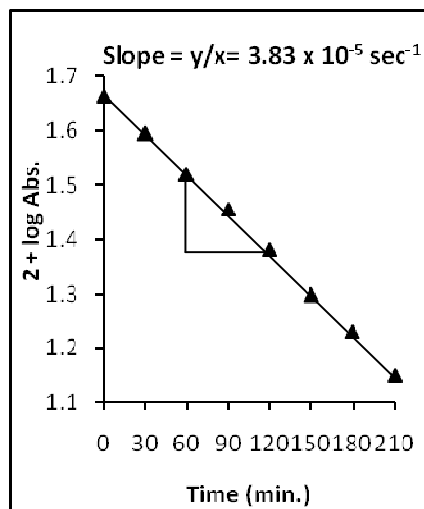


Fig-II: A plot showing a typical run of photobleaching of Reactive Yellow 86 by Photo-Fenton reagent under the optimized conditions.

Effect of variation in hydrogen ion concentration on the rate of decolorization of the dye

Fenton oxidation is known as a highly pH dependent process since pH plays an important role in the mechanism of $\cdot\text{OH}$ production in the Fenton's reaction. At high pH ($\text{pH} > 3$), the generation of $\cdot\text{OH}$ gets slower because of the formation of the ferric hydroxo complexes.

On the other hand, at very low pH (< 2.0), hydrogen ions acts as $\cdot\text{OH}$ radical scavengers. The reaction is slowed down due to the formation of complex species $[\text{Fe}(\text{H}_2\text{O})_6]^{+2}$, which reacts more slowly with peroxide compared to that of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{+2}$.

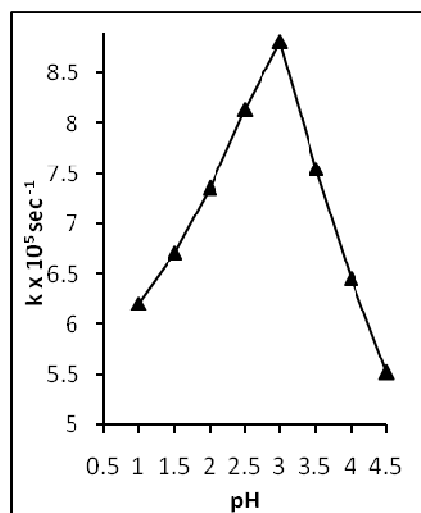


Fig- III: A plot showing effect of variation in hydrogen ion concentration on the rate of decolorization of the dye by Photo-Fenton reagent.

In this study, photodegradation was performed at different pH from 1 to 4.5. Fig - III also prove that pH 3 is the optimal pH for RY86 decolorization. Hence all subsequent experiments were carried out at pH 3.

Effect of variation in dye concentration on the rate of decolorization of the dye

The effect of dye concentration on the degradation of Reactive Yellow 86 was studied at different concentrations varying from 1.0×10^{-5} M to 8.0×10^{-5} M keeping all other factors identical. The result (Fig-IV) reveals that the rate of photobleaching of dye decreases with the increase in the concentration of the dye. The reason behind it is that the increase in the initial concentration of the dye lies in consistency of the hydroxyl radicals concentrations for all the dye molecules and therefore the rate of decolorization decreases.

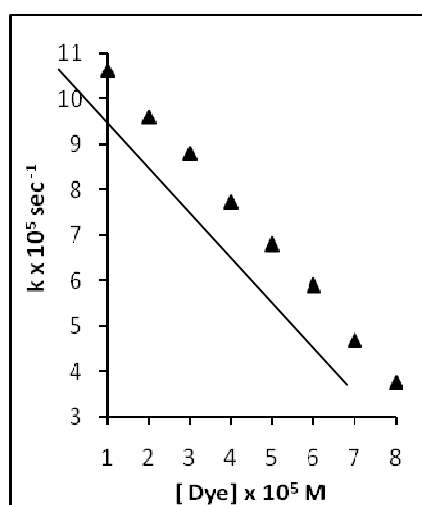


Fig- IV: A plot showing effect of variation in dye concentration on the rate of decolorization of the dye by Photo-Fenton reagent

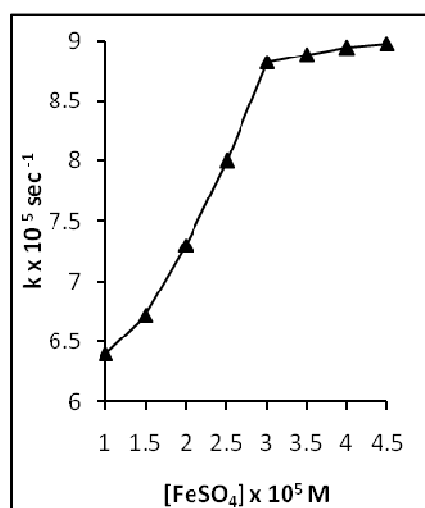


Fig- V: A plot showing effect of variation in catalyst concentration on the rate of decolorization of the dye by Photo-Fenton reagent.

Effect of variation in catalyst concentration on the rate of decolorization of the dye

Keeping all other factors identical, the concentration of catalyst was changed and its effect on the rate of photochemical degradation was observed. The result of Fig-V reveals that the rate of photobleaching of dye increases with the increase in the concentration of catalyst FeSO_4 up to 3×10^{-5} M. The increase in ferrous ions in the reaction mixture is accompanied by enhanced generation of $\cdot\text{OH}$ radicals, consequently increasing the rate of photodegradation. After the optimal Fe^{2+} addition, the higher dose of Fe^{2+} resulted in a brown turbidity that causes the recombination of $\cdot\text{OH}$ radicals and Fe^{2+} reacts with $\cdot\text{OH}$ as a scavenger. Therefore, on further increase, the rate becomes almost constant.

Effect of variation in hydrogen peroxide concentration on the rate of decolorization of the dye

The effect of H_2O_2 concentration on the degradation of RY86 is shown in Fig - VI. The result reveals that the rate of photobleaching of dye increases with the increase in the concentration of H_2O_2 upto 5.87×10^{-2} M. This can be explained on the basis that at higher concentration of H_2O_2 , more hydroxyl radicals are produced which degrade more dye molecules.

Further increase in $[\text{H}_2\text{O}_2]$ has negligible effect due to the recombination of $\cdot\text{OH}$ radicals and also hydroxyl radicals reaction with H_2O_2 contributing to the $\cdot\text{OH}$ scavenging capacity.

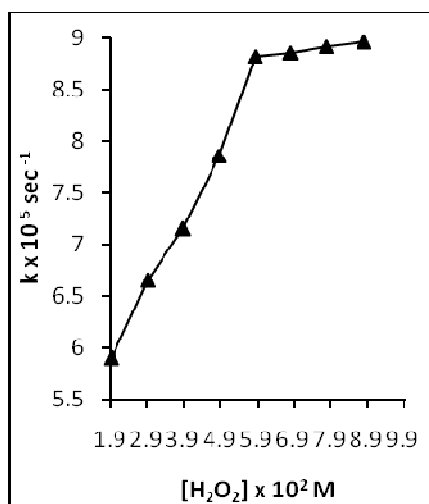
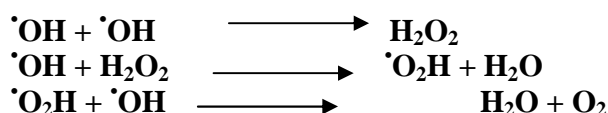
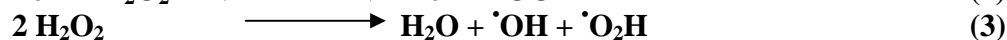
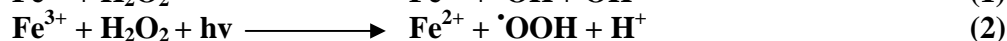
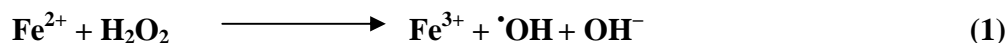


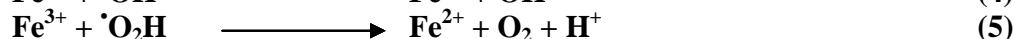
Fig- VI: A plot showing effect of variation in hydrogen peroxide concentration on the rate of decolorization of the dye by Photo-Fenton reagent.

Mechanism

The mechanism of Fenton oxidation is based on the generation of $\cdot\text{OH}$ radicals by the catalytic decomposition of H_2O_2 in acidic media. In presence of Fe^{2+} , the peroxide breaks down to $\cdot\text{OH}$ and OH^- , according to the following reactions (Eqn.1, 2, 3).



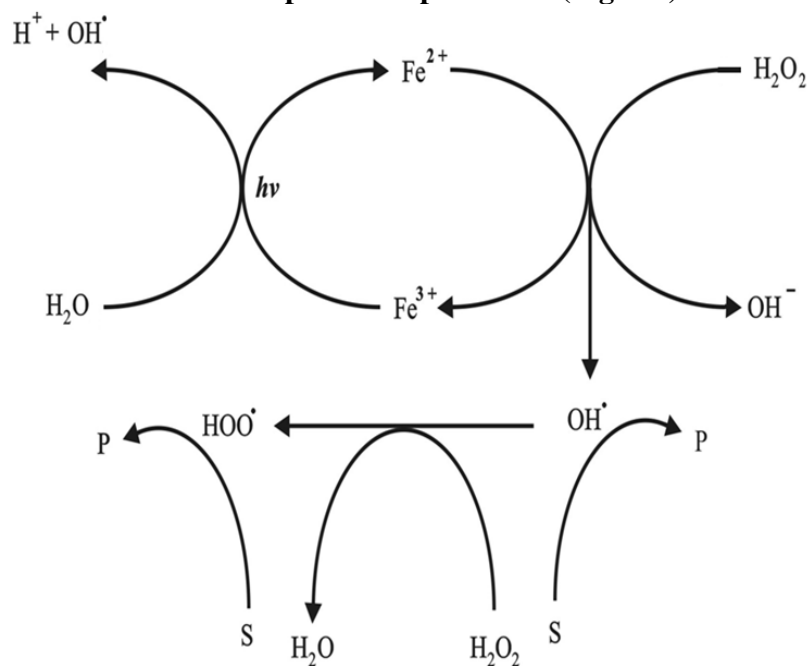
Ferrous ions will undergo oxidation to ferric ions by the addition of $\cdot\text{OH}$ radicals, while ferric ions are reduced to ferrous ions by the incorporation of $\cdot\text{OOH}$ radicals producing H^+ ions (Eq: 4,5).



$\cdot\text{OOH}$ radicals are highly unstable in water and undergo facile disproportionation rather than reacting slowly with the dye molecules. The participation of the $\cdot\text{OH}$ 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 bonds. After continuous irradiation, the complete mineralization of dye occurred via converting into end products.

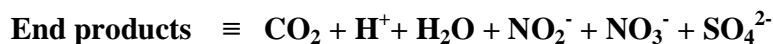
The whole process is picturised (Fig.VII).



Where S = Dye and P = End Products

Fig.VII: A Schematic representation of Photo-Fenton Chemistry

The end products are simple molecules or ions and less harmful to the environment (Eq: 6).



The end products were detected and their presence in the reaction mixture was ascertained either by chemical test or by ion selective electrode method.

Nitrate ions were detected and confirmed using nitrate ion selective electrode which is having a solid-state PVC polymer membrane. Nitrite 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 were detected and confirmed by gravimetric analysis in which excess of barium chloride solution was used and sulphate ions are precipitated as BaSO_4 . CO_2 was confirmed by introducing the gas to freshly prepared limewater. The test solution (limewater) turns milky which indicates its presence.

CONCLUSION

Photo-Fenton process was used for the photo-catalytic degradation of dye Reactive Yellow 86. Based on the results, it can be concluded that the decoloration of dye is strongly dependent on various reaction parameters e.g. pH, concentration of the dye, concentration of FeSO_4 and concentration of H_2O_2 .

The photocatalytic degradation of Reactive Yellow 86 was observed at 419 nm. The optimum conditions for the photobleaching of dye were $[\text{Dye}] = 3 \times 10^{-5} \text{ M}$, $[\text{FeSO}_4] = 3 \times 10^{-5} \text{ M}$, $[\text{H}_2\text{O}_2] = 5.87 \times 10^{-2} \text{ M}$ and $\text{pH} = 3$. Kinetic studies reveal that photocatalytic bleaching of Reactive Yellow 86 follows a first order kinetics.

The great interest of the academic community for the use of AOPs in waste water treatment is reflected by a number of publications that have been produced during the last decade. Major drawbacks of some methods is the use of costly chemicals, high operational cost, increased energy consumption as well as the formation of unknown intermediates which in some cases could be more toxic than the parent compounds. Based on the above, the main future challenges for using AOPs in waste water treatment could be the development of efficient and low cost materials to promote sufficient treatment, the use of renewable energy sources, the targeting of new classes of pollutants and the commercialization of processes which have been so far used in the laboratory.

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