



Use of Photo-Fenton reagent for the degradation of Basic Orange 2 in aqueous medium

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ABSTRACT

Photocatalytic decolorization of dyes using AOP is a new concern among researchers since it offers an attractive method for decolorization of dyes and breaks them into simple mineral form. The oxidation using Fenton Reagent has been found to be a promising treatment method for the effective decolorization and degradation of dyes. A detailed investigation of photodegradation of Basic Orange-12 (BO2) using H_2O_2/Fe^{+3} have been carried out. Results indicate that dye degradation is dependent on concentration of Dye (BO2), 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: Basic Orange-2, Photo- Fenton, Photocatalytic, Decolorization, AOPs.

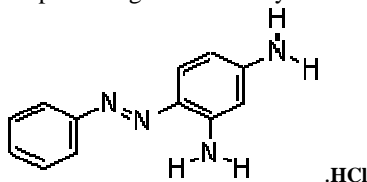
INTRODUCTION

The world is facing the challenge of purification of water and other resources. A lot of industries especially textile, dyeing and printing industries have generated environmental problems like aesthetic pollution, eutrophication and perturbation of aquatic ecosystem. Waste waters originating from dyes production and application industries pose a major threat to the surrounding ecosystems because of their toxicity and potentially carcinogenic nature [1]. Apart from the aesthetic problems relating to colored effluent, dyes strongly absorb sunlight. It affects the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem [2].

Therefore, this problem of textile waste waters caused by residual dyes during the dyeing process needs more effort to be studied and investigated. The limitations of conventional waste water treatment methods can be overcome by the application of the so called advanced oxidation processes (AOPs) [3].

AOPs are based on the generation of very reactive species such as hydroxyl radicals ($\bullet OH$), which have a strong oxidation potential [$E_0 = + 2.80 V$], second only to fluorine. Hydroxyl radicals rapidly and non-selectively oxidize a broad range of organic pollutants [4]. Common AOPs involve Fenton, Fenton-like processes, ozonation, high voltage electrical discharge (corona) process, TiO_2 , photo catalysis, radiolysis, wet-oxidation and various combinations of these methods [5-8]. Fenton's oxidation, one of the oldest AOPs, is relatively cheap, easily operated and maintained [9-12]. It has the advantages of coagulation and catalytic oxidation, as well as being able to generate oxygen in water. 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 [13-15].

For the present investigation, water soluble azo dye Basic Orange 2 (BO2), which is used for cotton, acrylic, viscous fiber, paper, leather and wood color, was used. BO2 dye is toxic and carcinogenic in nature. Thus it is considered worthwhile to see how dye BO2 could be degraded in aqueous medium by Fenton reagent. In this study, we report an easy, fast and economical method for the photo degradation of dye BO2 by Fenton reagent.



Molecular Formula C₁₂H₁₃ClN₄ and Molecular Weight 248.51

Fig.1: Structure of Basic orange 2

EXPERIMENTAL SECTION

Basic orange 2 (Krishna Chemicals, Ankleshwar), anhydrous FeCl₃ (SDFCL) and H₂O₂ (30%, SDFCL), were used in the present investigations. The dye solution of Basic Orange 2 was prepared in doubly distilled water. The photochemical degradation of BO2 was studied in the presence of Fe⁺³ ion, H₂O₂ and visible light. Stock solutions of Basic Orange 2 (0.1243 g, 1.0 × 10⁻³ M) and FeCl₃ (0.0860 g, 1.06 × 10⁻³ M) were prepared in doubly distilled water (500 and 500 ml, respectively). For the photochemical degradation of BO2, 25 ml of diluted stock dye solution (2.5 × 10⁻⁵ M) and 2.0 ml of diluted stock FeCl₃ solution (2.65 × 10⁻⁴ M) was exposed to light from a 200-watt Tungsten lamp. A water filter was used to cut off thermal radiations. The pH of the solution was measured with a digital pH meter (Toshniwal, Ajmer) and adjusted within a range of 3.0-6.5 by the addition of previously standardized hydrochloric acid and sodium hydroxide solutions. A G-3 sintered glass crucible was used for filtration during the measurement of the optical density at different time intervals. The λ_{max} of the dye was determined using a Shimadzu UV 1700 Pharmspec spectrophotometer. The light intensity was measured using a Solarimeter (CEL, Kodaikanal).

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 photochemical degradation of Basic Orange 2 was observed at λ_{max} = 445 nm. The results for a typical run are given in Table 1 and graphically represented in Fig. 2.

The optical density of Basic Orange 2 solution decreases with an increase in the time of irradiation, indicating that Basic orange 2 is consumed on irradiation. The plot of 2 + log OD against time (Fig. 2) was linear, following pseudo-first order kinetics. The rate constant was determined using the expression $k = 2.303 \times \text{slope}$, with an optimum rate constant of $k = 4.606 \times 10^{-4} \text{ sec}^{-1}$.

Table 1

Time (min.)	2 + log O.D.
0.0	1.51
5.0	1.45
10.0	1.39
15.0	1.33
20.0	1.27
25.0	1.21
30.0	1.15

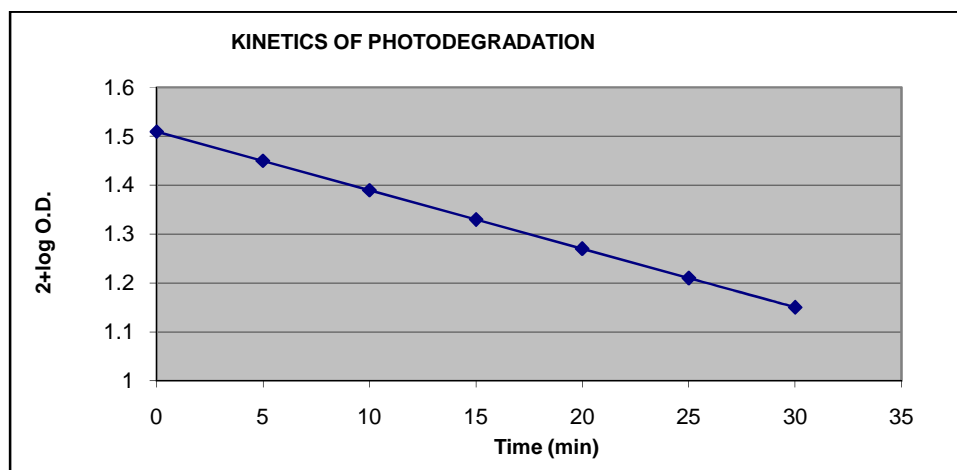


Fig.2: Typical photochemical degradation of Basic orange 2 observed at $\lambda_{\max} = 445$ nm under the optimized conditions of [Basic Orange 2] = 2.5×10^{-5} M, $\text{H}_2\text{O}_2 = 2.0$ mL, $[\text{Fe}^{+3}] = 2.65 \times 10^{-4}$ M, light intensity = 80.0 mW cm^{-2} and pH = 5.0.

Effect of variation in pH

The effect of pH on the rate of photocatalytic bleaching of dye was observed. The photodegradation was performed at different pH values from 3.0 to 6.5. The result of Fig-3 reveals that the rates of photobleaching of dye basic Orange 2 increases with an increase in pH up to 5.0, after which it decreases with increasing pH. At pH >5.0, Fe^{+3} decomposes H_2O_2 into water and oxygen, instead of forming hydroxyl radical which is the reactive chemical species for the photobleaching process. Thus, all subsequent experiments were carried out at pH 5.0.

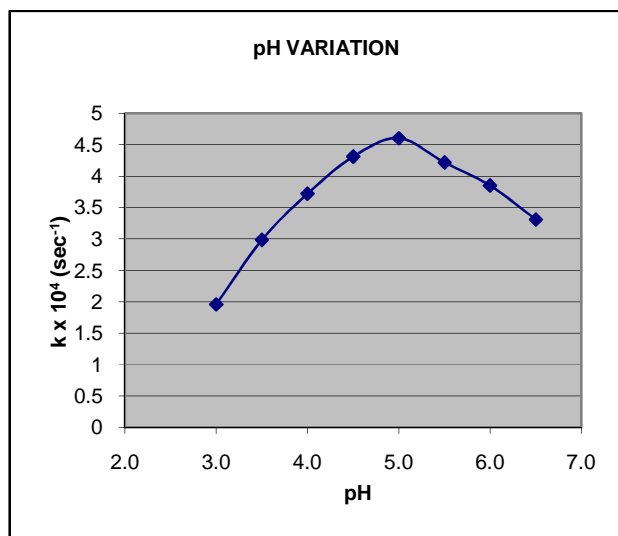


Fig.3: Effect of pH on the photochemical degradation of Basic orange 2 observed at $\lambda_{\max} = 445$ nm under the optimized conditions of [Basic Orange 2] = 2.5×10^{-5} M, $\text{H}_2\text{O}_2 = 2.0$ mL, $[\text{Fe}^{+3}] = 2.65 \times 10^{-4}$ M, light intensity = 80.0 mW cm^{-2} .

Effect of Dye (Basic Orange 2) concentration

The effect of the dye concentration on the degradation of Basic Orange 2 was studied at different concentrations varying from 1.0×10^{-5} M to 4.5×10^{-5} M keeping all other factors identical. The result (Fig- 4) reveals that the rate of photobleaching of dye decreases with the increase in the concentration of dye. It can be explained on the basis of these data that as the concentration of the dye is increased, the dye itself may act as a filter for the incident light, preventing sufficient intensity of light from reaching the dye molecules in the solution. Hence the rate photobleaching of dye decreases.

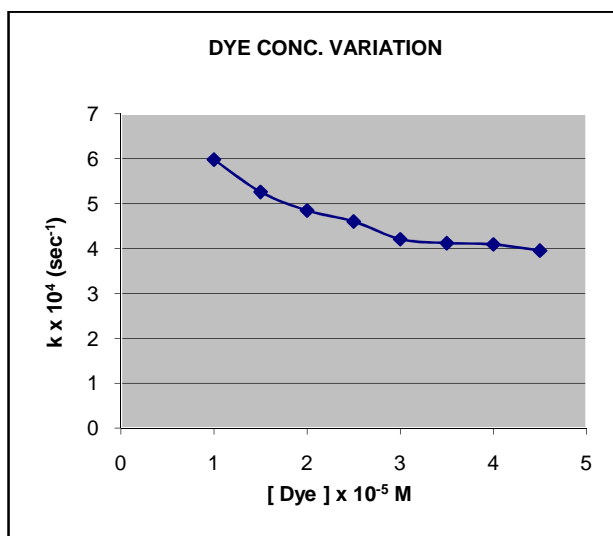


Fig. 4: Effect of dye concentration on the photochemical degradation of Basic orange 2 observed at $\lambda_{\text{max}} = 445 \text{ nm}$ under the optimized conditions of $\text{pH} = 5.0$, $\text{H}_2\text{O}_2 = 2.0 \text{ ml}$, $[\text{Fe}^{+3}] = 2.65 \times 10^{-4} \text{ M}$, light intensity = 80.0 mW cm^{-2} .

Effect of Ferric Ion concentration

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.5 reveals that the rate of photobleaching of dye increases with the increase in the concentration of Fe^{+3} ions up to $2.65 \times 10^{-4} \text{ M}$. The increase in Fe^{+3} ions in the reaction mixture are accompanied by enhanced generation of $\cdot\text{OH}$ radicals, consequently increasing the rate of photodegradation. After the optimal Fe^{+3} additions, the higher dose of Fe^{+3} resulted in a brown turbidity that causes the recombination of $\cdot\text{OH}$ radicals and Fe^{+3} reacts with $\cdot\text{OH}$ as a scavenger. Therefore, on further increase, the rate becomes almost constant.

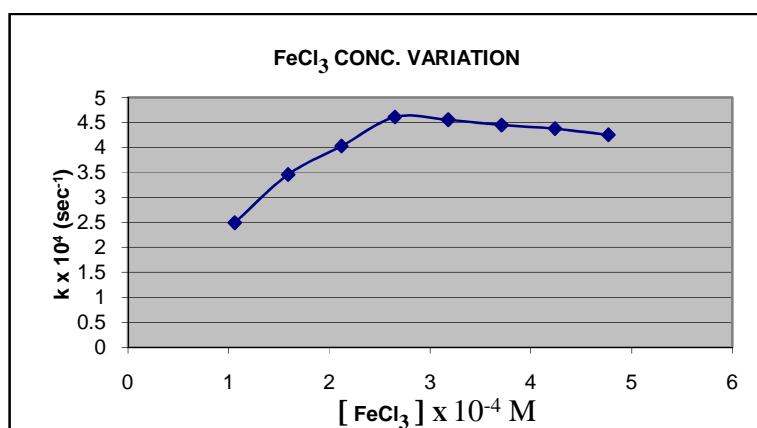


Fig.5: Effect of Fe^{+3} ion concentration on the photochemical degradation of Basic orange 2 observed at $\lambda_{\text{max}} = 445 \text{ nm}$ under the optimized conditions of $\text{pH} = 5.0$, $\text{H}_2\text{O}_2 = 2.0 \text{ ml}$, $[\text{Basic Orange 2}] = 2.5 \times 10^{-5} \text{ M}$, light intensity = 80.0 mW cm^{-2} .

Effect of H_2O_2 concentration

Keeping all other factors constant, the concentration of H_2O_2 was changed and its effect on the rate of photobleaching was studied. The result reported in Fig.6 reveals that the rate of photobleaching of dye increases with the increase the amount of H_2O_2 upto 2.0 mL . Further increase in H_2O_2 has negligible effect as H_2O_2 acts as a scavenger of $\cdot\text{OH}$ radicals to produce per hydroxyl radical ($\cdot\text{O}_2\text{H}$) which has much lower oxidation capacities than $\cdot\text{OH}$ radicals.

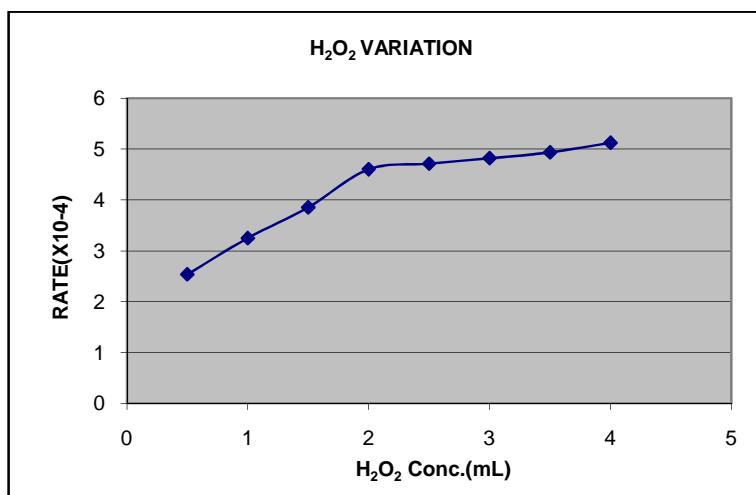


Fig.6: Effect of H₂O₂ concentration on the photochemical degradation of Basic orange 2 observed at $\lambda_{\text{max}} = 445 \text{ nm}$ under the optimized conditions of pH = 5.0, $[\text{Fe}^{3+}] = 2.65 \times 10^{-4} \text{ M}$, $[\text{Basic Orange 2}] = 2.5 \times 10^{-5} \text{ M}$, light intensity = 80.0 mW cm^{-2}

Effect of Light Intensity

A linear relationship was observed between the rate constant and light intensity (Fig-7), which indicates that a decrease in the light intensity decreases the rate of reaction. This may be attributed to the increased number of photons reacting with Fe^{3+} ions and, as a result, there is an increase in the number of hydroxyl radicals and a corresponding increase in the rate of reaction.

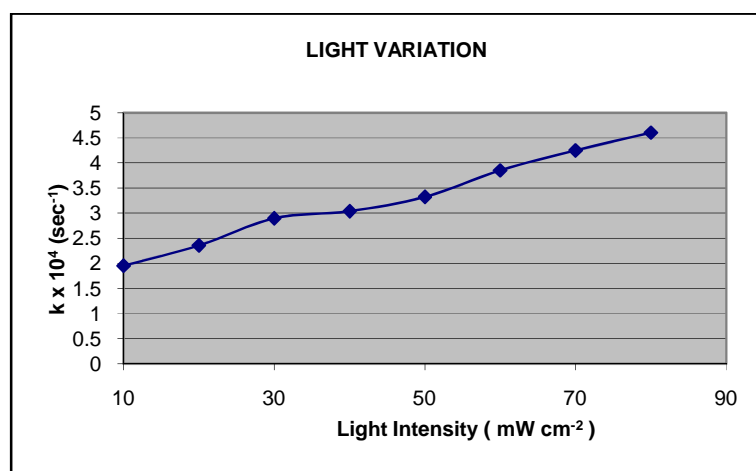
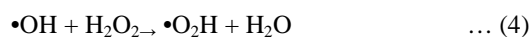
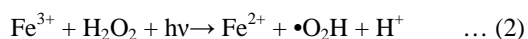
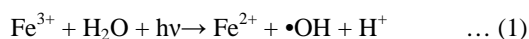
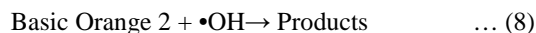
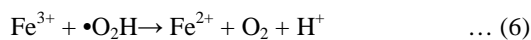


Fig.7: Effect of light intensity on the photochemical degradation of Basic orange 2 observed at $\lambda_{\text{max}} = 445 \text{ nm}$ under the optimized conditions of $[\text{Basic Orange 2}] = 2.5 \times 10^{-5} \text{ M}$, $\text{H}_2\text{O}_2 = 2.0 \text{ mL}$, $[\text{Fe}^{3+}] = 2.65 \times 10^{-4} \text{ M}$, and pH = 5.0

MECHANISM

On the basis of experimental observations, which corroborate the existing literature, a tentative mechanism has been proposed for photodegradation of Basic Orange 2 with the photo-Fenton reagent.

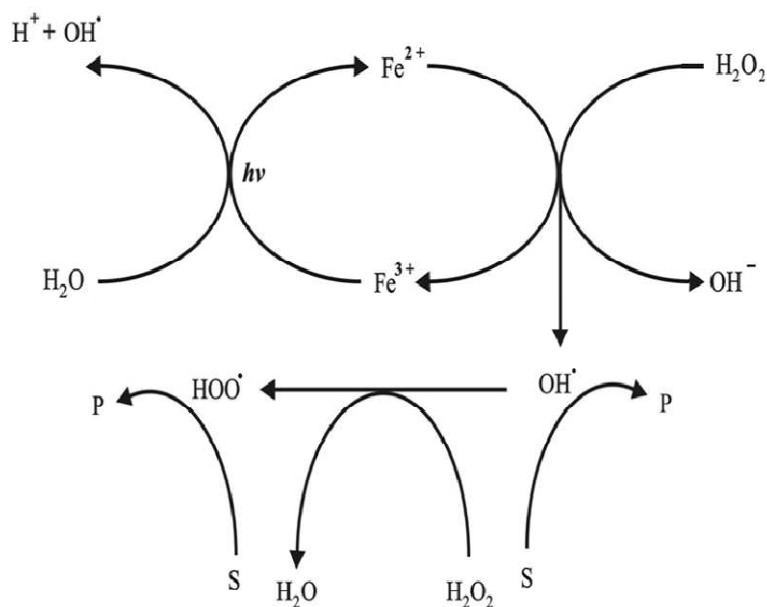




The aqueous solution of ferric ions on exposure to light dissociates water into a proton and $\bullet\text{OH}$ radical and ferric ions are reduced to ferrous ions (Equation 1). These ferrous ions will decompose H_2O_2 into a hydroxyl ion and a hydroxyl radical, while ferrous ions undergo oxidation to ferric ions (Equation 3). Ferric ions generate $\bullet\text{OOH}$ radicals due to dissociation of H_2O_2 in the presence of light (Equation 2). The incorporation of $\bullet\text{OH}$ with H_2O_2 also produces $\bullet\text{OOH}$ radicals (Equation 4). Ferrous ions will undergo oxidation to ferric ions by the addition of $\bullet\text{OH}$ radicals, while ferric ions are reduced to ferrous ions by the incorporation of $\bullet\text{OOH}$ radicals, producing H^+ ions (Equation 5, 6). $\bullet\text{OOH}$ radicals are highly unstable in water and undergo facile disproportionation rather than reacting slowly with the dye molecules. The participation of the hydroxyl radical as an active oxidizing species was confirmed using the hydroxyl radical scavenger 2-propanol, which drastically reduced rate of photodegradation (data not shown).

The two possibilities for the consumption of $\bullet\text{OH}$ radicals include, firstly, the dissociation of H_2O_2 into $\bullet\text{OOH}$ and water or combining to form H_2O_2 molecules (Equation 7), and, secondly, a reaction with Basic Orange 2 to give the colorless degradation products (Equation 8).

The main advantage of using the photo-Fenton reagent is the cyclic regeneration of the consumed Fe^{2+} ions on illumination. The amount of ferrous salt required in photo-Fenton process is small as compared to that when using the Fenton reagent, where ferrous ions must be added; otherwise the reaction will stop after conversion of ferrous ions to ferric ions. This is an important advantage of the photo-Fenton process for industrial use, as further separation of the ferric ions is not required after wastewater treatment. The whole process is pictured (Fig.8)



Where S = Dye and P = End Products

Fig.8: A Schematic representation of Photo-Fenton Chemistry

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