



Photodegradation of direct yellow-12 using UV/H₂O₂/Fe²⁺

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Abstract

A detailed investigation of photodegradation of direct yellow-12 (DY12) using UV/H₂O₂/Fe²⁺ has been carried out in a photochemical reactor. Experiments studied degradation as a function of concentration, decolorization and reduction in chemical oxygen demand (COD). The effect of operating parameters, such as UV, pH, amount of Fenton's reagent (H₂O₂ and FeSO₄), and amount of DY12 dye has also been determined. It has been observed that simultaneous utilization of UV irradiation with Fenton's reagent increases the degradation rate of DY12 dye. The dye quickly loses its color and there is an appreciable decrease in COD value, indicating that the dissolved organic have been oxidized. The kinetics of degradation of the dye in dilute aqueous solutions follows pseudo-first order kinetics. Final products detected at the end of the reaction include NO₃⁻, NO₂⁻, N₂O, NO₂, SO₂, CO₂ and CO. Results indicate that dye degradation is dependent upon pH, UV-intensity, concentration of Fenton's reagent and dye. Acidic pH has been found to be more suitable in comparison to neutral and alkaline. The optimum concentration of Fenton's reagent (H₂O₂/Fe²⁺) was found as 1500/500 mg l⁻¹ for 50 mg l⁻¹ DY12 dye in water at pH 4. The results indicate that the treatment of DY12 dye wastewater with UV/Fe²⁺/H₂O₂ system is efficient.

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Keywords: Direct yellow-12 (DY12); Fenton's reagent; Dye degradation; COD; Kinetics

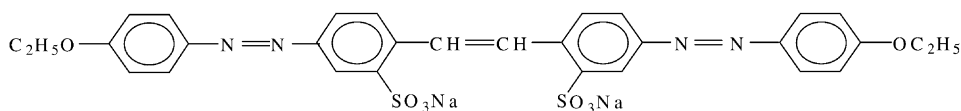
1. Introduction

Dyes are widely used for coloring in textile industries. Synthetic textile dyes and other industrial dyestuffs constitute a major class of chemicals. Significant losses occur during the manufacture and processing of dyes and these lost chemicals are discharged in the effluent.

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These effluents have adverse effect on the environment if not treated properly. Among the overall production of dyes, azo dyes constitute a significant portion and are very toxic to the surrounding environment if released untreated.

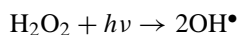
Direct yellow-12 (DY12; molecular weight 680, C.I. No. 24897) is an azo dye and widely used in textile, paper and leather industries. This dye is also extensively used in cosmetics, food additives, ink and paint. The structure of DY12 dye is shown below.



The effluent containing DY12 is yellow in color, toxic and has high biological oxygen demand (BOD). The dye's strong color causes considerable damage to the aquatic life. DY12 does not allow sunlight to pass through and thereby affects the photosynthesis of aquatic plants. Modern dyes are resistant to conventional biological treatment but these azo dyes are reduced to colorless primary amines by this treatment. These primary amines are even more toxic than the original dye [1]. Proper treatment of the dye plant effluent is thus, a matter of concern before discharge. The current protocols so followed for effluent treatment are mainly based on chemical and biological methods. Activated charcoal adsorption, reverse osmosis and coagulation treatment has also been utilized for this purpose. However, the efficiency of these methods has not been satisfactory in treating every dye effluent, due to the wide varieties of chemicals in the wastewater [2].

Chemical oxidation has been used for a broad spectrum of organic compounds such as mono-, di- and pentachlorophenol [3], acid red 44 [4], methylene blue and wastewater [5]. Hydrogen peroxide (oxidation potential 1.78 V) and ozone (oxidation potential 2.07 V) are chiefly used as oxidant [6].

The advanced oxidation process (AOP) was defined by Glaze et al. as the oxidation process, which generate hydroxyl radicals in sufficient quantity to affect water treatment [7,8]. AOP uses UV light in conjunction with oxidants such as H₂O₂, Fenton's reagent and ozone to achieve great performance. UV is used to split oxidant molecules, thereby producing highly reactive hydroxyl radicals [6,9]. This technique uses the oxidizing power of hydroxyl radicals (having the strongest oxidizing power after fluorine) to degrade organic hazardous effluents into CO₂ and H₂O [9]. The accepted mechanism for the photolysis of H₂O₂ in H₂O₂/UV system is:



These radicals may further react with organic substrate [6]. It has also been shown that oxidative catalytic system H₂O₂/Fe²⁺ system (Fenton's reagent) could be used for dye destruction and decolorization in industrial wastewater [5,10]. Fenton's reagent yielded a solution with powerful and extraordinary oxidizing capability [11]. Fenton's reagent along with UV-Vis radiation was reported to improve the degradation of various organic pollutants such as chlorophenol [12]. Fenton's reagent accelerated the oxidation rate by five to nine times the rate of UV/H₂O₂ process [13]. The reaction time needed for UV/Fenton's treatment was less when compared to the UV/H₂O₂, O₃/H₂O₂ reaction in removal of COD

from pharmaceutical wastewater [14]. It was reported, Fenton system is efficient in photochemical degradation of industrial effluent [15].

In present work, we carried out extensive observations on photodegradation of direct yellow-12 dye by using UV/Fenton's reagent (UV/H₂O₂/Fe²⁺).

2. Materials and methods

Direct yellow-12 was obtained from the Madhavdas & Manilal Co., Ahmedabad, India. Its purity was 98%. DY12 dye solution was prepared in double distilled MilliQ water (Millipore distillation unit). Other reagents namely, hydrogen peroxide (30% (w/v)) and FeSO₄·7H₂O (10% (w/v)) were of A.R. grade (procured from Merck, India). Both the reagents were used in a 1:1 ratio (v/v) for the experiments.

Studies were conducted in an annular type batch photoreactor of 1000 ml capacity. The photoreactor consisted of a reactor vessel, immersion well and UV lamp assembly (Fig. 1). In this arrangement lamp was housed in an immersion tube, which in turn was immersed in the liquid contained in the reactor vessel to be irradiated with UV radiation. This arrangement allowed the entire UV output to pass into the liquid, resulting in high radiation efficiency. Unabsorbed UV radiation by the liquid is safely absorbed by glass walls of the vessel, thus protecting the person from harmful effects of short-wave UV. The whole reactor assembly was covered with a photochemical safety hood, which was had a highly polished anodized aluminum surface. The immersion well of the reactor was double walled. It was constructed using high purity transparent quartz (transmission of 98% for UV light at 254 nm of peak intensity). It held an 8 W low-pressure mercury vapor lamp. The immersion well had an inlet and outlet arm to enable water circulation for temperature controls. The immersion well was inside the reactor with a standard joint at top so that the assembly was airtight.

The reactor vessel was made of borosilicate glass with a total effective reactor volume of 1000 ml after inserting the immersion well inside. The reactor vessel had a sintered disc at the bottom (Borosil G-2 grade, diameter 20–30 mm) for bubbling air into it (to ensure proper mixing of constituents), gas outlet at the top, sample port with stopcock at the side to enable gas monitoring, temperature measurement port and a teflon-coated thermocouple with temperature indicator.

The rate of DY12 dye degradation was quantified by measuring dye concentration as a function of time using UV-Vis spectrophotometer (GBC UV, Model Cintra 10). DY12 dye concentration was determined using an UV-Vis spectrophotometer at 394.9 nm and a calibration diagram. With this method the decrease in the absorbance was directly proportional to the dye concentration reduction. The chemical oxygen demand (COD) was measured as a function of time using standard acidic dichromate method [16]. The change in pH was monitored using a pH-meter.

2.1. Effect of oxidant concentration

In order to observe the effect of oxidant concentration on the rate of degradation of DY12, experiment were carried out by varying the dose of H₂O₂/Fe²⁺ from 450/150 to 1950/650 mg l⁻¹. The temperature of the process was maintained at 25 °C by water circulation. The effect of Fenton's reagent dose on the reduction in COD was also observed [18].

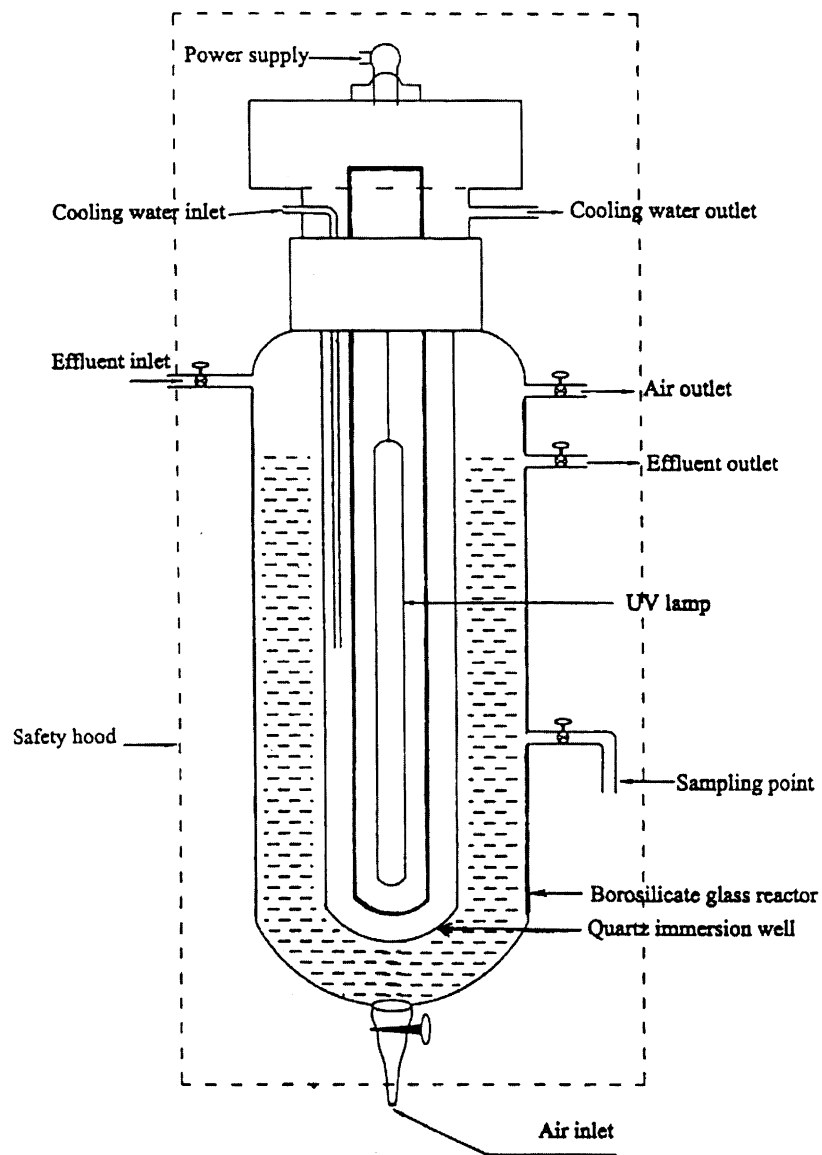


Fig. 1. Immersion well photochemical reactor.

2.2. Effect of pH

In order to optimize the pH, experiments were carried out under acidic, neutral and alkaline pH at 4.0, 7.0 and 10.5, respectively.

2.3. Kinetic study

Kinetic studies at varying Fenton's reagent dose were carried out to determine the order that the reaction follows during degradation.

2.4. Final products

Some gases and ionic species may result during DY12 degradation. Gases such as CO₂, CO, SO₂, N₂O and NO₂ can be detected by an ambient air quality Monitor (Model Sapphire 100 from Foxboro). SO₂ and NO₂ can also be checked by Indian Standard Procedure [17]. The ionic species content such as SO₄²⁻, NO₂⁻ and NO₃⁻ after degradation may be determined by using DR/2000 Hach spectrophotometer colorimetrically. This instrument is a micro-processor-controlled, single-beam instrument suitable for colorimetric measurement. The H₂O₂ can be measured by the reaction with titanium(IV) salt in acid solution [18].

2.5. Procedure

A synthetic dye solution 1000 ml of known concentration was mixed with Fenton's reagent and irradiated with an 8 W Hg vapor lamp. Air was circulated at a constant flow rate of 1 l min⁻¹ for complete mixing of constituents at constant temperature 25 °C.

3. Results and discussion

The control experiments were carried out at initial dye concentration (C_0) of 7.35×10^{-5} M (50 mg l⁻¹) pH 7.0 and concentration of H₂O₂/Fe²⁺ 1500/500 mg l⁻¹.

Initially we optimized the UV-intensity and found that the time required for DY12 degradation using an 8 W low-pressure Hg lamp was less than that using an 8 W medium pressure Hg lamp. The results indicate that the rate of dye degradation proceeds faster in combination with UV light and Fenton's reagent, rather than in absence of either one of the constituents. The rate of dye degradation was monitored by UV-Vis spectral changes at 394.9 nm (Fig. 2). The peak is due to n-π* transition of azo group. There is rapid decrease of absorption DY12 dye due to disappearance of the n-π* transition of azo group in DY12 dye, implying that these groups are affected by the photo-oxidative process. Photo-enhancement in this reaction is mainly due to reaction involving H₂O₂ and Fe salt, because the Fe²⁺ catalyzed the photochemical oxidation of DY12 dye by H₂O₂ [6]. Photolysis of H₂O₂/Fe²⁺ produces hydroxyl radicals (Eq. (1)) [9], which have a high oxidizing power. These hydroxyl radicals can not be produced in the dye/UV system alone. The OH• free radicals attack the dye molecules and undergo a very rapid and effective substitution reaction to form oxygenated intermediates. Acceleration in concentration reduction is a consequence of photoreduction of (Fe-OH)²⁺ to Fe²⁺ with greater production of reactive hydroxyl radicals [19]. However, the total rate of H₂O₂ decomposition is smaller in the presence of Fe³⁺ as compared to Fe²⁺ [20]. Hence, Fe²⁺ is a more efficient oxidant.

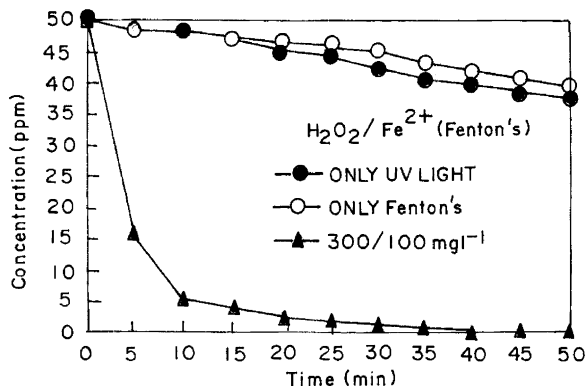


Fig. 2. Control experiments to show the effect of various oxidants on photodegradation of DY12.

The reaction occurring in the process is as follows:



The effect of pH on the rate of dye degradation was monitored at three different pHs 4.0, 7.0 and 10.5. The pH was adjusted by adding concentrated H_2SO_4 and NaOH . Acidity and alkalinity were monitored to keep their concentration constant at desired values throughout the duration of experiments as it has been observed (Fig. 6) that effective dye degradation is strongly dependent upon the pH of the solution.

The rate of DY12 dye degradation is faster in acidic pH than in neutral or alkaline system, because under acidic pH, OH^\bullet is the predominant reactive oxidant and under alkaline

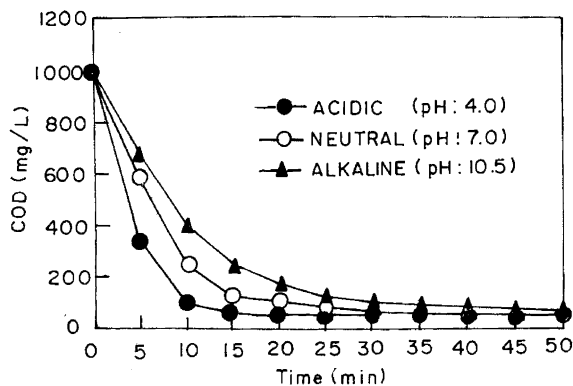


Fig. 3. Effect of pH on COD reduction of DY12 using Fenton's reagent.

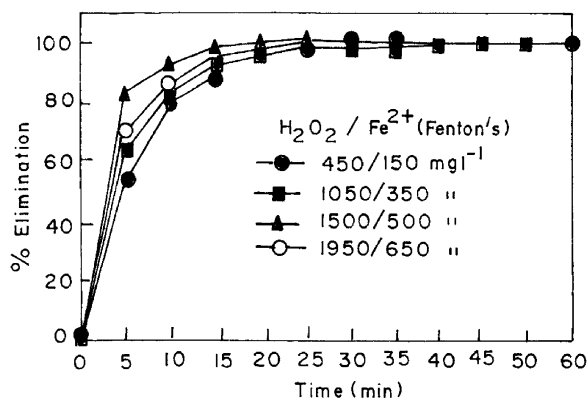
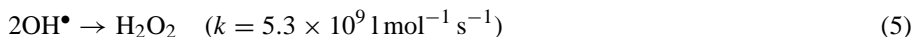
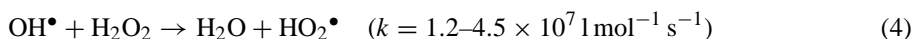


Fig. 4. Effect of oxidant dose on photo-oxidation of DY12 at pH: 4.0 and 50 mg l⁻¹ dye concentration.

pH, hydroperoxyl radicals are formed by reaction of hydroxyl radicals with H₂O₂. These hydroperoxyl radicals do not have as high oxidizing power as OH[•] [9]. Another reason for better results at lower pH is solubility of iron increased at lower pH.

A series of experiments was carried out over a wide range of H₂O₂/Fe²⁺ concentrations (450/150–1950/650 mg l⁻¹) at constant dye concentration of 7.35 × 10⁻⁵ M (50 mg l⁻¹) and at constant pH 4.0. These experiments are aided us in determining of rate kinetics. The rate and degree of DY12 degradation with time, is greatest at [H₂O₂/Fe²⁺] = 1500/500 mg l⁻¹ (Fig. 4). A further increase in the oxidant concentration slows the degradation process because when the H₂O₂ concentration is less, more OH[•] radicals are available to attack the dye molecule and the rate of the reaction is faster. But with increase in the concentration of oxidant, the following competing reaction increase at [H₂O₂] ≫ [Fe²⁺]:

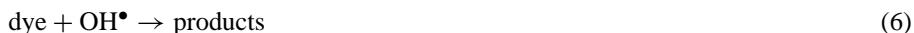


Due to above reactions H₂O₂ acts as a scavenger of highly reactive OH[•] free radicals to form hydroperoxyl radicals [21]. These radicals are much less reactive and do not contribute to oxidative degradation of organic substance [6].

It has been found that with the increase in dye concentration, the time required for degradation also increases. At low concentration of substrate, the percentage conversion is higher compared that at higher concentration [22,21] whereas the rate of degradation increases with an increase in the initial concentration of substrate.

3.1. Kinetic studies

The main reaction of dye degradation is shown further:



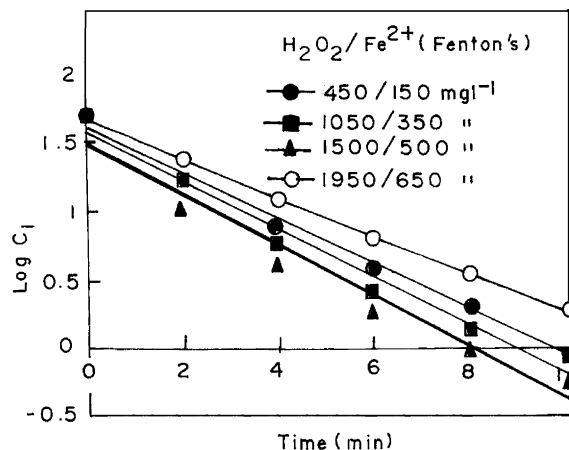


Fig. 5. Kinetic studies to show that the reaction follows pseudo-first order reaction at pH: 4.0 and 50 mg l⁻¹ dye concentration.

It is assumed that the rate of dye oxidation is first order but the hydroxyl radical concentration is greater than the dye concentration. Under such conditions the reaction may be considered as a pseudo-first order. The rate equation can be expressed as:

$$\log C_t = \log C_0 - \left(\frac{k}{2.303} \right) t \quad (7)$$

where C_0 is the initial dye concentration, C_t the concentration of dye at time ' t ', and k the overall rate constant, time⁻¹.

Fig. 5 shows the plot of $\log C_t$ versus t . Having the straight-line behavior this plot confirms the pseudo-first order reaction kinetics. The average overall rate constant (k) was 0.33 min⁻¹ and the average half value period ($t_{1/2}$) was 2.1 min (Table 1).

COD was monitored by using standard method [16,23]. COD measurements for experiments run at varying oxidant doses and pH. From COD analysis (Fig. 3), it was observed that under acidic conditions (pH 4.0) the percent reduction of DY12 was maximum reaching 95% at a concentration of 1500/500 mg l⁻¹ (H₂O₂/Fe²⁺). COD reductions in a range of 91–95% were observed indicating that the organic were oxidized. Lin and

Table 1
Effect of half life and H₂O₂ concentration on photo-oxidation of DY12 dye using Fenton's reagent^a

S. no.	Quantity of oxidant (mg l ⁻¹) (H ₂ O ₂ /Fe ²⁺)	k (min ⁻¹)	$t_{1/2}$	H ₂ O ₂ reduction (%)
1	450/150	0.33	2.10	70.2
2	1050/350	0.35	1.98	82.7
3	1500/500	0.37	1.87	95.0
4	1950/650	0.28	2.40	86.8

^a The conditions are pH 4.0, dye concentration is 50 mg l⁻¹.

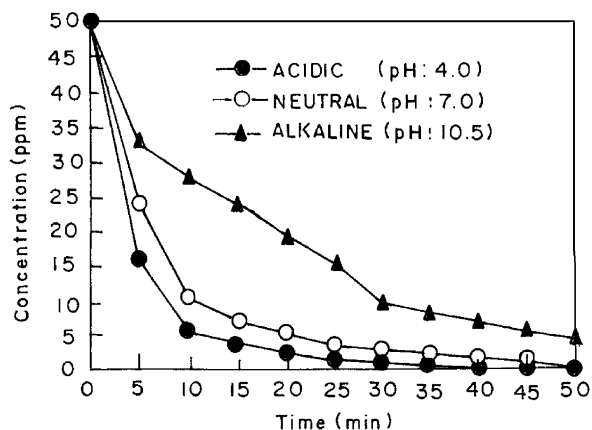


Fig. 6. Effect of pH on photo-oxidation of DY12 using Fenton's reagent and UV light.

Peng investigated the treatment of textile wastewater using Fenton's reagent at various pH values [24].

During degradation of DY12 dye, some traces of gas (mainly SO_2 , NO_2 and CO_2) were detected by the ambient air quality monitor. These byproducts may be due to the nitrogen, sulfur and organic carbon content of the DY12 dye. Some ionic species (NO_3^- , SO_4^{2-} and a negligible quantity of NO_2^-) were also detected.

Studies were carried out on actual textile industry wastewater reveal that optimum dose of Fenton's reagent of $1500/500 \text{ mg l}^{-1}$ ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) is effective in decolorization of the wastewater in 35 min (Fig. 7) under optimal condition. The initial COD value of waste dye was 1100 mg l^{-1} . Its pH was adjusted to 4.0. A COD reduction of 98% was achieved (Fig. 8) within 35 min. This result indicates that this technique is efficient in treatment of wastewater.

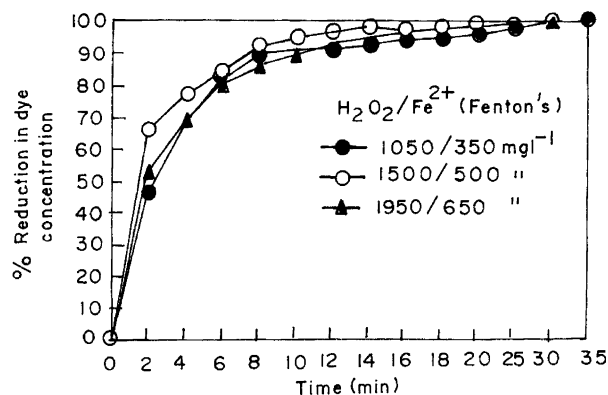


Fig. 7. Percent reduction in dye wastewater concentration using $(1500/500 \text{ mg l}^{-1})$ ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) of Fenton's reagent at pH: 3.9.

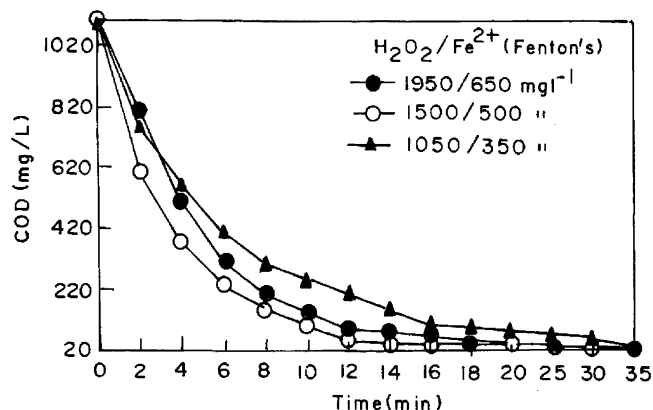


Fig. 8. Reduction in COD of dye wastewater using 1500/500 mg l⁻¹ of Fenton's reagent at pH: 3.9.

4. Conclusions

- Decolorization and degradation of DY12 dye is greatly enhanced by Fenton's reagent and UV light.
- Under all conditions the initial rate of conversion was extremely high as compared to the rate later in the reaction. The conversion attained within the initial 8 min accounted for more than 90% of conversion.
- Degradation is generally affected by pH and occurs faster at pH 4.0. The DY12 dye degradation is dependent on the initial oxidant concentration and exhibits a maximum at 1500/500 mg l⁻¹ (H₂O₂/Fe²⁺).
- Kinetic measurements show that the reaction follows pseudo-first order kinetics with a rate constant found of 0.33 min⁻¹.
- This technology can be applied for effective treatment of colored wastewater in a short period of time.
- The system would be effective in dye effluent treatment.

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