Optimization of Different Variables Used in Fenton Reagent Process for Removal of Direct Red 80 Dye

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***Abstract*—Increasing industrialization has resulted in a discharge of a lot of waste in to the environment. An enormous amount of dyes are used daily in many industries and all the waste generated is being disposed and is continuously polluting the environment. This waste should be treated before discharging into the water bodies. For the removal of these dyes from water, Fenton process can be used. Direct Red 80 dye was used to make aqueous solution having a concentration of 150 mg/L at different pH values & time intervals, and treating it with various concentrations of Hydrogen Peroxide & Ferrous Sulphate. The colour removal was monitored by a spectrophotometer & results were plotted to optimize different independent variables. The experimental study revealed 99.77% colour removal. The optimization results gave the best values as pH = 3.5, H202 dose = 330 mg/l and FeSO4 dose = 30 mg/l at 30 minutes of reaction time.**

***Keywords*— Direct Red 80, Fenton Reagent, Textile waste**

I. Introduction

A wide variety of dyes are used mainly in paper manufacturing and textile dying industries. Many natural waterways are contaminated and polluted because of the disposal of huge amount of dye waste from these industries. It is very important to remove these dyes from the water bodies with concerned to the hazardous effects they have on the environment (Su et al., 2011). The major industries which are responsible for the dye waste generation are textile, cosmetic, printing, drug and food processing which contain color compounds which are responsible for serious environmental problems (Karatas, et al., 2012).

Developing countries have textile industries as one of the major industries. The waste which is generated from these industries have a very high concentration of organic matter and dyes which impart colour to the water making it aesthetically unfit for use (Özdemir et al., 2011). Environment, aquatic life and human health are adversely affected by the waste water generated from these industries as they contain hazardous mixtures of organic and inorganic pollutants and also many heavy metals (Soon and Hameed, 2011). The colour of waste water depends on the colour of dye used in the industries nearby. The wastewater generated from textile industries can have an adverse effect on the living organisms also can affect the ecosystem and can hinder the assimilative capacity of environment (Yavuz et al., 2009). For the removal of different varieties of textile dyes and providing non-toxic and stable end-products, a lot of usage of different advanced-oxidation processes and their combinations has been reported over the last few years (Vajnhandl & Marechal, 2007).

In the experimental study, Direct Red 80 Dye was used for the preparation of aqueous solution. The Empirical formula of the dye is (Hill Notation) C45H26N10Na6O21S6 The molecular weight of dye was found out to be 1373.07. The structure of dye is shown in Fig 1.

Such type of Direct dyes when used and discharged into the environment causes huge amount of harm to living organisms by polluting water. Therefore the removal of these dyes is very important before discharging them. For the removal of these dyes three types of methods are used are Physical, Chemical & Biological.

Physical Techniques: In this method the dye present in the waste water are separated by physical processes like Adsorption, Precipitation, Ion exchange, Membrane separation, Coagulation/flocculation.

Chemical techniques: The dye molecule is broken into simpler fragments and the chromopore responsible for imparting colour is destroyed. These processes are like Ozonolysis, Chemical oxidation/reduction

Biological techniques: In this method activated sludge is used for the absorption of dyes and hence this absorption results in discoloration or the dye molecules are biologically degraded. Eg. Aerobic/anaerobic digestion.

Advanced oxidation processes (AOP's) are used widely in the removal of toxic organic and inorganic wastes in water and wastewater. They are based on the generation of highly reactive hydroxyl radicals which are exceptionally strong oxidizing agents [12]. For the removal of dyes the most popular methods used is oxidation with H_2O_2 which is stability in pure form and hence needs to be activated for the oxidation to take place. Hydrogen peroxide can be activated by different methods and it decomposes into $OH^\bullet$ radical and OH^- ion [13].

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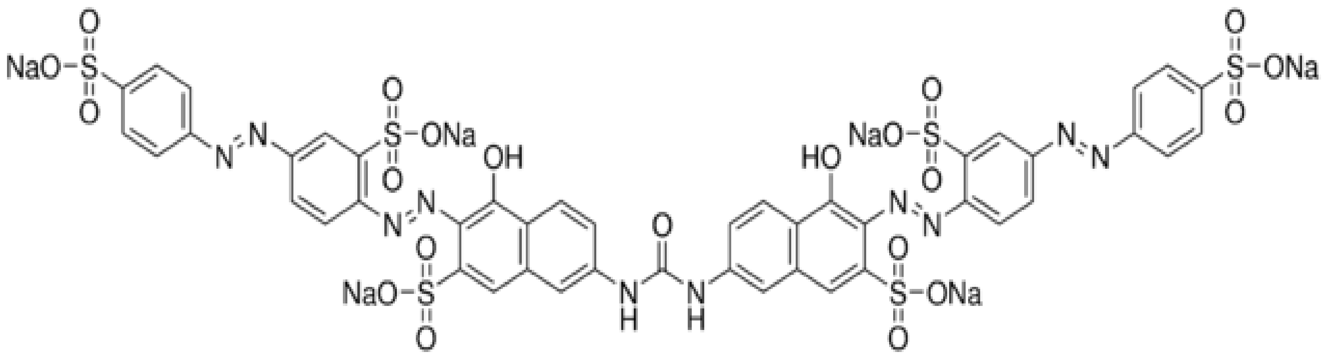

Fig. 1 Structure of Direct Red 80 Dye

A well-known Advanced Oxidation Process is Fenton's reagent in which ferrous ions Fe^{2+} and ferric ions Fe^{3+} are used as catalyst for the decomposition of H_2O_2 under acidic pH ranging from 2 to 5. This reaction produces free radicals such as $OH^{\bullet}$ & OH^{-} that almost non-selectively attack organic as well as inorganic pollutants [5]. There are various advanced oxidation processes present and out of them the most easy-to-handle process is Fenton's reaction which has been proved to be most effective when colour removal and operating cost are taken into consideration for the treatment of industrial wastewater. The Fenton's reagent is found to target water soluble, nucleophilic and aromatic pollutants [6].

The classification of Fenton process can be done as shown in the Figure 2

Fenton process is based on an electron transfer between hydrogen peroxide (H_2O_2) and a homogeneous metal catalyst (Fe^{2+}).

In Fenton process, hydrogen peroxide is catalyzed by ferrous ion to produce hydroxyl radicals. It is shown in Eq. (1)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad \text{........ Eq. (1)}$$

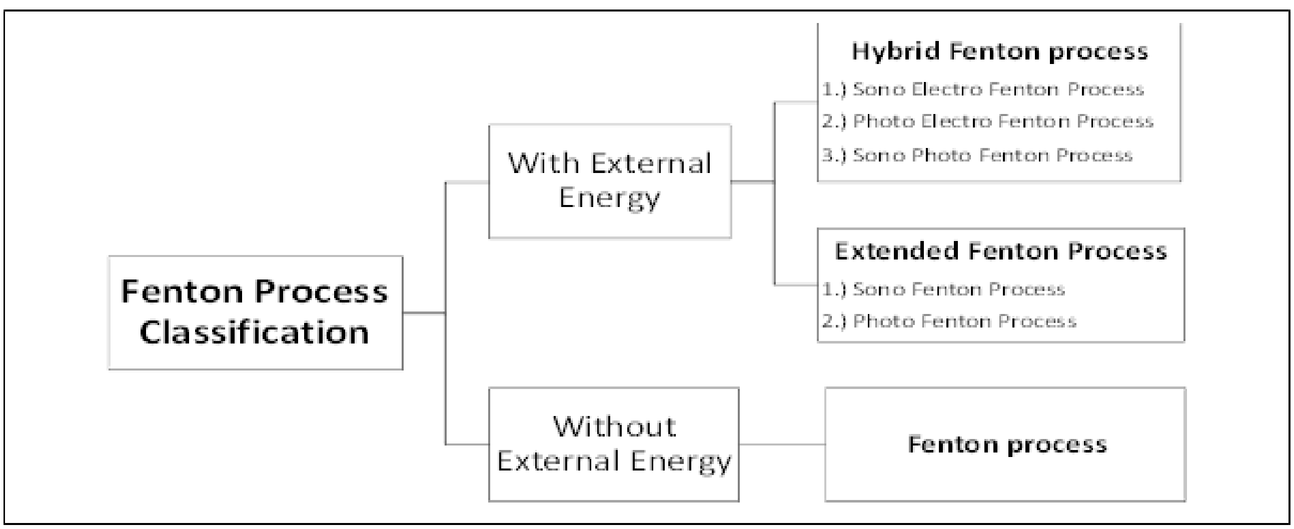

Fig. 2 Classification of Fenton's Process

The hydroxyl radical thus produced will react with the dye to produce dye radical and water molecule. Dye molecule is denoted by RH. It is shown in Eq. (2)

$$OH^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \quad \text{........ Eq. (2)}$$

The dye radical then reacts with Ferric ion to produce dye radical and water molecule. It is shown in Eq. (3)

$$R^{\bullet} + Fe^{3+} \rightarrow R^{+} + H_2O \quad \text{....... Eq. (3)}$$

This reaction is propagated by ferrous ion regeneration, which is mainly due to the reduction of the produced ferric species with hydrogen peroxide (Eq. (4)) *(Basturk & Karatas, 2014).*

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H_2O + OH^{\bullet} \quad \text{........ Eq. (4)}$$

In this study we will use Fenton process to remove dye form the aqueous solution prepared and then analyse the variation in the colour removal by the variation of concentration of different components of Fenton reagent.

II. MATERIAL AND METHODOLOGY

Direct Red D80 dye was purchased from a local vendor of Surat, Gujarat, India. The Ferrous Sulphate Heptahydrate ($FeSO_4 \cdot H_2O$) and hydrogen peroxide (H_2O_2) were purchased from FINAR - AR grade. Electronic precision balance used for measuring dosage of $FeSO_4 \cdot H_2O$ and Direct Red 80 dye. pH meter and UV Spectrophotometer which were used in the analysis were of HATCH.

An aqueous solution of dye was prepared by mixing distilled water and Direct Red 80 dye. The concentration of dye was 150 mg/l and 5-6 Liter aqueous solution was prepared at a time. The dye solution was of basic nature so to carry out the Fenton process the pH was maintained at 3.5. Out of the total solution prepared, 4 samples containing 500 ml of aqueous solution were taken in different jars. Then their pH was changed from basic to acidic by the addition of H_2SO_4 and mixing the solution with the help of magnetic stirrer. The Fenton reagent needs acidic medium for the oxidation to take place so the experiments were carried out on solutions havings pH 3.5. The pH of the solutions was maintained using senSION$^+$ HATCH pH meter. After this, Ferrous Sulphate Heptahydrate (($FeSO_4 \cdot H_2O$) and hydrogen peroxide solution were a is added simultaneously according to dosage (for ferrous sulphate heptahydrate 20mg/l, 30mg/l, 40mg/l and for hydrogen peroxide 220mg/l, 330mg/l, 440mg/l) and take a sample of 50mg for testing the removal efficiency at every five minutes intervals, UV visible spectrophotometer (HATCH) gives the results of samples at 509 nm wavelength which is suitable of Direct Red D80 dye. This UV spectrometer is having 200nm to 700 nm range of wavelength. Thus, optimum dosage $FeSO_4$ =mg/l , H_2O_2 =330 mg/l at 30 minutes for 150 mg/l concentred aqueous solution) is found for highest color removal. The Colour removal is shown in Figure 3.

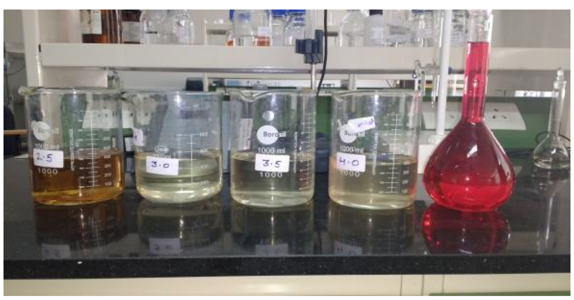

Fig. 3. Colour removal and original dye colour

III. RESULTS AND DISCUSSION

A. *Effect of Hydrogen Peroxide*

One of the major component of Fenton reagent is H_2O_2. It helps in the oxidation of the ferrous sulphate and also initiates the Fenton process reactions. $OH^\cdot$ (Hydroxyl Radical) is used as primary oxidant. It attacks the organic molecule present in the solution & takes hydrogen from the organic molecule or provides hydrogen to the double bond present. Hydroxyl ion makes new oxidized intermediates with lower molecular weight or carbon dioxide and water in case of complete mineralization. The Oxidation potential of hydroxyl ion is E0 = 2.8. The concentration of $H_2O_2$was varied along with the other parameters. The effect of the variation of H_2O_2 was also observed and plotted as shown in the figure 5. In the graph the percentage removal efficiency is plotted on the Y-axis and the Time is plotted on the X-axis. The curves represent the percentage color removal at pH 3.5 and different H_2O_2 concentrations. The concentrations of H_2O_2 taken for the experiment are 220 mg/l, 330 mg/l & 440 mg/l. From the graphs the results that can be incurred are that a dosage of 330 mg/l is found to be optimum for the dye removal. So form this we can conclude that and aqueous solution having 3.5 pH and 330 mg/l H_2O_2 concentration is found to be optimum dose and it gives an efficiency of 99.77 % color removal.

B. *Effect of Ferrous Sulphate*

Another major component of Fenton reagent is $FeSO_4$. In Fenton's process the ferric ions are converted to ferrous ions and again to ferric ions. Ferric salts can only be used in Fenton process as ferric ions are required to start the reaction. Simple Fe can also be used as it has low cost, more effectiveness, more organic molecule degradation capability. The corrosion of Fe produces Fe^{2+} ferric ions and thus initiates the Fenton's reaction. It helps in the formation of hydroxyl ion required in Fenton process. The concentration of $FeSO_4$ was varied. The effect produced by the variation of $FeSO_4$ was observed and plotted as shown in the figure 6. In the graph the removal efficiency percentage is plotted on the Y-axis whereas the Time is denoted on the X-axis. The curves show the colour removal percentage at pH 3.5, H_2O_2 = 330 mg/l and different $FeSO_4$ concentrations. The different concentrations of $FeSO_4$ taken for the experiment are 20 mg/l, 30 mg/l & 40 mg/l.

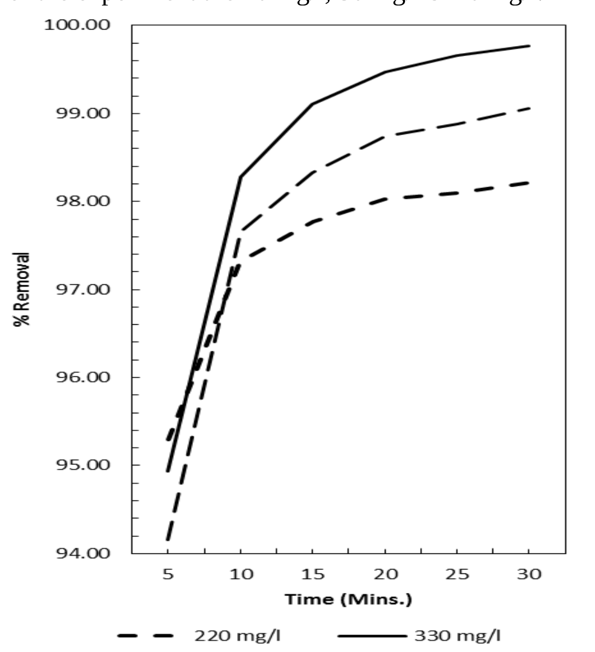

Fig. 5. Effect of different H_2O_2 dosage on colour removal efficiency with respect to time at 30 mg/l $FeSO_4$ and 3.5 pH

The results that were found out form the graph are that a dosage of 30 mg/l is found to be optimum for the dye removal.

So from this we can conclude that an aqueous solution having 3.5 pH, H_2O_2 concentration as 330 mg/l and $FeSO_4$ concentration as 30 mg/l is found to be optimum dose and it gives an efficiency of 99.77 % color removal.

IV. CONCLUSION

One of the major pollutants that threaten our environment are dyes. They are very harmful to the living organisms and also can destroy the environment if discharged directly in the ecosystem. One of the most powerful processes that is used for the removal of the dyes is Fenton process. Many processes have achieved total removal of dyes and thus prove very helpful in saving the environment. Catalyst concentration, pH, H2O2 concentration, dye concentration, and temperature are the components on which the processes used to remove dyes from the waste generated are dependent. The optimum dosage is found to be 30 mg/l for FeSO_4, 330 mg/l for H_2 O_2 at pH 3.5.Hence, Fenton processes is one of the best methods for dye degradation.

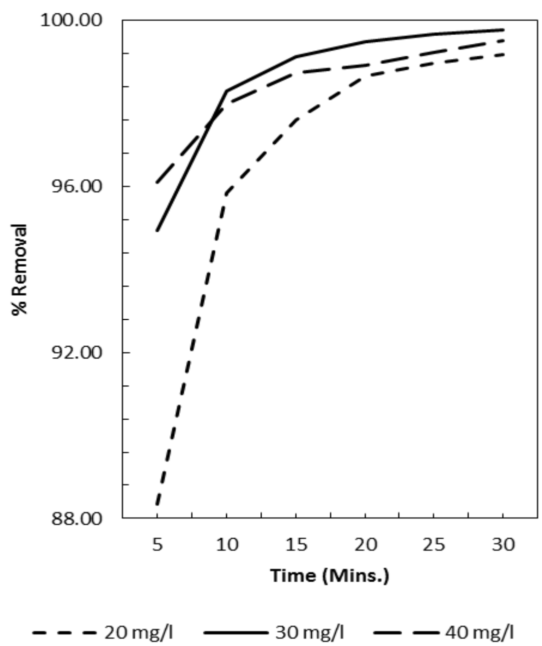

Fig. 6. Effect of different $FeSO_4$ dosage on colour removal efficiency with respect to time at 330 mg/l H_2O_2 and 3.5 pH

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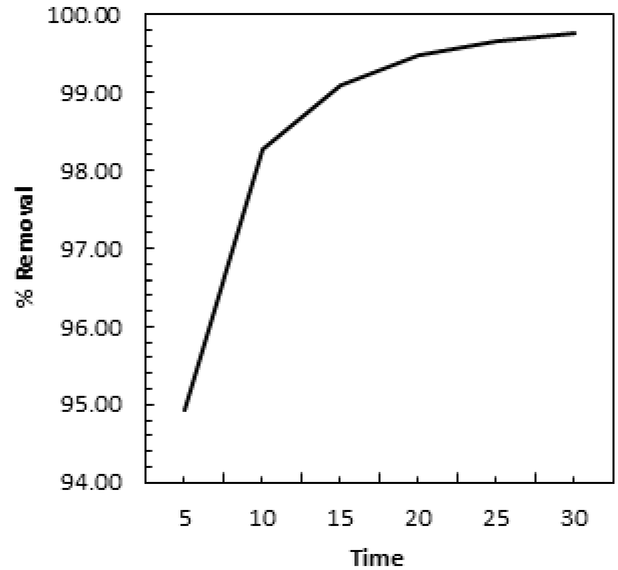

Fig. 7. Colour removal efficiency with respect to time at Optimum dosage i.e. 30mg/l $FeSO_4$, 330 mg/l H_2O_2 and 3.5 pH

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