"Decolourisation of Synthetic and Textile Wastewater by Fenton Process"

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Abstract: The main objective of the present paper were to exploit the process for the removal of color present in the synthetic wastewater and textile wastewater. This paper present the experimental results obtained on the removal of color using swarf as bed media. It also signifies the effect of flow rate and pH on the removal of color by column study. The present study mainly focused on the removal of color by column study by addition of hydrogen peroxide as an oxidizing agent. Finally comparison of both the column study conducted for synthetic and textile wastewater has been made to know the removal efficiency of the color from the wastewater. The present study investigated and concluded that, comparison to synthetic wastewater removal efficiency of textile wastewater is low. It can be concluded that the removal of the color from both synthetic and textile wastewater mainly depends on dissociation of iron ions in Fenton Process.

Keywords: Removal of color, Column study, Swarf as bed media, Synthetic and textile wastewater, Fenton process.

I. Introduction

Wastewater from textile industry is one of the major sources of aromatic amines in to the environment. There are more than 10,000 dyes used in textile industry and 280,000 tones of textile dyes are discharged every year worldwide. Degradation of dyes especially azo dyes, is difficult due to their complex structure and synthetic nature. Azo dyes are characterized by nitrogen to nitrogen double bond (–N= N–). The color of dyes is due to azo bond and associated chromophores, so disposal of dyes into surface water not only affects the aesthetic but cause also biotoxicity [1].

Synthetic dyes are present in many spheres of our everyday life and their application are continuously growing, e.g., in various branches of the textile industry, of the leather tanning industry, in paper production, in agricultural research, in photo electrochemical cells, and in hair colorings. Moreover synthetic dyes have been employed for the control of the efficiency of wastewater treatment. Wastewaters originating from dyes production and application industries pose a major threat to surrounding ecosystems, because of their toxicity and potentially carcinogenic nature. Apart from the aesthetic problems relating to colored effluent, dyes also strongly absorb sunlight, thus impeding the photosynthetic activity of aquatic plants and seriously threatening the whole ecosystem. So there is a clear need to treat dye wastewater prior to discharge into the effluent. Most of pollutants, except color, can be reduced by chemical, physical or biological methods. Therefore, the color problem of some textile wastewater caused by the residual dyes during the dyeing process needs more effort to be studied and investigated [2].

The production and finishing of textiles is often one of the most important industries in many developing countries. Waste water from textile mills is often discharged directly into rivers and lakes or directly into soil. Due to the biorecalcitrant nature of modern dyes, little dye would be decolorized or degraded, even if the wastewater were to be discharged to a conventional biological treatment plant. Possible treatment processes for some of the less water soluble dyes are adsorption or flocculation, but these processes result in solid wastes, thus creating new environmental problems [3]. Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand, heat, color, acidity, and other soluble substances. The removal of color from textile industry and dyestuff manufacturing industry wastewaters represents a major environmental concern [4].
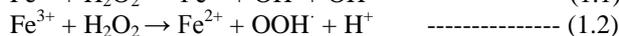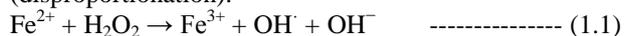
Azo dyes constitute the largest class of dyes used in industry. More than two thousand azo dyes are known and over half of the commercial dyestuffs are azo dyes. Azo dyes are broadly used in the textile industry, and also widely employed to color solvents, inks, paints, varnishes, paper, plastic, rubber, foods, drugs, and cosmetics. Azo dyes are resistant to aerobic biodegradation, since the conventional treatment (e.g. activated sludge) of wastewater contaminated with these dyes could not remove most azo dyes effectively. The resulting dye effluent may contain some components or moieties that could be toxic, carcinogenic or mutagenic to aquatic

life. Therefore, the degradation of azo dyes under alternative advanced oxidation technologies, like the Fenton reagent has to be explored [5].

Due to the complex polyaromatic structure and recalcitrant nature, dyes are not possible to degrade by means of biological methods. Aromatic amines which are formed as metabolites of reductive cleavage of azo bond under anaerobic conditions are more toxic than intact dye molecules and hence need further treatment [1].

A number of physical and chemical techniques have been used extensively to treat textile wastewaters. The classic methods such as chemical coagulation, sorption's are costly, rather inefficient, and often produce secondary wastes. Therefore, much attention has been paid to the development of treatment techniques that lead to complete destruction of dye molecules. Recently, chemical treatment methods, based on the generation of hydroxyl radicals, have been applied for pollution degradation, due to high oxidation power of hydroxyl radical [6]. Several physico-chemical methods like chemical precipitation, adsorption by activated carbon, natural absorbents, polycatalytic oxidation, ozonation, and Fenton's oxidation have been investigated to treat azo dye containing wastewater [1].

Fenton's reagent is a solution of hydrogen peroxide and an iron catalyst that is used to oxidize contaminants or wastewaters. Fenton's reagent can be used to destroy organic compounds such as trichloroethylene and tetrachloroethylene. It was developed in the 1890 by Henry John Horstman Fenton. Ferrous Iron (II) is oxidized by hydrogen peroxide to ferric iron (III), a hydroxyl radical and a hydroxyl anion. Iron (III) is then reduced back to iron (II), a peroxide radical and a proton by the same hydrogen peroxide (disproportionation).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^. + OH^- \qquad --------------- (1.1)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^. + H^+ \qquad --------------- (1.2)$$

Reaction (1.1) was first suggested by Haber and Weiss in the 1930, but is commonly referred to as 'the Fenton reaction'. In the net reaction the presence of iron is truly catalytic and two molecules of hydrogen peroxide are converted into two hydroxyl radicals and water. The generated radicals then engage in secondary reactions. In reaction (1.2) ferric iron (III) reacts with hydrogen peroxide to give ferrous Iron (II), this reaction is known as Fenton – like reaction.

The hydroxyl radicals which are second only to fluorine among common oxidants could react rapidly and non-selectively with nearly all−organic pollutants. Indeed, the $OH^.$ concentration determines the lifetimes of many compounds in the environment and, consequently, it has been called "mother nature's vacuum cleaner" [7]. The efficiency of Fenton's oxidation depends on H_2O_2 and Fe^{2+} concentrations, time and pH of the reaction. The pH value should be in the range of 2.5 to 4.0. Fenton's reagent has been found effective in treating various industrial wastewater components including aromatic amines and wide variety of dyes, pesticides and surfactants, as well as many other substances [8]. The main objective of the present study is to explore Fenton Process for removal of color from synthetic and textile wastewater. To determine the color removal efficiency with varying flow rate, pH in Fenton Process. To compare the efficiency of color removed in synthetic and textile wastewater by Fenton Process.

II. Materials and methodology

2.1 Materials Used

The chemicals used in this study hydrogen peroxide and Acid Fast Red A. The hydrogen peroxide 30% (H_2O_2) has been used in the study. Acid Fast Red A was used in the preparation of synthetic wastewater. The structure of the dye is as shown in Fig 2.1. Empherical formula of Acid Fast Red A is $C_{20}H_{13}N_2O_4$. Acid Fast Red A is soluble in water and is very slightly soluble in ethanol. Swarf is used as a catalyst, sodium hydroxide and other chemicals used in the experiments are of analytical grade.
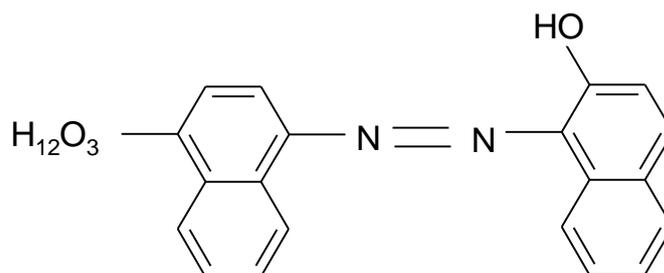

Fig. 2.1: Structure of the Acid Fast Red A

The swarf has been created during metal sawing and the particle size of swarf in the range of 0.5-2.5 mm. The swarf acts as heterogeneous catalyst for the activation of hydrogen peroxide with wastewater. When swarf used as a solid catalyst, iron ions are leached from the solid material. Then, the iron ions act as

homogeneous catalyst for the activation of H_2O_2 to generate hydroxyl radicals according to the Fenton reaction. Chemical constitution of the steel used as catalyst (swarf) is shown in Table 2.1. The carbon steel used as catalyst to hardened and tampered which is suitable for cylinder gears, machine tools, etc.

Table 2.1: Chemical constitution of the steel used as a catalyst (Swarf)

En Number	Chemical Constitution (%)			
	Copper	Manganese	Silicon	Specific gravity
9	0.50-0.60	0.50-0.80	0.05-0.35	0.060

Because the swarf releases Fe^{2+} ions to the solution under acidic conditions, iron dissolution is an initial step for the oxidation of contaminants (e.g. dyes) by the H_2O_2/swarf process. When dye oxidation occurs, the initial Fe^{2+} ions are consumed, and the oxidation rate will depend on the dissolution rate of Fe^{2+}. The proposed mechanisms of hydroxyl radical production in the presence of the swarf catalyst are presented in Fig 2.2.

This mechanism has three stages
➢ Dissolution of swarf and release of Fe^{2+} ions,
➢ The Fenton reaction including formation of hydroxyl radicals $OH^{\bullet}$, and
➢ Oxidation of dye.
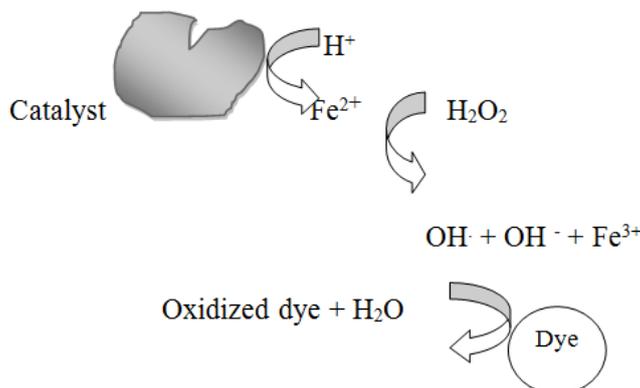
Fig. 2.2: The proposed mechanism of hydroxyl radical production in the presence of swarf as a catalyst

2.2 Reactor
A bench scale reactor was set up in the laboratory as shown in Fig 2.3. A column with diameter of 7.5 cm and height 50 cm with working volume of 923.25cm^3. Swarf was filled up to 27 cm depth in the column. The column has an inlet to feed and outlet to withdraw the effluent. A suitable capacity of glass beaker was used to collect the wastewater from the column.

1 = Wastewater tank
2 = Column
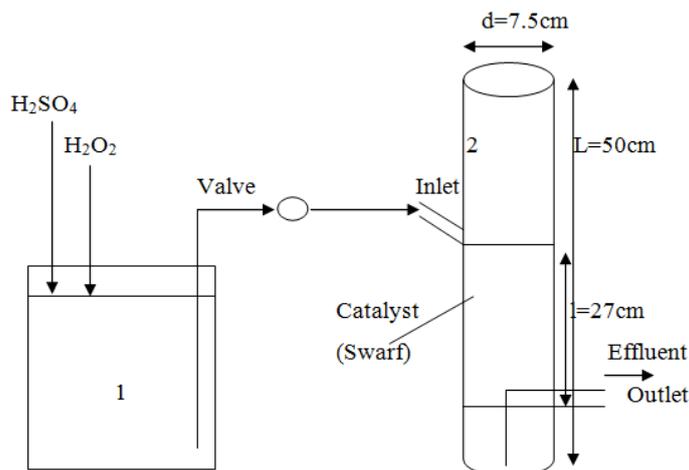
Fig. 2.3: Schematic flow diagram of experimental set-up of the Fenton reactor

2.3 Synthetic Wastewater preparation

The simulated dye wastewater was prepared by diluting commercial Acid Fast Red A with tap water. The dye has high purity and used without further purification. About 0.1mg of Acid Fast Red A dye was dissolved in 1 liter tap water and it gives the concentration of 100mg/dm^3. Dissolved synthetic wastewater produce an intensive red color. The initial characteristics of the synthetic wastewater were done as per the standard method 19th edition (2005). The parameters analyzed were pH, Color, Chloride, Total dissolved solids (TDS), BOD and COD.

2.4 Characterization of Synthetic and Textile Wastewater

About 4 liter of wastewater sample was collected from textile industry for the comparison with synthetic wastewater for the present study. Similar parameter (Synthetic Wastewater) was analyzed for the study purpose in the laboratory for textile wastewater. Initial characteristics of the synthetic and textile wastewater were analyzed have been presented in Table 2.2.

Table 2.2: Characteristics of Synthetic Wastewater

Parameter	Synthetic Wastewater	Textile wastewater
Color	Red	Pale pink
pH	7.3	6.6
Chloride mg/l	54.7	23.9
Total Dissolved Solids mg/l	236	304
BOD mg/l	-	308
COD mg/l	5	754

2.5 Column Study

The column study was done using 27cm bed with swarf as catalyst. The simulated dye wastewater is prepared for selected pH with varying amount of H_2SO_4 and 150 mg H_2O_2 was added for one liter of wastewater. The pH was varied from 2, 3, 4, 5 and 6 to determine the maximum color removal. The prepared solution are fed into the reactor at varied flow rates i.e., 2ml, 3ml, 4ml, 5ml and 6ml/min under gravity. For every 1hour the samples were withdrawn and add 0.1 N NaOH to maintain pH 9 in order to prevent further generation of hydroxyl radicals through the Fenton Process. Further, initial and final colors of the samples were analyzed by using UV-VIS Spectrophotometer with wavelength of 510 nm.

2.6 Measurement of Color
Preparation of Stock Solution

Dissolve 1.246g potassium Chloroplatinate, K_2PtCl_2 (equivalent to 500mg metallic platinum) and 1.00g crystallized cobalt us chloride, $CoCl_2.6H_2O$ (equivalent to 250mg metallic cobalt) in distilled water with 100ml concentrated hydrochloric acid and dilute to 1000ml with distilled water. Prepared stock solution produced color of 500Hazen.

Preparation of Standard graph

About 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1ml stock solution added to 10 numbers of 50ml capacity Nessler tube and make up to 50ml by adding distilled water. Each Nessler tube gives different color units such as 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10Hazen. The standard stock solutions concentrations were determined using spectrophotometer. Color unit (Hazen) v/s concentration was then plotted to get a standard calibration curve as shown in Figure 2.4. This standard curve was used to determine color unit in wastewater samples.
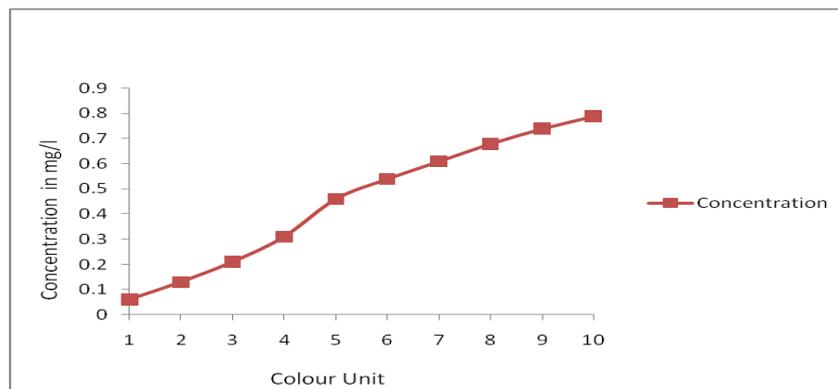
Fig. 2.4: Calibration curve for Color unit

2.7 Regeneration of Swarf

The efficiency of swarf may decrease due to the iron oxides forming on the surface hence it requires regeneration. In order to regenerate the catalyst, the Fenton reactor is flushed with distilled water and filled with H_2SO_4 at 1:9 ratios. After 1 hour, the Fenton reactor is once again flushed with distilled water to remove excess accumulation of H_2SO_4 in the reactor.

III. Results and Discussions

3.1 Optimization of flow rate

In first phase color removal efficiency was observed with varying flow rate from 2, 3, 4, 5 and 6 ml/min to optimize the same. The first set of experiment was carried out by keeping the pH in acidic range at 3 and flow rate of 2 ml/min. The samples were collected for every 1 hour from the reactor for the analysis. Initial concentration of dye in the synthetic wastewater was found to be 1.85 mg/l with color of 21 Hazen. Iron concentration of synthetic wastewater found to be 1.14 mg/l. For the present condition, maximum color removal was observed to be 90.47% under 4 hour duration. Finally, it was observed that the percentage of color removal increase with time. The variations of color and iron concentration with time are shown in Fig 3.1. From figure it was clear that dissociation of iron into the wastewater takes place, in other words there was reduction of color with increase in time.

The second set of experiment was carried out by keeping the pH in acidic range at 3 and flow rate of 3 ml/min. Initial concentration of the sample was 1.85 mg/l which reduced to 0.14 mg/l after 4 hour duration. A maximum color about 90.47% was removed after 4 hour. Fig 3.2 shows variation of iron concentration and color with time. From Fig, iron dissociation increased with time and substantial color removal was observed.

The third set of experiment was carried out by keeping the pH in acidic range at 3 and flow rate of 4 ml/min. A maximum color removal of 90.47% was achieved at 2 Hazen in 4 hour duration. Fig 3.3 shows variation of color and iron concentration with time. From figure it was clear that color reduced gradually from 21 Hazen to 5, 4, 3 and 2 Hazen with increase in time and at each point there was slight increase in iron concentration.
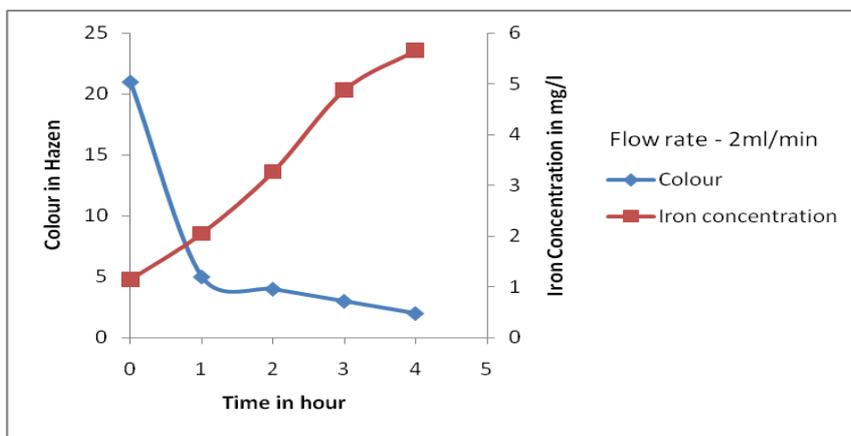

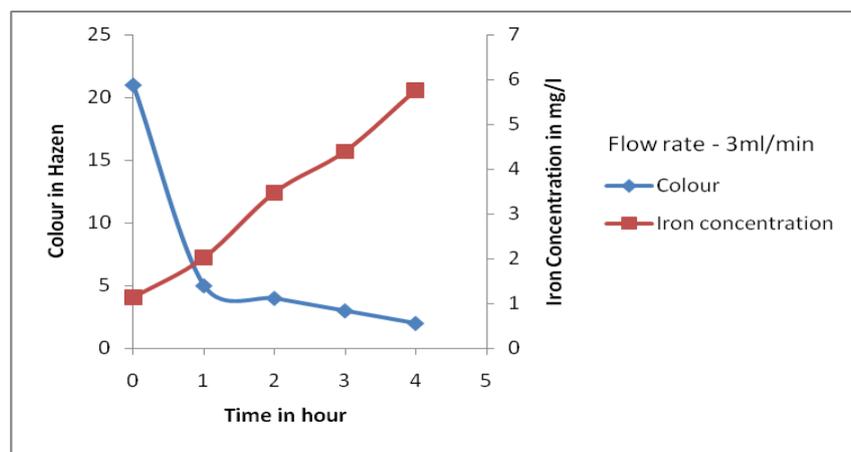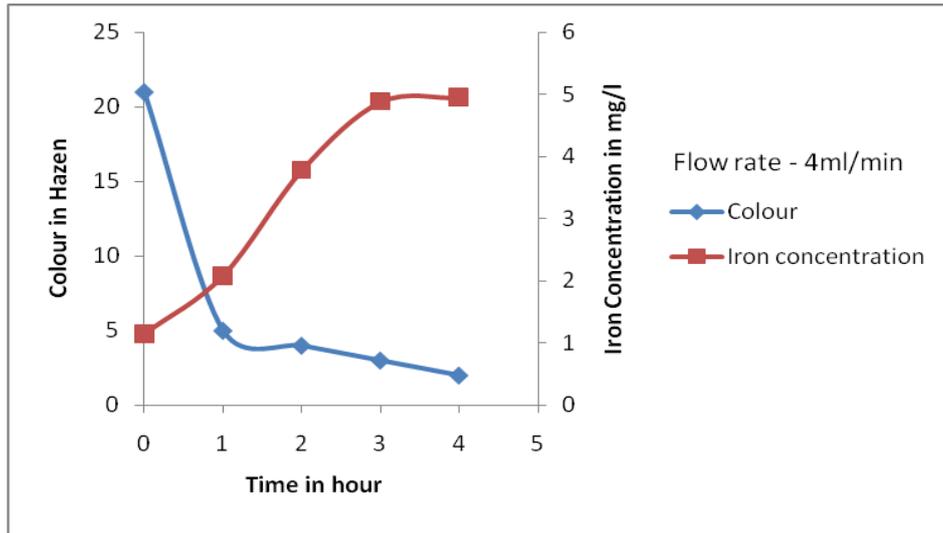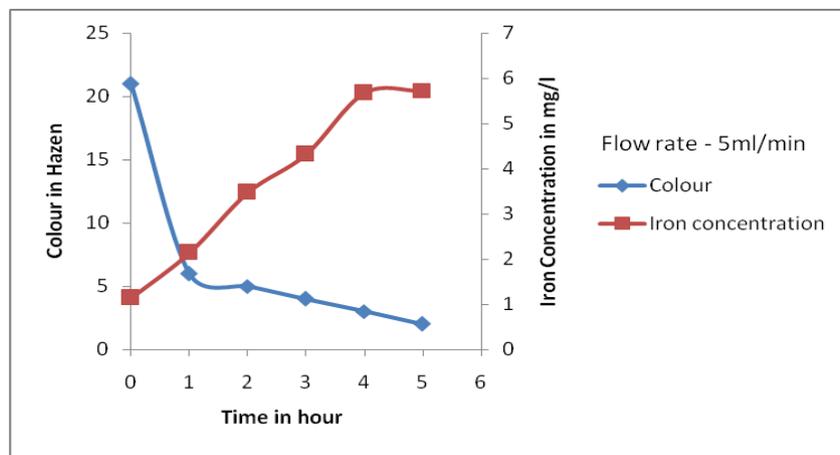**Fig. 3.1:** Variation of Color and Iron concentration with time

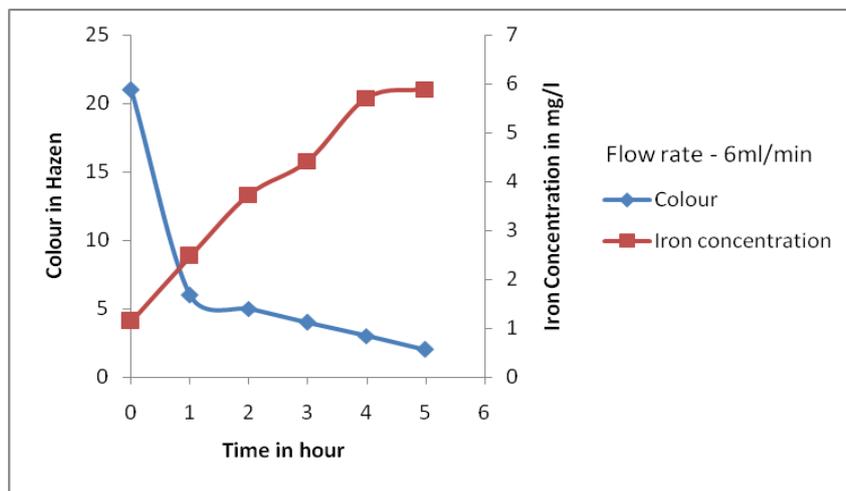**Fig. 3.2:** Variation of Color and Iron concentration with time

Fig.3.3: Variation of Color and Iron concentration with time

The fourth set of experiment was carried out by keeping the pH in acidic range at 3 and flow rate of 5 ml/min. A maximum of 90.47% was obtained after 5 hour. Fig 3.4 shows variation of color and iron with time. The fifth set of experiment was carried out by keeping the pH in acidic range at 3 and flow rate of 6 ml/min. An optimum efficiency about 90.47% in 5 hour duration was achieved. Fig 3.5 shows variation of color and iron concentration with time. Iron concentration gradually increased in 5 hour with significant reduction in color.

Fig. 3.4: Variation of Color and Iron concentration with time

Fig. 3.5: Variation of Color and Iron concentration with time

3.2 Optimization of pH

Optimized flow rate value 4 ml/min was selected (ie. maximum percentage color removal of 90.47% after 4 hour) in the column study with varied pH conducted using swarf as bed media for up to 5 hour at an interval of one hour. The same bed depth and the influent dye concentration was maintained .

The first set of experiment was carried out by keeping the flow rate constant at 4 ml/min with pH 2. For the present condition, maximum color removal was observed to be 85.71% under 4 hour collection time. Variation of color and iron concentration with time was shown in Fig 3.6. For the present case, color of the synthetic wastewater was decreased from 21 Hazen to 3 Hazen. Also iron concentration increased from 1.14 mg/l to 5.36 mg/l with time. The second set of experiment was carried out by keeping the flow rate constant at 4 ml/min with pH 3. Maximum efficiency of about 90.47% was achieved in 4hour duration. Fig 3.7 shows variation of cooler and iron verses time. The third set of experiment was carried out by keeping the flow rate constant at 4 ml/min with pH 4. Highest efficiency of 85.71% was achieved. Compare to pH 3, the dissociation of iron into wastewater reduced and even there was minor decrease in the removal effectiveness. Fig 3.8 shows variation of color and iron concentration with time.
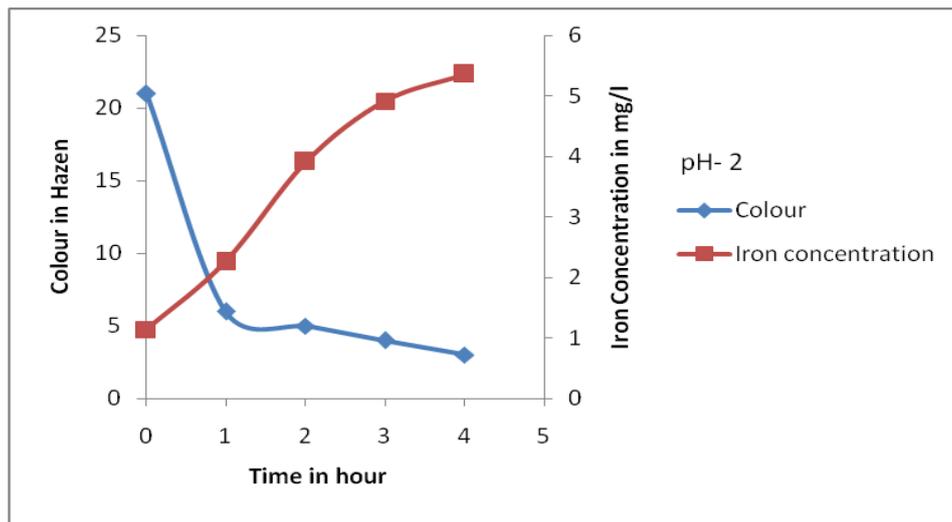

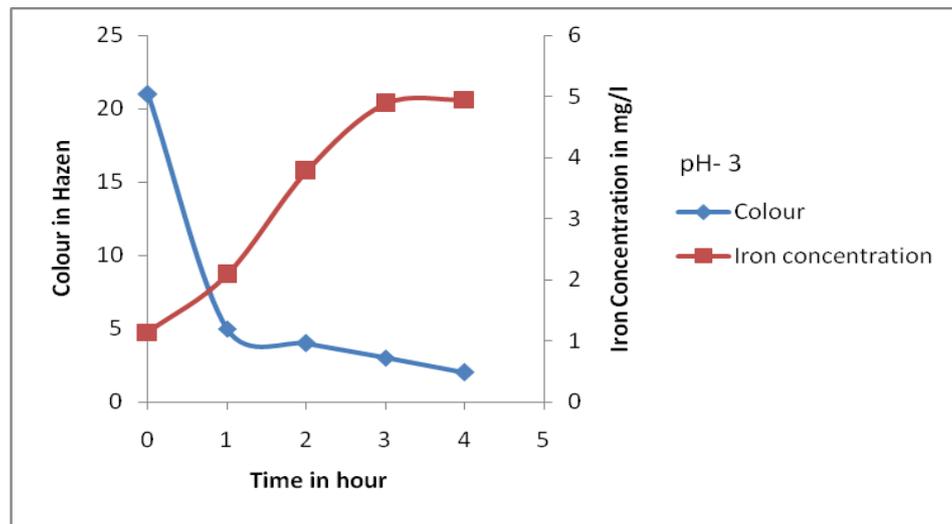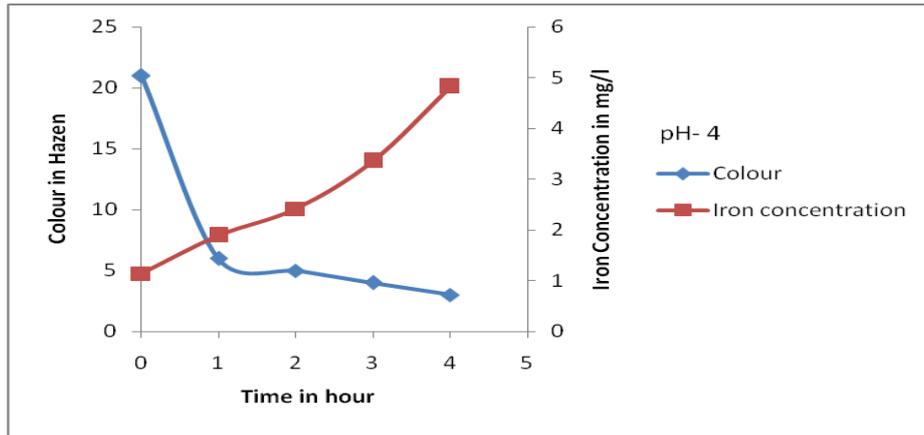**Fig. 3.6:** Variation of Color and Iron concentration with time .
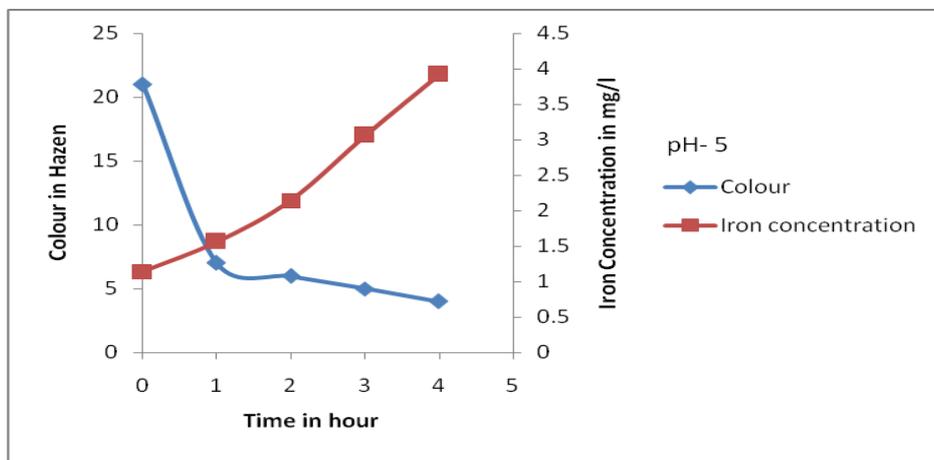

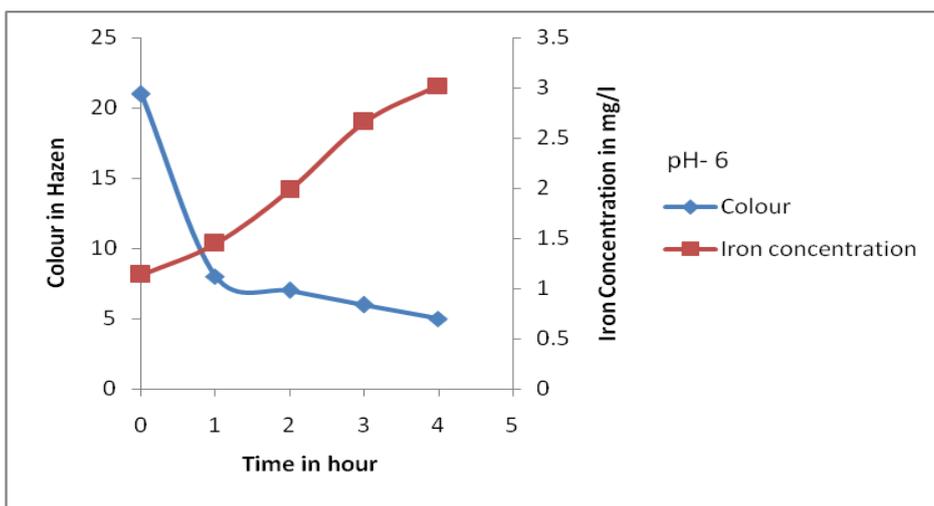**Fig.3.7:** Variation of Color and Iron concentration with time

Fig. 3.8: Variation of Color and Iron concentration with time

The fourth set of experiment was carried out by keeping the flow rate constant at 4 ml/min with pH 5. Initial concentration of dye in synthetic wastewater sample was 1.85mg/l with color 21 Hazen. Maximum color removal efficiency of about 80.95% was achieved in 4 hour. Fig 3.9 shows color and iron variation verses time. Iron dissociation reduced with the increase in pH and reached maximum of 3.92 mg/l in 4 hour. The fifth set of experiment was carried out by keeping the flow rate constant at 4 ml/min with pH 6. Color removal efficiency decreased to minimum of about 76% after 4 hour. This clearly shows, with increase in pH there was decrease in color removal and iron dissociation. Fig 3.10 shows variation of color and Iron concentration with time. Iron dissociation was less in pH 6, after 4 hour 3.02 mg/l of iron was recorded.

Fig. 3.9: Variation of Color and Iron concentration with time

Fig. 3.10: Variation of Color and Iron concentration with time

3.3 Comparison of color removal efficiency between Synthetic and Textile wastewater

Column studies conducted for both synthetic and textile wastewater has been discussed herein. As per the discussion for synthetic wastewater it was observed that maximum color removal efficiency at the flow rate 4 ml/min was 90.47%. Further, studies also identified the maximum color removal efficiency achieved about 90.47% at pH 3 for synthetic wastewater. Finally the studies also conducted to know the maximum removal efficiency at optimum flow rate (4 ml/min optimum in synthetic wastewater) was selected for textile wastewater. Under the selected flow rate of 4 ml/min the maximum removal efficiency was achieved about 72.72% at pH 3 for textile wastewater. Fig 3.11 shows variation of color and iron concentration with time for synthetic and textile wastewater. From figure, it was clear that iron dissociation in synthetic wastewater sample was higher compare to textile wastewater sample. Similarly, the percentage of color removal for textile wastewater was less in contrast with synthetic wastewater sample.
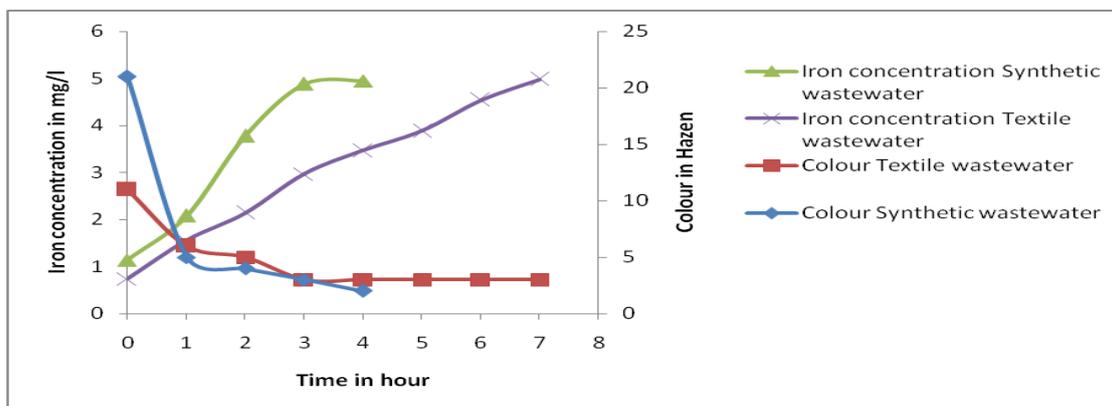
Fig. 3.11: Comparison of Color and Iron removal for synthetic and textile wastewater

IV. Conclusions

Based on the experimental results obtained from column studies on the removal of color using swarf as a bed media, the following conclusions have been drawn. As per the discussion for synthetic wastewater it was observed that maximum color removal efficiency at the flow rate 4 ml/min was 90.47%. Further, studies concluded that the maximum color removal efficiency achieved about 90.47% at pH 3 for synthetic wastewater. Finally the studies also conducted to know the maximum removal efficiency at optimum flow rate (4 ml/min optimum in synthetic wastewater) was selected for textile wastewater. Under the selected flow rate of 4 ml/min the maximum removal efficiency was achieved about 72.72% at pH 3 for textile wastewater. The present study investigated and concluded that, comparison to synthetic wastewater removal efficiency of textile wastewater is low. Overall, it can be concluded that the removal of the color from both synthetic and textile wastewater mainly depends on dissociation of iron ions in Fenton Process.

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