Treatment Of Textile Wastewater Using Solar Photofenton Process

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***Abstract*—The treatment of textile wastewater by photo-Fenton oxidation process was investigated using natural sunlight as energy source. The dyes present in the wastewater were Remazol Red F 3B, Olive R and Ramazol Turquoise blue CG. The degradation of dyes was evaluated by the decrease in COD and colour. The influence of reaction time, Fe^{2+} concentration, concentration of H_2O_2 and solar light intensity was studied at a pH of 3. The best results were obtained using 4 mg/L Fe^{2+} concentration, 60 mM H_2O_2 concentration and 30 min. reaction time at a light intensity of 44 w/m^2. Under these experimental conditions 87% COD removal and 93% colour removal was obtained.**

Keywords- textile; dyes; solar light; photo-fenton; COD removal

I INTRODUCTION

The textile industry, a major consumer of water for its different wet processing operations, is also a major producer of effluent wastewater containing organic surfactants, salts, acids, alkalis, solvents and the residual dyes. Water pollution from textile dyeing industry becomes a matter of concern owing to significant organic matter and dyeing agents that produce colours[1,2]. The cotton textile industry is a growing industry in India with over 1000 process units. In general, the wastewater from a typical cotton textile industry is characterized by high values of BOD, COD, colour, and pH [1]. The textile wastewater with high amount of COD is found to be toxic to biological life [7]. The intensive colour causes problems to the aquatic life and makes the water unfit for use at the downstream side of the disposal point. To prevent the above adverse effects, the textile industry wastewater needs to be treated and discharged as per the standards laid down under Central Water (Prevention and Control of Pollution) Act, 1974, legislated by the Government of India.

The advanced oxidation processes (AOP) are currently considered as an effective treatment for the dye removal and COD reduction of textile wastewater. Although AOPs include different reacting systems, their mechanisms are basically characterised by the in situ generation of highly reactive and non-selective hydroxyl radicals (HO·, E^o = 2.8V), able to oxidise and mineralise almost all organic compounds to CO_2 and inorganic ions [5,6]. Advanced oxidation processes (AOPs) were developed to generate hydroxyl free radicals using different oxidants under different combinations. These radicals were found to destroy components that are not destroyed under conventional oxidation processes[8,10]. AOP using ozone, ultra violet, TiO2, fenton, photo-phenton and hydrogen peroxide can be used to treat textile dyes. The main advantage of AOPs over the other treatment processes is its pronounced destructive nature and mineralization of organic contaminants present in wastewater[5].

Among AOPs, the fenton process is an interesting solution since it allows high degradation levels at room temperature and pressure conditions using cheap chemicals and easy to handle reactants. Fenton's oxidation is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions [9-11]. The production of highly oxidizing species can be enhanced by applying solar light on Fenton reactants, supporting sustained chemical reactions as well as an increase in efficiency compared to other AOP-based methods. This process is known as solar photo-fenton oxidation and the high rate of oxidation of dyes and other recalcitrant pollutants accounts for the capacity of solar radiation to influence the direct formation of $HO^\bullet$ radicals.

$$H_2O_2 + UV \rightarrow HO^\bullet + HO^\bullet$$

$$Fe^{3+} + H_2O + UV \rightarrow HO^\bullet + Fe^{2+} + H^+ \quad [7]$$

Furthermore, the solar photo-fenton process has advantages like very less or no sludge generation and use of a free cost energy source than conventional fenton process[23].

The aim of this work is to determine the influence of factors like contact time, concentration of Fe^{2+} and H_2O_2 and solar light intensity in the solar photo-fenton reaction for the treatment of textile wastewater and also to optimise the same.

II MATERIALS AND METHODS

A. Chemicals

The chemicals used in the experiment include 1N H_2SO_4 or NaOH to adjust the pH, Ferrous sulphate ($FeSO_4.7H_2O$) as a source of Fe^{2+} and 30% H_2O_2 to generate peroxide radicals. Also, 0.1N Sodium bisulphite ($NaHSO_3$) was added to stop the reaction of H_2O_2.

B. Analytical methods

The parameters like pH, COD, BOD5, TSS, TDS, Alkalinity, Turbidity, Sulphides, Chlorides, Hardness and Colour were analyzed as per procedures in standard methods (APHA, 1971).

C. Solar photofenton experiment

The solar photofenton experiment was carried out in a glass beaker of capacity 1L. The volume of the sample used was 500 mL. The desired pH value was adjusted using 1N H_2SO_4 or NaOH before start-up. Then a given weight of iron salt ($FeSO_4.7H_2O$) was added. The iron salt was mixed very well with wastewater for 10 min. The experimental setup was placed under the sunlight and given volume of H_2O_2 was then added. The reaction time starts with the addition of H_2O_2 and the reagents has to be thoroughly mixed. The light intensity was measured using a lightmeter. When required contact time is reached, 0.1N Sodium bisulphite ($NaHSO_3$) was added to stop the reaction of H_2O_2.

The factors influencing the photo-fenton reaction are pH, Fe^{2+} concentration and concentration of H_2O_2. Thus to enhance the BOD/COD ratio to 0.5, several trials were done based on these factors. In this experiment, pH of wastewater is kept as 3 based on the information in previous researches that the generation of $OH^{\cdot}$ radicals through the decomposition of H_2O_2 as well as the catalytic activity of Fe^{2+} is maximum at this pH (Ahmed R.Mobarki et al, 2013). Also, concentration of Fe^{2+} and H_2O_2 in the range of 2 to 10 mg/L and 20 to 70mM was applied to find out the optimum dosage. The reaction time between 15 to 75 minutes was selected. The available solar light intensity at the project site was up to 44 W/m^2.

III RESULTS AND DISCUSSION

A. Sampling of real textile wastewater

The samples of untreated real textile wastewater were collected from Cannanore Handloom Exports Ltd, Kannur. The water requirement for the industry is 40 to 50 m^3/day and the dying process generates 20 to 30 m^3 coloured wastewater while processing 200kg cotton every day.

The dyes mostly used by the industry are Remazol Red F 3B, Olive R and Ramazol Turquoise blue CG. The wastewater samples are stored at 4^0C and analysed to determine the characteristics. Table 1 shows the characteristics of untreated real textile wastewater.

Table 1. characteristics of untreated real textile wastewater

Parameter	***concentration***
BOD	210 mg/L
COD	980 mg/L
pH	12
TSS	125 mg/L
TDS	970 mg/L
Alkalinity	1200 mg/L
Chloride	180 mg/L
Turbidity	64 NTU
Hardness	140 mg/L
Sulphide	44 mg/L

B. Effect of reaction time

The experiments are carried out to find the influence of reaction time by keeping all other factors as constants. It can be seen from the figure 1 that COD removal and colour removal increase up to 30 min. and then it is more or less the same. So a contact time of 30 min is chosen as the optimum reaction time.

Table 2 effect of reaction time on solar photo-fenton process

Reaction time (min)	***COD removal (%)***	***Colour removal (%)***
15	28	32
30	72	76.2
45	74	79
60	74	80
75	74	77

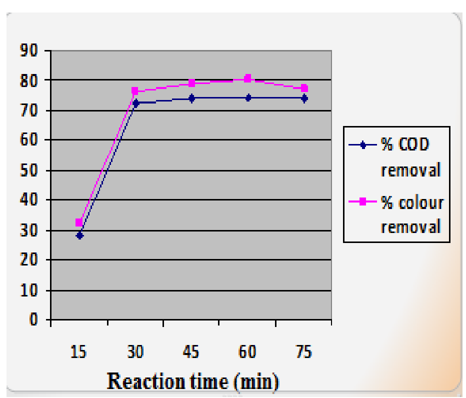

Figure 1 effect of reaction time (at 3 mg/L Fe^{2+},30mM H_2O_2, pH=3, 25 w/ m^2 intensity)

C. Effect of Fe^{2+} concentration

In subsequent steps of fenton reaction, hydroxyl radical can react with $Fe^{2+}$and oxidise it to Fe^{3+} ions. From table 3 and figure 2, it is clear that maximum COD removal is at a concentration of 4 mg/L and the removal efficiency decreases on higher concentrations of Fe^{2+}. It may be due to the self-scavenging of $OH^{\cdot}$ radical by converting it to hydroxyl ions during oxidation of Fe^{2+}.

$$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^{-} \quad [9].$$

Table 3 effect of Fe^{2+} concentration

Fe^{2+} conc. (mg/L)	***COD removal (%)***	***Colour removal (%)***
2	52	42.9
3	73.6	76
4	74.4	78
5	62	72
10	48.8	69

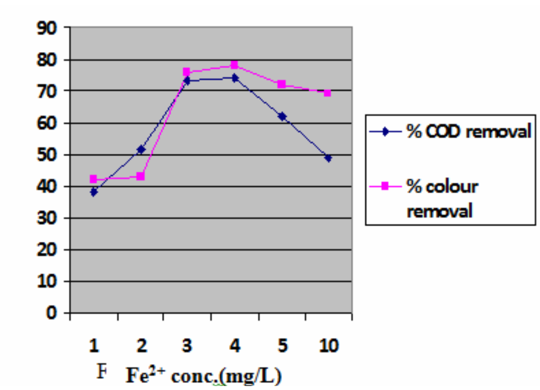

Figure 2 Effect of Fe^{2+} concentration(at 30 min reaction time,30mM H_2O_2, pH=3, 20 w/ m^2 intensity)

D. Effect of H_2O_2 concentration

The increase in dosage of H_2O_2 causes an increase in COD and colour removal. But beyond a concentration of 60 mM there is not much improvement in the removal efficiency. It may be due to the fact that the addition of higher dosages of H_2O_2 can produce hydroperoxyl radicals that are much less reactive than hydroxyl radicals [9].

Table 4 Effect of H_2O_2 concentration

H_2O_2 conc. (mg/L)	***COD removal (%)***	***Colour removal (%)***
20	63.92	61
30	76.4	79
40	77.2	83
50	79.6	85.2
60	80.4	85.7
70	80.4	84.6

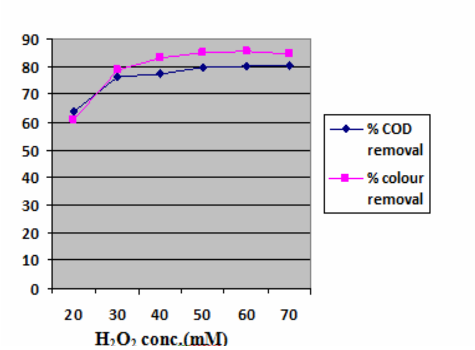

Figure 4 Effect of H_2O_2 concentration(30 min reaction time, 4 mg/L Fe^{2+}, pH=3, 20 w/ m^2 intensity)

E. Effect of solar light intensity

The photo-fenton reactions were carried out at different light intensities and at 4mg/L Fe^{2+} concentration and 60mM. After a irradiance time of 30 min. the COD and colour removals were determined. It is clear from table 5 and figure 4 that the COD removal and colour removal increases as the light intensity increases and COD removal efficiency of 81% can be achieved at 25 w/m^2.

Table 5 Effect of solar light intensity

Solar light intensity (w/m^2)	***COD removal (%)***	***colour removal (%)***
Nill	34	37
6	59	62
10	62	64
15	73	79
20	80	83
25	81	89
30	84	90
35	86	92
40	86.5	92
44	87	93

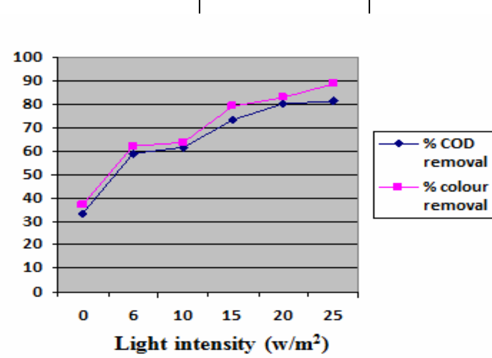

Figure 4 Effect of solar light intensity (at 4 mg/L Fe^{2+}, 60 mM H_2O_2 , 30 min. reaction time at pH = 3)

Fig.3.5 wastewater before and after treatment (at 4 mg/L Fe^{2+}, 60 mM H_2O_2 , pH=3, 20 w/ m^2 intensity, 30 min reaction time)

F. Characteristics of wastewater after treatment

Table 6 characteristics of wastewater after treatment

Parameter	***concentration***
BOD	184 mg/L
COD	196 mg/L
pH	5.4
TSS	34 mg/L
TDS	1210 mg/L
Alkalinity	420 mg/L
Chloride	86 mg/L
Turbidity	23 NTU
Hardness	80 mg/L
Sulphide	9 mg/L

IV CONCLUSION

The treatment of textile wastewater by solar-photofenton reaction was evaluated through this work and the following remarks are concluded. (i) The reaction is optimised for COD and colour removal and the optimum parameters are obtained as 4 mg/L Fe^{2+} concentration, 60 mM H_2O_2 concentration and 30 min. reaction time at a pH of 3 and light intensity of 20 w/m^2. The COD and colour removal of 80.4% and 85.7% is obtained in the optimum chemical dosage at the most available intensity of 20 w/m^2 (ii) The COD and colour removal efficiency increases with the increase in solar light intensity and 87% COD removal and 93% colour removal is obtained at an intensity of 44 w/m^2. Even though the reaction rate is a little low on cloudy days, the costless solar energy utilization can compensate for small differences in photo-degradation rates, especially in tropical regions like India where solar energy is abundant.

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