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Decolouring of Synthetic Waste Water by Chemical Oxidation

Rathinakumar Vedachalam[1]*, Sugumaran Karuppiah[2]

[1]*School of Civil Engineering, SASTRA University, Thanjavur-613401, Tamilnadu, India*

[2]*School of Chemical and Biotechnology, SASTRA University, Thanjavur-613401, Tamilnadu, India*

ABSTRACT

Discharge of waste water from the textile industry into the natural water bodies causes serious problem to the aquatic environment. This waste water contains dyes which are mainly made of chemicals in which majority of these chemicals categorized as inorganic. General methods used to treat this waste water can remove organic chemicals, also these methods consumes more time. Hence treating this waste water has become a great challenge to the chemists and environmental engineers. As the dyes which are used in the textile industry are inorganic in nature, the common practices used to treat this is waste water are no longer useful. Hence new methods are required to treat these inorganic chemicals and these methods must be must faster than the common practices. Hence chemical oxidation methods came into existence. The paper deals with chemical oxidation process for the color removal of waste water by using Fenton's reagent. In this process Hydrogen Peroxide is used as oxidant. Fenton's reagent uses ferrous ions to make OH- radicals. These OH-oxidizes the chemicals present in waste water and decolorizes it. So, in this paper focuses on preparation of Fenton reagent and optimum time requirement that can remove methylene blue (MB) color.

Keywords: Chemical oxidation, Color removal, Methylene blue, Waste water, Fenton

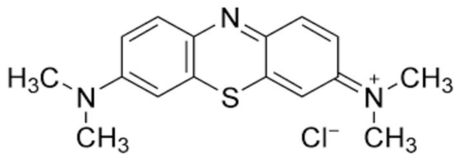
INTRODUCTION

Wastewater emerging from Textile industries includes a large distribution and addition of chemicals and dyes that make the real challenge for the concerned industries in environmental aspects [1,2]. Pollution in textile industry raised in dyeing and finishing processes. These processes demand a wide range of dyestuffs and chemicals which is having highly complied organic chemicals. It is causing very serious problems in their disposal as all of them are not contained in the final product. Apart from the color, some other pollutants found in textile wastewaters are HSS, COD, heat, acidity, and other soluble substances [3]. Despite many test, the procedure prescribed by the American Dye Manufacturers Institute (ADMI) is considered as best experimental system to analysis the color of the waste water [4]. Experimental studies focuses on the removal of color from textile industry and dyestuff manufacturing industry needs more attention with reference to environmental concern [5]. In the last few decades a rather fast evolution of the research activities attributed to the environmental protection has been witnessed as the consequence of the special attention paid to the environment by social, political and legislative international authorities leading in some cases to the delivery of very severe regulations. One of the major steps taken in this process is treating the waste effluent water from the industries before disposing it. The textile industry consumes about 20% of fresh water resources have been developing various process to treat their effluent waters. Some of the methods developed are incineration, chemical adsorption, and advanced oxidation processes. Studies have shown that the variation of initial azo dye concentration produces a variation in kinetics [6]. Over the years there have been many developments in these processes. With increase in chemicals in dye manufacturing, the conventional methods are no longer can be adopted. Hence advanced methods like chemical oxidation processes have been evolved. Exposure of strong oxidizing agent exposed to UV which generates hydroxyl free radicals is the key factor in the Advance Oxidation Process (AOP) [7]. When a water or wastewater containing H_2O_2 is irradiated with UV, hydroxyl radicals are formed. These hydroxyl radicals were identified as strong oxidants to oxidize organic compounds present in waste water [8]. The organic compounds degraded by radicals by, which lead to either an abstraction of hydrogen atoms or addition to double bonds [9]. Chemical oxidation aims at the mineralization of the contaminants to carbon dioxide, water and inorganic or, at least, at their transformation into harmless products. Apart from this many researchers contribute for the chemical oxidation process [10,11]. Obviously the methods based on chemical destruction, when properly developed, give complete solution to the problem of pollutant abatement differently from those in which only a phase separation is realized with the consequent problem of the final disposal.

MATERIALS AND METHODS

Methylene blue

Methylene Blue dye (MB) is basic aniline dye, $C_{16}H_{18}N_3SCl$ that forms a deep blue solution when dissolved in water. It is utilized in coloring and dyeing industry. The removal of methylene blue from any wastewater is of very important due to its serious threats to the environment.



Molecular formula of Methylene blue

Hydrogen peroxide (H_2O_2)

Hydrogen peroxide is a colorless liquid with bitter taste. Naturally it was presented in mere amounts especially in gaseous form. It is very unstable, having greater affinity to oxygen and water with liberated of enormous heat. It is one of the powerful oxidizing elements when it aligned with organic matters. It is also plays a crucial role in minor concentration (3-9%) especially in hair bleach and clothes. Higher concentration of H_2O_2 finds its place in textile industry, rubber industry and organic chemical industry. Hydrogen peroxide is a strong oxidizing agent used in aqueous solution as a ripening agent, bleach, and topical anti-infective. It is relatively unstable and solutions deteriorate over time unless stabilized by the addition of acetanilide or similar organic materials.

Ferrous sulphate ($FeSO_4.7H_2O$)

Ferrous Sulphate is a green colour crystalline compound generally obtained in nature. It plays a significant role in preparation of various chemical compounds and also it is act as a reducing reagent. It is also used a catalyst for hydrogen peroxide.

Preparation of solutions

Stock solution is also known as a base solution for the preparation of the various solutions as for preparing concentrations of 1ppm and smaller concentrations are more difficult. Hence a higher known concentration of the required solution is prepared and by diluting the stock solution we can get the required concentration of the solution Solid methylene blue of 25 mg is correctly weighed in the machine and is added to the 500 ml of distilled water. Hence obtaining 50 ppm stock solution. Similarly, various concentrations of stock solutions can be prepared.

The sample solutions are then undisturbed and lids are closed so that dust and other particles may not mix as this would change its properties. This is how the dye solutions are prepared.

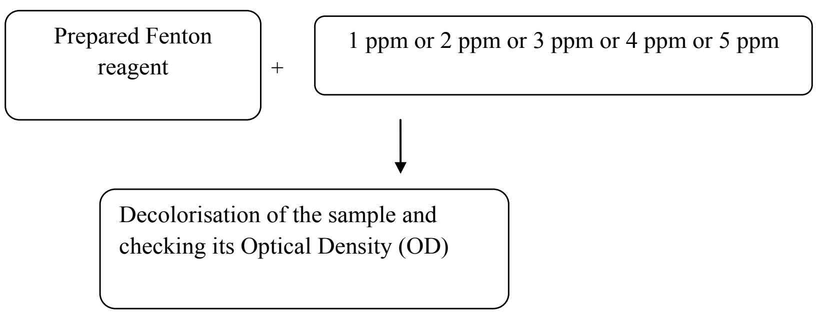
Preparation of $FeSO_4$ solution

It is similar to the preparation of the stock solution i.e., suitable amount of $FeSO_4$ is added to water and dissolved in it. Here 1000ppm, 300 ppm solutions are prepared.

Preparation of Fenton reagent

To prepare Fenton's reagent take $FeSO_4$ solution, H_2O_2 solution and water in the ratio of 1:4:4. Addition of water is just to make the solution diluted which is little safer to use. Concentrated Fenton reagent can also be made for better results. Storage of Fenton reagent should be in a dark place as it can react in sunlight.

Experimental methodology



Preparation of stock solution

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Procedure

Solid methylene blue of 25 mg is correctly weighed in the machine and is added to the 500 ml of distilled water. Hence obtaining 50 ppm stock solution. Similarly, various concentrations of stock solutions can be prepared. Note: Stock is to be prepared in higher concentrations than the sample concentrations.

Sample solutions

1) **1 ppm:** From the stock solution 2 ml is taken and it is diluted to 100 ml water.
2) **2 ppm:** From the stock solution 4 ml is taken and it is diluted to 100 ml water.
3) **3 ppm:** From the stock solution 6 ml is taken and it is diluted to 100 ml water.
4) **4 ppm:** From the stock solution 8 ml is taken and it is diluted to 100 ml water.
5) **5 ppm:** From the stock solution 10 ml is taken and it is diluted to 100 ml water.

The sample solutions are then undisturbed and lids are closed so that dust and other particles may not mix as this would change its properties. This is how the dye solutions are prepared (Figure 1).

Figure 1: Image of sample solutions

Calculation of optimum dosage of Fenton reagent

In order to estimate the optimum dosage of Fenton reagent, 50 ml sample of MB samples are taken of various concentrations of 1-5 ppm. Now Fenton reagent is added to each sample in a calculated amount and changes in the sample water. Dosage of Fenton reagent is decided on the reaction that is taking place. Once the reaction starts, the pH and OD values are calculated for every 10 min duration. This procedure is conducted for each sample of MB. All the final pH and OD values are noted down.

RESULTS AND DISCUSSION

The experimental programme was carried out by conducting tests on MB sample before and after the treatment. To find initial characteristics of MB sample water pH test and Colorimeter test are conducted. Initial characteristics of waste water were found as in Table 1 and Figure 2.

Effect of pH

The synthetic waste water prepared using methylene blue has a wide range of Hydrogen ion concentration values (pH) and the concentration of pH plays a predominant role in the colour removal efficiency**.** It was found that the reaction rates of Fenton oxidation of the dyes are rather slow in alkaline medium while they are fast in acidic medium [12]. In a particular study related to colour removal capacity by chemical oxidation, the maximum yield was obtained at pH 3.0 by the Fenton's oxidation process [13] (Table 2).

Figure 3 shows the pH reducing efficiency of Fenton reagent at different time intervals at 10, 20 and 30 min. It was found that increase in time is an important function of reduction in pH concentration. At the end of 10 min, the pH reducing efficiency was found as 39.02% at the lower concentration, it was observed as 40.02% and 53.66% at the end of 20 and 30 min of experiment time.

Table 1: Value of pH and OD for different concentration

Concentration of sample	pH value	Optical density
1 ppm	8.2	0.1
2 ppm	8.1	0.16
3 ppm	8.1	0.2
4 ppm	8.2	0.23
5 ppm	8.1	0.33

Table 2: Effect of pH values at different time intervals

Concentration	Initial pH Con	Final pH Con	Efficiency
10 min			
1 ppm	8.2	5	39.02
2 ppm	8.1	5.1	37.04
3 ppm	8.1	5	38.27
4 ppm	8.2	5.1	37.80
5 ppm	8.1	5.1	37.04
20 min			
1 ppm	8.2	4.9	40.24
2 ppm	8.1	4.7	41.98
3 ppm	8.1	4.6	43.21
4 ppm	8.2	4.4	46.34
5 ppm	8.1	4.2	48.15
30 min			
1 ppm	8.2	3.8	53.66
2 ppm	8.1	3.7	54.32
3 ppm	8.1	3.7	54.32
4 ppm	8.2	3.6	56.10
5 ppm	8.1	3.2	60.49

Figure 2: Image showing change in color after treatment

Even in the higher concentration of 5 ppm of MB same trend was witnessed. It was 33.04%, 48.15% and 60.45% at the end of 10, 20 and 30 min. So it was evidently proved that the concentration of pH was reduced even in higher concentration of MB on increased residence time of Fenton reagent.

Effect of decolouring capacity

Initial concentration of dyes is an important parameter in practical application. The effect of colour removing capacity of the Fenton reagent at different concentration of MB 1-5 ppm was investigated at different time intervals like 10, 20 and 30 min (Table 3).

In Figure 4 graph shows 100% efficiency in the lower concentration (1 ppm) when the experiment was conducted for 30 min. We can observe the change in OD values by addition of Fenton reagent (1:4:4 concentrations). The change in pH values indicate that the sample water has converted to acidic in nature. We can also find that about 100% color has been removed and that left color is due to

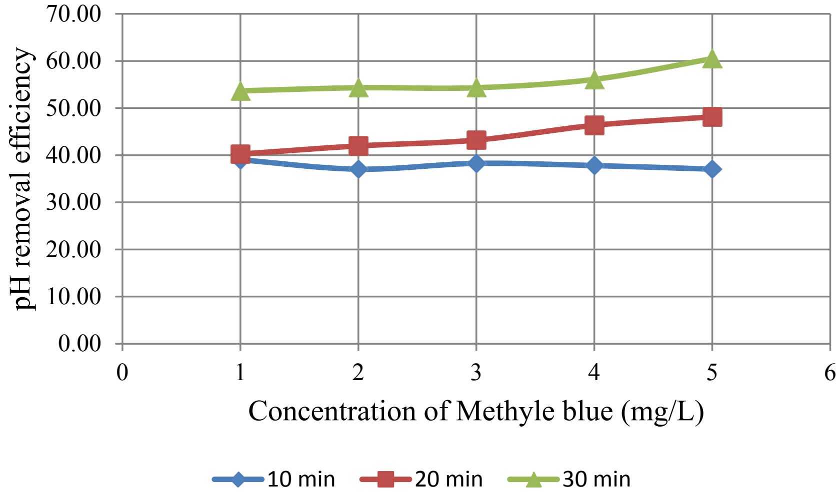

Figure 3: Effect of pH removal at different time intervals

Table 3: Table showing color removal efficiency of Fenton reagent at different time interval

Initial concentration	Initial OD	Final OD	Color removal efficiency
		10 min	
1 ppm	0.1	0.05	50.00
2 ppm	0.16	0.05	68.75
3 ppm	0.2	0.06	70.00
4 ppm	0.23	0.08	65.22
5 ppm	0.33	0.1	69.70
		20 min	
1 ppm	0.1	0.01	90.00
2 ppm	0.16	0.02	87.50
3 ppm	0.2	0.03	85.00
4 ppm	0.23	0.04	82.61
5 ppm	0.33	0.06	81.82
		30 min	
1 ppm	0.1	0	100.00
2 ppm	0.16	0.01	93.75
3 ppm	0.2	0.02	90.00
4 ppm	0.23	0.02	91.30
5 ppm	0.33	0.03	90.91

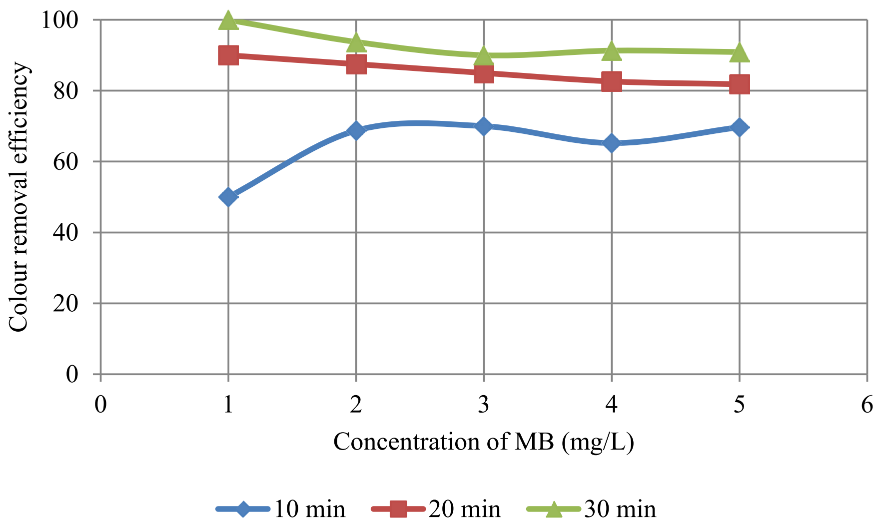

Figure 4: Graph showing relation between time and color removal efficiency

Fe^{3+} ions. This Fe^{3+} is due to addition of $FeSO_4$. Hence 5 ml of Fenton reagent for every 50 ml of synthetic waste water removes 90% of color. When the experiment was conducted for 10 min only 50% of color was removal, so the remaining 50% of color was found removed when it runs for additional 20 min. Even when the experiment was investigated for 20 min even 90% of color removal efficiency was witnessed. In the higher concentration of MB (5 ppm) trails conducted for 10 min delivers 70% of color removal efficiency, whereas 85% was found when it was analyzed for 30 min. In addition to this observation, increasing trend was observed color removal efficiency with reference different concentration in 10 min. But the efficiency was found decreased with respect to concentrations of MB in 20 and 30 min. In the higher concentration (5 ppm) the difference in color removal efficiency was not shown a big difference, in case of 10 min it was 69.70% for 20 min it was 81.82% whereas for 30 min it was found as 90.92%, so the ultimate difference between 10 min and 30 min was found to be 20%. So in order to reduce the time constraints in the experiments 20 min found to be the optimum duration for this investigation.

CONCLUSION

From the investigations we came to the following conclusions are drawn:

1) With the application of Fenton reagent as chemical oxidant it is possible to remove the color even up to 100%.
2) The effect of pH plays a significant role in decolourization as the solution turn to be acidic after the addition of Fenton reagent the process found to be very simple.
3) Fenton reaction is a time dependent process and along with time the color is removed more but the rate of color removal will tend to decrease after certain point.
4) Overall cost evaluations so far available indicate that AOP systems are not more expensive than the well-established technologies for pollutant abatement.
5) Based on the results observed from this experiment, the time plays a crucial role in the colour removal capacity. Among the three difference choices, 20 min found to be optimum for all concentrations.

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