Removal of Malachite Green Dye from aqueous solution by Fenton Oxidation

Sandeep Thakur [1], M.S. Chauhan [2]

[1]*Research Scholar, Department of Civil Engineering, Maulana Azad National Institute of Technology Bhopal, India- 462003.*
[2]*Professor, Department of Civil Engineering, Maulana Azad National Institute of Technology Bhopal, India- 462003.*

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Abstract - *In order to see the influence of different variable parameters (initial pH of the solution, Fe++ concentration and H_2O_2 concentration) and the efficiency to remove Malachite Green dye (Basic Green 4) from aqueous solution, Fenton Oxidation method was employed. Then different parameters were studied using known concentration (150 mg/l) and initial COD (256 mg/l) of prepared dye synthetic solution in a batch mode. The results showed a very high decolorization of 99.40% and the reduction of COD upto 100 % achieved at pH 12 and Fe++ concentration and H_2O_2 concentration of 400mg/l and 6 ml/l. This confirms the efficient removal of dye by Fenton oxidation.*

Key Words:Dyes, Fenton oxidation, Advance oxidation, Malachite Green Dye, COD, Color removal.

1. INTRODUCTION

Dyeing and finishing are the two chief processes usually applied in most of the textile industries generates great amount of wastewater contains strong color, dissolved and suspended solids and high chemical oxygen demand (COD) concentration. The disposal of these dye wastewaters causes a great problem for the industry as well as a threat to the environment.

The majority of synthetic dyes are noxious substances to human and aquatic life. In textile industries, due to low dye fixing efficiency of 60–90% on textile fibers, large amounts of unfixed dyes are released in effluents. In the estimates around 1–15% of the dye is released into wastewaters during dyeing and finishing processes [1]. The removal of dyes from colored effluent particularly from textile industries is one of the major environmental concerns these days and it is necessary to treat dye wastewater before discharged into water [2].

Malachite green (Basic Green 4 Dye) is one of the widely used dye which is used for dyeing silk, wool, leather, jute, and cotton, as a biological stain, as an acid-base indicator, as a dye for paper these vast use of Malachite Green result in its release to the environment through various waste streams. There are many harmful effect of this dye to environment and the human health such as when it is heated to decomposition it emits very toxic fumes of nitrogen oxide and hydrogen chloride. Ingestion causes diarrhea and abdominal pain. It is injurious to eyes, can cause bilateral blindness due to corneal problem [3]. Hence, Malachite green was chosen for this research work.

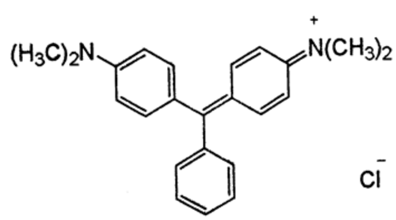

Fig-1: Molecular structure of Malachite Green Dye, [4] There are various techniques employed worldwide for removal of dyes from wastewater. The majority of these conventional methods is becoming inadequate and inefficient; because of the dye effluent contain mainly complex aromatic molecular structures. Dye compounds are usually made to resist fading on exposure to soap; water, light and this make them more stable against biodegradation [5]. There are number of physical, chemical and biological treatment processes employed for the treatment of dye wastewater like Adsorption [6], Chemical coagulation, Electrochemical treatments, Advanced oxidation processes (AOPs) including treatment with oxidizing agents, such as hydrogen peroxide (Fenton), ozone, UV light or their combinations, biological treatments such as anaerobic process, oxidation ponds, trickling filters, activated sludge process, etc. Physical methods such as Adsorption, Coagulation usually need additional chemicals which cause secondary pollution and a huge volume of sludge [7]. In these processes there is excess generation of huge amounts of sludge and increases the total dissolved solids in the effluent. In biological treatment the microorganisms such as algae, fungi, bacteria, and yeasts are capable to degrade certain type of dyes. But, the application of biological treatment is limited as they requires a large land area, has sensitivity toward toxicity of certain chemicals and treatment time is very high. Further, in general some dyes are toxic and are not easily biodegraded by biological process [8]. The sensitivity of biological treatment processes and secondary pollution caused by conventional chemical methods make advance treatment processes more popular.

The Fenton oxidation process is the well known advance oxidation process used in wastewater treatment. It was reported by Fenton over a century before for maleic acid oxidation:

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH$ ………………… (1)

In the presence of excess amounts of hydrogen peroxide the rate constant for the reaction of Fe ion with H_2O_2 is more and Fe (II) oxidizes to Fe (III) in a few seconds to minutes. Fe (III) catalytically decomposes hydrogen peroxide and generates again hydroxyl radicals according to the reactions:

$Fe^{3+} + H_2O_2 \leftrightarrow H^+ + Fe{-}{-}OOH^{2+}$ …………………(2)

$Fe{-}{-}OOH^{2+} \Rightarrow HO_2 + Fe^{2+}$ ………………… (3)

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH$ ………………… (4)

For this reason, it is assumed that the majority of waste destruction catalyzed by Fenton's reagent is simply a Fe (III)–H_2O_2 system catalyzed destruction method, and Fenton's reagent with an overdose of H_2O_2e is Fe(III)–H_2O_2 process also known as Fenton-like reagent. Therefore, the ferric ion can replace the ferrous ion in Fenton's reagent. For hydrogen peroxide decomposition iron salts act as a catalyst, in further reactions Fe (II) regenerated. In the previous studies it has been observed that Fenton's reagent can be utilized as a promising oxidant for soil contaminants. Fenton's reagent is capable to destroy different phenols, herbicides, and nitrobenzene in water also reduces COD in municipal wastewater. The use of Fe (II)/H_2O_2 as an oxidant for treatment of wastewater is attractive due to the facts that:

1. Iron is a very abundant and non-toxic element.
2. Hydrogen peroxide is eco friendly and simple method.

Thus, the Fenton process is very effective for generation of Fe(III)–H_2O_2 OH radicals; On the other hand, it involves consumption of single molecule of Fe^{2+} for every OH radical generated, require a high amount of Fe(II) [9].

In this study, effect of Fenton Oxidation has been examined with reference to the removal of Malachite green dye from a synthetic solution.. Effect of various operating parameters such as initial pH, Fe^{++} concentration, H_2O_2 concentration and initial dye concentration Fenton Oxidation, where examined and optimized. The optimum values of these parameters were primarily determined on the basis of color and COD removal.

2. MATERIALS AND METHODS

The Fenton method was conduct in 1000 ml beaker containing 500mL sample of prepared synthetic dye wastewater. The Fenton oxidation process serves both oxidation and coagulation functions. In the Fenton oxidation, H_2O_2 solution and $FeSO_4 \cdot 7H_2O$ powder (Merck, 30%) was added to a sample, and then it was mixed slowly for 5 min and then allowed for sedimentation for 30 minutes to find the removal efficiency of color and COD while using Fenton oxidation.

The dye solution was prepared by dissolving Malachite Green (Basic Green 4) in distilled water. The dye was purchased from Oswal Udhyog, Mumbai, India was used as such without further purification. For the preparation of sample 150 mg of the dye was dissolved per liter of distilled water which is close to real industrial dye effluent.

Intensity of color is measure based on various absorbance λ (nm) which are characteristics wavelength of various color. A UV-VIS Doublebeam spectrophotometer (Systronics AU-2701) was employed to measure the maximum absorption wavelengths for Malachite Green dye. Maximum absorption of Malachite Green dye used in experiments was λ_{max} 617 nm.

Color removal efficiency can be determined from the formula, Color removal efficiency (%) =100x $\frac{(C0-C)}{C0}$

Where, C_0 and C are the concentrations of dye before and after electrocoagulation respectively.

COD was measured by closed reflux method as given in Standard Methods for the Examination of Water and Wastewater Analysis Manual 20th Edition [10] by suitable dilution of wastewater in distilled water if needed.

3. RESULTS AND DISCUSSION

3.1 Effect of pH on Basic Green 4 Dye

To determine the optimum value, pH was changed between 2 to 12. The pH for both Fenton oxidation and coagulation experiments was adjusted with 0.1 N H_2SO_4 and NaOH. It has been observed that Fenton oxidation takes place in the acidic pH range for this particular dye so the results were shown from pH 6 to 12 because at lower pH less than 7 no significant color removal was observed. Result shows 99.45% color and 87.50% COD removal in the range of 12.00 pH. Chart 1 shows percentage removal of color and COD at various pH. When Fenton process was applied to Basic Green the removal efficiency was better in higher pH. High pH results in a decrease of free iron species in the mixed solution, which impedes the further reaction of $Fe^{2+}$with H_2O_2 and the regeneration of $Fe^{2+}$from Fe^{3+}. On the other hand, the low removal efficiency at lower pH is due to the formation of the complex species $(Fe^{2+} (OH) (H_2O)_6)^+$ which reacts more slowly with H_2O_2 than $(Fe^{2+} (OH) (H_2O)_5)^+$. In addition, the scavenging effect of .OH by H^+becomes more prominent at a relatively low pH level, which hinders the oxidation as well. At lower pH, the reaction of hydrogen peroxide with Fe^{2+} is seriously affected causing the reduction in hydroxyl radical production [11].

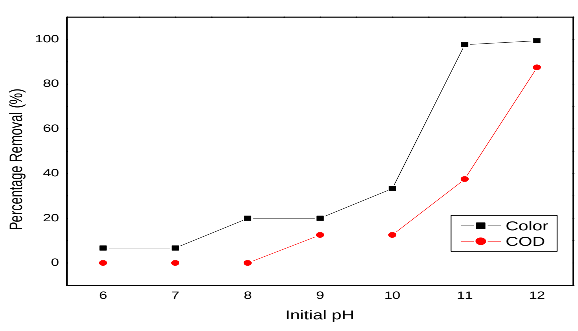

Chart – 1: Percentage removal of color and COD on varying initial pH

3.2 Effect of Fe^{++} Concentration on Malachite Green Dye

Experiments were conducted to see the removal of color and COD under different ferrous (Fe^{++}) dosages at a constant H_2O_2 dosage of 6 ml and 12 pH. Fe^{++} dose was varied from 100mg, 200mg, 300mg, 400mg and 500mg in experiments. At Fe^{++} dose of 200 mg, the color removal was 99.54% and COD removal was 87.50 % respectively. It is obvious that the ferrous dosage significantly affects the color and COD removal. Chart 2 shows the decolorization of dye and decreases in COD with varying Fe^{++} concentration. Both COD and color removal were increased with Fe^{2+} dosage. It might be clarified by the redox reactions since $HO^{\bullet}$ radicals may be scavenged by the reaction with the hydrogen peroxide or with another Fe^{2+} molecule. The lower degradation capacity of Fe^{2+} at small concentration is probably due to the lowest $HO^{\bullet}$ radicals production available for oxidation [12]. However, further addition of Fe^{2+} above optimum dose there is a decrease in removal efficiency due to unbalancing of the oxidant [13] *and* the overdose of Fe^{2+}led to the self-scavenging of **.**OHas shown in the reaction : **.**OH + $Fe^{2+} \rightarrow Fe^{3+} + OH^-$ [11].

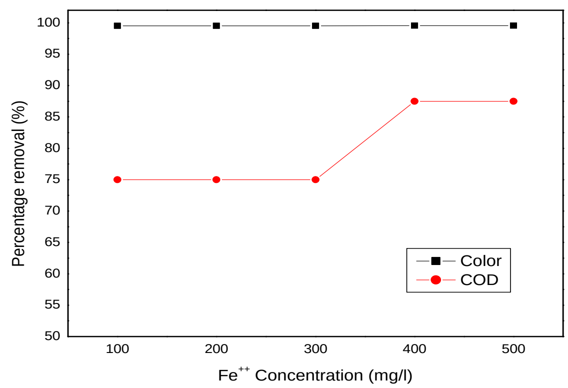

Chart – 2: Percentage removal of color and COD on varying Fe^{++} concentration

3.3 Effect of H_2O_2 dose on Malachite Green Dye

Experiments were done at different H_2O_2 dosages to see its effect on removal of color and COD. The pH was controlled at 2 and the ferrous dosage was 400 mg/l. In dose 6.00 ml H_2O_2, the 99.40 % color and COD removal reached upto 87.51 %, respectively. Chart 3 shows the decolorization of dye and decreases in COD with varying H_2O_2 concentration. As the H_2O_2 concentration increases, the decolorization of dye enhanced because more Fe^{++} and OH are formed at higher H_2O_2 concentrations in solution. On the other hand, when the H_2O_2 concentration is greater, the degradation rate of dye somewhatget reduced. This can be understand by the scavenging effect when using a higher H_2O_2 concentration [14].

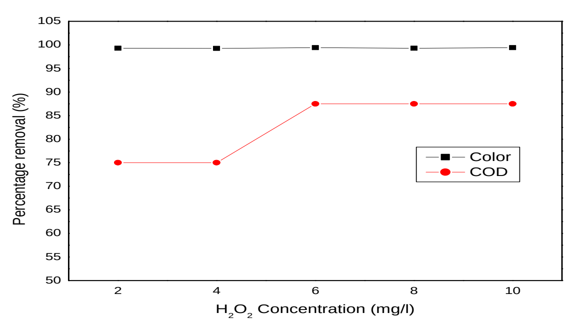

Chart – 3: Percentage removal of color and COD on varying H_2O_2 concentration

3.4 Effect of Initial concentration of Dye on Malachite Green Dye

The effect of various dye concentration on color and COD removal has been be investigated. Under optimized operational conditions i.e. optimum pH, optimum Fe^{++} and H_2O_2 Concentration, the concentration of dyes varied from 50 mg/l, 100 mg/l, 200 mg/l, 250 mg/l, and 300 mg/l. It has been observed that on varying concentration of dye there is not that much difference in the color removal from Malachite Green dye more than 99 % color removal was achieved. In case of COD it is seen that higher the dye concentration, lower the COD removal efficiency. This decrease in removal efficiency is due to the formation of insufficient number of hydroxyl radicals. The probable reason is that when the initial concentration of dye is increased, the •OH concentration is not increased equally [15]. Therefore, it is quite clear that, the lower is the dye concentration the better is the decolorization efficiency. Chart 4 shows percentage removal of color and COD on varying initial concentration of dye.

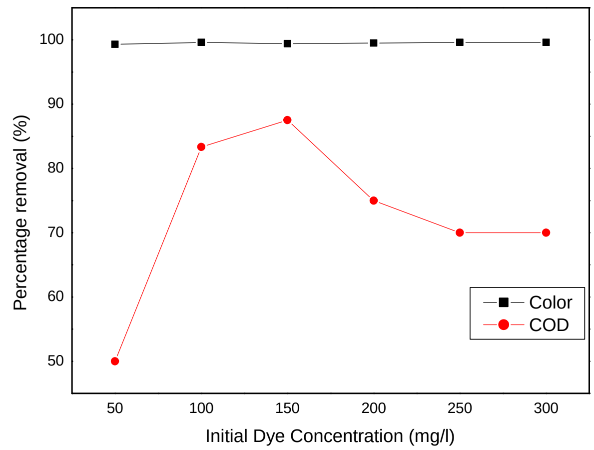

Chart – 4: Percentage removal of color and COD on varying initial dye concentration

4. CONCLUSION

Fenton's oxidation was carried out to eliminate malachite green dye from the aqueous solution synthetically prepared in the laboratory. This work summarizes the results of the studies performed on malachite green dye sample wastewater. The results showed that FO process is veryefficientin removing color and COD from dye. At optimum conditions pH 12 and Fe++ concentration of 400mg/l andH_2O_2 concentration of 6 ml/l removal of color (99.40%) and COD (100 %) was achieved. Hence, it is suggestedthat the Fenton process be better used as a decolorizingagent for dyes.

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Sandeep Thakur, Research Scholar Department of Civil Engineering, Maulana Azad National Institute of Technology Bhopal. Email: sandeep.manit@rediffmail.com

Dr. M.S. Chauhan, Professor, Department of Civil Engineering, Maulana Azad National Institute of Technology Bhopal.