REMOVAL OF COLOR AND COD OF DYE MANUFACTURING WASTEWATER BY COMBNATION OF FENTON OXIDATION AND SBR

Kunj S. Patel[1], Neha R. Patel[2], Arti N. Pamnani[3]

[1] *M.E. Student, Environmental engineering, BVM Engineering College, Vallabh Vidyanagar, Gujarat*
[2] *Associate Professor, Civil Engineering Department, BVM Engineering College, Vallabh Vidyanagar, Gujarat*
[3] *Lecturer, Civil Engineering Department, B &B Inst. of tech, v.v.nagar, Gujarat*

ABSTRACT

A dye is a natural or synthetic substance used to add a color to or change the color of something. Synthetic dyes are further described as Acetate rayon dyes, Acid dyes, Azoic dyes, Basic dyes, Direct dyes, Mordant or chrome dyes, Lake or pigment dyes, Sulfur or sulfide dyes and Vat dyes. More than 70% of total dye is azo dye. Maharashtra and Gujarat represent 90% of dyestuff generation in India because of the accessibility of raw materials and dominance textile industry in these regions. They are considered as a more perilous wellspring of environmental issue. High chemical oxygen demands (COD), biochemical oxygen demands (BOD), suspended solids and intense color because of color intermediates or deposits and assistant chemicals describe from the dye production process. As synthetic dye are found to be water soluble which can give color to water this can be seen when even in small amount, dye are found to be poisonous and carcinogenic when disposed directly to water source, dye are often found in waste water in manufacturing unit as well as textile dye process. It is necessary to remove dye from waste water before disposal as they are hard to remove biologically and can be harmful for further use of water. Fanton oxidation converts dye molecules into simple molecular structures, which can easily degrade by microorganisms. This study was done combining both e Fenton oxidation and biological(aerobic) treatment for effective treatment line.. Experiments were carried out to find the optimum conditions for Fenton oxidation and Aerobic treatment. The optimum conditions are as follows for Fenton Oxidation pH is 3, $FeSO_4$ concentration is 60 ppm, H_2O_2 concentration is 500 ppm and time is 45 minutes. 57.73% Color and 40.06% COD reduction is achieved in Fenton Oxidation. For aerobic treatment Sequential Batch Reactor(SBR) is applied. Experiments carried out to find out reaction time of SBR. Optimum reaction time is 24 hr. with 2500 mg/L MLSS. After SBR process Further 70% and 66% reduction of Color and COD respectively is achieved to Fenton oxidation treated wastewater. And the total reduction in Color and COD achieved are 87.8% and 79.6% respectively.

Keyword: - *Fenton Oxidation, SBR, Dye wastewater, $FeSO_4$, H_2O_2*

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1. INTRODUCTION

Dye is a natural or synthetic substance used to add a color to or change the color of something. Mankind has utilized colors for a many years and the first known utilization of a, colorant is accepted to be by Neanderthal man around 1,80,000 years ago. In any case, the primary known utilization of a natural colorant was much later, being almost 4000 years back, when the blue color indigo was found in the wrappings of mummies in Egyptian tombs [1]. Dye industry is also known as Dyestuff industry, which is one of the quickly developing commercial industry because of development of material textile, ceramic and cosmetic industry. Colors are broadly utilized in industries like textile industries, printing industries, food Industries, cosmetic Industries, leather industries, paper industries and so forth [2]. There are more than 100,000 sorts of business dye produce in globe out of which 70% are Azo dye as they are generally utilized [3].

The Indian dyestuff industry is just around 40 years of age however a couple MNCs set up dyestuff units in the pre independence era. Like any other chemical industries, the dyestuff industry is additionally exceedingly divided. In India small, medium and large industrial units are producing dye and dye intermediates [5]. In India 65% of dye produce by organized industry and 35% of dye produced by unorganized industry. The Indian dyestuff industry is comprised of around 1000 small scale units and 50 large scale units, who produce around 130,000 tons of dyestuff. The real clients of dye in India are textiles, paper, plastics, printing ink and foodstuffs. The textile business devours around 80% of the dye because of high demand for polyester and cotton, comprehensively [4] [5]. Maharashtra and Gujarat represent 90% of dyestuff generation in India because of the accessibility of raw materials and dominance textile industry in these regions. More than 750 units are occupied with the manufacturing of the dyes in Gujarat, adding to more than 60% of Indian exports of dye and dye intermediates [6].

Dyes are mainly bifurcated in two types natural and synthetic. Synthetic dyes are further described as Acetate rayon dyes, Acid dyes, Azoic dyes, Basic dyes, Direct dyes, Mordant or chrome dyes, Lake or pigment dyes, Sulfur or sulfide dyes and Vat dyes [2]. The principle effluent generated is from filter press and gear washing after batch operation. For the most part, wastewater from dye manufacturing is exceedingly variable in creation and contains a substantial number of various mixes, for example, raw materials, intermediate products, and even the dyes themselves. They are considered as a more perilous wellspring of environmental issue. High chemical oxygen demands (COD), biochemical oxygen demands (BOD), suspended solids and intense color because of color intermediates or deposits and assistant chemicals describe from the dye production process [5]. As synthetic dye are found to be water soluble which can give color to water this can be seen when even in small amount, dye are found to be poisonous and carcinogenic when disposed directly to water source, dye are often found in waste water in manufacturing unit as well as textile dye process. It is necessary to remove dye from waste water before disposal as they are hard to remove biologically and can be harmful for further use of water [7].

Conventional treatments for dye wastewater are coagulation, flocculation and adsorption on activated carbon. Membrane separation and ion exchange are recovery processes for dye wastewater. Advance oxidation process, selective bioadsorbents are the emerging removal processes for treatment of dye wastewater. Advance Oxidation (AOP) Process is one of the promising Technology foe removals of dye from wastewater [7].

Fenton Oxidation is one of the Advance Oxidation Process(AOP). Fenton Treatment is essential for Treatment of dye wastewater. Fenton process converts dye molecules into simple end products or biodegradable products. So aerobic treatment followed by fanton process is very effective. Fenton process reduces COD and Color of dye wastewater upto very effectively [14, 15, 16, 17, 18]. As in Fenton process, its produce OH' radical and OH' radical is highly unstable. OH' radical break the dye molecules and converts them into simple end products or simple biodegradable products [8]. SBR (Sequential Batch Reactor) is followed by Fenton process as aerobic process. SBR is modification of Activated Sludge Process. Operation of SBR is simple than ASP and effectively reduce the COD and Color [13]. Though Fenton process is capable for breaking of dye molecules the main handicap lies is the high cost of reagent, energy and production of sludge which contain high amount of Fe (III), which needs to be managed by safe disposal methods [10]. Hence, there is need for further research for finding an efficient and economical treatment method for complete mineralization of dye. Mineralization of azo dye can be achieved using AOP–aerobic sequential treatment. Oxidation treatment prior to biodegradation delivered the best performance for treating the dye effluent rather than only biological and biological prior to the Oxidation treatment [12]. Dye contains high organic load and to remove this biological process are widely uses. But due to the toxicants (like phenol and aromatic compounds) in the dye waste water, biological process can't be used directly so that chemical treatment like oxidation process are used as an first phase and in second phase biological treatment is applied.[11]. Most of the previous researchers have focused on only one method of treatment, i.e. either biological process or advanced oxidation process for treating recalcitrant compound. Whereas the preferred method for treatment of recalcitrant compound is to use AOP (for partial degradation) followed by aerobic biological process. In recent years, the combined Fenton-SBR process has been used to treat dyestuff, landfill leachate, textile effluent, antibiotic wastewater, recalcitrant wastewater and bamboo industry wastewater.

2. MATERIAL AND METHOD

2.1 Materials

Wastewater is collected from Durga Dye Chem Industry, located at G.I.D.C. Kalol, Dist - Gandhinagar, Gujarat. The effluent generates from filter press and washing of equipments during production of dye. Color and COD of industry are upto 3600 to 3750 pt.co. unit and 4150 to 4400 mg/l respectively.

$FeSO_4$, H_2O_2, and H_2SO_4 and other equipments are provide by Samata Consultancy, Gandhinagar, Gujarat

10% $FeSO_4$ solution is made by dissolving 100 gm $FeSO_4$ into 1000 ml water and Dosage of $FeSO_4$ is applied as 100 mg/l dosage of $FeSO_4$ is 1 ml of 10% $FeSO_4$ Solution. 80 mg/l dosage of $FeSO_4$ is 0.8 ml of 10% $FeSO_4$ Solution. Concentrated (30%) H_2O_2 is used, The dosages were taken in ppm(mg/l). 1.33 ml of Concentrated (30%) H_2O_2 is equal to 400 ppm (mg/l) H_2O_2 dosage. 1.66 ml of concentrated (30%) H_2O_2 is equal to 500 ppm (mg/l) dosage.

For SBR treatment Sludge collected from the nearer sewage treatment plan from after the secondary clarifier sludge bottom. Reactor capacity: 10 liter plastic reactor Volume: Added 5 liter waste treated by Fenton's oxidation. MLSS: Added 1.44 liter sludge for maintaining the 2500 MLSS concentration in 5 liter dye wastewater. After the filling phase there having every 2 hour sample being collected provide 30 minute settlement and after that supernatant is measure for COD. DO is maintained about 2 mg/l and MLSS is maintained 2500 mg/l. Every 2 hours sample is collected and after settlement the samples are preserved with 1 N H_2SO_4 up to pH 2 preserved sample is measure for COD and Color

2.2. Methods

Experimental study is designed to obtain maximum COD and Color removal at optimum pH, Time, $FeSO_4$ dosage and H_2O_2 dosage for Fenton oxidation with 5 liter wastewater volume. pH, COD and Color are measured by IS 3025 (p - 11) : 1983, IS 3025 (p-58) : 2003, IS 3025 (p-4) : 1983 Methods respectively. After getting the optimum values of H_2O_2 dosage, $FeSo_4$ dosage, pH, and Time, the Fenton Oxidation is done 5 times with optimum conditions and Removal of COD and Color is measured. The Fenton Oxidation treated wastewater is than applied to SBR to obtain further removal in COD and Color.

In SBR treatment, Reactor capacity: 10 liter plastic reactor Volume: Added 5 liter waste treated by Fenton's oxidation. MLSS: Added 1.44 liter sludge for maintaining the 2500 MLSS concentration in 5 liter dye wastewater. After the filling phase there having every 2 hour sample being collected provide 30 minute settlement and after that supernatant is measure for COD. DO is maintained about 2 mg/l and MLSS is maintained 2500 mg/l. Every 2 hours sample is collected and after settlement the samples are preserved with 1 N H_2SO_4 up to pH 2 preserved sample is measure for COD and Color. In SBR fill phase is of 10 minutes, settle phase is of 30 minutes, Decant is of 10 minutes. The experiment is carried out to find out optimum reaction time for SBR.

3. RESULT AND DISCUSSION

Optimum conditions for variable parameters are found for Fenton oxidation and SBR to remove Color and COD from Dye manufacturing wastewater. The optimum value of pH, Time, Concentration of H_2O_2, Concentration of $FeSO_4$ are found for Fenton oxidation and optimum Reaction time, HRT are found for SBR treatment.

3.1 Effect of pH on Color and COD Removal

$FeSO_4$ concentration is 30 ppm, H_2O_2 concentration is 300 ppm, Time is 1 hr, Initial Color is 3670 pt.co. unit and Initial COD 4290 mg/l. it is found that with decrease in pH the color and COD removal increases. At 2 and 3 pH Color and COD values of wastewater are 2035 pt.co unit and 3028.7 mg/L and 2113.9 pt.co. unit and 2732.7 mg/L respectively. pH value 3 is optimum for both Color and COD reduction. The reduction showed in Figure 1. pH 3 is optimum.

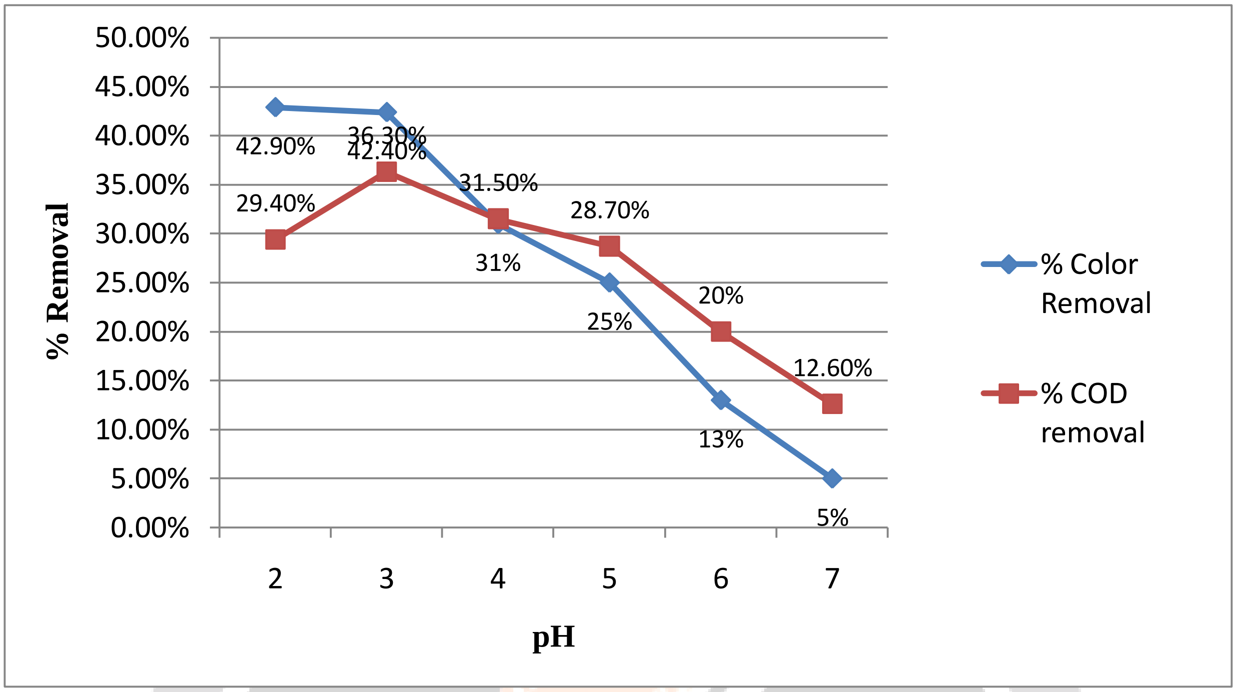

Figure 1: effect of pH on Color and COD reduction

3.2 Effect of $FeSO_4$ Concentration on color and COD removal

.pH is 3, Concentration of H_2O_2 is 300 ppm, time 1 hr, Initial Color is 3670 pt.co. unit and Initial COD is 4290 mg/L. When experiment carried out to find optimum $FeSO_4$ concentration, it is found that 60 ppm concentration is optimum. At 60 ppm $FeSO_4$ concentration Color and COD values are 1520 pt.co. unit and 3011.5 mg/L respectively. Showed in Figure 2 the reduction of Color and COD reduction. 60 ppm $FeSO_4$ dosage is optimum.

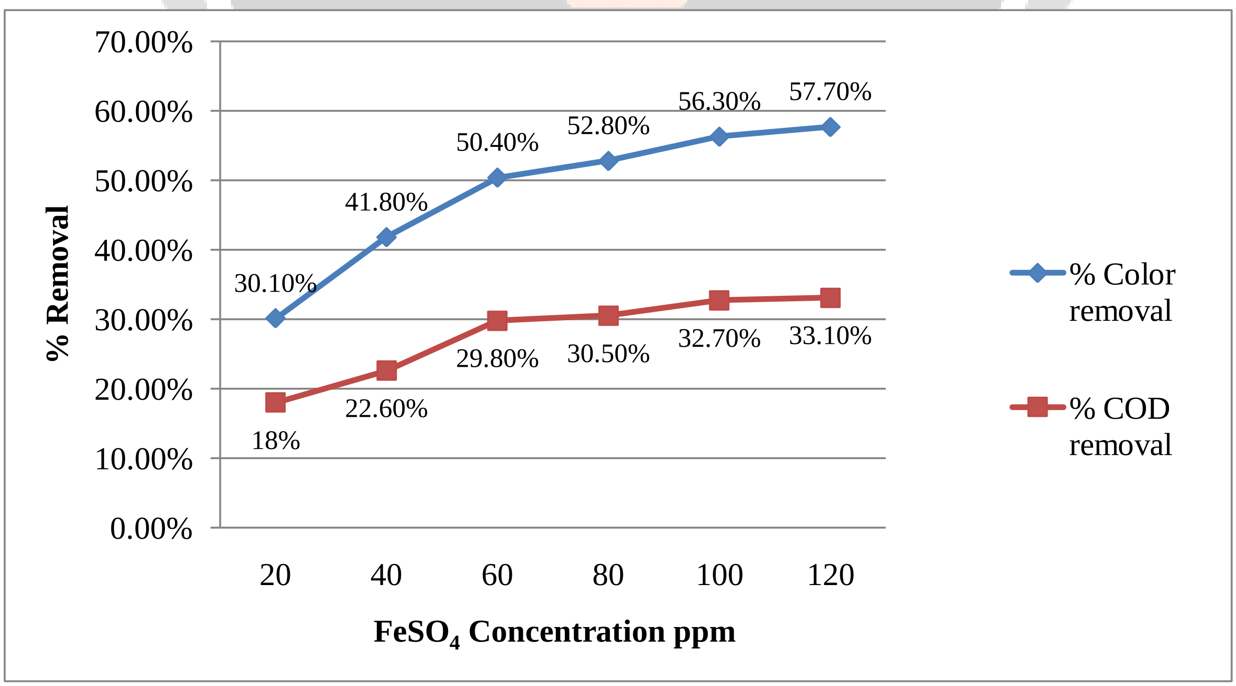

Figure 2: Effect of $FeSO_4$ concentration on Color and COD reduction

3.3 Effect of H_2O_2 concentration on Color and COD removal

pH is 3, $FeSO_4$ concentration is 60 ppm, time 1 hr, Initial Color is 3670 pt.co. unit and COD is 4368 mg/L. When experiment carried out to find optimum H_2O_2 concentration, it is found that 500 ppm concentration is optimum. At 500 ppm H_2O_2concentration Color and COD values are 1493 pt.co. unit and 2542 mg/L respectively showed in figure 3. 500 ppm H_2O_2 dosage is optimum.

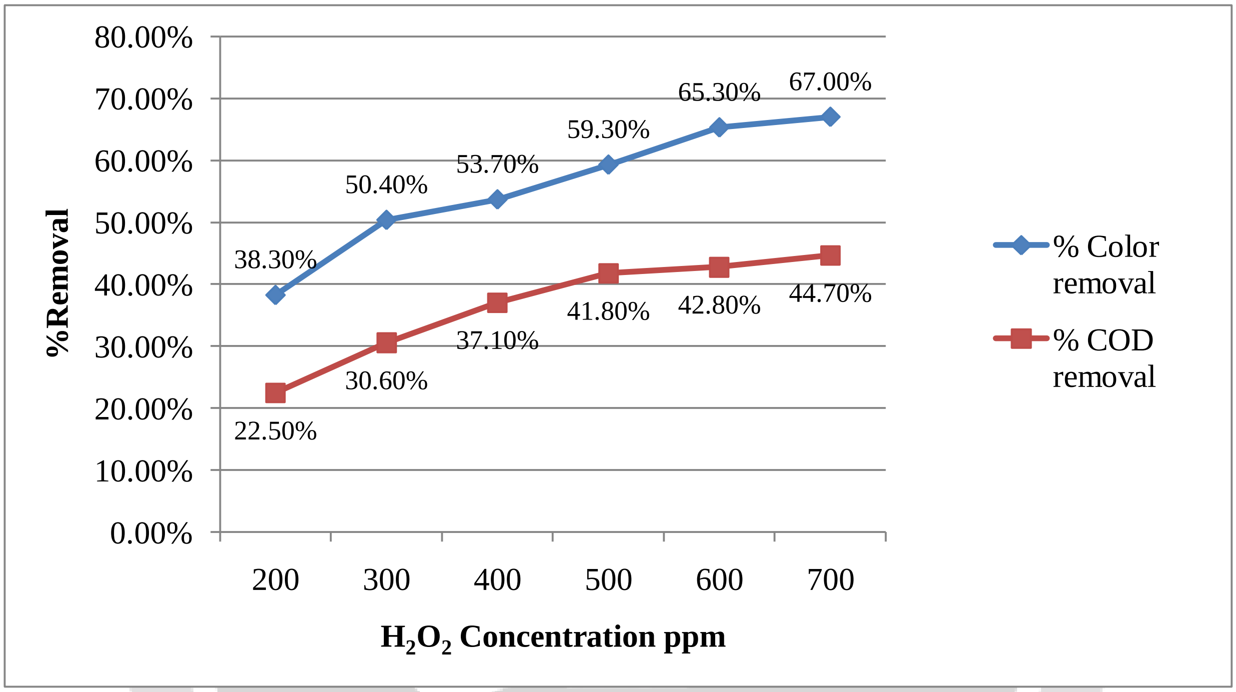

Figure 3: Effect of H_2O_2 Concentration on Color and COD reduction

3.4 Effect of Time on Color and COD removal

pH is 3, $FeSO_4$ concentration is 60 ppm H_2O_2 concentration is 500ppm, initial Color is 3650 pt.co. unit and initial COD is 4382 mg/L. When experiment carried out to find optimum Time, it is found that 45 min is optimum. At 45 min time interval Color and COD values are 1547 pt.co. unit and 2637.9 mg/L respectively showed in figure 4. Optimum time foe Fenton oxidation is 45 minutes.

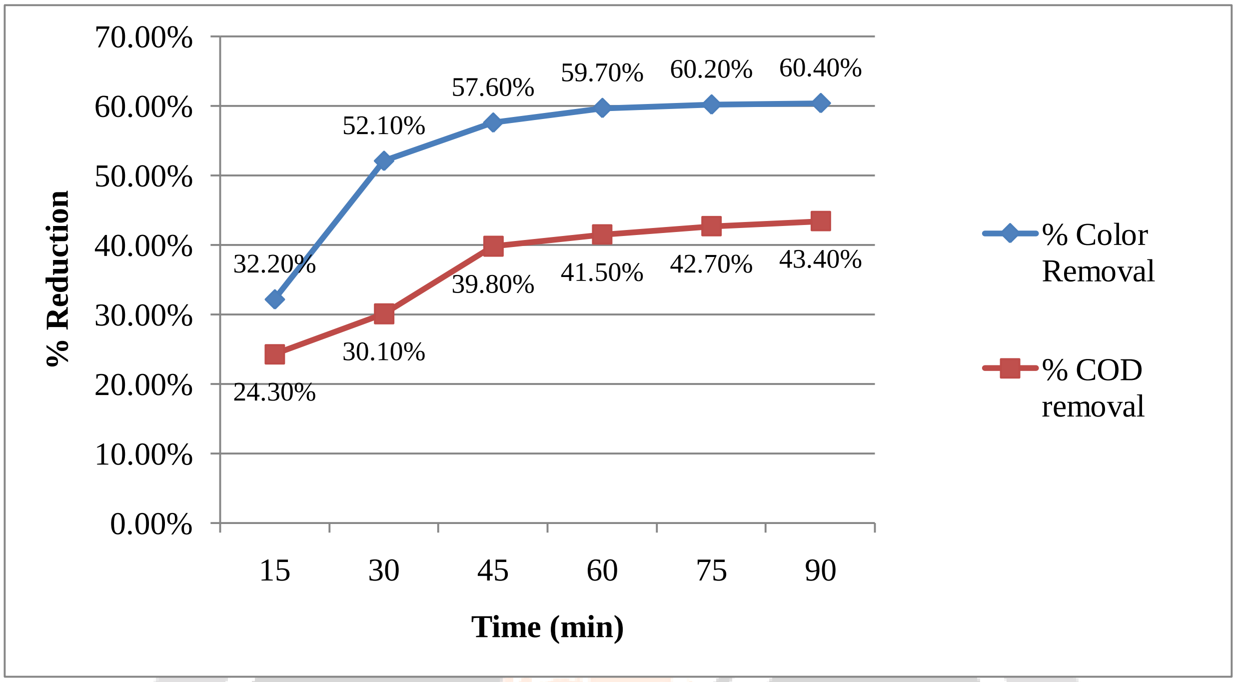

Figure 4: effect of time on Color and COD reduction

3.5 Average Reduction in Fenton Oxidation

After getting optimum condition for Fenton Process, Fenton oxidation is done five times with dye manufacturing wastewater and average reduction in Color and COD is calculated. Average Color reduction is 57.73%, and average COD reduction is 40.06% showed in table 1.

Sr. No	Initial Color (pt.co. unit)	Final Color (pt.co.unit)	% reduction	Initial COD mg/L	Final COD mg/L	% Reduction
1	3650	1547	57.60%	4382	2637	39.80%
2	3657	1534	58.03%	4423	2644	40.22%
3	3643	1536	57.83%	4397	2624	40.31%
4	3653	1550	57.56%	4386	2635	39.92%
5	3669	1554	57.64%	4372	2620	40.06%
Average			**57.73%**			**40.06%**

Table 1: average reduction through Fenton oxidation

3.6 Reaction Time in SBR

In SBR process takes place in 5 phases fill, react, settle, decant and idle. Experiment is carried out to find the reaction time of SBR for Fenton treated dye wastewater. In SBR the MLSS is 2500 mg/L maintained. Three times running carried out to find out reaction time. Samples were taken when SBR reactor in reaction phase, taken sample than allowed to settle for 30 minutes than after Color and COD were measured. Samples were taken in 2 hr interval. Figure 5, 6 and 7 shows the reduction in Color and COD with the different reaction time. 24 hr reaction time is optimum.,

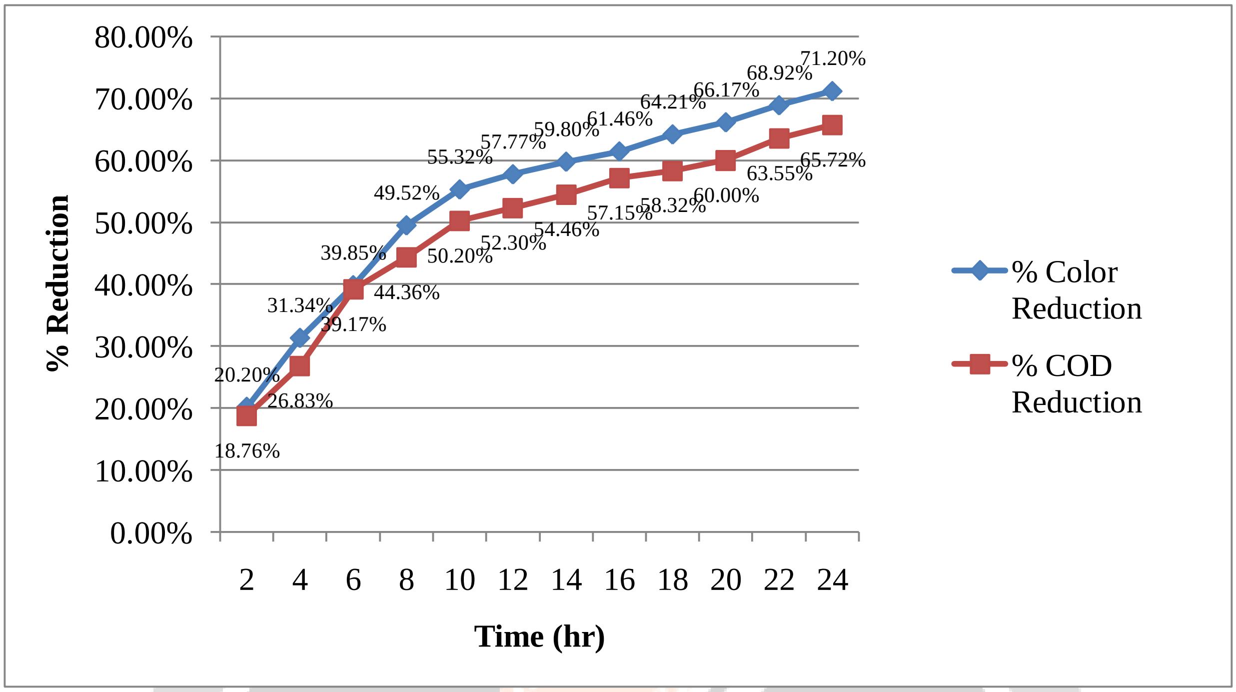

Figure 5: Trial 1: Reduction in COD and Color in SBR

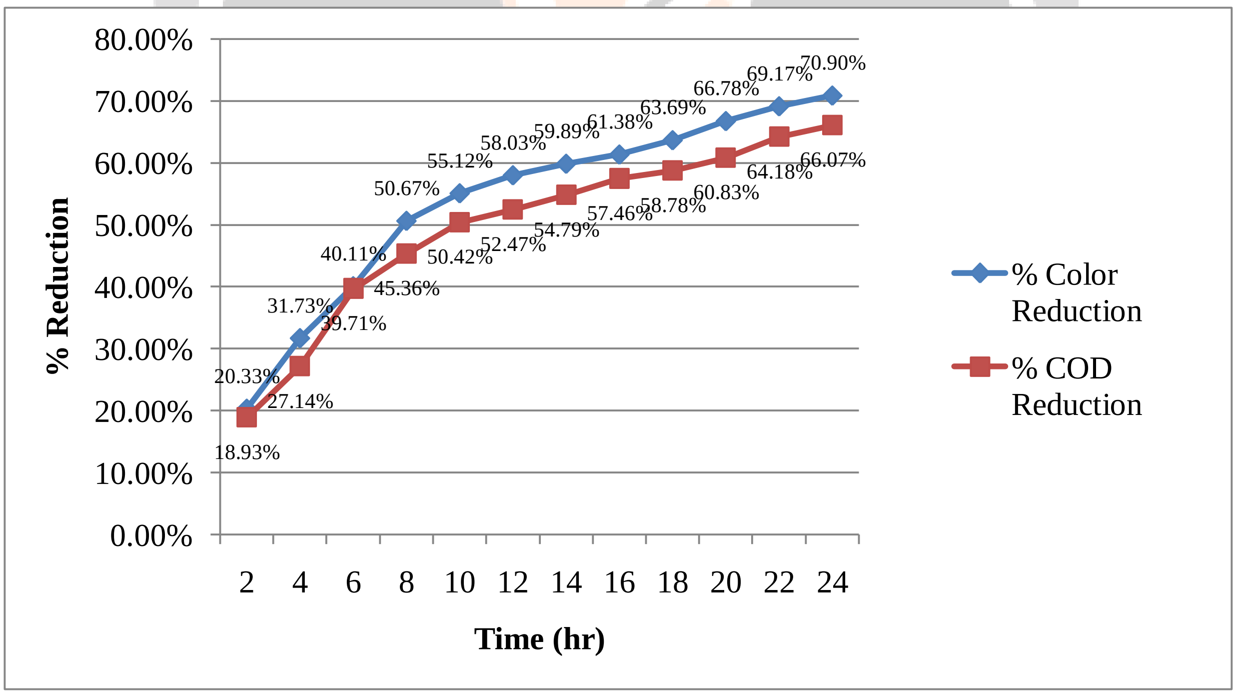

Figure 6: Trial 2: Reduction in COD and Color in SBR

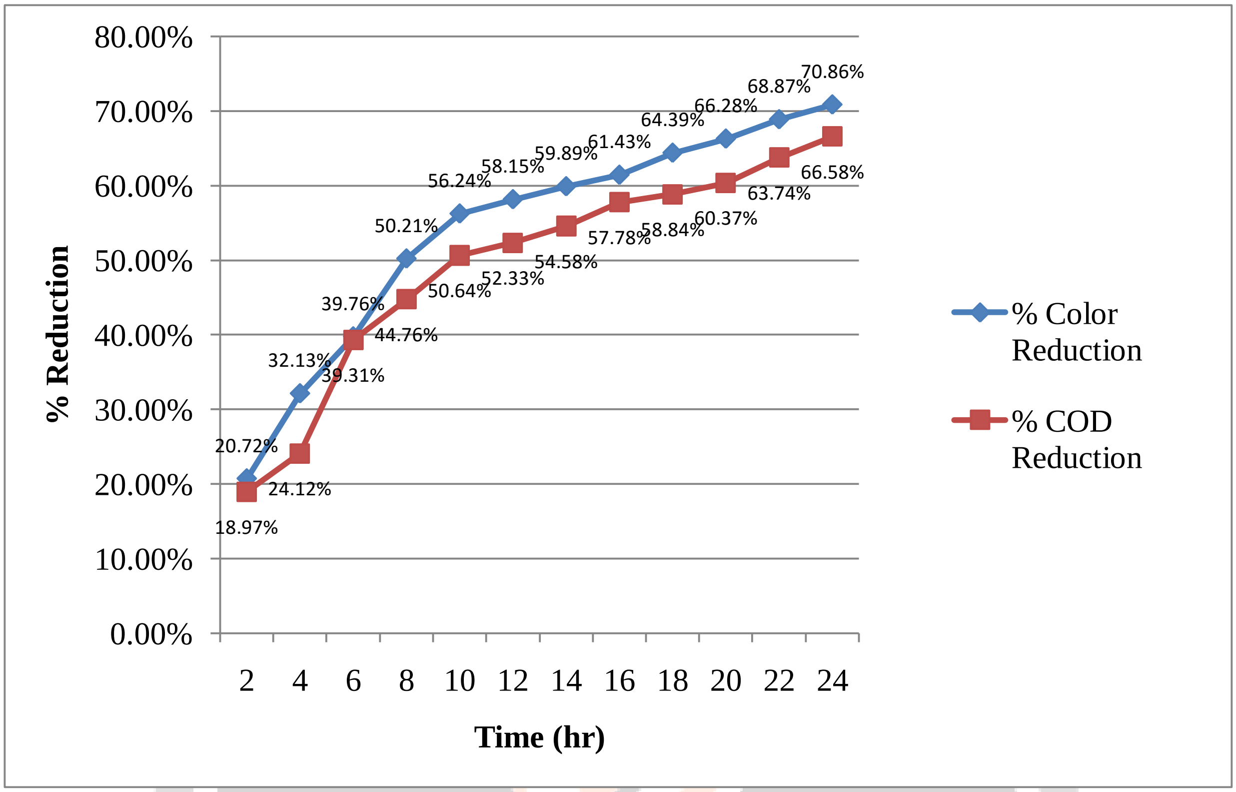

Figure 7: Trial 3: Reduction in COD and Color in SBR

5. Conclusion

From the above Experiments it is found that for real dye manufacturing industry wastewater the combination of Fenton and aeration Treatments are very effective. In Fenton oxidation average Color and COD reduction is 57.30% and 40.03% respectively. The optimum conditions for Fenton process are ph 3, $FeSO_4$ Concentration is 60 ppm, H_2O_2 concentration is 500 ppm and reaction time is 45 minutes. The Fenton treated wastewater than applied to SBR unit, where further reduction in Color and COD is achieved. 70% and 66% further reduction is achieved of Fenton treated wastewater of Color and COD respectively. The total reduction in Color and COD are 87.8% and 79.6% respectively.

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