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# Treatment of Dye Wastewater by AOP's

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***Abstract****: The study was carried out on dye wastewater treated by AOPs (advanced oxidation process) for the removal of residual COD on a laboratory scale. This study compares the treatment efficiency of COD removal by Fenton's treatment & combined Fenton & Ultrasonic cavitation performed at the same time interval. Raw wastewater showed COD around 2800 – 2900 mg/l. The effect of different parameters & dosage combinations such as pH, COD/ $H_2O_2$ & $H_2O_2/Fe^{+2}$ were analyzed. About 81% reduction in COD is observed at pH 3, COD: $H_2O_2$ as 2:1 and $H_2O_2$: $Fe+^2$ as 10:1 by Fenton's treatment & 88% by combined Fenton & Sonolysis treatment. Hence, it is suggested that combined Fenton & Ultrasonic cavitation proves to be more efficient treatment for COD reduction and thereby improving biodegradability of the wastewater.*

***Keywords: Dye wastewater, COD removal, Advanced Oxidation Process, Fenton's treatment, Ultrasonic cavitation***

## 1. Introduction

Dye industry consumes maximum amount of water in dyeing & finishing process. The textile effluents consists of high TDS, COD, chloride, BOD, colour, surfactants and are refractory organic matter due to which these cannot be used as carbon source neither as an energy source by micro-organisms. Conventional treatment of textile effluent is not effective due to the complex structure of dyes and less biodegradability also when COD is high. Therefore, Advanced Oxidation Process have been widely used as in generating hydroxyl ions (OH•) as a primary oxidant. AOPs are applied as an alternative to achieve reduction in COD & eventually improve biodegradability of the wastewater.

The two AOPs used are Fenton treatment & Ultrasound cavitation. Fenton's reagent as they effective to decolourize wastewater & reducing COD thereby treating various industrial wastewaters in generating hydroxyl ions (OH• ).Fenton's reagent refers to aqueous mixture of Fe (II) and hydrogen peroxide.The basic mechanism of Fenton's treatment includes oxidation, chemical coagulation of dye molecules ,therefore degrading organic pollutants.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\cdot + OH^-$$

The Hydroxyl radical is very strong and attacks on organic compounds and thus yields to reduction in colour of the dye or even colourless. It has also been studied that Fenton's treatment is quite efficient to treat wastewater having >5000 mg/l COD and removal of AOX (Adsorbable Organic Halogen) but the most important point in this treatment is that pH should be 2-3.High concentration of $H_2O_2$ acts like a radical scavenger while low concentration of $H_2O_2$ is not enough to COD. The $H_2O_2/Fe^{+2}$ concentration ratio 10:1 is advantageous for removal of AMX, AMP, and CLX wastewater Liu et al. **[13]**. It is also observed that removal of Aniline and COD greatly depends on $H_2O_2$ concentration it is observed that 93% of COD removal was obtained by adding 1200 mg/l of $H_2O_2$.

Sonochemistry involves chemical processes in presence of ultrasound irradiation. When waves of large amplitudes pass through the solution it causes cavitation i.e. formation of bubbles, coupling of these bubbles takes place by the acoustical wave at a microscale level and reach to a critical size. Further compression leads to collapse of bubbles, resulting to chemical reaction, heat and light emissions. The present study is carried out on real dye wastewater i.e. Basic Red 39.

Several methods have been introduced to treat dye wastewater in this paper, two major objectives are:

1. To investigate and compare efficiency of Fenton's treatment and combine Fenton and Ultrasound cavitation treatment of real dye wastewater for COD removal.
2. To check and improve biodegradability of the wastewater after AOPs.

## 2. MATERIALS AND METHODS

### 2.1 The Dye Wastewater

The raw wastewater was obtained from a Dye manufacturing industry located at Ankleshwar, Gujarat, India. The company manufactures products such as Basic Red & Tartrazine. The presence of colour is mainly due to Rhodamine, minimum 5-6% of colour do exist even after carrying out treatment on the wastewater. The COD of raw wastewater ranges about 2800 – 2900 mg/l. The characteristics range of secondary-treated wastewater collected from the unit used in the present study is shown in Table 1.

### 2.2 Fenton Treatment

The sample of dye wastewater sample having initial COD 2860 mg/l with Fenton's treatment oxidation reactions were carried out in a 500ml beaker. Prior to the treatment pH in all the samples was adjusted to 2, 2.5 & 3 for different sets of combination. Then iron catalyst (Ferrous Sulphate) was added on the basis of molar ratios such as $H_2O_2/Fe^{+2}$ 10:1, 15:1 & 20:1 followed by drop to drop addition of $H_2O_2$ based on COD: $H_2O_2$ concentration ratio of 2:1, 4:1, 6:1 with continuous stirring as shown in fig.1. The reaction was allowed to run for 3hrs, after which, pH was adjusted to 9 by hydrated lime and then bought down to pH 7 by adding Alum. Different sets of experiment were performed keeping pH & COD: $H_2O_2$ concentration ratio value constant at a time and varying $H_2O_2$: $Fe^{+2}$ molar ratios i.e. 10:1, 15:1 & 20:1 for each set.

### 2.3 Ultrasonic Cavitation

Sonochemistry involves passing acoustical waves of finite amplitude waves through solutions causing cavitation. About 125ml of Fenton sample was taken in beaker. Sonication probe was dipped in the beaker filled with sample and allowed to run the reaction for 172 second cycle for 3hours the phase is such as the cavitation occurs for 172 sec. and pauses for next 172 seconds. The frequency at which sonication works is 20 kHz. As a result, sludge is settled and supernatant is tested for COD. Fig.2 shows the Ultrasonication apparatus with the probe in the sample for sonication.


*Figure 1. Adding $H_2O_2$ and $Fe^{+2}$ in Raw Wastewater on Magnetic Stirrer*


*Figure 2. Ultrasonic Cavitation Apparatus*

*Table 1: Characteristics of OBA Wastewater Used in Present Study*

| Characteristics | Value of parameters |
|---|---|
| pH | 5.0 – 6.0 |
| COD (mg/l) | 2800- 2900 |
| TDS (mg/l) | 13,400 – 14,750 |
| Chloride (mg/l) | 691- 770 |

### 2.4 Analytical Methods

Total Dissolved Solids, Chemical Oxygen Demand, Chloride, pH tests were performed according to procedure described in standard methods.

## 3. RESULTS & DISCUSSION

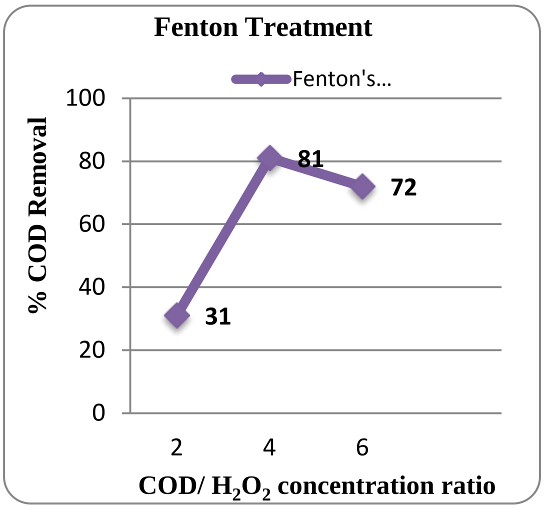
The experimental work was oriented towards the best combination of AOPs that can be applied on the current wastewater to achieve best COD removal.

In this study, COD removal obtained is 87% by combine Fenton & Ultrasonic cavitation is more efficient than 81% by only Fenton process for COD removal. The table.2 shows the results of maximum COD removal amongst all the sets of experiments. The increase in efficiency may be due to additional generation of $OH^-$ by Sonolysis and cavitation causing pyrolysis of organics. Also the treatment efficiency depends on organics characteristics.

**Table: 2 COD Removal Achieved by Fenton and Combine Fenton + Ultrasonic Cavitation treatment at pH 3**

| Sr. No | $COD/H_2O_2$ molar ratio | $H_2O_2/Fe^{+2}$ molar ratio | COD after Fenton's Treatment (mg/l) | % COD removal by Fenton's Treatment | COD after combine Fenton + ultrasonic cavitation (mg/l) | % COD removal by Fenton + ultrasonic cavitation |
|---|---|---|---|---|---|---|
| **19** | 6:1 (0.4ml) | 10:1 | 2000 | 31% | 2567 | 11% |
| **20** | 4:1(0.59ml) | | 650 | 78 % | 1100 | 62% |
| **21** | 2:1(1.19) | | 814 | 72% | 540 | 87% |

Following figure 2 (A) and figure 2 (B) shows % COD removal by Fenton and Fenton + Sonolysis both the treatments.



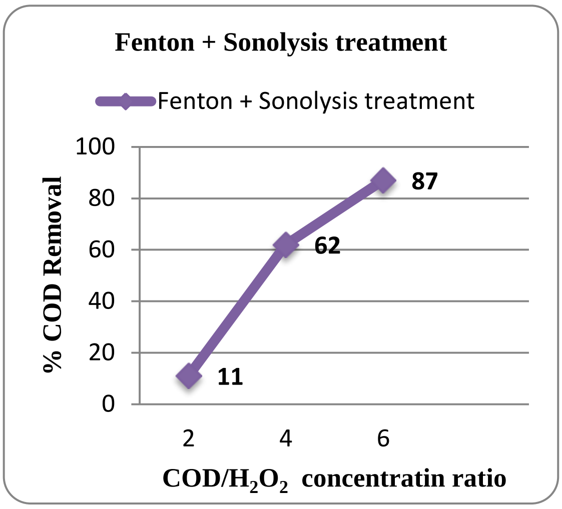




**Figure 2 (A) % COD Reduction at pH3, $H_2O_2/Fe^{+2}$ molar ratio 10:1 and varying COD/ $H_2O_2$: 2:1 by Fenton's treatment**

**Figure 2 (B) % COD reduction at pH 3, $H_2O_2/Fe^{+2}$ molar ratio 10:1 by combined Fenton + Sonolysis treatment**

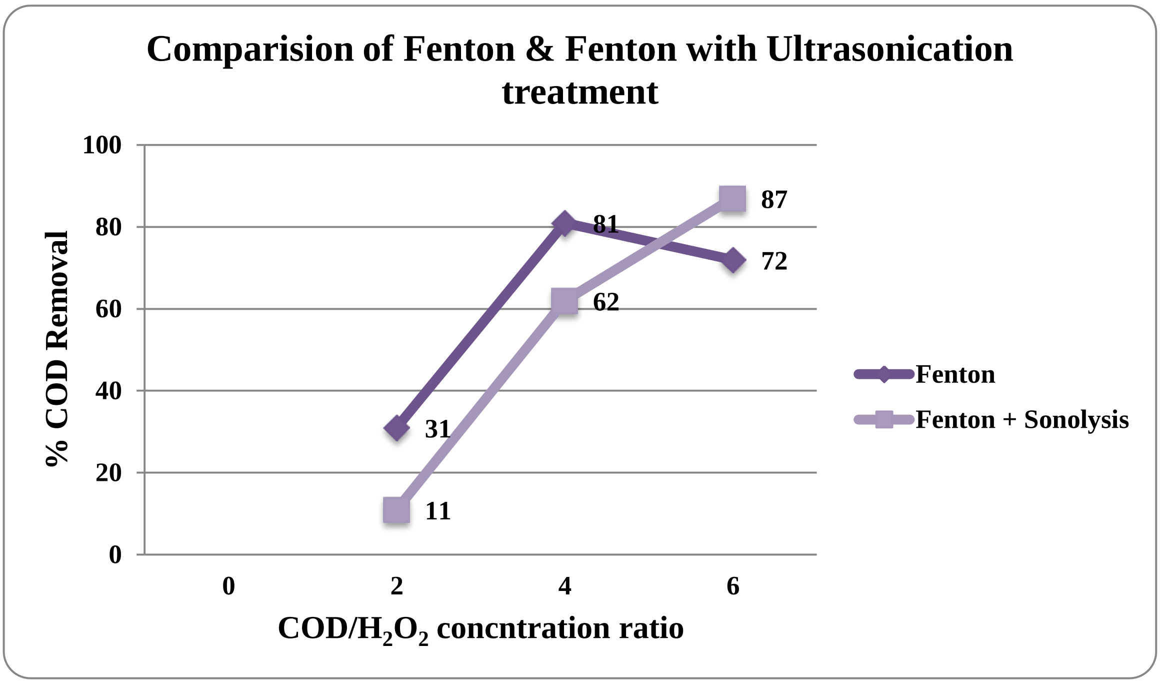



**Figure 3. Comparing Fenton and combine Fenton + Ultrasonic cavitation treatment %COD reduction at pH 3 and $H_2O_2/Fe^{+2}$ molar ratio 10:1**

## 4. CONCLUSION

Two advanced oxidation treatments were performed on the waste by varying parameters of Fenton's reagent .Both the treatments have better performance compared to conventional treatment The results draws to conclusion that Fenton's treatment works best at pH 3. Although the COD values exceed limits of safe discharge standard but considerable reduction in COD is observed.

By only Fenton's treatment COD removal achieved is 81% for COD:$H_2O_2$ ratio of 4:1 & $H_2O_2$: $Fe^{+2}$ ratio of 15:1 & by combined Fenton & Sonolysis %COD removal obtained is 87% for COD: $H_2O_2$ ratio of 6:1 & $H_2O_2$: $Fe^{+2}$ of 20:1.Therefore, it is seen that Fenton's treatment combined with ultrasonic cavitation proves to be more efficient treatment for COD removal.

**REFERENCES**

[1] Alenka Majcen Le Marechal, Boštjan Križanec, Simona Vajnhandl, Julija Volmajer Valh, 'Textile Finishing Industry as an Important Source of Organic Pollutants'.

[2] Antonio Marco, Santiago Esplugas , Gabriele Saum, "How and Why combine Chemical And Biological Processes for wastewater treatment" , Wat. Sci. Tech. 1997, Vol. 35, No.4, pp. 321-327

[3] Benatti, C.T., Tavares, C.R.G, Fenton's Process for the Treatment of Mixed Waste Chemicals. Organic pollutants ten years after the Stockholm Convention-Environmental and Analytical Update, 2012, Pp 247–268

[4] Claus Hoft, Gerhard Sigl, Oliver Specht, lIse Wurdack and Dietrich Wabner, "Oxidative Degradation of AOX and COD by different advanced oxidation process: A comparative study withtwo samples of pharmaceutical wastewater", War. Sci. Tech. Vol. 35, No.4, 1997, pp. 257-264

[5] C. Allegre a, P. Moulin, M. Maisseu , F. Charbit, "Treatment and reuse of reactive dyeing effluents", Journal of Membrane Science 269 , 2006, 15–34

[6] Cláudia Telles Benatti1 and Célia Regina Granhen Tavares., "Fenton´s Process for the Treatment of Mixed Waste Chemicals." Analytica Chimica Acta 561 ,2006, 210–217

[7] Erik J. Rosenfeldta,b, Karl G. Lindenb, Silvio Canonicaa, Urs von Gunten, "Comparison of the efficiency of dOH radical formation during ozonation and the advanced oxidation processes $O_3$/$H_2O_2$ and UV/$H_2O_2$", Water Research 40 ,2006, 3695 – 3704

[8] Horsch, P., Speck, A. & Frimmel, F.H, Combined advanced oxidation and biodegradation of industrial effluents from the production of stilbene–based fluorescent whitening agent. Water Research 37, 2003 ,2748–2756.

[9] Jiju M. Joseph, Hugo Destaillats, Hui-Ming Hung, and Michael R. Hoffmann, "The Sonochemical Degradation of Azobenzene and Related Azo Dyes: Rate Enhancements via Fenton's Reactions", J. Phys. Chem. A, 104, 2000, 301-307

[10] Julia Garcıa-Montano a, Francesc Torrades b, Jose A. Garcia-Hortal, "Degradation of Procion Red H-E7B reactive dye by coupling a photo-Fenton system with a sequencing batch reactor", Journal of Hazardous Materials B134 ,2006, 220–229

[11] K. Ranganathan ., K. Karunagaran, D.C. Sharma, "Recycling of wastewaters of textile dyeing industries using advanced treatment technology and cost analysis—Case studies", Resources, Conservation and Recycling 50 ,2007, 306–318

[12] Lee, E., Lee, H., Kim, Y.K., Sohn, K. & Lee, K , Hydrogen peroxide interference in chemical oxygen demand during ozone based advanced oxidation of anaerobically digested livestock wastewater. International Journal of Environmental Science and Technolog 8(2): 381–388. 2011

[13] Liu, Q.Y., Liu, Y.X. & Lu, X.J. 2012. Combined photo Fenton and biological oxidation for the treatment of aniline wastewater Procedia Environmental Sciences 12: 341–348.

[14] Manoj Yadav1 and Dharmendra.," A Critical Review on Performance of Wastewater Reuse Systems" , International Journal of Environmental Research and Development. ISSN 2249-3131 Volume 4, Number 3 ,2014, pp. 233-238

[15] O. Legrini, E. Oliveros, and A. M. Braun," Photochemical Processes for Water Treatment", Chem. Rev. 1093, 1993, 671-698

[16] Sheng H. Lin & Chi F. Peng, "A Continuous Fenton's Process for Treatment of Textile Wastewater" Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954, 2014

[17] Zongping Wang, Miaomiao Xue, Kai Huang and Zizheng Liu , Textile Dyeing Wastewater Treatment ,chapter 5