

Degradation of Azo Dye Pollutants in the Textile Wastewater Using Advanced Oxidation Process

Pramod Gopinathan ¹, Veena G.Nair ¹, Shoniya ² and Charuvelil Aravindakumar ¹⁺

1. Post Graduate Department of Chemistry, NSS Hindu College, Changanassery, Kerala, India
2. School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India

Abstract. The application of Fenton reaction for generating $\cdot\text{OH}$ radical, which is used for performing AOP for the degradation of textile effluent. The purpose of the study is to investigate the most cost effective pre-treatment in the textile effluent plant (TEP) in order to enhance the rate of biodegradability of the textile waste water, unless otherwise, which is one of the most man made water pollutants on earth crust. The relevance of this topic is not only beneficial to the textile manufactures but as to look through the general view in order to fight effectively against a general cause of gross water pollution because of textile effluent and examine the possibilities of suggesting a suitable solution.

The results showed a general trend that the concentration of Fe^{2+} and pH of the sample increased together with the maximum value of optical density (OD) at minimum duration of only 1 hour. This trend gives a conclusive idea that the effective pre-treatment in TEP is to increase the concentration of Fenton reagent ($[\text{Fe}^{2+}]$ as 10^{-3} moldm⁻³ and $[\text{H}_2\text{O}_2]$ as 10^{-2} moldm⁻³) for the significant enhancement of the rate of biodegradability, which was found to be the most cost effective pre-treatment for TEP. The spectral parameters showed maximum absorbance ranging from 200 to 400 nm and these results have obtained more or less the same agreement with photodegradation using sunlight.

Keywords: Advanced oxidation process (AOP), optical density (OD), textile effluent plant (TEP)

1. Introduction

It is highly relevant to host the 2011 International Conference on Climate Change and Social Issues (CCSI 2011) in Colombo, the capital of Sri Lanka. The Republic of Sri Lanka is blessed with highly conducive climatic and soil conditions and mineral resources. In addition, it has recently revamped its technical and university education so that it is, geared toward developing a strong industrial culture and improving its potential for accelerated industrial development. As a highly populated country (about 300 per sq. km.) any programme on sustainable (industrial) development should emphasize the importance of protecting the environment for the future. This can be completely achieved through well -organized infrastructure development in industrial estates (zones). After liberalization of the economy in 1977, the private sector has become the engine of growth.

Environment scientists recently observed an alarming increase in the degree of pollution in the Kelani River, which is the major water source in Colombo ^[1]. "Less attention is paid on effluent monitoring mechanisms during project approval and even after implementation by the relevant authorities". The main culprits are textile industries [Textile dyeing and bleaching] who discharge harmful chemicals, dyes and detergents to waterways. The Ministry of Environment and Natural Resource, Sri Lanka, has also launched a people-friendly programme [*Pavithra Ganga*] to purify river water.

Textile Engineering has a direct connection with environmental aspects. The main reason is that the textile industry plays an important role in the economy of the country like India and it accounts for

⁺ Corresponding author. Tel.: +91-481 -2732620, 2732120; fax: +91-481-2731009
Email: CT-Aravindakumar@rocketmail.com

around one third of total export. Out of various activities in textile industry, chemical processing contributes about 70% of pollution.

How the degradation of Azo Dye Pollutants affects social issues and climate changes!? Scarcity of drinking pure water, which is the primary need of human being and if the natural resources of water from the water shed, is contaminated grossly with textile effluent, is a major threat of the sustainability of the society . Moreover, temperature of textile effluent water varying around 65-75 °C that would be considered as heat reservoir and the prolonged contamination of the multiple tons of effluent may lead to affect the thermal equilibrium of the surroundings where the textile industries are located. This may directly affect environmental conditions, which will be one among the consequences of climate changes.

Thus, the purpose of this work is to look the possibilities of suggesting a suitable and cost effective method in order to keep the natural water shed away from textile effluent contamination. Therefore, this communication highlights the present studies, which can be carried out in the area of effective textile effluent treatment.

In fact, a practical estimate of the total materials used, it has been found that 45% material in preparatory processing, 33% in dyeing and 22% are re-processed in finishing ^[2].

Table1. 1: Properties of Waste Water from Textile Chemical Processing

| Property | Standard | Cotton | Synthetic | Wool |
|-------------------|-----------|-------------|-------------|-----------------|
| pH | 5.5 – 9.0 | 8 – 12 | 7 – 9 | 3 – 10 |
| BOD, mg/l, 5 days | 30 – 350 | 150 – 750 | 150 – 200 | 5000 – 8000 |
| COD, mg/l, day | 250 | 200 – 2400 | 400 – 650 | 10,000 – 20,000 |
| TDS, mg/l | 2100 | 2100 – 7700 | 1060 – 1080 | 10,000 – 13,000 |

The bleaching / dyeing units in Coimbatore district consume 6,16,000 metric tons of firewood annually for water heating and contribute to deforestation and global warming. The industries in Tiruppur consume about 90 million liters of water per day and generate about 87 million liters of effluent per day. This has adversely impacted agriculture and fisheries in the vicinity of the units. This case study captures the situation and discusses options for reducing the impact on the water bodies.

1.1. Major Findings

There are 729 dyeing and bleaching units in Tiruppur generating 87 million liters of wastewater per day, 50 units in Coimbatore town generating 8 million liters of effluent per day, and around 10 units in Mettupalayam generating 7 million liters of effluent per day. The pollution load during the period 1980 – 2000 was total dissolved solids 23.54 lakh tons, Chloride 13.11 lakh tons, Sulphate 1.25 lakh tons, total suspended solids 0.97 lakh tons, Chemical oxygen demand 0.9 lakh tons, Biochemical oxygen 0.29 lakh tons, oil and grease 0.01 lakh tons. High concentration of Total Dissolved Solids and Chlorides persist in ground and surface water in spite of having Common Effluent Treatment Plant and Individual Effluent Treatment Plant.

1.2. Objectives

1. To measure the Total Organic Carbon (TOC) for evaluate the mineralization efficiency of textile effluent.

- To observe the enhancement of biodegradation efficiency of pre-ozonized sample [both unexposed and exposed to sunlight].
- To optimize the significant enhancement of Biological Oxygen Demand [BOD] level.
- Help the farmers near the industries in enhancing the fertility of the soil by effective and efficient degradation of hazardous materials contaminated their paddy field
- To expose electron beam radiation technology in order to enhance the biodegradability for an activated sludge process.
- To examine the analytical methods of the prediction of useful end products and transfer the technical know-how to the collaborative industries.
- To understand the possibility of recycling and reuse of textile waste water - an effective remedy for water scarcity.
- To compare Photo degradation of azo dyes using UV – H₂O₂, UV & VIS – ZnO/TiO₂
- To compare the results of photodecolourisation efficiencies with solar irradiation and UV irradiation and examine the possibility of a cost effective method be transferred to increase significantly the efficiency of (TEP)
- To optimize the geometries of the species by quantum chemical calculations.

2. Experimental

2.1. Materials Used

- Fenton reagent [mixture of ferrous sulphate (10^{-3} , 5×10^{-4} , 10^{-4} , 5×10^{-5} mol dm⁻³) and H₂O₂ (10^{-2} mol dm⁻³)]
- Azo dye (Diazo amino benzene [DAB] [10^{-4} mol dm⁻³])
- Dil. HCl. (10^{-1} mol dm⁻³)
- Primary Amine (99% purity [Nice Chemicals Pvt Ltd])
- Sodium Nitrite (99% purity [Nice Chemicals Pvt Ltd])
- β-Naphthol (99.9% [Qualigens Fine Chemicals]).

2.2. Preparation of Azo dye (Diazo amino benzene [DAB])

Primary amine is dissolved in dilute HCl, and kept it in ice cold temperature in order to arrest/ passify the reaction at a desired thermal range and mixed it with sodium nitrite followed by vigorous shaking. A clear yellow solution is formed, which was yellow in colour. The system was retained still at ice cold temperature in which β-Naphthol dissolved in minimum quantity of 10% NaOH, were thoroughly mixed using electronic shaker (Heavy Rotary Shaker) for 5 minutes. The resulted dye formed, which was imparted scarlet-red colour and this solid in amorphous form was used for the entire experimentation. Aromatic primary amines were diazotized and the diazonium salt coupled with β-Naphthol forming the azo dye (DAB) [7-9].

From the stock solution of ferrous sulphate (10^{-3} mol dm⁻³), samples of varied concentrations, such as (5×10^{-4} , 10^{-4} and 5×10^{-5}) mol dm⁻³ was prepared for experimental work. A mixture of 5 ml azo dye prepared in deionized water and the concentration of the sample in which the concentration of ferrous sulphate was adjusted as (10^{-4} mol dm⁻³) and mixed with H₂O₂ (10^{-2} mol dm⁻³) using heavy rotary shaker at about 5 minutes.

Adjust the pH of the system around 2 using dil. HCl (10^{-1} mol dm⁻³) and enhance the entire volume of the mixture as 100ml using standard flask. In a similar way, samples of different pH were adjusted as 4 and 6 respectively for the comparative works. Each sample of volume 5 ml covered well with black paper for observing optical density measurements using photochem colorimeter. After this, all these samples are irradiated in the presence of sunlight. Optical density of sample I showed in Table.1 of *Result & Discussion* was irradiated 1 hour and subsequently measured optical density by following the above instrumental parameters. For the purpose of comparing the optical density data, three more samples were irradiated in sun light at an interval of 30 minutes up to 2 ½ hours. The experiments were repeated using

samples of two more pH (4 and 6) and performed the remaining part of the experimental works^[10] at the special instrumentation lab of the School of Chemical Sciences, Mahatma Gandhi University. The samples were irradiated in uv lamp at intervals of 10 minutes up to 30 minutes. Spectral parameter of the above samples was studied using spectrophotometer (uv-vis 1700, SHIMADZU).

3. Result and Discussion

Due to an increasing environmental pollution a search for the treatment and disposal of the dyes from the textile effluents is getting more and more importance. Oxidation and reduction processes play important roles in the degradation treatments of the azo dyes. The latter process is more effective and in consequence its mechanism is also better understood^[1-4,11-19]. Much less information is available on the mechanism of the oxidation processes, the intermediates involved in these reactions and their role in the effectiveness of the oxidative degradation of the azo dyes. $[\text{Fe}^{2+}]$ having various concentration were added to each sample, is considered as a major component of Fenton reagent and irradiated in the presence of sun light and uv-light simultaneously^[10]. One of the spectral parameters is the optical density (OD) measurement (colourimeter used) at different time scale for each sample. The results obtained were tabulated in tables (3.1 & 3.2).

The result of OD values showed a gradual increasing trend in accordance with the increasing pH values from 2 to 6. The OD results in each column of the two tables in a same pH seemed to be a falling trend. The maximum value for optical density in Table 3.1 and 3.2 is also obtained corresponds to the sample I with pH 6. The reason for this significant achievement was due to the increase in absorbance as the pH gets increased.

Table 3.1: Variation of optical density at different pH of a mixture of Fenton reagent ($[\text{Fe}^{2+}] = 10^{-3} \text{ mol dm}^{-3}$ + $[\text{H}_2\text{O}_2] = 10^{-2} \text{ mol dm}^{-3}$)

| Sample (DAB solution [5 ml]) $10^{-4} \text{ mol dm}^{-3}$ of azodye + H_2O_2 $10^{-2} \text{ mol dm}^{-3}$ | OPTICAL DENSITY(OD) | | |
|---|---------------------|------|------|
| | pH 2 | pH 4 | pH 6 |
| Sample I (1hr) | 1.04 | 1.06 | 1.97 |
| Sample II (1 1/2hr) | 1.02 | 1.05 | 1.95 |
| Sample III (2hr) | 1.01 | 1.03 | 1.94 |
| Sample IV (2 1/2hr) | 0.99 | 1.01 | 1.92 |

Table 3.2: Variation of Optical Density at different pH of a mixture of Fenton reagent ($[\text{Fe}^{2+}] = 10^{-4} \text{ mol dm}^{-3}$ + $[\text{H}_2\text{O}_2] = 10^{-2} \text{ mol dm}^{-3}$)

| Sample soln(5 ml) $10^{-4} \text{ mol dm}^{-3}$ azodye + $10^{-2} \text{ mol dm}^{-3} \text{H}_2\text{O}_2$ | OPTICAL DENSITY | | |
|---|-----------------|------|------|
| | pH 2 | pH 4 | pH 6 |
| Sample I (1hr) | 1.05 | 1.07 | 1.96 |
| Sample II (1 1/2hr) | 1.04 | 1.05 | 1.93 |
| Sample III (2hr) | 1.02 | 1.04 | 1.92 |
| Sample IV (2 1/2hr) | 1.01 | 1.02 | 1.90 |

3.1. Results of Spectrum Analysis

The discussion could be able to lead based on the spectral parameters in the following figures from Fig 3.1 [(a) & (b)]; it is clear that the spectra having maximum concentration show minimum absorption. In both the cases, up to 20 minutes absorption decreases linearly. In Fig 3.1 (b), a scan from visible region ranging 450 to 800 nm, all the spectra superimpose and almost parallel to X-axis indicating no significant absorption.

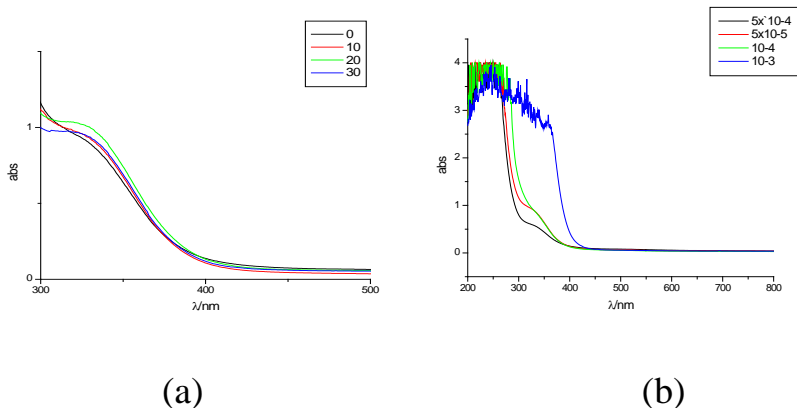


Fig.3.1: Electronic absorption spectra obtained on irradiation during photo Fenton reaction using UV lamp. Reaction conditions: (a): $[\text{Fe}^{2+}]_0 = 5 \times 10^{-5} \text{ moldm}^{-3}$, $\text{DAB}[\text{dye Stuff}]_0 = 10^{-4} \text{ moldm}^{-3}$, $[\text{H}_2\text{O}_2]_0 = 10^{-2} \text{ moldm}^{-3}$, $\text{pH}=4$; (b): $\text{DAB} [\text{dyestuff}]_0 = 10^{-4} \text{ moldm}^{-3}$, $[\text{H}_2\text{O}_2]_0 = 10^{-2} \text{ moldm}^{-3}$ at $\text{pH} 4$.

4. Conclusion

The purpose of the study is to investigate the most cost effective pre-treatment in the textile effluent plant (TEP) in order to enhance the rate of biodegradability of the textile waste water, unless otherwise, which is one of the most men made water pollutants on earth crust. The relevance of this topic is not only beneficial to the textile manufactures but as to look through the general view in order to fight effectively against a general cause of gross water pollution because of textile effluent and examine the possibilities of suggesting a suitable solution.

Using the application of Fenton reaction for generating $\cdot\text{OH}$ radical, which is used for performing AOP in the present contest. The results of Table I to IV showed a general trend that the concentration of Fe^{2+} and pH of the sample increased together with the maximum value of OD at minimum duration of only 1 hour. This interesting trend gives a conclusive idea that the effective pre-treatment in TEP is to increase the concentration of Fenton reagent up to $([\text{Fe}^{2+}] 10^{-3} \text{ moldm}^{-3} + [\text{H}_2\text{O}_2] = 10^{-2} \text{ moldm}^{-3})$. Then, expose the textile effluent by following the above concentration of Fenton reagent for the significant enhancement of the rate of biodegradability, which was found to be the most cost effective method in minimum duration.

Comparison of the results of spectra among figures 1 to 3 showed maximum absorbance even up to 4 ranging from 200 to 400 nm spectral width (blue line) gave most important information that the above summary of results may get good and effective inference for preparing the concentration of Fenton reagent the most cost effective pre-treatment for TEP.

A comparative study at the end of the project using sun light as source of performing photo degradation of dyestuff, also gave more or less the same conclusive ideas.

The above noticeable facts lead us with stimulating research views of the chance of obtaining some useful end products after degradation of hazardous solid wastes, already reported by the earlier researchers.

5. Acknowledgements

I acknowledge Prof.Dr.Charuvelil Aravindakumar, Dean & Hon. Director, *School of Environmental Sciences*, offered collaborative works at *Common Instrumentation Centre (CIC)*, *Mahatma Gandhi University*, Kerala, India. I would like to extend acknowledgement to my parental institution [*NSS Colleges' Central Committee*] and my research centre [*Post Graduate and Research Department of Chemistry, SB College, Changanassery, Kerala, India*]. I am indebted with *National Science Academy, Government of India* from where applying for financial assistance.

6. References

- [1] Shanika Sriyananda, *Sunday Observer*, 2003
- [2] Sivaramakrishnan, C.N., *Colourage*, 2004, **9**, 27-32.
- [3] J. Zielonka, R. Podsiadły, M. Czerwińska, A. Sikora, J. Sokołowska, A. Marcinek; *J. Photochem. Photobiol. A: Chem.* 2004, **163**, 373–379.
- [4] R. Podsiadły, J. Sokołowska, A. Marcinek, J. Zielonka, A. Socha, M. Kaźmierska; *J. Photochem. Photobiol. A: Chem.* 2005, **171**, 69–76.
- [5] H.J.H Fenton, *Chem Soc.* 1994, **65**, 899.
- [6] H.J.H Fenton, *proc. Chem. Soc.* 1999, **15**, 224.
- [7] P. Neta, H. Levanon, *J. Phys. Chem.* 1977, **81**, 2288–2292.
- [8] L. Flamingi, S. Monti, *J. Phys. Chem.* 1985, **89**, 3702–3707.
- [9] S. Monti, L. Flamingi, *J. Phys. Chem.* 1986, **90**, 1179–1184.
- [10] G G Davies, N Sutin, O. Walkins, *J Am Chem. Soc.* 1920, **92**, 1892.
- [11] Vannikov, *High Energy Chem.* 2002, **36**, 7–9.
- [12] A. Albin, E. Fasani, S. Pietra, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1021–1024.
- [13] K. Vinodgopal, P.V. Kamat, *J. Photochem. Photobiol. A: Chem.* 1994, **83**, 141–146.
- [14] C. Lagrasta, I.R. Bellobono, M. Bonardi, *J. Photochem. Photobiol. A: Chem.* 1997, **110**, 201–205.
- [15] K.K. Sharma, B.S.M. Rao, H. Mohan, J.P. Mittal, J. Oakes, P. O'Neill, *J. Phys. Chem. A*, 2002, **106**, 2915–2923.
- [16] H. Tada, M. Kubo, Y. Inubushi, S. Ito, *Chem. Commun.* 2000, 977–978.
- [17] P. Neta, H. Levanon, *J. Phys. Chem.* 1977, **81**, 2288–2292.
- [18] L. Flamingi, S. Monti, *J. Phys. Chem.* 1985, **89**, 3702–3707.
- [19] S. Monti, L. Flamingi, *J. Phys. Chem.* 1986, **90**, 1179–1184.