# TREATMENT OF TEXTILE WASTEWATER CONTAINING DYE STUFF BY FENTON OXIDATION PROCESS AND ADSORPTION

Dilani Parimalarajah

(168877L)

Thesis submitted in partial fulfillment of the requirements for the

degree Master of Science in Environmental Management

Department of Civil Engineering

University of Moratuwa

Sri Lanka

September 2021

**DECLARATION**

"I declare that this is my own work and this thesis does not incorporate without acknowledgement any material previously submitted for a degree or Diploma in any other University or institute of higher learning and to the best of my knowledge and belief, it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

Also, I hereby grant to the University of Moratuwa the non-exclusive right to reproduce and distribute my thesis, in whole or in part in print, electronic or other medium. I retain the right to use this content in whole or part in future works (such as articles or books)."

Signature: Date:

The above candidate has carried out research for the Master's thesis under my supervision.

Name of the supervisor: Prof. M. W. Jayaweera

Signature of the supervisor: Date:

The above candidate has carried out research for the Master's thesis under my supervision.

Name of the co-supervisor: Prof. (Ms.) W. B. Gunawardana

Signature of the supervisor: Date:

**Abstract**

Environmental pollution is the most severe global issue threatening our ecosystem in the current scenario. Pollution is present in every strata of the earth, and the negative effects associated with it are a major source of concern in the modern era. Textile industry hazardous effluents are regarded as one of the major contributors to water pollutants discharged untreated into bodies of water. The discharged effluents from these industries have been demonstrated to bear a high pollution load (high dissolved solids, COD, colour and chloride content) with poor biodegradability. Therefore, untreated textile wastewater causes severe damage to the environment if discharged without treatment. Many techniques like electrochemical coagulation, reverse osmosis, nanofiltration, adsorption using activated materials etc., draw attention to treatment. With traditional approaches, treating textile wastewater, which is of great strength and complexity, has become a significant challenge.

Advanced oxidation processes represent a powerful treatment for refractory and toxic pollutants in textile wastewaters. The present investigation is focused on COD removal, using Fenton oxidation and combined treatment with materials of $TiO_2$, Commercial activated carbon and $TiO_2$ impregnated activated carbon (AT). Initial COD level of 2100mg/l decrease up to 710 mg/l through Fenton oxidation process. Further to discharge treated wastewater into the water body (<250mg/l) is achieved with 8g of $TiO_2$,7 g of CAC, and 6g of $TiO_2$ impregnated AC. CAC was selected as the best material economically for post-treatment. Many factors influenced the degradation rate in the Fenton process, such as initial hydrogen peroxide concentrations(0.65ml/l), initial iron concentration (1.5 g/l) and pH (2-3).

CAC gave maximum COD removal at pH 2. The data were fitted to the Langmuir adsorption isotherm, with a maximum adsorption capacity of 8.16 mg/g and monolayer dye adsorption to the material. The Langmuir adsorption separation factor was 0.033, indicating that the Langmuir adsorption is favourable. The reaction proceeded in a pseudo-second-order, implying chemisorption to the substance. The optimum regeneration agent was found to be NaOH, and the material was exhausted after two regeneration cycles.

From the results Fenton with CAC adsorption is most efficient treatment method at higher dye concentrations and for textile industry effluent.

Keywords: Adsorption, Fenton, COD, $TiO_2$, Iron

**ACKNOWLEDGEMENT**

It is pleasant time to impress my gratitude for all who supported me throughout the journey. I would begin my thanks giving with the almighty without whose blessings, my thesis entitled "Treatment of textile wastewater containing dye stuff by Fenton oxidation and adsorption" would have not been completed.

First of all, I would like to extend my heartfelt gratitude to my supervisor Prof. Mahesh Jayaweera, for giving me the opportunity to complete the research. Your guidance and encouragement given at every step of the way in the research helped me to achieve the goals. Your support was immense, and I am very fortunate to have you as my supervisor. I extremely appreciate the advice given in experiments, writings and moral assistance given to complete this research.

I am very grateful to my co-supervisor Prof. Buddhika Gunawardana, for providing her guidance and support for the research project. Your feedback on my experiments, writing, helped me to complete a very productive study. Furthermore, I would like to extend my gratitude to Prof. Jagath Manatunge for guiding me to conduct fruitful and successful research. Your advice and guidance helped me to complete a very productive study.

I extend my sincere thanks to the laboratory staff of Environmental Engineering Laboratory, Department of Civil of Engineering, University of Moratuwa; Ms. Nilanthi Gunathilake, Mr. Kasun Zoysa, Mr. Justin and Mr.Dhananjaya for the assistance received to conduct my research experiments successfully in the Environmental engineering laboratory.

I would like to thank head and the staff of Analytical Laboratory, Department of Materials Science and Engineering, University of Moratuwa for allowing me to use laboratory equipment.

I would like to thank Mahesh, Madusha, Thilini and Nipuni for their friendship, guidance, strength and assistance given in the period of the research study.

I am grateful to my family for being there for me, giving their unconditional love and support to fulfill my aims. Finally, I would like to thank my spouse for supporting, encouraging, and understanding me in my quest.

**TABLE OF CONTENTS**

DECLARATION ..... i
ABSTRACT ..... iii
ACKNOWLEDGEMENT ..... iv
TABLE OF FIGURES ..... viii
LIST OF TABLES ..... x
LIST OF ABBREVIATIONS ..... xi
1.INTRODUCTION ..... 1
1.1 General ..... 1
1.2 Scope of the study ..... 4
1.3 Objectives of the study ..... 4
1.4 Approach ..... 5
2.LITERATURE REVIEW ..... 6
2.1 Properties of dyes ..... 6
2.2 Textile Dye Classification ..... 7
2.2.2 Basic dyes ..... 8
2.2.3 Direct or Substantive dyes ..... 8
2.2.4 Reactive dyes ..... 8
2.2.5 Vat dyes ..... 8
2.2.6 Disperse dyes ..... 8
2.2.7 Sulphur dyes ..... 9
2.2.8 Azoic dyes ..... 9
2.3 Dye intermediates ..... 9
2.4 Toxicity of dyes ..... 9
2.5 Textile dyeing processes ..... 10
2.5.1 Pre-treatment processes of dyeing ..... 10
2.6 Wastewaters from textile processing ..... 11
2.7 Treatment and disposal of textile industry wastewater ..... 13
2.8 Primary treatment ..... 14
2.9 Advanced oxidation process ..... 16
2.9.1 Uses of the Fenton's reagent ..... 16
2.10 Adsorption ..... 22

2.11 Titanium dioxide ..... 23
2.12 Treatment methods and their advantages and limitations ..... 25
3.MATERIAL AND METHODS ..... 28
3.1Textile Industry Effluent ..... 28
3.2 Classification of dyes ..... 29
3.3 Chemical Oxygen Demand analysis ..... 32
3.4 Synthesis of $TiO_2$ ..... 34
3.5 Synthesis of $TiO_2$ impregnated Activated Carbon ..... 34
3.6 Fenton Oxidation process ..... 35
3.7 Evaluation of COD removal efficiency for different combination of synthesized $TiO_2$ and AC ..... 36
3.8 Selection of Best Material for COD removal ..... 36
3.9 Characterization of CAC using SEM, EDX, XRD, and FTIR ..... 36
3.10 Optimization of experiment condition for the CAC for COD removal ..... 38
3.10.1 Optimum Contact time ..... 38
3.10.2 Optimum pH ..... 39
3.11 Adsorption isotherms and kinetic studies for CAC ..... 39
3.11.1 Adsorption isotherms ..... 39
3.11.2 Kinetic studies ..... 40
3.12 Regeneration Studies for Commercial Activated Carbon ..... 41
4.1 Wastewater Characterization ..... 42
4.2 Operating Parameters of Fenton Oxidation Process ..... 42
4.3 Best pairing selection of AC: $TiO_2$ ratio to remove COD ..... 44
4.4 Effect of $(AT)_{opt}$ on COD removal ..... 44
4.5 Effect of $TiO_2$ loading on COD removal ..... 46
4.6 Effect of Activated Carbon loading on COD removal ..... 47
4.7 Selection of best material for COD removal ..... 48
4.8 Characterization of Activated carbon using SEM, EDX, XRD and FTIR ..... 50
4.8.1 ESEM and EDX Analysis ..... 51
4.8.2 XRD Analysis of AC ..... 53
4.8.3 FTIR analysis for AC ..... 54
4.9 Optimum condition for COD removal using AC ..... 54

4.9.1 Impact of contact time ..... 54
4.9.2 Effects of pH ..... 56
4.10 Adsorption Isotherms and kinetic studies ..... 58
4.10.1 Adsorption isotherms for COD removal by AC ..... 58
4.10.2 Kinetic studies ..... 61
4.11 Regeneration studies for AC ..... 64
A schematic diagram of a wastewater treatment module for dyestuffs is shown below. ... 65
5. CONCLUSIONS AND RECOMMENDATIONS ..... 66
5.1 Conclusions ..... 66
5.2 Recommendations ..... 67
LIST OF REFERENCES ..... 69

**TABLE OF FIGURES**

Figure 2. 1: Classification of textile dyes (Christie 2007, Hunger 2003, Sabnis 2010) .....7
Figure 2. 2: The constituents and wastewater characteristics from various textile processing steps (Verma et al., 2012) .....12
Figure 2. 3: Stages of wastewater treatment .....13

Figure 3. 1 : Structure of Disperse red .....29
Figure 3. 2: Structure of Disperse yellow .....30
Figure 3. 3: Structure of Disperse orange .....30
Figure 3. 4: Structure of Disperse navy blue .....30
Figure 3. 5 : Structure of Sunset yellow .....30
Figure 3. 6: Structure of Suncid red .....31
Figure 3. 7: Structure of Disperse Rubine .....31
Figure 3. 8: Structure of Disperse blue8 .....31
Figure 3. 9: COD reflux condenser .....33
Figure 3. 10: Titration setup and color change .....33
Figure 3. 11: Aerating the wastewater with Fenton reagent .....35
Figure 3. 12: The laboratory setup for the batch studies on the mechanical stirrer .....36
Figure 3. 13: Environmental Scanning Electron Microscopy- Energy-Dispersive X-ray Spectroscopy .....37
Figure 3. 14: Fourier Transform- Infrared Spectroscopy .....37
Figure 3. 15: X-Ray Diffraction spectroscopy .....38
Figure 3. 16: The experimental setup for batch experiments .....38

Figure 4. 1: COD Removal efficiency with different $AT_{opt}$ dosages .....45
Figure 4. 2: COD Removal efficiency with different dosage of $TiO_2$ .....47
Figure 4. 3: COD removal efficiency with different CAC dosage .....48
Figure 4. 4: Final COD with different dosage of CAC, $TiO_2$ and $TiO_2$ impregnated AC .....49
Figure 4. 5: Treatment cost for 1l of Fenton treated water for three materials .....50
Figure 4. 6 SEM image of AC before Adsorption .....51
Figure 4. 7: SEM image of AC After Adsorption .....51
Figure 4. 8: The EDX image of CAC .....52

Figure 4. 9: XRD analysis of AC.....53
Figure 4. 10: FTIR analysis of AC before and after adsorption .....54
Figure 4. 11: Final COD vs the contact time .....55
Figure 4. 12: Final COD with different pH.....57
Figure 4. 13: The Langmuir isotherm for COD removal with AC .....59
Figure 4. 14: The Freundlich isotherm for COD removal with AC.....60
Figure 4. 15: Pseudo first order kinetic model for adsorption onto AC .....62
Figure 4. 16: The reaction kinetic data is fitted to second order kinetic model.....63
Figure 4. 17: The COD removal efficiency of AC after each regeneration cycle .....64

## LIST OF TABLES

Table 2. 1: Highlights of published work on Fenton's/photo-Fenton oxidation of textile dyes/ wastewater.....17
Table 2. 2: Available COD removal methods and their advantages and limitation .....25
Table 3. 1: Characteristics of textile industry effluent before treatment .....28
Table 3. 2:Properties of dyes .....29
Table 3. 3: Mixing weight ratio of AC and $TiO_2$.....35
Table 4. 1:Characteristics of effluent.....42
Table 4. 2: COD removal percentage for different ratio of AC:$TiO_2$.....44
Table 4. 3: COD removal percentage with different dosage of $AT_{opt}$ .....45
Table 4. 4: COD removal percentage with dosage of synthesized $TiO_2$ .....46
Table 4. 5: COD removal percentage with dosage of AC .....48
Table 4. 6:The analyzing method with the relevant analyzed characteristics.....50
Table 4. 7: The weight and atomic composition of the CAC .....52
Table 4. 8: The Optimum contact time for COD removal.....55
Table 4. 9: Optimum pH investigation .....56
Table 4. 10: Adsorption data fitted to Langmuir isotherm .....58
Table 4. 11: Adsorption data to fitted Freundlich isotherm.....60
Table 4. 12: The pseudo first order reaction results.....61
Table 4. 13: The kinetic experiment results of AC.....62

## LIST OF ABBREVIATIONS

| Abbreviation | Description |
|---|---|
| COD | Chemical Oxygen Demand |
| BOD | Biochemical Oxygen Demand |
| DO | Dissolved Oxygen |
| AOP | Advance Oxidation Process |
| CAC | Commercial Activated Carbon |
| FTIR | Fourier-Transform Infrared spectroscopy |
| SEM | Scanning electron microscope |
| EDX | Energy-dispersive X-ray spectroscopy |
| XRD | X-ray Diffraction Analysis |