Removal of Dyes from Industrial Effluents Using Combination of Advanced Oxidation Processes (AOPs) and Biological Treatment

by

Che Zulzikrami Azner bin Abidin
(841210324)

A thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

School of Environmental Engineering
UNIVERSITI MALAYSIA PERLIS

2014

ACKNOWLEDGEMENTS

First and foremost, utmost praise is to Allah, the Almighty for blessings me with the desire and emotional strength to fulfil and materialize my dream to complete this thesis.

I would like to express my deepest gratitude to my supervisor, Dr. Fahmi Muhammad Ridwan, for his academic guidance, suggestions and support. His constructive criticisms, valuable suggestions, insights and patients have truly encouraged me. His help and encouragement are sincerely appreciated, and thus making this research possible. I would also like to thank my co-supervisor, Assoc. Prof. Dr. Ong Soon-An for his valuable time, insightful comments and encouragement during the period of this research.

Special and sincere thanks are extended to my fellow graduate student and lab mates, Ms. Fatin Nadhirah for her invaluable contributions and suggestions. I would also like to thank Ms. Janna, Ms. Hazirah, Ms. Sakinah, Ms. Lai Li Lze and Ms. Ling Ching Swan and many others for their valuable assistance. Their friendly and helpful contributions have always encouraged me.

I am thankful to numerous persons who, in many ways, supported, encouraged and assisted me in the completion of my study. Mr. Nazerry, Mrs. Zuraini, Mr. Razi, Mr. Roshasmawi, Mr. Affandi, Mr. Munif, Mr. Mokhzani, Mr. Shukri, Mr. Zahir, Mr. Andi, Mr. Ahmad Saiful and other colleges that have been close to me during these four years with their help and supports. Similarly, my gratitude goes to anybody who has directly or indirectly contributed to the successful completion of this research.

Last but not least, my deepest gratitude to my beloved family members, particularly my parent, Hj. Abidin Ahmad and Hjh. Asiah Mohamood for their encouragement, blessings and motivation at each and every step throughout my life.

I would also like to say thank you, still it is not the perfect word to describe my appreciation, to my beloved wife, Mrs. Saparina Mohd Alip for her unconditional patient, understanding and encouragement during this journey. And to my children, Ahmad Zulzikry and Syadza Nur Aimy for understanding and appreciating me. They shared all my happiness and painfulness, in the whole process of my research. It would not been possible to complete this study without them.

THESIS DECLARATION FORM

UNIVERSITI MALAYSIA PERLIS

DECLARATION OF THESIS

Author's full name	:	Che Zulzikrami Azner bin Abidin
Date of birth	:	18 December 1978
Title	:	Removal of Dyes from Industrial Effluents Using Combination of Advanced Oxidation Processes (AOPs) and Biological Treatment
Academic Session	:	2013 / 2014

I hereby declare that this thesis becomes the property of Universiti Malaysia Perlis (UniMAP) and to be placed at the library of UniMAP. This thesis is classified as:

☐	**CONFIDENTAL**	(Contains confidential information under the Official Secret Act 1972)
☐	**RESTRICTED**	(Contains restricted information as specified by the organization where research was done)
√	**OPEN ACCESS**	I agree that my thesis is to be made immediately available as hard copy or on-line open access (full text)

I, the author, give permission to the UniMAP to reproduce this thesis in whole or in part for the purpose of research or academic exchange only (except during a period of _____ years, if so requested above).

Certified by:

SIGNATURE	**SIGNATURE OF SUPERVISOR**
781218-09-5001	Dr. Fahmi Muhammad Ridwan
(NEW IC NO. / ~~PASSPORT NO.~~)	**NAME OF SUPERVISOR**
Date: ____________	Date: ____________

NOTES: *If the thesis is CONFIDENTIAL or RESTRICTED, please attach with the letter from the organization with period and reasons for confidentiality or restriction.

Removal of Dyes from Industrial Effluents Using Combination of Advanced Oxidation Processes (AOPs) and Biological Treatment

ABSTRACT

Nowadays, the removal of dyes from industrial effluents is still far away to a satisfactory solution. Even though the AOPs are known strong technologies for wastewater treatment, it still requires further advancement and extent. Hence, a new promising treatment is their combination with biological treatment, by taking the advantages of the individual potentials. Therefore, this research evaluated four treatment techniques, namely ozonation, ozone/hydrogen peroxide (O_3/H_2O_2), ultraviolet/hydrogen peroxide (UV/H_2O_2), and a combination of ozonation-biological for synthetic dyes, consist of monoazo Methyl Orange (MO), disazo Reactive Red 120 (RR120) and anthraquinone Reactive Blue 19 (RB19). Finally, the treatments are evaluated with batik wastewater as a real wastewater sample from industries. The finding revealed that ozonation, O_3/H_2O_2, UV/H_2O_2, and ozonation-biological become an effective treatment for monoazo, disazo, anthraquinone, and real wastewater. The treatments accomplish, under appropriate conditions, a full decolourization and a substantial mineralization. However, O_3/H_2O_2 and ozonation works well with the dyes, in contrast to UV/H_2O_2. It reveals that complete decolourization by ozonation and O_3/H_2O_2, with less than 20 min contact. Two decolourization curves of ozonation and O_3/H_2O_2 almost overlapped suggesting that H_2O_2 hardly affects decolourization rate. Contrariwise, it takes more than 60 min for complete decolourization with UV/H_2O_2 for RR120, but requires more than 120 min for MO and RB19. Nevertheless, there was a significant difference for COD and TOC removals. It is apparent that O_3/H_2O_2 showed higher removal, suggesting that the presence of H_2O_2 promote the oxidation reaction. The final COD removal of O_3/H_2O_2 reached 100% within less than 10 min for RR120 and RB19, while 15 min for MO. Likewise, the higher TOC removal was observed for O_3/H_2O_2 in comparison to ozonation and UV/H_2O_2. On the whole, the COD removal was similar to TOC removal for each treatment. It is obvious that high decolourization from the start of biological was contributed from ozonation pre-treatment. In addition, the results indicate that 59.6 and 69.4% COD removal from ozonation and ozonation-biological, respectively for MO. While, resulted about 40.7 and 72.9% removal for RR120, and 51.4 and 59.8% for RB19, respectively. Thus, it represents small organic molecules that contribute considerably to the COD that cannot be completely removed by ozonation-biological treatment. Similar to COD, the results indicate that 49.1 and 73.7% TOC removal from ozonation and ozonation-biological, respectively for MO. While it leads to 39.3 and 64.3% removal for RR120 and 37.5 and 70.8% removal for RB19, respectively. It is clear that the biological further degrades the dyes from ozonation. In addition, each dye shows different decolourization pattern and degradation behaviour according to its chemical structure. The change in UV-vis and FT-IR spectra indicated the evidence of dye structure cleavage and intermediates formation. While, the NO_3^-, SO_4^{2-} and Cl^- anions formed indicate dye mineralization. The decolourization conform first-order kinetics, with R^2 values greater than 0.92. The O_3/H_2O_2 performs better with the batik wastewater, as compared to ozonation and UV/H_2O_2. Therefore, the results for synthetic wastewater support its application for real wastewater, even though the batik wastewater was more difficult to be decolourized and degraded because of its complex composition.

Penyingkiran Pewarna daripada Efluen Perindustrian Menggunakan Gabungan Proses Pengoksidaan Lanjutan (PPL) dan Rawatan Biologi

ABSTRAK

Pada masa kini, penyingkiran pewarna dari pelepasan efluen industri masih jauh lagi untuk mencapai penyelesaian yang memuaskan. Walaupun PPL dikenali sebagai teknologi yang baik untuk rawatan air sisa, ia masih lagi memerlukan penambahbaikan. Oleh itu, rawatan baru yang adalah gabungan PPL dengan rawatan biologi, dengan mengambil kira kelebihan potensi individu. Oleh itu, kajian ini dinilai empat teknik rawatan, iaitu pengozonan, ozon/hidrogen peroksida (O_3/H_2O_2), ultraungu/hidrogen peroksida (UV/H_2O_2), dan gabungan pengozonan-biologi pewarna sintetik, yang terdiri daripada *monoazo Methyl Orange* (MO), *disazo Reactive Red 120* (RR120) dan *anthraquinone Reactive Blue 19* (RB19). Akhir sekali, rawatan dinilai dengan air sisa batik sebagai sampel air sisa sebenar dari industri. Hasil kajian mendapati pengozonan, O_3/H_2O_2, UV/H_2O_2, dan pengozonan-biologi menjadi satu rawatan berkesan untuk pewarna *monoazo*, *disazo*, *anthraquinone*, dan air sisa sebenar. Rawatan telah mencapai (dalam keadaan yang sesuai), penyingkiran penuh warna dan degradasi yang besar. Walau bagaimanapun, O_3/H_2O_2 dan pengozonan berfungsi dengan lebih baik dengan pewarna, berbanding UV/H_2O_2. Ia menunjukkan bahawa penyingkiran sepenuhnya warna dengan pengozonan dan O_3/H_2O_2 dalam masa kurang daripada 20 min. Dua lengkung penyingkiran warna daripada pengozonan dan O_3/H_2O_2 hampir bertindih mencadangkan bahawa H_2O_2 tidak memberi kesan kepada kadar penyingkiran warna. Sebaliknya, ia mengambil masa lebih daripada 60 minit untuk penyingkiran sepenuhnya dengan UV/H_2O_2 untuk RR120, tetapi lebih daripada 120 min untuk MO dan RB19. Walau bagaimanapun, terdapat perbezaan yang signifikan untuk peyingkiran COD dan TOC. Ia adalah jelas bahawa O_3/H_2O_2 menunjukkan penyingkiran yang lebih tinggi, dan kehadiran H_2O_2 menggalakkan pengoksidaan. Penyingkiran COD akhir O_3/H_2O_2 mencapai 100% dalam masa kurang daripada 10 minit untuk RR120 dan RB19, manakala 15 min untuk MO. Begitu juga, penyingkiran TOC yang lebih tinggi untuk O_3/H_2O_2 berbanding pengozonan dan UV/H_2O_2. Pada keseluruhannya, penyingkiran COD adalah sama dengan TOC untuk setiap rawatan. Ia adalah jelas bahawa penyingkiran warna yang tinggi dari permulaan rawatan biologi disumbangkan dari pra-rawatan pengozonan. Di samping itu, keputusan menunjukkan bahawa 59.6 dan 69.4% penyingkiran COD dari pengozonan dan pengozonan-biologi, masing-masing untuk MO. Manakala, kira-kira 40.7 dan 72.9% untuk RR120, dan 51.4 dan 59.8% untuk RB19. Oleh itu, ia menunjukkan molekul organik kecil telah menyumbang dengan ketara kepada COD yang tidak boleh disingkirkan sepenuhnya oleh rawatan pengozonan-biologi. Sama seperti COD, keputusan menunjukkan bahawa 49.1 dan 73.7% penyingkiran TOC dari pengozonan dan pengozonan-biologi, masing-masing untuk MO. Walaupun, ia membawa kepada 39.3 dan 64.3% bagi RR120, dan 37.5 dan 70.8% bagi RB19. Ia adalah jelas bahawa rawatan biologi mendegradasikan lagi pewarna dari pengozonan. Selain itu, setiap pewarna menunjukkan corak yang berbeza mengikut struktur kimianya. Perubahan dalam spektrum UV-vis dan FT-IR menunjukkan bukti pemecahan struktur dan pembentukan produk perantaraan. Manakala, anion NO_3^-, SO_4^{2-} dan Cl^- yang terbentuk menunjukkan degradasi pewarna. Penyingkiran warna menepati kinetik tertib-pertama, dengan nilai R^2 yang lebih besar daripada 0.92. O_3/H_2O_2 merawat air sisa batik dengan lebih baik, berbanding pengozonan dan UV/H_2O_2. Oleh itu, keputusan untuk air sisa sintetik menyokong penggunaan untuk air sisa sebenar, walaupun air sisa batik lebih sukar untuk penyingkiran warna dan degradasi disebabkan komposisinya yang lebih kompleks.

LIST OF PUBLICATIONS

No. Journal

1. Che Zulzikrami Azner Abidin, Fahmi, Ong Soon An, Siti Nurfatin Nadhirah Mohd Makhtar, Nazzery Rosmady Rahmat (2014). Decolorization and COD Reduction of Textile Wastewater by Ozonation in Combination with Biological Treatment. Science of the Total Environment. *(Impact Factor 3.789) – draft*

2. Che Zulzikrami Azner Abidin, Fahmi, Ong Soon An, Siti Nurfatin Nadhirah Mohd Makhtar, Nazzery Rosmady Rahmat (2014). Partial Oxidation of Mono and Disazo Reactive Dyes by the O_3 and O_3/H_2O_2 Processes. Desalination and Water Treatment. *(Impact Factor 0.852) – under review*

3. Che Zulzikrami Azner Abidin, Fahmi, Ong Soon-An, Siti Nurfatin Nadhirah Mohd Makhtar, Nazerry Rosmady Rahmat (2014). Ozonation of Azo Dye Reactive Red 120: Performance and Decolourization Kinetics. ScienceAsia. *(Impact Factor 0.398) – under review*

4. Fahmi Muhammad Ridwan, Che Zulzikrami Azner Abidin, Nazerry Rosmady Rahmat (2010). Multi-stage Ozonation and Biological Treatment for Removal of Azo Dye Industrial Effluent. International Journal of Environmental Science and Development (IJESD), 1(2), 13-18.

No. Proceeding

1. Che Zulzikrami Azner Abidin, Fahmi, Ong Soon-An, Siti Nurfatin Nadhirah Mohd Makhtar, Nazzery Rosmady Rahmat, Razi Ahmad. Effect of pH and H_2O_2 Dosage on the Photooxidative Degradation of Reactive Red 120 (RR120) by UV/H_2O_2, *The 4th International Malaysia-Ireland Joint Symposium on Engineering, Science and Business (IMiEJS 2014), June 25-26, 2014, Penang. –* ***SCOPUS cited***

2. Che Zulzikrami Azner Abidin, Muhammad Ridwan Fahmi, M.A. Umi Fazara, Siti Nurfatin Nadhirah. Degradation Characteristic of Monoazo, Diazo and Anthraquinone Dye by UV/H_2O_2 Process, *The 3rd International Conference on Fundamental and Applied Sciences (ICFAS 2014), June 3-5, 2014, Kuala Lumpur. -* ***SCOPUS cited***

3. Che Zulzikrami Azner Abidin, Fahmi, Ong Soon-An, Siti Nurfatin Nadhirah Mohd Makhtar, Nazzery Rosmady Rahmat, Razi Ahmad. Decolorization and COD Reduction of Textile Wastewater by Ozonation in Combination with Biological Treatment, *Proceedings of Malaysian Technical Universities Conference on Engineering & Technology (MUCET 2013), December 3-4, 2013, Universiti Malaysia Pahang (UMP), Kuantan, Pahang.*

4. Siti Nurfatin Nadhirah Mohd Makhtar, Fahmi Muhammad Ridwan, Nasrul Hamidin, Che Zulzikrami Azner Abidin, Wan Nurhazirah Kamaruzaman. Methyl Orange Removal by Photocatalysis Process (UV/Hydrogen Peroxide), *UTAR National Postgraduate Fundamental and Applied Sciences Seminar (UTAR NPFASS 2013), May 13-14, 2013, Universiti Tunku Abdul Rahman, Kampar, Perak.*

5. Muhammad Ridwan Fahmi, Che Zulzikrami Azner Abidin, Nazerry Rosmady Rahmat, Ong Soon An. Trend in biodegradability improvement of azo dyes by ozonation, The 4th *Asia-Pacific Young Water Professionals Conference*, December 7-10, *2012, Tokyo, Japan*.

6. Che Zulzikrami Azner Abidin, Fahmi Muhammad Ridwan, Ong Soon An, Nazerry Rosmady Rahmat. Comparative study on the degradation of reactive dyes by O_3 and O_3/H_2O_2 processes, *2nd International Malaysia-Ireland Joint Symposium on Engineering, Science and Business (IMiEJS 2012), June 18-20, 2012, Kuala Lumpur.*

7. Che Zulzikrami Azner Abidin, Fahmi Muhammad Ridwan, Ong Soon An, Nazerry Rosmady Rahmat. Degradation of Reactive Red 120 by O_3 and O_3/H_2O_2 Process, *International Postgraduate Conference (IPCE 2011), October 22-23, 2011, Universiti Malaysia Perlis (UniMAP), Perlis.*

8. Nazerry Rosmady Rahmat, Fahmi Muhammad Ridwan, Che Zulzikrami Azner Abidin, Apipah Ariffin, Suhaida Mohamed Arshad. Ozonation and Biological Treatment for the Removal of Azo Dye Industrial Effluent, *International Postgraduate Conference (IPCE 2011), October 22-23, 2011, Universiti Malaysia Perlis (UniMAP), Perlis.*

9. Fahmi Muhammad Ridwan, Che Zulzikrami Azner Abidin, Nazerry Rosmady Rahmat. Characteristic of Colour and COD Removal of Azo Dye by Advanced Oxidation Process and Biological Treatment, *International Conference on Biotechnology and Environmental Management (ICBEM 2011), September 16-18, 2011, Singapore.*

10. Fahmi Muhammad Ridwan, Che Zulzikrami Azner Abidin, Nazerry Rosmady Rahmat, Ong Soon An. Study of Advanced Oxidation Process and Biological Treatment Mechanisms for Azo Dye Industrial Effluent, *International Congress on Green Process Engineering (GPE 2011), September 6-8, 2011, Kuala Lumpur.*

11. Che Zulzikrami Azner Abidin, Fahmi Muhammad Ridwan. Characteristic of COD and Colour Removal of Azo Dye in Ozonation and Biological Treatment, *National Postgraduate Conference (NPC 2011), September 19-20, 2011, Universiti Teknologi Petronas (UTP), Tronoh, Perak. - **SCOPUS cited***

12. Che Zulzikrami Azner Abidin, Fahmi Muhammad Ridwan, Nazerry Rosmady Rahmat, Suhaida Mohamed Arshad. Decolorisation of Azo Dye by Ozonation, *International Postgraduate Conference on Engineering (IPCE 2010), Oktober 16-17, 2010, Universiti Malaysia Perlis (UniMAP), Perlis.*

13. Fahmi Muhammad Ridwan, Apipah Ariffin, Suhaida Mohamed Arshad, Che Zulzikrami Azner Abidin, Nazerry Rosmady Rahmat. Decolourization and COD removal of Azo Dye Solution by Repeated Ozonation and Biodegradation, *International Conference on Environmental Science and Technology (ICEST 2010), April 23-25 2010, Bangkok, Thailand.*

14. Che Zulzikrami Azner Abidin, Fahmi Muhammad Ridwan, Haidar S. Al- Maroof, Nazerry Rosmady Rahmat. Application of Multi-Stage Ozonation / Advance Oxidation Process (AOP) and Biological Treatment for Colour, Bod and COD Removal of Azo Dye Industrial Effluent, *Proceeding of Engineering Postgraduate Conference (EPC 2009), July 26-27, 2009, Universiti Malaysia Perlis (UniMAP), Perlis.*

LIST OF SYMBOLS

%	Percentage
^0C	Degree Celsius
a	Weight concentration of H_2O_2
A	Weight of dried filter plus dried residue
Abs	Absorbance
B	Weight of filter
C	Concentration
C_0	Concentration at time = 0
C_t	Concentration at time = t
cm^{-1}	Wavenumber
d	Dilution factor
D	Chromogen
g/mol	Grams per mole
f	Correction factor (ratio of the COD value of the H_2O_2 concentration)
h	Hour
$HO^{\bullet}$	Hydroxyl radicals
hv	Photon
k	Reaction rate constant
λ	Wavelength
λ_{max}	Maximum absorption wavelength
L	Litre
lb	Pound (mass)
min	Minute
mg/L	Milligram per litre
mL/min	Millilitres per minute
mM	Milimolar
N_{MnO4}	Normality of $KMnO_4$ titrate
nm	Nanometre
Q	Linker or bridge
RG	Reactive groups
Pt-Co	Platinum-Cobalt Scale (colour scale)

t	Time
T_{MnO4}	Volume of $KMnO_4$ titrate
μl	Microliter
USD/m^3	United States dollar per cubic meter
v	Volume
V	Volts
W	Water-solubilising group
W/m^2	Watts per square meter
X	Leaving group

LIST OF ABBREVIATIONS

ADMI	American Dye Manufacturers Institute
Ag_2SO_4	Silver sulphate
AOPs	Advanced oxidation processes
AOX	Absorbable organic halogens
ATR	Attenuated Total Reflection
ASP	Activated-sludge Process
BOD	Biochemical oxygen demand
BOD_5	Biochemical oxygen demand for 5 days
CAS	Chemical Abstract Service
CMAS	Complete-mix activated sludge
CI	Colour Index
Cl	Chlorine
Cl_2	Chlorine gas
CiO_2	Chlorine dioxide
Cl^-	Chloride anions
ClO^-	Hypochlorite
CMC	Carboxymethyl cellulose
COD	Chemical oxygen demand
COD_c	Chemical oxygen demand (corrected)
COD_m	Chemical oxygen demand (measured)
DO	Dissolved oxygen
DOE	Department of Environment
EOP	Electrochemical oxidation potential
EQA	Environmental Quality Act
F	Fluorine
FT-IR	Fourier Transforms-Infrared
GAC	Granular activated carbon
H_2SO_4	Sulphuric acid
$HO^\bullet$	Hydroxyl radicals
H_2O_2	Hydrogen peroxide
H_2O_2/Fe^{2+}	Fenton

H_2SO_4	Sulphuric acid
HCl	Hydrochloric acid
$HgSO_4$	Mercury(II) sulphate
IC	Ion-chromatography
ID	Internal diameter
$K_2Cr_2O_7$	Potassium dichromate
KI	Potassium iodide
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
Mn_2O_7	Manganese(VII)
Mo	Microorganism
MO	Methyl Orange
N_2	Nitrogen gas
$Na_2S_2O_3$	Sodium thiosulphate
NaOH	Sodium hydroxide
NBR	Nitrile butyl rubber
NHAr	Aromatic amines
NR	Natural rubber
NRE	Ministry of Natural Resources and Environment
NO_3^-	Nitrate anions
NO_2^-	Nitrite anions
O_2	Oxygen (molecular)
O_3	Ozone
O_3/H_2O_2	Ozone / Hydrogen peroxide, Perozone process
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PU	Polyurethane
RB19	Reactive Blue 19
rpm	Revolution per minute
RR120	Reactive Red 120
SBR	Sequencing batch reactor
SO_4^{2-}	Sulphate anions

TDS	Total Dissolved Solids
TiO_2	Titanium dioxide
TOC	Total organic carbon
TSS	Total suspended solids
UBAF	Up-flow biological aerated filter
UV	Ultraviolet
UV/H_2O_2	Ultraviolet irradiation / Hydrogen Peroxide, H_2O_2 photolysis process
UV-vis	Ultraviolet-visible
VSS	Volatile suspended solids
V-UV	Vacuum-ultraviolet
ZnO	Zinc oxide

LIST OF FIGURES

LIST OF TABLES

TABLE OF CONTENTS