



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

by

**Che Zulzikrami Azner bin Abidin
(841210324)**

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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.

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LIST OF SYMBOLS

%	Percentage
$^{\circ}\text{C}$	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
$h\nu$	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_{MnO_4}	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

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LIST OF ABBREVIATIONS

ADMI	American Dye Manufacturers Institute
Ag ₂ SO 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
ClO 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 ₂ SO ₄	Sulphuric acid
HO [•]	Hydroxyl radicals
H ₂ O ₂	Hydrogen peroxide
H ₂ O ₂ /Fe ²⁺	Fenton

H ₂ SO ₄	Sulphuric acid
HCl	Hydrochloric acid
HgSO ₄	Mercury(II) sulphate
IC	Ion-chromatography
ID	Internal diameter
K ₂ Cr ₂ O ₇	Potassium dichromate
KI	Potassium iodide
MLSS	Mixed liquor suspended solids
MLVSS	Mixed liquor volatile suspended solids
Mn ₂ O ₇	Manganese(VII)
Mo	Microorganism
MO	Methyl Orange
N ₂	Nitrogen gas
Na ₂ S ₂ O 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 ₂ O 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 ₂ O ₂	Ultraviolet irradiation / Hydrogen Peroxide, H ₂ O ₂ photolysis process
UV-vis	Ultraviolet-visible
VSS	Volatile suspended solids
V-UV	Vacuum-ultraviolet
ZnO	Zinc oxide

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