

Hybrid O₃/UV/Fe process using rebar flakes waste for removal of congo red dye in wastewater

Fathiya Allisa Zahrandika^{1*}, Sandyanto Adityosulindro¹, Syaza Nadya Felia¹, and Kusrestewardhani¹

¹Universitas Indonesia, Indonesia

Abstract. In Indonesia, textile is one of the labour-intensive industries that makes an important contribution to the national economy sectors. This industry tends to develop rapidly to meet domestic and export needs. This phenomenon increases wastewater generation from the textile industry. Textile wastewater contains dyes that are designed to be durable to resist sunlight and washing process. These properties pose a challenge to the treatment of dye wastewater. The complex structure of dye molecules is generally difficult to degrade by conventional biological processes, while the physical-chemical precipitation process will generate hazardous sludge. Therefore, alternative treatment processes for dye removal are urgently required. In this work, ozonation (O₃), ozone and ultraviolet (O₃/UV), and catalytic ozone coupling with ultraviolet (O₃/UV/Fe) processes were tested for decolourisation of synthetic Congo red dye wastewater. Laboratory assays were carried out under various operating conditions: pH (3-7); ozonation mode (continuous, sequential); and catalyst dose (0.5-2 g/L). Ozonation in sequential mode and the utilisation of rebar flake waste from building construction project as iron catalyst presents a degree of novelty in this work. Congo red decolourisation up to 97% was achieved in less than one-hour of reaction by the continuous O₃ process. Mineralisation in terms of COD reduction (50%) can be increased by either performing ozonation in sequential mode (79%) and coupling with UV irradiation (86%). Nevertheless, the effect of the iron catalyst was found to be negligible.

1 Introduction

Indonesia's textile industry was proliferating in 2019 with 15% growth and was recorded as the highest-growing industry [1]. While the pandemic has halted every growing industry process, the textile industry remains one of the seven primary sectors prioritised for the Industry 4.0 era. All the production process of textile products has resulted in wastewater byproduct, which accounts for up to 58-81% of all water used for production, and more than half of the water is being disposed of without further treatment [2]. The primary pollutant in textile wastewater is dyes that can withstand in the food chain as toxic, mutagenic, and

* Corresponding author: fathiya.allisa@ui.ac.id

carcinogenic compounds showing worse side effects if present in higher trophic organisms. Of all the dyes present in wastewater, azo-dyes are likely to be persistent in wastewater since 15-20% of azo-dyes is not perfectly tied to the fabric and will be carried away by wastewater as a pollutant [3].

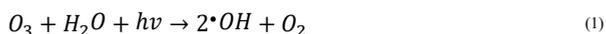
Dyes are persistent and cannot be degraded by relying on biological processes because of their reactive and toxic traits in nature. The toxicity in dyes will harm the biological system and ruin the microbes in the system. One of the most common biological processes is the Sequencing Batch Reactor (SBR). SBR can only remove 67% of anthraquinone and azo dye after 24 hours [4]. Another experiment mentioned that Reactive black 5 and Navy 106, part of an azo dye, are more challenging to degrade in anaerobic conditions. This happened because of the biomass characteristic and low nitrate and sulphate in sludge, which hinders the decolorisation process [5]. Likewise, the coagulation-flocculation process is also not efficient for Congo Red (CR) removal in alkaline conditions, while most of the textile wastewater is in alkaline conditions [6].

To overcome the challenge in textile wastewater treatment, development new treatment technology is urgently indispensable. Advanced Oxidation Process (AOPs) is one of the most promising new technology thanks to its potent oxidation level. The formation of powerful and also non-selective oxidant (for example, hydroxyl radical ($\cdot\text{OH}$)) is the base process of AOPs. The oxidant will then break organic contaminants into small aliphatic compounds, carbon dioxide and water without sludge as by product [7]. In the textile industry, various AOPs technologies have been implemented including non-photochemical combinations such as O_3/OH^- and $\text{O}_3/\text{H}_2\text{O}_2$ [8], a photochemical variety such as O_3/UVC [9], also Fenton and Photo-Fenton oxidation process [10]

In the full-scale application, actually AOPs are constrained by the high energy or chemical consumption compared to typical conventional biological process. When the AOPs process involves O_3 , not only the operational cost but also the safety concern related to ozone production [11]. Moreover, AOPs need rigorous laboratory test to determine the optimum reagent, energy, and experimental condition. Without optimum operating condition, AOPs may undergo scavenging reaction, limited COD/TOC removal, and produce effluent with a high toxicity level than initial condition due to the formation of toxic intermediates during reaction [12,13].

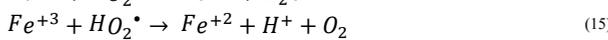
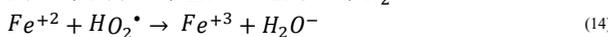
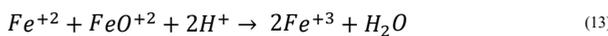
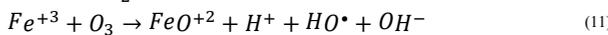
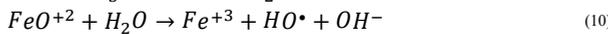
Combining two or more treatment process or called hybrid process is an emerging strategy to overcome AOPs drawbacks through synergically systems between two or more processes. By coupling some processes, more radicals are produced thus increasing the reaction rate and removal efficiency [14]. Moreover, combination of AOPs could provide different degradation mechanisms that may increase mineralization efficiency, reduce reagent and energy consumption [12,13].

In this work, O_3 process was coupled with UV light irradiation and iron catalyst to enhance the free radicals generation process through synergistic reaction. O_3 molecule will be injected towards the system, and the molecule will then react with water to produce hydroxyl radical ($\cdot\text{OH}$) to eliminate pollutants [7]. To enhance the ozonation process, ultraviolet irradiation (UV) can be applied to generate additional hydroxyl radical (equation 1). Furthermore, the propagation and termination steps resulted from the reaction between ultraviolet and ozone (O_3) also lead to the formation of hydrogen peroxide (H_2O_2) (equations 2-5) [15]. Subsequently, the excess of hydrogen peroxide can initiate additional radicals from both $\text{O}_3/\text{H}_2\text{O}_2$ (equation 6) [16] and $\text{UV}/\text{H}_2\text{O}_2$ mechanisms (equation 7).





Besides UV irradiation, catalytic ozonation is another way to enhance the ozonation process. In catalytic ozonation processes, the ozonation rate is accelerated by adding an active metallic catalyst, as shown in equations 8-15 [17]. Catalytic ozonation can be performed homogeneously via ozone decomposition by active soluble metal species or heterogeneously using the organic compound and catalyst via complex formation process [18]. The heterogeneous system is more practically more interesting due to the easy catalyst separation after the reaction.



The objective of this study is to assess the effectiveness of ozonation (O_3), ozone/ultraviolet (O_3/UV), and catalytic ozone/ultraviolet ($O_3/UV/Fe$) processes in decolorizing dye wastewater. The model contaminants for this experiment is Congo Red (CR) because of its toxicity and is used widely in the textile industry [19]. Previous studies have documented the degradation of CR through ozonation and catalytic ozonation [20]. Nevertheless, further research is required to examine the impact of the ozone injection method and the utilization of catalysts derived from waste. In this work, the ozonation of CR was assessed in continuous and sequential steps, while the catalytic ozonation was carried out using rebar flake waste as a catalyst.

2 Materials and methods

2.1 Chemicals and catalyst

Congo Red (CR), H_2SO_4 , and NaOH were acquired from Merck. A synthetic CR standard solution was created by dissolving 0.5 g of CR powder in 1 L of deionized water. The CR working solution at 50 mg/L was subsequently prepared by diluting the CR standard solution. For pH adjustment throughout the experiment, 1M H_2SO_4 and 1M NaOH were employed.

Rebar flakes waste (RFW) was collected from a building construction site in Jakarta. RFW was prepared by sieving through 200 mesh and screening with a magnetic bar to remove coarse and fine impurities. Then, it was washed with deionised water and dried at 105°C for 24 h.

2.2 Experimental setup and protocols

Batch reactor consists of a beaker glass, a magnetic agitator, an ozone generator (11 W; 10 mg/min O_3 ; Diodel Indonesia) and two low-pressure mercury lamps (6 W and 8 W; $\lambda=254$ nm; Hitachi) were used to carry the experiments. The UV lamps were placed 10 cm from the

water surface on the beaker glass perpendicularly (figure 1). In addition, an air purifier with an activated carbon filter was used to collect and decompose the ozone gas.

The breaker glass was filled with a 250 mL Congo Red (CR) working solution, and agitation was set to 300 rpm. To achieve the desired initial pH, a pH adjuster (1 M H₂SO₄ and/or 1 M NaOH) was introduced. The first sample (t_0) was then collected. Subsequently, the ozone generator was activated to initiate the reaction. In the cases of O₃/UV and O₃/UV/Fe processes, the UV lamp was switched on, and the RFW catalyst was added immediately after starting the ozone generator. Samples were withdrawn at specific time points ($t = 5, 10, 20, 30,$ and 60 min), centrifuged, and diluted for analysis. All experimental runs were duplicated to ensure the reproducibility of the concentration-time profile of CR during the reaction.

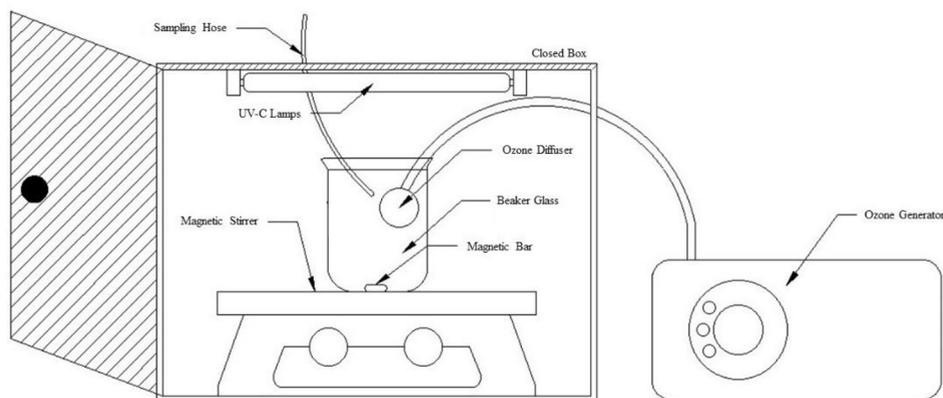


Fig. 1. Experimental set up

2.3 Analytical method

The solution's pH was gauged with a pH meter, and the concentration of CR in water was assessed spectrophotometrically at 499 nm using a UV-Vis Spectrophotometer (DR6000, HACH). Chemical oxidation demand (COD) as an indicator of organic contaminant was determined spectrophotometrically (DR6000, HACH) using HACH method 8000.

3 Results and discussion

3.1 Effect of pH on ozonation

To examine the impact of initial pH on the ozonation process, the experiment is conducted under three distinct pH conditions: acidic (pH 3), neutral (pH 7), and alkaline (pH 10.5). After 1 hour reaction, three different pH conditions result in relatively similar CR removal. The highest removal was achieved at alkaline conditions (pH 10.5) at 97%. It is crucial to highlight that the removal of CR at alkaline conditions happens fastest compared to other conditions. After 20 minutes of reactions, the removal of CR at alkaline conditions has achieved 91%, while the acidic and neutral conditions appear to have 75-80% CR removal. The trend for dye removal can be observed in Figure 2. This shows that ozonation was best executed at alkaline conditions.

At acidic conditions (pH 3), the O₃ molecule was responsible for CR removal. Meanwhile, in the alkaline condition (pH 10.5), the O₃ molecules were shifted to hydroxyl radical (·OH) [21]. The main differences between hydroxyl radical (·OH) and ozone

molecule (O_3) are their oxidation potential and reactivity when degrading pollutants in the system. The oxidation potential of hydroxyl radicals ($\cdot OH$) is greater than that of ozone (O_3). ($2,07 \text{ V } O_3 < 2,80 \text{ V } \cdot OH$) [21]. Higher oxidation potential value in hydroxyl radical ($\cdot OH$) results in slight faster and higher CR removal.

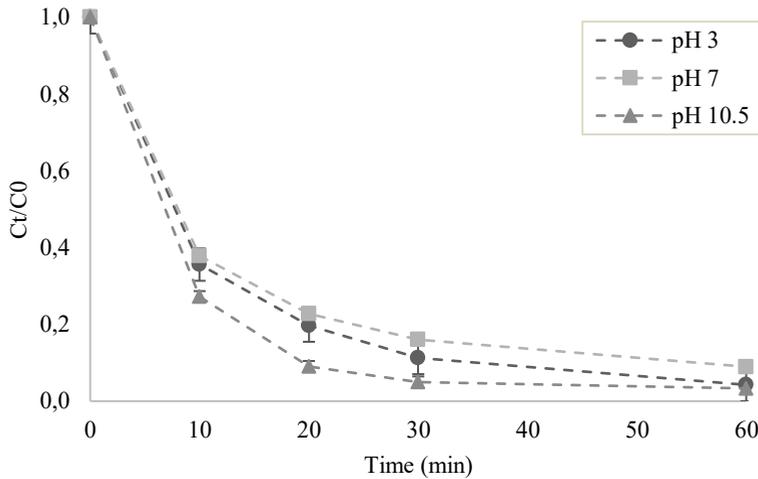


Fig. 2. Effect of pH on ozonation

3.2 Continuous vs sequential ozonation

When observing the conditions where the ozone generator is turned on for 60 minutes straight (60' On), the ozonation process is considered efficient enough to remove CR almost completely. However, noting that AOPs are less desirable because of the high operational cost [22], energy saving could be achieved by reducing the duration of ozonation. This experiment divided the ozonation mode into three conditions: 60' On, 10' On-10' Off, and 5' On-10' Off, corresponding to 150, 75 and 50 mg/L of O_3 doses, respectively.

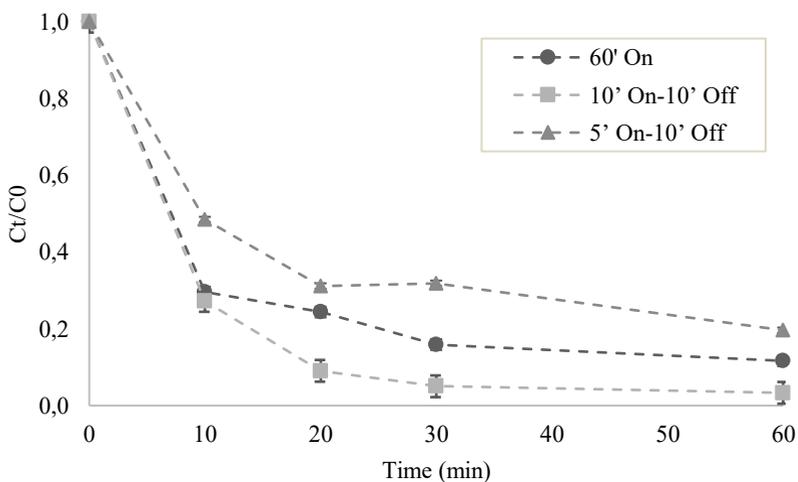


Fig. 3. Effect of Scheme on ozonation

It was observed that the change in O₃ dosage has a significant effect on CR degradation with trends 60' On > 10' On-10' Off > 5' On-10' Off correspond to 97%>88%>81% CR removal in 60 min as observed in Figure 3.

Interestingly, CR removal showed a different trend compared with COD removal efficiency. Highest COD removal efficiency up to 79% was obtained in sequential mode (5' On-10' Off) where theoretical lowest ozone dosage was applied (figure 4). The observed phenomenon can be elucidated by the prevalence of radical scavenger reactions involving ozone molecules and hydroxyl radicals (equations 16-17 [23]) attributable to the surplus of O₃ in continuous ozonation.

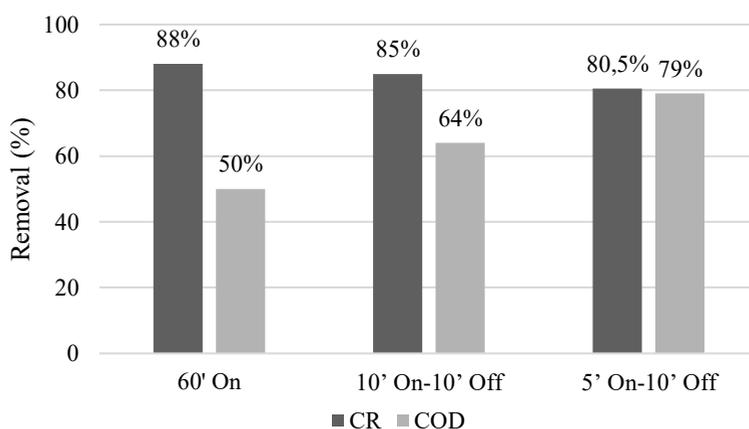
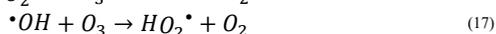
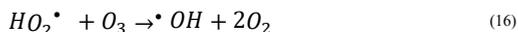


Fig. 4. Comparison of dye removal and COD removal value for schematic ozonation

3.3 Effect of UV irradiation on ozonation

Coupling O₃/UV was observed at optimum pH conditions (10.5) and sequential ozonation with 5' On-10' Off scheme. Then, the result was compared to ozonation-only and UV irradiation-only processes. As depicted in Figure 5, CR removal during UV process was found to be very limited (only 10% removal). This may happen due to the nature of textile dyes that designed to withstand light exposure.

On the other hand, UV irradiation showed additional effect on O₃ process. Compared to the single O₃ process (CR removal: 80%), the combination of O₃/UV obtained higher CR removal up to 89%. This happened due to the contribution of UV (*hν*) towards the reaction of O₃ and water, increasing the concentration of hydroxyl radical and producing hydrogen peroxide (H₂O₂) as an additional oxidant in the system (equations 8-14). Furthermore, the synergistic effect was clearer in term of COD removal. While UV only showed no COD removal, the addition of UV on O₃ process can enhance COD removal from 79% to 86%. This finding indicates that the intermediates formed by radical attack may be susceptible to photolysis.

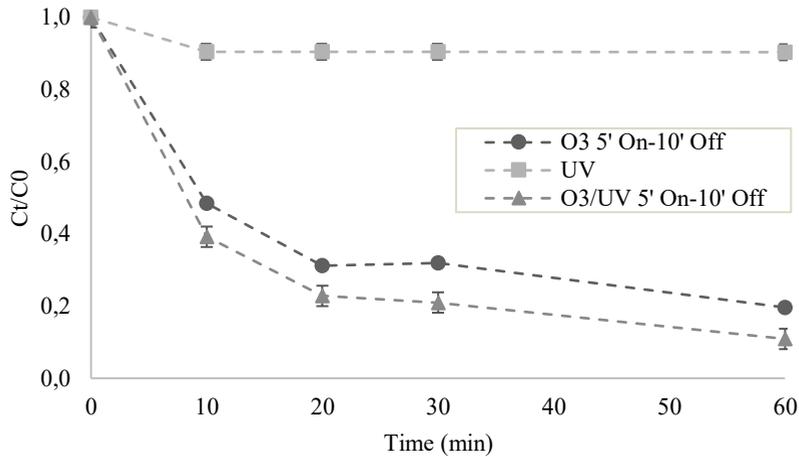


Fig. 5. Comparison of dye removal using O₃, UV, and O₃/UV

3.4 Effect of iron catalyst

The combination between O₃/UV/Fe was conducted to assess the impact of iron catalyst on O₃/UV process. Rebar Flake Waste (RFW) was used as source of iron to induce catalytic reaction (equations 8-15). Based on a previous study, this catalyst can mediate Fenton reaction for removal of methyl orange in water [24]. In this work, the catalyst dose of 0.5, 1, and 2 g/L were tested in O₃/UV/Fe process. Upon closer observation in figure 6, there is no appreciable difference in CR degradation in the presence and absence of RFW. This finding could be explained by the domination of oxidation by ozone over catalytic ozonation mechanisms.

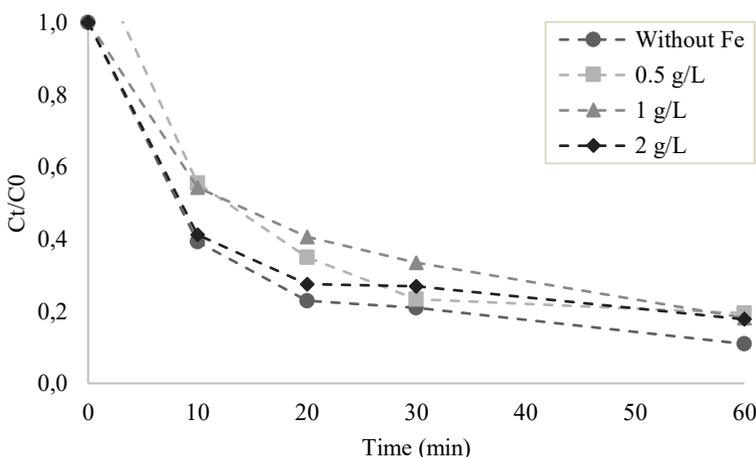


Fig. 6. Effect of Fe catalysts on congo red dye removal

3.5 Kinetic, Energy Consumption and Potential Applications

The kinetic decolorisation of CR by O₃, O₃/UV and O₃/UV/Fe was initially calculated by the first-order, pseudo first-order and second-order kinetic model (data not shown), then the

result found that the CR decolorisation well-fitted the second-order kinetic model. From table 2 it can be seen that the fastest decolorisation was achieved in continuous ozonation process ($k_2 = 0.0089$ L/mg.min). In sequential ozonation process, the decolorisation rate was also almost triple in O₃/UV process ($k_2 = 0.0027$ L/mg.min) compared to O₃ process ($k_2 = 0.001$ L/mg.min).

In the context of energy consumption, the EEO (Electrical Energy per Order) value is employed for a holistic comparison of the studied AOPs, considering both consumption and removal efficiency. This value quantifies the electric energy required to achieve a tenfold reduction in contaminants (kWh/m³/order) [25,26]. The determination of the EEO value involves equation 18, where P stands for the power input (measured in kW by a Watt meter), t is the reaction time (60 min), V represents the volume of the CR solution (0.25 L), and c_i and c_f indicate the initial and final COD concentrations (mg/L).

$$EEO = \frac{P \times t \times 1000}{V \times \log\left(\frac{c_i}{c_f}\right)} \quad (18)$$

Comparison of EEO value from the studied process describes in table 1. Continuous ozonation process which give best CR removal turns out to be the most energy-intensive process (EEO = 186 kWh/m³/order). Interestingly, shifting from continuous to sequential ozonation (5' On-10' Off) can significantly reduce the EEO four times to 48 kWh/m³/order with similar CR removal.

Table 1. Summary of experiments

Process	O ₃ injection	Fe (g/L)	CR (%)	COD (%)	k ₂ * (L/mg.min)	R ²	EEO** (kWh/ m ³ /order)
O ₃	60' On	(-)	97	50	8.9×10^{-3}	0.964	186
O ₃	10' On-10' Off	(-)	88	64	2.2×10^{-3}	0.948	81
O ₃	5' On-10' Off	(-)	81	79	1.0×10^{-3}	0.926	48
UV	NA	(-)	10	0	(-)	(-)	(-)
O ₃ /UV	5' On-10' Off	(-)	89	86	2.7×10^{-3}	0.987	89
O ₃ /UV/Fe	5' On-10' Off	0.5	84	89	1.5×10^{-3}	0.905	81
O ₃ /UV/Fe	5' On-10' Off	1	82	NA	1.3×10^{-3}	0.994	(-)
O ₃ /UV/Fe	5' On-10' Off	2	82	NA	1.3×10^{-3}	0.932	(-)

*CR decolorization kinetics

**EEO calculation based on COD removal

Regarding potential applications of O₃/UV process, both kinetic and EEO are important parameters. Kinetic constant is related to the design of reactor volume while EEO describe energy requirement aspect. AOPs can be implemented using batch mode and continuous-flow mode. In batch reactors, the AOP is carried out in a single vessel for chemical oxidation of the target contaminants. The UV lamps can be integrated by being immersed in the centre of the reactor or placed above the reactor. In O₃/UV/Fe process, RFW catalyst separation can

be carried out by sedimentation or magnetic separation. On the other hand, continuous-flow mode can be performed using pipeline (plug-flow system) combined with membrane separation to remove RWF catalyst at the end of reaction.

4 Conclusion

The decolorisation of Congo Red (CR) dye in water was investigated using ozonation (O_3), ozonation-UV (O_3/UV) and catalytic ozonation ($O_3/UV/Fe$) process. The highest CR removal up to 97% in 1 hour reaction was obtained in continuous ozonation process, while sequential ozonation processes surprisingly superior in terms of COD removal (50% in continuous vs 79% in sequential). This finding could be explained by the occurrence of radical scavenger reactions between ozone molecules and hydroxyl radicals due to the excess of ozone molecule in continuous ozonation process. The UV irradiation effects on ozonation of CR was also found to be beneficial in mineralization efficiency. Nevertheless, the effect of rebar flakes waste as iron catalyst in hybrid $O_3/UV/Fe$ process was negligible. Electrical energy assessment showed ozonation in sequential method (5' On-10' Off) was the most promising process from techno-economical point of view.

Acknowledgements

The author expresses gratitude to the SEED scholarship, generously provided by the Alumni of Civil and Environmental Engineering at Universitas Indonesia for the support for this work. Technical support provided by Licka Kamadewi and Pipit Fitriah from Laboratorium Rekayasa dan Kualitas Air (Laboratory of Engineering and Water Quality) Fakultas Teknik Universitas Indonesia was also acknowledged.

References

1. Kementerian Perindustrian, *Mendorong Kinerja Industri Tekstil Dan Produk Tekstil Di Tengah Pandemi*, Buku Analisis Pembangunan Industri.
2. H. Patel and R. T. Vashi, *Characterization of Textile Wastewater*, in *Characterization and Treatment of Textile Wastewater* (Elsevier, 2015), pp. 21–71.
3. K. Rehman, T. Shahzad, A. Sahar, S. Hussain, F. Mahmood, M. H. Siddique, M. A. Siddique, and M. I. Rashid, *Effect of Reactive Black 5 Azo Dye on Soil Processes Related to C and N Cycling*, *PeerJ* **6**, e4802 (2018).
4. I. C. Gonçalves, S. Penha, M. Matos, A. R. Santos, F. Franco, and H. M. Pinheiro, *Evaluation of an Integrated Anaerobic/Aerobic SBR System for the Treatment of Wool Dyeing Effluents: Purification of Wool Dyeing Effluent in a SBR*, *Biodegradation* **16**, 81 (2005).
5. R. Ganesh, G. D. Boardman, and D. Michelsen, *Fate of Azo Dyes in Sludges*, *Water Research*.
6. K. Sarayu and S. Sandhya, *Current Technologies for Biological Treatment of Textile Wastewater-A Review*, *Applied Biochemistry and Biotechnology*.
7. S. C. Ameta and Rakshit. Ameta, *Advanced Oxidation Processes for Wastewater Treatment*, in *Advanced Oxidation Processes for Waste Water Treatment* (Elsevier, 2018), pp. 1–12.
8. I. Arslan, *Treatment of Reactive Dye-Bath Effluents by Heterogeneous and Homogenous Advanced Oxidation Processes*, Bogaziçi, 2000.

9. Y. Dadban Shahamat, M. Masihpour, P. Borghei, and S. Hoda Rahmati, *Removal of Azo Red-60 Dye by Advanced Oxidation Process O₃/UV from Textile Wastewaters Using Box-Behnken Design*, Inorg Chem Commun **143**, 109785 (2022).
10. S. Chakma, L. Das, and V. S. Moholkar, *Dye Decolorization with Hybrid Advanced Oxidation Processes Comprising Sonolysis/Fenton-like/Photo-Ferrioxalate Systems: A Mechanistic Investigation*, Sep Purif Technol **156**, 596 (2015).
11. H. M. Solayman, Md. A. Hossen, A. Abd Aziz, N. Y. Yahya, K. H. Leong, L. C. Sim, M. U. Monir, and K.-D. Zoh, *Performance Evaluation of Dye Wastewater Treatment Technologies: A Review*, J Environ Chem Eng **11**, 109610 (2023).
12. S. Adityosulindro, C. Julcour, D. Riboul, and L. Barthe, *Degradation of Ibuprofen by Photo-Based Advanced Oxidation Processes: Exploring Methods of Activation and Related Reaction Routes*, International Journal of Environmental Science and Technology **19**, 3247 (2022).
13. G. A. Ismail and H. Sakai, *Review on Effect of Different Type of Dyes on Advanced Oxidation Processes (AOPs) for Textile Color Removal*, Chemosphere **291**, 132906 (2022).
14. F. I. Hai, K. Yamamoto, and K. Fukushi, *Hybrid Treatment Systems for Dye Wastewater*, Crit Rev Environ Sci Technol **37**, 315 (2007).
15. M. A. Oturan and J. J. Aaron, *Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review*, Critical Reviews in Environmental Science and Technology.
16. H. Wang, S. Zhang, X. He, Y. Yang, X. Yang, and S. W. H. Van Hulle, *Comparison of Macro and Micro-Pollutants Abatement from Biotreated Landfill Leachate by Single Ozonation, O₃/H₂O₂, and Catalytic Ozonation Processes*, Chemical Engineering Journal **452**, 139503 (2023).
17. A. Ziylan and N. H. Ince, *Catalytic Ozonation of Ibuprofen with Ultrasound and Fe-Based Catalysts*, Catal Today **240**, 2 (2015).
18. B. Kasprzyk-Hordern, M. Ziótek, and J. Nawrocki, *Catalytic Ozonation and Methods of Enhancing Molecular Ozone Reactions in Water Treatment*, Applied Catalysis B: Environmental.
19. E. I. Yakupova, L. G. Bobyleva, I. M. Vikhlyantsev, and A. G. Bobylev, *Congo Red and Amyloids: History and Relationship*, Biosci Rep **39**, (2019).
20. P. O. Oladoye, M. O. Bamigboye, O. D. Ogunbiyi, and M. T. Akano, *Toxicity and Decontamination Strategies of Congo Red Dye*, Groundwater for Sustainable Development.
21. T. Tapalad, A. Neramittagapong, S. Neramittagapong, and M. Boonmee, *Degradation of Congo Red Dye by Ozonation*, Chiang Mai Journal of Science.
22. S. Sundararaman, V. Kavitha, A. J. Mathew, and S. M. Seby, *Performance Analysis of Heterogenous Catalyst Support for the Decolourisation of Azo Dye (Congo Red) by Advanced Oxidation Process*, Biocatal Agric Biotechnol **15**, 384 (2018).
23. P. K. Rai and P. Kumar, *Role of Post-CCSD(T) Corrections in Predicting the Energetics and Kinetics of the OH[·] + O₃ Reaction*, Physical Chemistry Chemical Physics **24**, 13026 (2022).
24. S. Adityosulindro, A. Rahdhani, and D. M. Hartono, *Heterogeneous Fenton Oxidation Catalysed by Rebar Flakes Waste for Removal of Methyl Orange in Water*, Journal of Applied Science and Engineering **25**, 481 (2021).
25. J. Farkas, M. Náfrádi, T. Hlogyik, B. Cora Pravda, K. Schrantz, K. Hernádi, and T. Alapi, *Comparison of Advanced Oxidation Processes in the Decomposition of Diuron and Monuron-Efficiency, Intermediates, Electrical Energy per Order and the Effect of Various Matrices*, Environ Sci (Camb) **4**, 1345 (2018).

26. J. R. Bolton, K. G. Bircher, W. Tumas, and C. A. Tolman, Figures-Of-Merit For The Technical Development And Application Of Advanced Oxidation Technologies For Both Electric-And Solar-Driven Systems † (IUPAC Technical Report), 2001.