Decolorization of Peat Water by Catalytic Ozonation Process

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***Abstract-*. Peat water is a potential source of raw water in Indonesia, especially on the island of Kalimantan. However, the high concentration of natural organic matter, color, dissolved iron, and low pH in peat water is challenging for conventional water treatment systems such as coagulation-flocculation. This work investigated ozonation-based processes as potential pre-treatment for color and organic removal. Experimental comparisons were made between O_3, O_3/UV, O_3/Fe, and O_3/UV/Fe to analyze the effect of UV and iron catalysts on the effectiveness of the ozonation process. The most promising result was obtained in the O_3/UV/ZVI process at pH 5 with initial conditions including stirring speed during ozonation 300 rpm, temperature 27°C, system volume 250 mL, and ZVI catalyst dosage (1 g/L) with a continuous process for 60 minutes. O_3/UV/ZVI was able to color removal (77%), COD (72%), and total Fe (90%). In addition, the figure-of-merit of studied processes was carried out through Electric Energy per Order (EEO). In conclusion, the catalytic ozonation process as a pre-treatment proved efficient for removing color, organic compounds, and neutralizing pH.**

Keywords; Peat Water, Ozonation, Hybrid Process, Color Removal, Water Treatment

I. Introduction

Indonesia is the fourth country with the largest percentage of peatlands in the world [1] . However, the potential of peat water has not been optimally utilized as a source of drinking water for the community, especially in Central Kalimantan. The high organic matter content makes it unsuitable for sanitation purposes [2]. The high concentration of NOM in peat water, specifically hydrophobic NOM in the form of humic and fulvic acids, causes the water to be acidic and brownish [3][4].

Peat water represents peat water that is characterized by high concentrations of organic compounds and poses significant health risks due to its unsuitability for direct consumption. The challenge of removing color and organic substances using conventional wastewater treatment methods remains a major concern. To address this issue, Indonesia has invested in developing various treatment methodologies, including coagulation-flocculation-sedimentation, adsorption, filtration, and ozonation [5]. However, the efficacy of these techniques varies depending on the specific contaminants present. Coagulation-flocculation, while effective for removing larger particles, exhibits limitations in precipitating fine particles such as organic dyes, heavy metals, and certain organic compounds [6]. Similarly, filtration processes, while demonstrably viable, encounter challenges related to membrane fouling, leading to decreased filtration rates and increased operational costs [7].

One of the most promising peat water treatment processes is ozonation. Ozonation is a treatment method using ozone to oxidize and remove organic compounds, chemicals, and microorganisms in peat wastewater [8]. Typical ozone process characteristics include non-toxic, environmentally friendly material, relatively harmless and can react specifically to complex organic compounds (aromatic organics, phenol groups). The ozonation process involves the injection of ozone through an ozone generator, which will react with organic compounds and microorganisms in wastewater. Ozonation using microbubbles has been widely used in water and wastewater treatment to reduce various pollutant concentrations [9].

The ozonation process is enhanced by using UV light illumination and catalysts. It is an advanced oxidation process that includes photochemical and catalytic methods. The addition of iron ions (Fe^{3+} or Fe^{2+}) has been reported to accelerate UV-enhanced ozonation of some pollutants. Fe(III) is thought to increase the amount of hydroxyl radicals through the reduction of O_3 with Fe^{2+} generated by Fe^{3+} photoreduction[10]. O_3/UV and O_3/UV/Fe (III) combinations were compared with single ozonation, with respect to TOC and COD reduction, respectively, for experiments conducted at room temperature, free pH and 7.4 g/h ozone production [10]. There was no difference of TOC reduction from single and photolytic ozonation of 40-45%. However, photo-fenton reaction of aqueous ferrous iron with UV resulted in higher efficiency. As for COD reduction, the difference was smaller, reaching 85% COD elimination after two hours with single and photolytic ozonation and 100% with UV/Fe (III)-enhanced ozonation [10]. Another study related to O_3/UV in congo red colour removal obtained a high colour removal efficiency of up to 97% in 1 hour [11]. In addition, this study also found that the effect of UV irradiation on ozonation is beneficial in mineralisation efficiency.

This study aims to evaluate the decolorization of peat water by the ozonation process with and without the addition of UV light and iron catalyst. The scope of this study is limited to the parameters to be tested including pH, COD, color, UV365, UV465, and Total Fe.

II. MATERIAL AND METHODS

Preparation of Peat Water

Peat water samples were collected from the Sebangau River in Sebangau National Park, Palangkaraya, Central Kalimantan. Peat water was taken by grab sampling method at 18 L of surface water and collected in a jerry can. The samples were then preserved at low temperatures in a freezer before analysis. Before the ozonation process began, peat water was filtered using a cellulose acetate (CA) filter combined with Whatman 1001-047 filter paper (20 µm pore size) and a continuous vacuum pump. The filtration process was conducted to simulate field conditions in preparation for subsequent ozonation treatment.

Catalyst

Iron (Fe) powder catalysts in the ozonation process will compare commercial catalysts namely ZVI (Zerovalent Iron) and construction waste catalysts namely Rebar Flakes Waste (RFW). The iron content in the RFW catalyst was 60.19% [12]. Meanwhile, ZVI catalyst with ≥99% iron content, was supplied from Sigma-Aldrich.

Analytical

The peat water samples were analyzed using a pH meter for pH measurement, color concentration was measured with a UV-Vis spectrophotometer DR 6000 using the HACH 8025, COD was measured with a spectrophotometer DR 2000 using the HACH 8000, total Fe was analyzed using the HACH 10249 method, and UV 365 and UV 465 measurements were performed with a spectrophotometer DR 6000 following the standard method 5910.

Experimental Procedures

The ozonation process was evaluated using two distinct operational schemes: continuous (60 minutes ON) and sequential (5 minutes ON, 10 minutes OFF) for a total duration of 60 minutes. The experimental setup included an ozone generator, a reactor box equipped with UV lamps (6W + 8W), syringe filters (0.45 µm), a hot plate maintaining room temperature (25–27°C), and a magnetic stirrer set to 300 rpm for consistent agitation.

In the catalytic ozonation process (O_3/UV/Fe), the procedure begins by pouring 250 mL of peat water into a beaker, followed by adding the catalyst at the predetermined dosage. The ozone generator is then activated with a power of 11 watts, and the UV lamps are turned on with a combined power of 6W and 8W, while maintaining constant agitation throughout the process. After 60 minutes of ozonation, samples were collected at specific intervals which were t0, t10, t20, t30, and t60. Moreover, each sample was filtered through a 10 mL syringe filter and then diluted 5-fold with distilled water for subsequent analysis.

III. RESULT AND DISCUSSION

Characterization of Peat Water

Filtration of natural peat water showed a persistent brownish-red color, which suggests the presence of lignin compounds and substances from the humification process, including minerals like iron (Fe) and manganese (Mn). This high color indicates a natural color with positively charged colloidal particles that cannot be deposited by gravity [13]. The 20 µm filter effectively retained larger particles but failed to remove dissolved colorants. The peat water exhibited a low pH, attributed to fulvic and humic acids. Other parameters, including removal of total dissolved solids (24,4%), alkalinity (10,8%), organic matter (2,7%), and turbidity (5%), showed minimal reduction post-filtration, with the decrease in TDS correlating with turbidity, indicating a low concentration of suspended solids. The test results of natural pH peat water samples with a temperature of 25-27℃ are shown as follows.

Tab. 1. Characteristics of Peat Water After Filtration

Parameters	Units	Filtered Peat Water
Total Coliform	MPN/100 mL	26
Color	PtCo	708
TDS	ppm	34
pH	-	4.56
Alkalinity	mg/L	36.6
Iron	mg/L	0.55
Organic Substances	mg/L	11.066
Soluble CO	mg/L	161
UV 365	-	0.1
UV 465	-	0.05
Turbidity	NTU	10.5

Continuous vs Sequential Ozonation

Ozonation experiments were conducted on peat water samples at natural pH and room temperature (25–27°C).

The highest color reduction after 60 minutes was achieved using the continuous ozonation method, with an efficiency of 72.71%, compared to 53.74% in the sequential ozonation process. The most significant decrease in color occurred between 10 and 20 minutes of ozonation, with a reduction of 285 PtCo as seen in **Figure 1**. During the ozonation process, ozone molecules decompose into highly reactive hydroxyl radicals (OH-), which are produced in greater quantities in continuous ozonation. These free radicals then attack hydrophobic compounds, breaking them into smaller particles that dissolve in water.

In contrast, during the sequential ozonation process, an increase in color intensity was observed between 20 and 30 minutes, which coincided with the ozone device being turned off. Initially, a decrease in color occurs as organic compounds break down into smaller, colorless molecules. However, over time, ozone continues to react with these smaller molecules, resulting in the formation of colored intermediate compounds. These intermediate compounds can cause an increase in color intensity during testing [14].

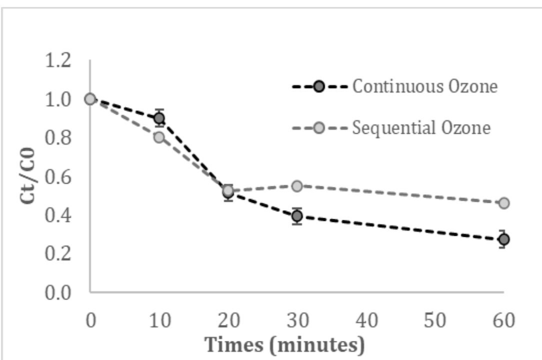

Fig. 1. Effect of Continuous vs Sequential Ozonation

Effect of UV Light Irradiation on Ozonation

UV experiments were conducted on peat water samples at natural pH and room temperature (25–27°C) using UV (6+8W) treatment. The results indicated that UV treatment slightly increased the color by 3.41%. In contrast, the combination of ozone and UV (O_3/UV) led to significantly greater color removal than ozone alone. The O_3/UV treatment achieved a color removal efficiency of 90.26% after 60 minutes, surpassing the 72.91% color removal observed in continuous ozonation. The highest color reduction in the O_3/UV experiment occurred within the first 10 minutes, with a reduction of 262 PtCo.

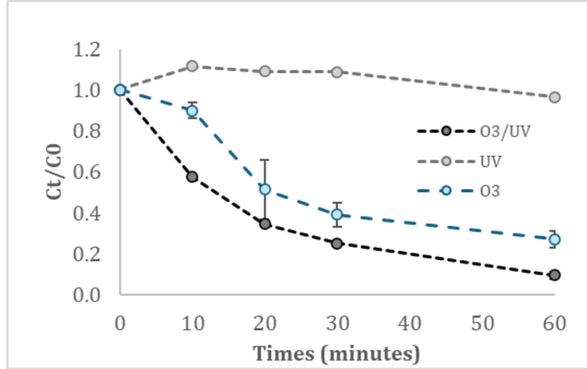

Fig. 2. Effect of UV Irradiation on Ozonation

Electric Energy per Order (EEO)

The O_3/UV/ZVI process effectively reduces COD from 161 mg/L to 45 mg/L, demonstrating its high efficiency with an EEO of 110 kWh/m^3. This significant COD removal reflects the enhanced degradation of organic compounds, which is achieved through the synergistic action of ozone and the ZVI catalyst, resulting in the generation of more hydroxyl radicals (•OH). These radicals are key to breaking down complex organic pollutants effectively. The low EEO value of 110 kWh/m^3 indicates that this process is more energy-efficient compared to continuous ozonation and O_3/UV processes, which have higher EEOs of 135 kWh/m^3 and 137 kWh/m^3, respectively. The combination of the iron catalyst and UV light optimizes energy use, leading to greater COD reduction at lower energy consumption.

Tab. 2. Total Electrical Energy Requirement for Each Experiment

Schemes	Total Ozonation Duration (minutes)	Relative Dose O_3 (mg/L)	Light Intensity	Electricity Consumption during 60 minutes (Watt.hour)[1]	EEO (kWh/m3/order)
O_3 60 ON	60	150	-	14	135
O_3 5 ON 10 OFF	20	50	-	8	188
UV	-	-	96	11	1408
O_3/UV	60	150	96	25	137
O_3/ZVI	60	150	-	14	603
O_3/UV/ZVI	60	150	96	25	110

Effect of Catalyst on Ozonation

In color removal with a variation of four doses, the optimum dose was obtained at a dose of 1 g/L at 95% compared to a dose of 0.5 g/L at 84%, a dose of 0.25 g/L at 84%, a dose of 2 g/L at 50%. The dose of 1 g/L ZVI catalyst was able to reduce the color up to 33 PtCo at the end of 60 minutes. The ZVI catalyst, in this case homogeneous catalytic, will act to initiate ozone decomposition and result

[1] F. A. Zahrandika, S. Adityosulindro, and S. N. Felia, "Hybrid O 3 / UV / Fe process using rebar flakes waste for removal of congo red

in the production of hydroxyl radicals through indirect processes (O_2- and O_3-). HO· reacts mainly by abstracting H atoms or adding to unsaturated bonds [15]. The higher yield of radicals will be utilized to achieve rapid removal of organic compounds.

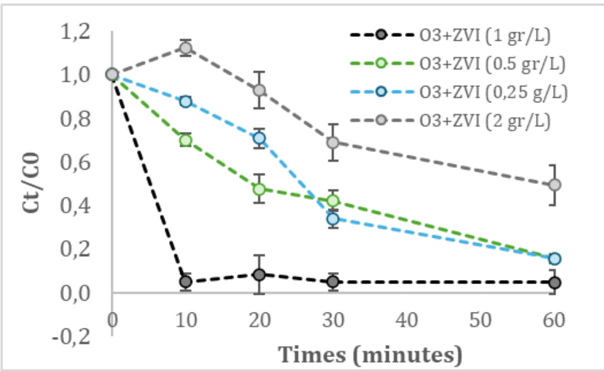

Fig. 3. Effect of Catalyst Dosage on O_3/ZVI

From Figure 3, the value in Ct/Co values exceeding 1 at a 2 g/L catalyst dose during the ozonation process is likely due to the high catalyst dose interacting with other compounds in the sample, thereby altering the measured color and absorbance. The formation of by-products can lead to the generation of new aromatic compounds or result from imperfections in the ozonation process.

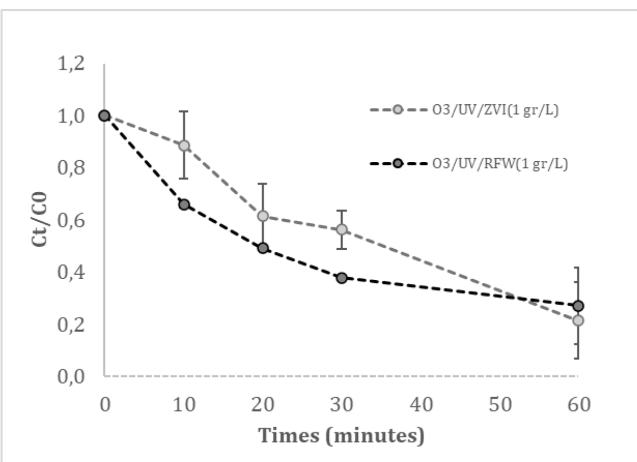

Fig. 4. Effect of Catalyst Dosage on O_3/UV/Fe

Furthermore, the graph above shows the downward trend of O_3/UV/Fe, where after 60 min, O_3/UV/ZVI decreased significantly at 60 min of 188 PtCo from 922 PtCo compared to O_3/UV/RFW of 285 PtCo from 798 PtCo. The stability of a catalyst impacts its oxidizing ability, with RFW being prone to frequent degradation over time. Ozonation can erode its surface, reducing its active area and effectiveness. In contrast, ZVI is more stable and durable due to its inert nature, enabling higher performance. ZVI is particularly effective in breaking down complex, hard-to-degrade organic compounds, offering longer-lasting decoloration effects.

Evaluation on pH, Iron, COD and E3/E4

The highest absorbance observed in natural peat water was 317 nm, indicating the presence of aromatic organic compounds like humic acid. The E365/E465 ratio was used to assess organic matter decomposition, with a higher ratio indicating greater humification and an older peat sample, while a lower ratio suggests younger peat. This ratio is proportional to dissolved organic carbon (DOC) content, with a higher ratio reflecting higher DOC and oxygen demand. Absorbance readings were taken at t0 and t60 for each sample, with the ratio linked to the molecular size of organic fractions in the peat water. The E365/E465 ratio is associated with the molecular size of the organic fractions present in the peat water [16]. From the several experiments conducted, the experimental results are summarised in the following figure.

No	Schemes	pH		Fe	COD	E3/E4		Color removal
		t0	t60	(mg/L)	%removal	to	t60	%removal
1	O_3 Continuous	4.26	4.66	-	61	2.03	5.96	73
2	O_3 sequential	4.43	4.54	-	25	3.8	4.7	54
3	UV	3.8	3.56	-	10	4.46	4.46	3
4	O_3/UV	3.94	3.5	-	81	4.24	4.63	90
5	O_3/ZVI (0,25 g/L)	3.93	4.88	0.15	17	4.04	7	84
6	O_3/ZVI (0,5 g/L)	3.97	4.96	0.03	1	7.97	18	84
7	O_3/ZVI (1 g/L)	4.08	5.04	0.01	19	4	2	95
8	O_3/ZVI (2 g/L)	4.12	5.22	0.02	29	4.27	1.26	50
9	O_3/UV/ZVI	4.62	5.89	0	88	4.07	5.66	79
10	O_3/UV/RFW	4.4	5.09	0.03	76	4.24	5.7	67
11	O_3/UV/ZVI pH 5	5.4	6.38	0.07	72	3.7	4.64	77
12	O_3/UV/ZVI pH 7	7.01	5.97	0.45	65	1.05	4.86	28
13	O_3/UV/ZVI pH 8	8.18	6.47	0.25	68	5.67	1.97	38

Fig. 5. Recapitulation of Whole Experiment Results

The COD analysis following continuous ozonation revealed a reduction of 61%, with concentrations decreasing from 161 mg/L to 62 mg/L. In contrast, sequential ozonation (5 minutes ON, 10 minutes OFF) achieved a lower COD reduction of 25%, with concentrations decreasing from 161 mg/L to 120 mg/L. These results demonstrate that continuous ozonation optimizes ozone utilization by providing a constant supply of the reactive species, which enhances the oxidation process and improves COD removal efficiency. Furthermore, the E3/E4 ratio in the continuous ozonation treatment increased significantly from 2.03 at t0 to 5.96 at t60, indicating a higher abundance of aromatic organic compounds with lower molecular weight lignin in the peat water. This shift suggests that continuous ozonation promotes the breakdown of larger, more complex organic molecules into smaller, aromatic fractions. The combined COD reduction and increased E3/E4 ratio demonstrate the improved effectiveness of continuous ozonation in treating organic contaminants in peat water.

A similar pattern was observed for COD reduction in the O_3/UV system proportional to the E3/E4 ratio, with the E3/E4 value increasing from an initial value at 4.26 to 4.63 after 60 minutes, compared to 4.46 for UV treatment, remaining stables from an intial value. The higher E3/E4 ratio in the O_3/UV treatment indicates a significant alteration in the dissolved organic matter (DOM) structure, where ozone effectively degrades aromatic compounds (with high E3 absorbance) into smaller oxidized products (with high E4 absorbance). Beside that, the COD concentration in the O_3/UV experiment decreased to 30 mg/L after 60 minutes, representing an 81.3% removal efficiency. In comparison, the UV-only method achieved a COD reduction of 9.93%, with the final concentration reaching 145 mg/L. These findings highlight the significantly greater efficacy of the O_3/UV combination in reducing both color and COD levels compared to using UV or ozone alone.

Meanwhile, in the process of adding iron catalyst (O_3/ZVI), the highest total Fe reduction was at a ZVI catalyst dose of 1 mg/L by 99%, but it was not effective in COD removal by 19%. Although HO· is highly reactive, its slightly electrophilic nature makes it slower to attack organic compounds with strong electron-withdrawing groups, such as carbonyl groups [15]. This means to show in some cases that COD reduction in peat water is not always maximal, especially for certain organic compounds that are more difficult to oxidize.

Therefore, the highest efficiency of ozonation was obtained at O_3/UV/ZVI 1 gr/L with pH 5 with removal of color (77%), COD (72%), Fe (90%). In this process, acidic conditions enhance the formation of hydroxyl radicals (•OH), which are highly reactive and increase the degradation of organic pollutants, where ZVI (Zero-Valent Iron) enhances the reduction of Fe and promotes the generation of reactive species like hydroxyl radicals. In addition, UV light accelerates the breakdown of ozone (O_3) into hydroxyl radicals, making the ozonation process more efficient in degrading contaminants.

IV. CONCLUSION

This study shows that the combined O_3/UV/Fe process is the most effective in treating peat water. Continuous ozonation without catalysts showed higher efficiency in removing color (73%) and COD (61%) than sequential ozonation in removing color (54%) and COD (25%). While the combination of ozone and UV light (O_3/UV) gave higher removal rates but higher energy consumption. However, the addition of zero-valent iron (ZVI) to the O_3/UV process with pH 5 adjustment improved color removal (77%) and was effective in reducing COD (72%), and total iron (90%). Overall, the O_3/UV/Fe with pH 5 process offers a promising approach for peat water treatment due to its high efficiency in removing organics and color, and low energy consumption (110 kW h m^{-3} $order^{-1}$).

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