Advanced Oxidation Process Using UV-H_2O_2 For Organic Substance Removal in Peat Water Based on Discoloration Signatures

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Abstract: Peat water is surface water that has high color intensity, low pH (pH 3-5) and contains the high organic substance, so it has influenced the health if it's used. Purpose of this research was conducted to the removal of organic substance (%R) in peat water using in UV-Peroxidation process as discoloration signatures indication. UV-Peroxidation is one of AOP (Advanced Oxidation Processes) base on the reactiveness radical hydroxyl ($HO^{\bullet}$) that originated from the existence of H_2O_2 with UV radiation. The research doing by varying the concentration of H_2O_2 0,0 – 0,11% in the wavelength of UV lamp 360 – 240 nm for 0-240 minutes. The result of that condition was shown that the higher concentration of H_2O_2 and longer of radiation time led to the bigger efficiency of the removal organic substance (%R). From the experiment, it can be concluded that the optimum dose of H_2O_2 was gained in at 0,07% and the removal of organic concentration found to 98,56% within 240 minutes. The measurement of water discoloration indicated up to 5TCU clarity.

Keywords: AOP, H_2O_2, organic substance concentration, peat water, UV-Peroxidation

1 INTRODUCTION

Peat water is surface water found in peat areas. Visually, peat water is reddish brown, tasted acid and smelly. In Indonesia, The study of Geology Resource Center of Energy and Mineral Resource Ministry reported that till 2006 the peat areas coped to 26 million hectares (ha) that spread in Kalimantan (± 50%), Sumatera (± 40%) while the rest of them spread in Papua and other islands. Especially for the peats area, Indonesia owns the fourth biggest area in the world after Canada, Rusia dan Amerika Serikat [1]. Based on this data, peat water in Indonesia is potentially utilized as a source of water for daily use if it has been processed properly.

Theoretically, the reddish brown color in peat water is caused by high content of dissolved organic substances (topsoil materials), particularly acid and its derivation, so the range of the pH is 2-5, high content of organic substances and metal, turbidity and the content of low suspension particles. The topsoil acid comes from organic decomposition such as leaves, trees or wood. Therefore, the technology of peat water processing to be clear water can

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be measured by the change of organic and metal contents which meet the standard of clean water.

Some methods of peat water processing have been done in both laboratory scale and real areas, unfortunately, they did not show the maximum results, yet. Conventional coagulation method in laboratory scale which done by using cockle shell and corals in processing peat water in Greudong Pase could only remove 5-58% of Fe concentration and were not able to change the water color which was still brownish yellow. The one of research about peat water treatment using the *Two-Stage Coagulation* method was capable to remove the organic compound of peat water in Bangkinang, Riau up to 88% by using Alum as the coagulant in dose of 280-300 mg/L but still was not significantly good in removing Fe concentration which was stable to the organic.

According to Watts [2] organic compound will easily oxidize by using radical hydroxyl ($HO^{\bullet}$), so it can be mineralized to be carbon dioxide (CO_2) and water (H_2O). *Advanced Oxidation Processes (AOP)*method is an advanced oxidation process that able to create radical hydroxyl ($HO^{\bullet}$) as an excellent oxidizer to oxidate all materials found in water.AOP method based on H_2O_2 was explained as the application of AOP by using H_2O_2 as a source reagent in producing radical hydroxyl which has oxidation potential (E^0=2,80 V) bigger than the oxidation potential of hydrogen peroxide (H_2O_2, E^0=1,80 V) itself.

Based on the prior research, UV-Peroxidation in laboratory scale managed to remove 77% of organic concentration (TOC) and 96% of Fe substance in peat water for 60 minutes in the 360 nm wavelength and constant concentration of H_2O_2 0,05% (Elfiana and Zulfikar, 2012) in [3]. The process of UV-Peroxidation was proved managed in removing Fe concentration in groundwater up to 92,10% [4]. In line with the previous study, it is expected that the using of UV/H_2O_2can give an appropriate way out to the alternative technology in processing peat water by supplying high efficiency to the removing of organic concentration and peat watercolor. Therefore, it is necessary to conduct a study to observe the optimum H_2O_2dose that can be used as $HO^{\bullet}$ source after being radiated by UV at 250-400 nm wavelength.

Based on the knowledge of the cause and color content in water and its characteristics, the process and the method that can be applied in processing natural color of water are; oxidation process, adsorption, coagulation-flocculation and separation with the membrane.

Organic substances consisted in nature might originate from plants, oil fibers, animal fat, starch, sugar, cellulose, and others. Those organic materials are related closely to the alteration of the physical characteristics of water, especially with the undesired changing of color, scent, taste, and turbidity. [5] states that AOP is work properly in the process of removing the contaminant in water to reduce the mixing of organic and nonorganic substance, COD, and BOD, which were not oxidated. If the process works completely, the result of organic substance oxidation is carbon dioxide and water, although it is difficult to gain a perfect result. AOP process, according to [6] has a basic rule in producing radical hydroxyl maximally, it is very reactive and also a strong oxidizer that can damage the organic and nonorganic contaminant which reacted with it.

In its development, the combination from several processes has been used such as ozone, hydrogen peroxide, ultraviolet light, titanium oxide, photocatalyst, sonolysis, electron beam or also known as AOP (Advanced Oxidation Processes) method which is a process to produce radical hydroxyl [7].

According to [5] a chemical compound that is hard to be broken through chemical oxidation can be oxidated by using radical hydroxyl (HO*) which is a reactive substance formed from intermediate reaction process. Its oxidation potential (E^o = 2,8 V) is bigger than

other oxidators. Radical hydroxyl formed through AOP is caused by UV radiation simulation and hydrogen peroxide [8].

The mechanism of the radical hydroxyl formation using hydrogen peroxide (H_2O_2) as a limiting reagent was known in three processes i.e Fe[II]/H2O2), UV/H2O2 dan O3/H2O2, as shown in Figure 1.

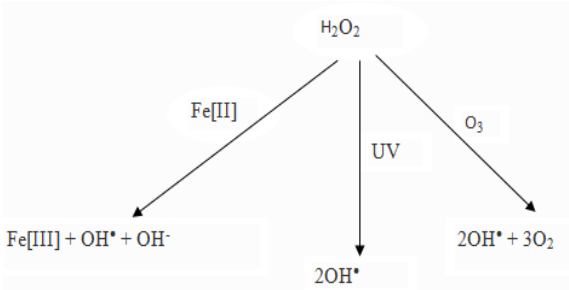


Fig. 1 The production of radical hydroxyl in AOP method based on H_2O_2 through reagent Fenton (Fe[II]/H2O2), UV/H2O2, and O3/H2O2 [9].

Radical hydroxyl reacts with all dissolved constituents, usually in series until the constituents are mineralized completely. It is not selective in zapping the constituents, without any specific class limit or compound group, which is different from other oxidants, and its reaction can be operated in normal temperature and pressure [6].

1.1 Photochemical process of UV

Ultraviolet (UV) was reported by Petersen *et.al*. (1988) as a ray that can be used to oxidate organic pollutant, known as photooxidation.The addition of energy in a system that contains organic substance is a principle process of photooxidation. The reaction of organic compound oxidation with UV ray occurred because the ray induces photochemical in water which produced radical hydroxyl following the reaction below (Cervera and Esplugas, 1983 in Jones, 1999):

$$H_2O \xrightarrow{hv} H^{\bullet} + HO^{\bullet} \quad (1)$$

1.1.1 Light Source

Light is one of electromagnetic wave types. The types of light that radiate ray can be classified based on its wave, i.e:

- Ultraviolet vacuum λ = 100 nm – 200 nm
- Ultraviolet λ = 200 nm – 400 nm
- Tampak (visible) λ = 400 nm – 800 nm
- Infra λ = 800 nm – 106 nm

Based on UV ray source, UV can be classified on:

Natural UV; UV, originated from the sun, consist of “UV-A” (400-320 nm) and more energetic UV which is shortwave “UV-B” (320-290nm). Shortwave radiation is adsorbed stronger by various types of pollutant and biomolecules. However, the basic mechanism of photochemical is same and the difference only happens in chromophore group of the receiver molecule.

Artificial UV, The wavelength is smaller than 290 nm and known as “UV-C”. The example of this UV is UV which is created of mercury bar. The intensity produced is usually higher and surely more energetic than sun UV [6].

Based on the UV ray function for photolysis, the effectivity of UV ray can be distinguished from the types of light that produce ray source i.e, polychromatic and monochromatic light. The main characteristic of this light is based on the wavelength emission around UV ray. The shorter energy of light wave the bigger radiation of energy happen. Polychromatic light radiates its ray in 180-400 nm wavelength, while the monochromatic light is in 254 nm (Froelich, 1992) in [5] states that good photolysis result will occur around polychromatic light length wave area, however, the result of photolysis in removing organic substances is more effective in monochromatic light.

1.1.2 UV-Peroxidation (H_2O_2/UV)

UV- Peroxidation is a chemical oxidation process that used Hydrogen Peroxide as a reagent to excited state becomes radical hydroxide ($HO^{\bullet}$)with the UV radiation. [9] reports that UV-peroxidation has been applied for remediation of good water from several contaminant areas in Nort America and Europe. One of the food industries in the USA used UV-peroxidation for good water contaminated with trichloroethylene (TCE) so the well water is reusable.The result showed that TCE was reduced from 4000 μg/l to 0,83 μg/l in the rate of flow 14 m^3/hour, with H_2O_2 50 mg/l and UV 30 kW light.

UV-peroxidation was proven to produce radical hydroxyl and able to oxidate water contaminant according to the reaction mechanism as below :

Initiation Phase:

$$H_2O_2 \xrightarrow{h\nu} 2\,HO^{\bullet} + HO^{\bullet} \quad (2)$$

Propagaation Phase:

$$H_2O_2/H_2O^{\bullet} + HO^{\bullet} \xrightarrow{h\nu} H_2O/OH^{-} + HO_2^{\bullet} \quad (3)$$

$$H_2O_2/H_2O^{\bullet}/O_2 \xrightarrow{h\nu} HO^{\bullet} + H_2O/OH^{-} + O \quad (4)$$

Termination Phase

$$HO^{\bullet} + HO^{\bullet} \xrightarrow{h\nu} H_2O_2 \quad (5)$$

$$HO^{\bullet} + H_2O^{\bullet}/O_2 \xrightarrow{h\nu} H_2O/\,HO^{\bullet} + O_2 \quad (6)$$

$$H_2O^{\bullet} + H_2O^{\bullet}/O_2 \xrightarrow{h\nu} H_2O_2\,/HO_2^{-} + O_2 \quad (7)$$

Due to radical hydroxide that reacts with Hydrogen peroxide, the existence of hydrogen peroxide is influential to radical hydroxide in decomposing process. Therefore, the addition of hydrogen peroxide is suggested in optimal concentration to have the optimum decomposition.

2 Methods

2.1 Peat water Characteristics

The sample of peat water from Ek Tren village in Samudra district of Aceh Utara was examined its physical chemistry characteristic based on the parameters; pH, TDS, turbidity, Fe

ion and organic substance ($KMnO_4$). The result of peat water characteristic used is compiled in Table 1 below :

Table 1. The Characteristic of Peat water from Ek Tren Village in Samudra District, Aceh Utara refer to PERMENKES RI No.416/MENKES/PER/IX/1990

Parameter	Unit	Level	Limit of Requirement
pH	-	5,7	6,8-8,5
TDS	mg/L	250	1.500
Turbidity	NTU	4,55	25
Fe iom	mg/L	16,18	1
Organic Substance (KMnO4)	mg/L	395	10

(Source: The result of analyzation in Laboratory, 2016)

2.2 Reagent

The material used in this research were peat water from Simpang Ek Tren in Samudra district, Aceh Utara; technical hydrogen peroxide ($H_2O_2$35%; density 1,11 kg/l; BM 34 g/mol; BE 17); aquadest; H_2SO_4; $NH_2OH.HCl$; HCl; $NH_4.C_2H_3O_2$; $H_2C_2O_4.2H_2O$ and $KMnO_4$.

2.3 Prototype of AOP reactor

The installation prototype of UV-Peroxidation reactor refers to the principles of water treatment with AOP in general, which is as shown in process chart flow in Picture 2, therefore the prototype of UV-peroxidation reactor instrument resulted in this research can be seen in Figure 3 and 4.

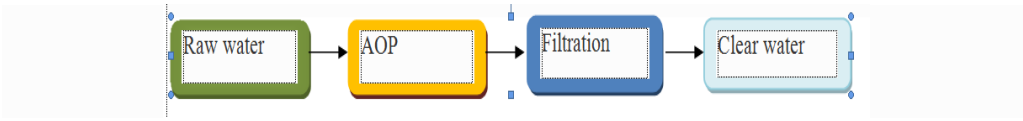


Fig. 2 The Principle of Water Treatment with AOP

The batch system of UV-peroxidation reactor UV-Peroksidasiin laboratory scale is shown in picture 3. The reactor is made from *pyrex-glass*with2 L capacity equipped with a stirrer, pH measurement, temperature, and filter.

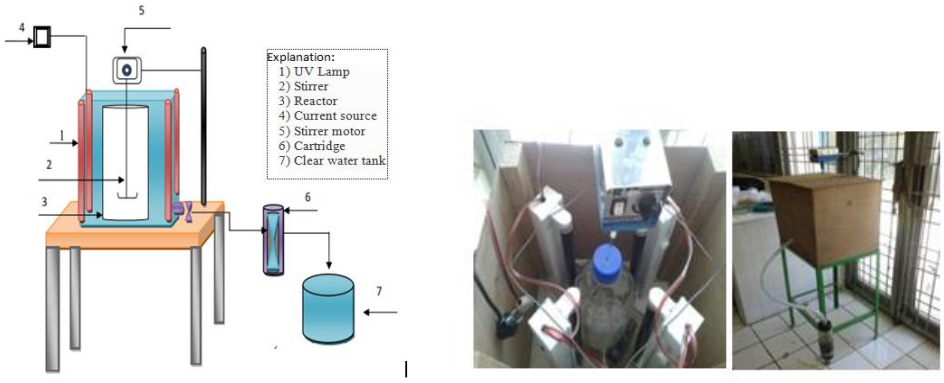


Fig. 3 UV-Peroxidation reactor with batch system in laboratory scale with10 watt UV lamp, brand Elite SK F 10 W T8 BLB (λ=360 nm)

In Figure 4, the equipment series of UV- Peroxidation process consisted of feedback tank 25 L, recirculation pump, peroxidation reactor (Aspirator with 5L capacity, with work volume 3,8L) , reagent tank of H_2O_2in upper side, Quartz Sleeve UV Lamp 10 Watt brand SNXIN, piping systems (distribution pipe, circulation pipe and bypass pipe, each has 3/8 diameter) connected the UV-peroxidation reactor with cartridge 03µ and 01µ,as the finishing process, filtration is intended to get clean and clear peat wate and has organic concentration and low Fe ion after the process.

Fig. 4 UV-Peroxidation with batch system batch in laboratory scale using 10 WUVlamp brand SNXIN (λ=240 nm)

2.4 Analysis

Ph measurement of peat water used Ph meter brand HANA HI 8424, the analysis of organic substance used Permangometry method with titration while the analysis of water peat color was used by using PtCo Spektrofotometry method.

The performance of each process can be seen from the percentage of removal (%R) parameter concentration gained from the following equation:

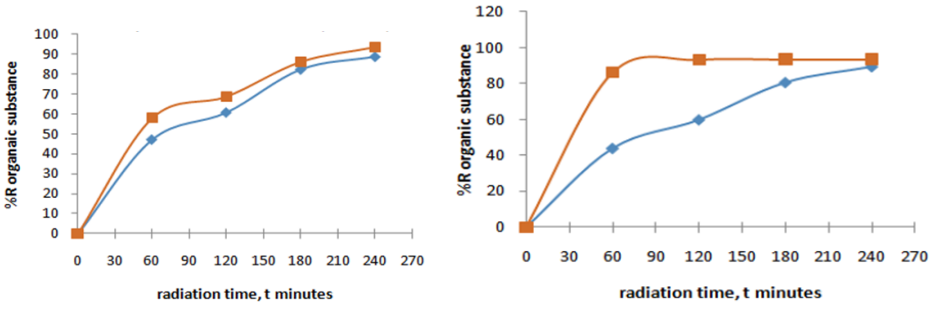
$$\%R = \frac{Concentration_{(\text{int hebeginning})} - concentration_{(inime)}}{Concentration\,(\text{int hebeginning})} x\,100\% \quad (8)$$

3 Result and Discussion

Referring to PERMENKES RI No. 416/MENKES/PER/IX/1990 , it can be concluded that the resulted characteristic of peat water did not meet the requirement as consumptive water because it was beyond the allowable level, the concentration of Fe ion was 16,18 mg/L (>1 mg/L) and the concentration of organic substance was 395 mg/L $KMnO_4$ (>10 mg/L $KMnO_4$). It can be concluded that the values of these three parameters were beyond the determined level, hence it is necessary to carry out the treatment process to improve the quality of the peat water before it ready to use.

3.1 The effect of H2O2 concentration in UV-Peroxidation process to the percentage of the reduction organic substance concentration

In UV-peroxidation process, H_2O_2 is used as the basic reagent of radical hydroxide forming which is formed during the UV- peroxidation process with the existence of UV ray energy. Thus, it is necessary to observe the influence of H_2O_2concentration in the treatment process of peat water, because oxidation reactivity would be different in each color water type that will be processed. In this research, the effect of $H_2O_2$was observed by looking at the changed values of organic substance concentration contained in peat water by processing the peat water with and without the addition of H_2O_2concentrated 0,05% along with the radiation in 360 nm and 240 nm wavelength. The result gained in this treatment is shown in the graph in Figure 5.



a) UV Lamp Elite SK F 10W T8 BLB (360 nm) b) Quartz Sleeve UV Lamp SNXIN 10 W (240 nm)

Fig. 5 Plot of %Rorganic substance with time at different wavelength radiation are 360 and 240 nm from the process with and without H2O2. The color is represented as follow: blue is UV ray + H2O2 0% ; and red is UV ray + H2O2 0,05%

3.2 The effect of UV ray wavelength to the reduction percentage of Organic Substance Concentration

In this research, the effect of UV ray wavelength was observed to find out the change of values from organic substance concentration contained in peat water by comparing two processes of UV-peroxidation using UV ray 360 nm and 240 nm. The process of peat water without adding H_2O_2 concentrated in various concentration H_2O_2 (0,0; 0,03; 0,05; 0,07; 0,09; dan 0,11%). The result obtained in this treatment is shown in the graph in Figure 6.

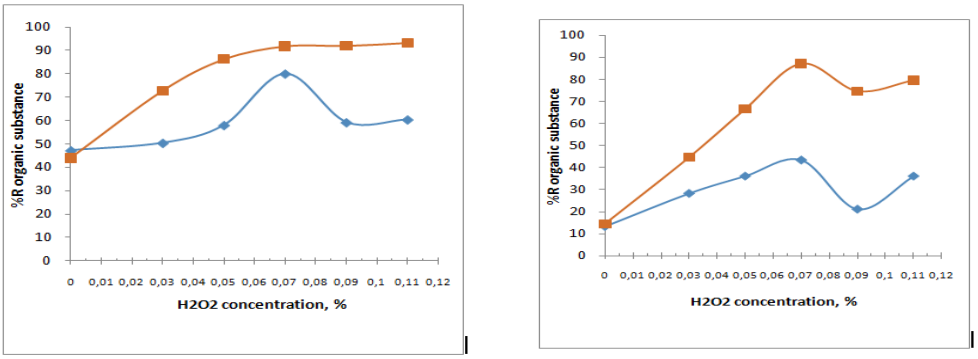


Fig. 6 Profile $\%R_{organic\ substance}$ in every time from the various concentration of H2O2 with wavelength UV ray. The color is represented as follow: blue is UV ray 360 nm, and red is UV ray 240 nm

From the graph in picture6it can be seen that $\%R_{organic\ substance}$ that gained from UV-Peroxidationprocess with UV ray radiation in the wavelength of 360 nm and 240 nm in various concentration of H_2O_2gave the different attained value percentage of gained organic substance reduction.The treatment using UV ray 240 nm gave a better percentage of organic substance reduction compared to the treatment using UV ray 360 nm. This is due to the resulted photon energy of UV ray 240 nm was bigger than resulted from UV ray 360 nm thus the process reactivity became bigger.The shorter of UV ray wave that radiated into the water, the bigger photon energy resulted because photon energy (E) is inverse with the wavelength (λ) in light velocity (c).

3.3 The performance of UV-Peroxidation process based on reduction percentage of Organic Substance (%Rorganic substance

From the previous treatment, it has been known that the concentration of $H_2O_2$and the UV ray influenced to $\%R_{organic\ substance}$ that resulted once the performance of UV – peroxidation process can be known based on the biggest value of $\%R_{organic\ substance}$ resulted from varying the dose of H_2O_2in various concentration and length of the wave from UV ray.The result shown from this treatment is displayed graphically in Figure 7

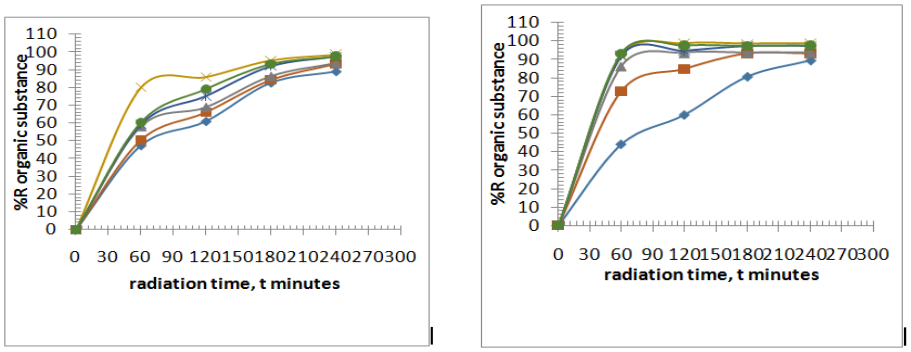


Fig. 7 The Performance of UV-peroxidation Process based on the percentage of organic substance reduction (%Rorganic Substance)

From the graph in picture 7, it is known that the optimum condition for the UV-peroxidation process that gave the best performance based on the efficiency of organic substance reduction. From the graph, it is also known that the percentage of organic substance reduction was gained in the concentration of 0,07%H_2O_2, the type of UV lamp with the beginning organic was 395 mg/L $_{KmnO4}$can be reduced up to 98% became 5,6 mg/L 60-120 minutes radiation time.Several samples of water around the damn were shown in picture 8.

Fig. 8 Sample of peat water and processed peat water

4 Conclusions

The conclusions achieved from part of the research are the characteristic of peat water in Ek Tren Village in Samudra district, Aceh Utara contains 395 mg/L organic substance, 16,18 mg/LFe_{total}, 9,85 mg/LFe^{2+}. The optimum dose of H_2O_2 optimum gained based on the percentage of organic substance concentration reduction (%$R_{organic\ substance}$) which is the biggest of H_2O_2concentration variation (0,0% – 0,11%), which is 0,07% with %$R_{organic\ substance}$ = 98%.

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