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Advanced Oxidation Processes (AOPs) for Refinery Wastewater Treatment Contains High Phenol Concentration

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Abstract. Petroleum Refinery wastewater is characterized by a high phenol content. Phenol is toxic and resistant to biological processes for treatment of the petroleum refinery wastewater. The combination of an AOP and a biological process can be used for treatment of the refinery wastewater. It is necessary to conduct a study to determine the appropriate condition of AOP to meet the phenol removal level. Two AOP configurations were investigated: H_2O_2 / UV and H_2O_2 / UV / O_3. From each process samples, COD, phenol and pH were measured. The oxidation was carried out until the targeted phenol concentration of treated effluent were obtained. The better result obtained by using process H_2O_2 / UV / O_3 with the H_2O_2 concentration 1000 ppm. After 120 minutes, the final target has been achieved in which phenol concentration of 37.5 mg/L or phenol degradation of 93.75%.

1 Introduction

Currently increasing of fuel consumption of about 5% per year make Indonesia have a very high fuel deficit if there is no additional oil processing capacity in the country. As a state-owned enterprise engaged in the energy sector, Pertamina continues to work hard in sustaining the availability of public fuel and achieving national energy security. Various oil and gas projects were established, one of which is the Residual Fluid Catalytic Cracking project, known as RFCC Project in Cilacap, Central Java. The RFCC refinery will increase premium production to 91,000 barrels per day or up 30,000 barrels per day (Pertamina.com).

The oil refinery consumes a minimum of 75.7 liters to 227.1 liters of clean water to process 1 barrel of crude oil [1]. The amount of waste water produced is about 41% of the amount of water used in the process [2,3]. From several previous laboratory tests it was found that refinery waste water had COD concentrations of 750-1600 mg / L, BOD about 300 mg / L, oil and mud concentrations 500-3000 mg / L, sulphide 13-17 mg / L, ammonia 14 mg / L, phenol around 960 mg / L, temperature around 30^0C and pH above 7 [4-6].

The use of AOPs is proven to be effective for wastewater treatment, but it tends to be expensive because intermediate oxidation is formed during the process and makes a long chemical degradation, requiring considerable energy [7]. AOPs technology is one or a combination of several processes such as ozone (O3), hydrogen peroxide (H_2O_2), UV radiation, titaniumoxide (TiO_2-photocatalyst), Fenton process, as well as several other processes that can produce hydroxyl radicals). OH radical is the active species that has the highest relative oxidation potential, which is about 2.8 V, bigger than ozone having an oxidation potential of 2.07 V. This makes the OH very easy to react with other compounds around it [8].

The UV / O_3 / H_2O_2 method as an alternative technology and further development of UV / O_3 and UV / H_2O_2 methods. The AOPs technology was developed to obtain a rapid and nonselective concentration or amount of hydroxyl radicals for processing and removing persistent contaminants, as well as pollutants of EDCs (endocrine disrupting contaminants). Oxidizing agents, H_2O_2 and O_3 are added to the body of the liquid to be treated, and then activated with UV radiation photon energy so that spontaneously generate hydroxyl radical (• OH).

RFCC wastewater has a high phenol content. Phenol is toxic and resistant to biological processes, and required further process in order to be biologically processed in the existing refinery wastewater plant [9]. The use of biological treatment processes will be constrained by high levels of phenol which interfere the nitrification process. Some toxic compounds that can inhibit the nitrification process include: cyanide,

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thiourea, phenol, aniline, and heavy metals such as silver, mercury, nickel, chrome, copper and zinc.

In order to be biologically processed, wastewater must contain Dissolved Oxygen (DO) about above 2 mg / L, COD 500-3000 mg / L, ammonia 20 mg / L, phenol 50-100 mg / L, temperature around 30^0C and pH about 5-10 [10-12]. In dealing with the problem proposed biological system of two stages. There was the addition of aeration tubs that require larger place and longer time [11].

The combination of AOPs processes and biological processes can be used in refinery wastewater treatment [13]. The main drawback of the AOPs process is the high cost due to large energy consumption. Selection of AOPs processes and operating conditions need to take into account the most extreme wastewater characteristics. From the existing wastewater data the process UV / H_2O_2 and UV / H_2O_2 / O_3 process have to be studied. The oxidation of organic pollutants in wastewater by AOP process utilizes the hydroxyl radical (OH) obtained by combining processes such as ozone O_3, UV, and H_2O_2 [14]. The number of OH radicals formed is influenced by the type of reaction and the presence of a strong oxidizer in the form of a mixture of hydrogen peroxide with ultraviolet light, a mixture of ozone with ultraviolet light and a mixture of ozone with hydrogen peroxide.

Phenol is classified in alcohol so can be oxidized to ketones, aldehydes and carboxylic acids [15]. Morkini et al., [16] states that carbon in ortho positions and the phenol compounds are electron donors so in such positions the electrons has high density. Hence the OH radical has a tendency to strike that position forming intermediate compounds of catechol, hydroquinone, and benzokuinon. The end product of the oxidation reaction is carboxylic acid and ketone which can be processed in biological process [17]. The phenol degradation reaction is a first-order reaction, so the oxidizing concentration and reaction time will direct the fast-moving and precise reaction to form carboxylic acids and ketones. The more oxidizing concentrations and reaction time may not necessarily produce the desired product, whereas to obtain low phenol content requires high energy and cost. It is necessary to conduct a study to determine the condition of AOPs process that meets the target.

The experiment will evaluate the processing of AOPs with UV / H2O2 and UV / H_2O_2 / O_3 process and determine the operating conditions of AOPs target effluent with phenol concentration 50-100 mg / L.

2 Experimental

2.1 Materials

This experimental uses synthetic and real wastewater. Synthetic wastewater was made by dissolving phenol PA with deionized water. The real wastewater come from Pertamina RU IV Cilacap. Hydrogen peroxide (technical). UV Lamp Model Viqua Sterilight Silver S12Q-PA UV System 15 gpm Serial 131219515, 110-240v 50/60 Hz. Ozonator model Viqua Sterilight Model S8Q-OZ/2 Serial 13060530, 110-240v 50/60 Hz; Fe_2SO_4; H_2SO_4 and NaOH (*Analytical Grade*) as pH controller.

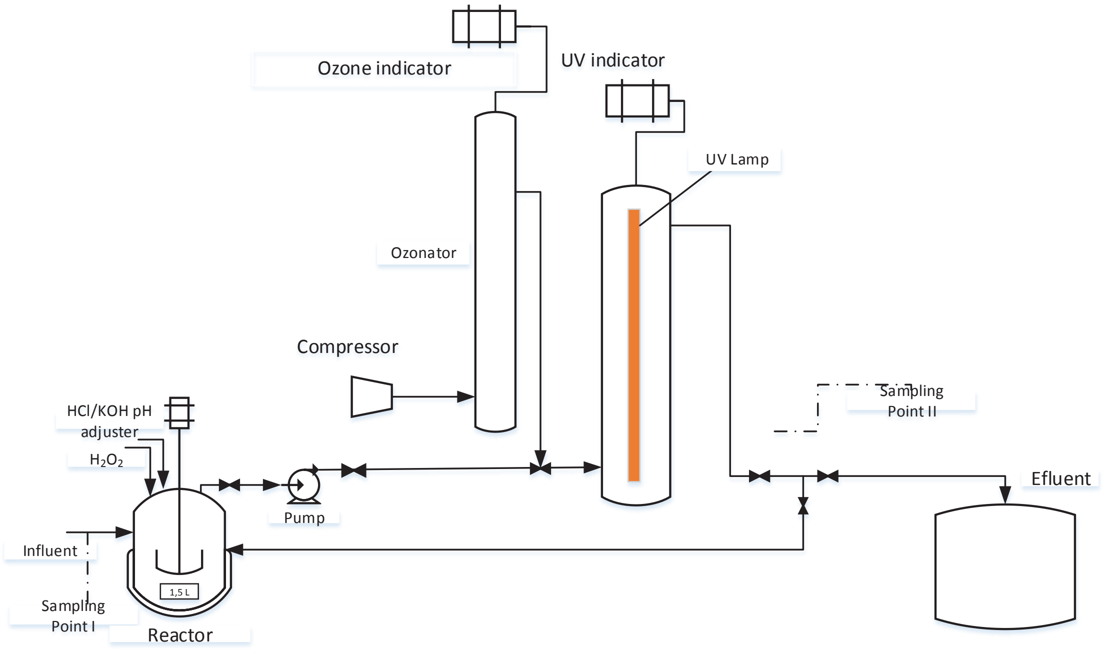

Fig 1. Advanced Oxidation Processess System

2.2 Method

Pertamina refinery waste water is first separated from solid impurities such as sand, stone, and solid waste. Prior to processing, wastewater was carried out by preliminary test, ie COD, phenol, and pH. A total of 20 liters of waste water goes into the reactor for AOPs processing using H_2O_2, ozone, and UV. Wastewater (influent) analyzed the COD, phenol, and pH content first. Then added H_2O_2 on various variables and arranged at pH using HCl and KOH. Influent is pumped into a UV process that is equipped with an ozone generator. (See Fig 1.).

After the process is done the analysis of effluent characteristics. The process is circulated with various time and hydrogen peroxide variables then analyzed effluent characteristics to obtain the required conditions to achieve the biological treatment on existing waste water treatment plant. The experiments were carried out with variations of the combination of H_2O_2 / UV and H_2O_2 / UV / ozone.

For Fenton system, prepare 250 ml wastewater on Schotts Bottle, then adjust pH into 3 by adding H_2SO_4. Add the Fe_2SO_4 catalyst then hydrogen peroxide for each variable. This experiment run with time variable from30 until 180 minutes. The results analyzed as like as the AOPs process.

2.2 Analytical

Influent and Effluent are analyzed Phenol, COD, and pH using Hanna Instruments HI 3864, HI 93754C-25 HR, and HI 8424 in order.

3 Results and discussion

3.1 UV/H_2O_2 process

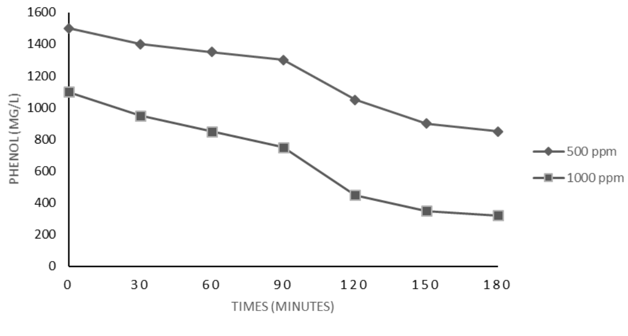

Fig 2. Phenol Degradation for synthetic RFCC wastewater by adding 500 mg/L H_2O_2 and 1000 mg/L H_2O_2

Fig 2. illustrates the experimental values of phenol final concentration in those wastewaters which have been put under advance oxidation process for reaction time 180 minutes. It can be concluded from Fig. that increasing the reaction time and the higher H_2O_2 concentration can lead more phenol degradation and reduction the final concentration of phenol in wastewater. The increase in H_2O_2 concentration increased the phenol degradation and COD removal. Both 500 mg/L and 1000 mg/L H_2O_2 have not reach targetted phenol concentration yet. The initial phenol concentration 1100 mg/L decreases to 320 mg/L and COD removal of 2090 mg/L from initial COD 2186 mg/L.

H_2O_2/UV process was chosen for this purpose because it is known to be simple and effective for the removal of moderate to low amounts of nonbiodegradable organic compounds. Eliminate the ozon process means energy and cost saving, so it will be reliable if H_2O_2/UV process has similar result with $H_2O_2/UV/O_3$ process. Hence, it can be concluded that the H_2O_2/UV process needs longer time and higher H_2O_2 concentration removed the phenols from the solution to levels below the target.

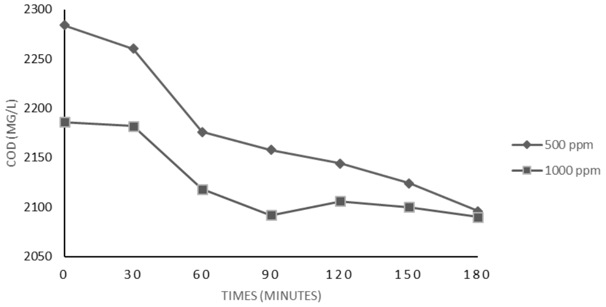

Fig 3. COD removal for synthetic RFCC wastewater by adding 500 mg/L H_2O_2 and 1000 mg/L H_2O_2

Figures 3. We can see that the COD removal show the descending trend againt increasing the H_2O_2 concentration. By adding 500 mg/L H_2O_2 concentration just remove a little amount of COD. While adding more concentration to 1000 mg/L, COD removal reach 2090 mg/L in 180 minutes. From the figures above can be concluded that the COD removal show the descending trend againt increasing the H_2O_2 concentration.

However, when H_2O_2 concentration exceeded the optimum concentration, amount of phenol degradation and COD removal was reduced. Although scavenging effect of hydrogen peroxide towards •OH occurs at higher concentrations [18], this is expected to give asymptotic values for phenol degradation. But reduction in phenol and COD removal observed may be due to the reaction of •OH and H_2O_2 and combination two •OH to form H_2O_2 [19]. In the other hand, the formation of •OOH which are significantly less reactive than hydroxyl radicals also reduces the reaction rate.

3.2 UV/H_2O_2/O_3 process

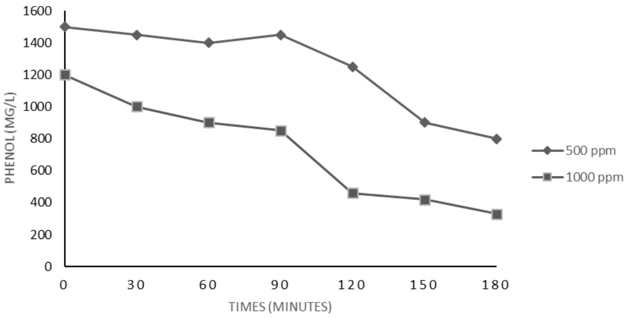

Fig 4. Phenol Degradation for synthetic RFCC wastewater by adding 500 mg/L H_2O_2 and 1000 mg/L H_2O_2

The effect of H_2O_2 concentration on the phenol degradation are despicted in Fig 4. It can be seen from the figures that the phenol concentration show the descending trend againt increasing the H_2O_2 concentration. By adding 500 mg/L H_2O_2 we get phenol degrades from 1500 mg/L to 800 mg/L. Then by adding 1000 mg/L H_2O_2 we get phenol degrades from 1200 mg/L to 330 mg/L In other hand COD removal on synthetic RFCC wastewater a bit lower too. COD decreases from 2360 mg/L to 2130 mg/L with 500 mg/L H_2O_2 and 2360 mg/Lto 2072 mg/L by adding 500 and 1000 mg/L H_2O_2 respectively.

The phenol degradation using the H_2O_2/UV and H_2O_2/UV/O_3 are not having significant result. Phenol degradation using H_2O_2/UV process has efficiency 70,9 % then using H_2O_2/UV/O_3 process has efficiency 72,5 %. Irradiation of H_2O_2 with UV generated •OH radicals with powerful oxidizability, so the time for phenol degradation was higher those for H_2O_2/UV/O_3 The •OH radicals generated by photocatalysis were distributed more widely than the •OH radicals generated from dissolved ozone [20]. Ozone is unstable in solution, and •OH radicals are generated by an autolytic process [21].

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (1)$$
$$O_3 + HO_2^- \rightarrow O_3{-} + HO_2 \quad (2)$$
$$O_3^- + H^+ \rightarrow HO_3 \quad (3)$$
$$HO_3 \rightarrow {\bullet}OH + O_2 \quad (4)$$
$$O_3^- + (H_2O) \rightarrow {\bullet}OH + O_2 + OH^- \quad (5)$$

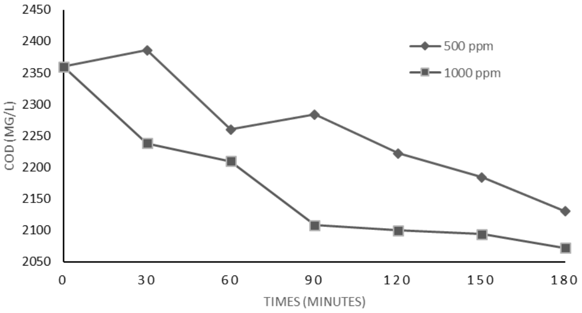

Fig 5. COD removal for synthetic RFCC by adding 500 mg/L H_2O_2 and 1000 mg/L

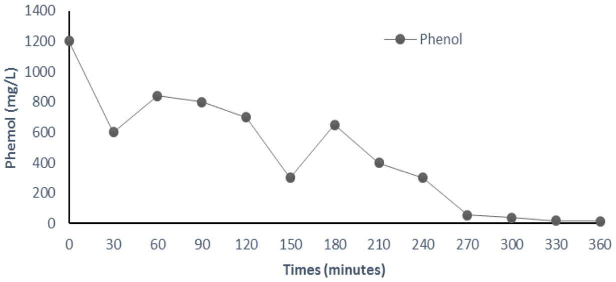

Fig 6. Phenol degradation for real RFCC by adding 500 mg/L H_2O_2

From the figure 6 we can see phenol degradation on real RFCC wastewater mostly symmetrical with the synthetic RFCC wastewater. Although we get a lower degradation there. The reason for this variation could be explained by the following reaction :

$$H_2O_2 + h\nu \rightarrow 2OH\,\bullet \quad (6)$$
$$H_2O_2 + OH\,\bullet \rightarrow HO_2\,\bullet + H_2O \quad (7)$$
$$O_3 + H_2O_2 + h\nu \rightarrow 2OH\,\bullet + 3O\,\bullet \quad (8)$$

Theorically, if the initial H_2O_2 concentration increases, higher hydroxyl radicals can be produced and phenol can be converted to CO_2 and H_2O more easily.

Fig 6. illustrates the experimental values of phenol concentration in RFCC wastewater which have been put under H_2O_2/UV/O_3 process for different reaction time. It can be conclude from Fig 6. that increasing reaction time will lead more phenol degradation and reducing the final concentration of phenol.

However there is an targeted condition of hydrogen peroxide concentration and reaction time. We see on Fig 6, adding 500 mg/L hydrogen peroxide have not reach target yet. The lowest phenol concentration reach at reaction time 150 minutes with 300 mg/L or degraded 57% from the initial concentration. While, by adding more 500 mg/L hydrogen peroxide on the next reaction reached to 55 mg/L along reaction time 270 minutes. The Ghaly et al. experimental observation confirmed the above statement. It can be clearly seen from Fig 2. that high initial concentration of H_2O_2 consumes the hydroxyl radicals according to desired reaction (7) and reduces the phenol degradation extent (increases the final concentration of phenol as despicted in Fig 6.)

The degradation mechanism of the real RFCC wastewater organic compounds, mostly aromatic-containing structures, is an electrophilic •OH addition to the rings that results in benzene ring conversion to phenol and then to dihydroxybenzene derivatives [22]. Both benzene and phenol produces dihydroxybenzene derivatives, along with quinines and several ring-opened products (namely carboxylic acids groups) [22;23]. This implies that as phenol is degraded, more is generated by the degradation of benzene. The direct reaction of •OH with the phenol molecules also gives rise to phenoxy radical. This radical, as detailed by Hosseini et al. (2007), is in resonance with radical structures in *o*- and *p*- positions [24] and becomes the starting point for the formation of different intermediates. More hydroxylated compounds such as catechol, hydroquinone, benzoquinone or hydroxyl hydroquinone are then produced from subsequent reactions of the intermediates with •OH [25]. So, the degradation rate are less than the synthetic RFCC wastewater.

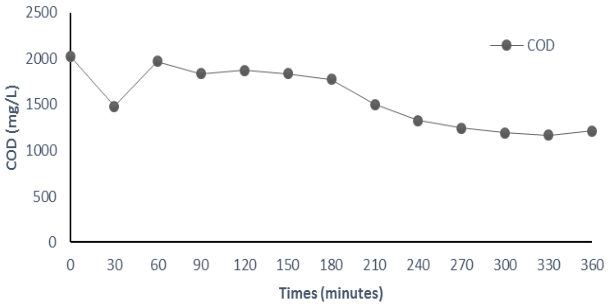

Fig 7. COD removal for real RFCC by adding 500 mg/L H_2O_2

Fig 7. illustrates COD removal as a function of time at different H_2O_2 concentration. COD removal are approximately symmetrical with the phenol degradation. The plots show that increasing reaction time will lead more COD removal and reducing the final concentration COD. By adding 500 mg/L H_2O_2 concentration just remove a little amount of COD typically same with the phenol degradation has not reach the target yet with this condition. While adding more concentration 500 mg/L, COD removal reach 1166 mg/L in 3300 minutes.

From the figures above can be seen from that the COD removal show the descending trend againt increasing the H_2O_2 concentration. Removal effieciencies are reduced at 180 minutes reaction time. It may cause by the alkaline media that dissociated form of hydrogen peroxide (HO_2^-) reacts with hydroxcyl radicals (reaction 2.) more than two orders of magnituted faster than observed hydrogen peroxide, leading loss of carbon oxidation potential which is confirmed by a slight decrease in COD removal under alkaline condition [26].

4 Conclusion

Phenol degradation in RFCC wastewater using AOP was found to be possible. For UV/H_2O_2/O_3 process target phenol concentration 55 mg/L easily reached by adding 500 mg/L H_2O_2 along 180 minutes then adding more 500 mg/L H_2O_2 along reaction time 90 minutes. For H_2O_2/UV process both 500 mg/L and 1000 mg/L H_2O_2 have not reach targetted phenol concentration yet. The initial phenol concentration 1100 mg/L decreases to 320 mg/L and COD removal of 2090 mg/L from initial COD 2186 mg/L. It can be concluded that the H_2O_2/UV process needs longer time and higher H_2O_2 concentration removed the phenols from the solution to levels below the target. In other hand COD removal on synthetic RFCC wastewater a bit lower too. This implies that as phenol is degraded, more is generated by the degradation of benzene. The direct reaction of •OH with the phenol molecules also gives rise to phenoxy radical.

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