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ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) COMPOUNDS FROM SEDIMENT IN THE WATERS KAYU BANGKOA PORT AND DEGRADATION OF PHENANTHRENE IN SEDIMENT BY USING $KMNO_4$ OXIDIZER

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ABSTRACT

Research about analysis of Polycyclic Aromatic Hydrocarbon (PAH) from sediments in water of Kayu Bangkoa Port and degradation of phenanthrene from sediments by using $KMnO_4$ have been conducted by Gas Chromatography Mass Spectrophotometry (GC-MS). The samples of sediment were taken at three location in the waters of the Kayu Bangkoa Port. Measurements of phenanthrene performed by standard internal method and analyzed using GC-MS. The results show that $KMnO_4$ oxidizing agent capable of degradated the whole phenanthrene with concentration of 137,13 ng/g in sediment.

Key words: Degradation, Phenanthrene, Gas Chromatography Mass Spectrophotometry, Polycyclic Aromatic Hydrocarbon (PAH), Standard Internal.

1. INTRODUCTION

Kayu Bangkoa Port is a boat harbor people who are used as a transit commuters who come from small islands to the Makassar City. The commuters from the small islands usually use Kayu Bangkoa Port as a transit point for destinations within the city of Makassar to shop for household purposes, food, fuel and oil [1].

Various activities around Kayu Bangkoa Port which often looks like, up and down passengers, take apart and contain goods, raise goods such as gas, groceries and fuel commuters who usually under the heading of small islands [1], making it less spillage of cargo transported in particular in the form of fuel pollutes surface leeks ran on Kayu Bangkoa Port, remember that according to the petroleum substances classified oganic aromatic [3].

Aromatic compounds containing aromatic compounds such as Polycyclic Aromatic Hydrocarbons (PAH) which is an aromatic compound consist of two or more benzene rings. In research on the content and source of PAH compounds in aquatic sediments of Pakis Jaya Karawang found that PAH contained in aquatic sediments derived from oil spills, burning fossil fuels and burning of organic material [3]. PAH compounds are compounds that are toxic, which in relatively high levels often found in sediments adjacent to urban areas and into the general pattern of accumulation PAH [7]. In addition to coming from a natural activity, PAH compounds also derived from anthropogenic sources like industrial activities, transportation and household activities [15].

PAH compounds at concentrations 0.1 to 0.5 ppm can potentially cause

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poisoning in living beings and at low levels can reduce the rate of growth, development and eat aquatic creatures [7]. PAH also are lipophilic compounds and carcinogenic and can enter the body through a variety of ways including through the process of respiration, absorbed through the pores of the skin as well as through the food and drink consumed [6]. PAH compounds effects on the organism can be a faster warning indicator to determine their impact on human health [3]. PAH compounds can be harmful because these compounds are difficult to unravel. If absorbed in the body of biota it will cause strong odors [7].

PAH compounds are more likely to accumulate in sediments than in the water [4]. PAH compound concentration in certain sediments can range between µg/kg till g/kg, this amount also depends on the distance between the source region of PAH compounds such as industrial, municipal and water currents [13]. However, until now there has been no environmental standards for PAH analysis in sediments in Indonesia [3]. PAH compounds in sediments are usually dominated by 4-6 ring that more hydrophobic [13].

Several studies conducted to prevent the bad effects of pollution PAH by degradation using microorganisms and chemical compounds. La Nafie [5], conducting research to degraded PAH using Fenton reagent. Murniasih, et al., [9] do biodegradation using a marine bacterium *Pseudomonas sp* to degraded phenanthrene. Veignie, et al., [12], conduct research to determine the role of hydrogen peroxide in the compound to degrade benzo[a]pyrene by *Fosarium solani* fungus. In the 18th World Congress of Soil Science [14], to investigate the efficiency of Fenton reagent and $KMnO_4$ in degrade phenanthrene, and pyrene in the soil and found that Fenton and $KMnO_4$ are efficient in degrade phenanthrene. In research conducted by Chen, et al., [2], obtained that $KMnO_4$ is the most effective oxidizer to degrade 16 PAH compounds.

To avoid the impacts pollution of PAH compounds to people, especially people around Kayu Bangkoa Port then in research analyzed of PAH compounds in sediment in the waters of the Kayu Bangkoa Port and analysis of the potential KMnO4 to degrade phenanthrene classified as PAH compounds consisting of three benzene rings.

2. METODE

2.1 Extraction and Sample Preparation

Approximately 250 g of sediment samples taken at each location. Sediment samples were put in glass bottles that have been in the rinse with n-hexane and have been labeled, then stored in the *ice box*. The sediment samples were taken to the laboratory and placed over the gutter that has been cleaned. The samples were then dried in air for 9 days, then homogenized with a mortar and sieved.

2.2 Analysis of PAH in The Sediment Which Were Taken from Water of Kayu Bangkoa Port

The initial process is performed sample extraction. A total of 5 g sample is weighed carefully and then extracted with 10 mL dichloromethane using *Soniclean* 160 HT. The extraction was done 2 times for 15 minutes. Results of extraction was centrifuged for 10 minutes at 2000 rpm to separate the solid phase and liquid phase. After a phase of solid and liquid phases were separate, then the liquid phase is taken and put in a 50 mL Erlenmeyer, and evaporated using nitrogen gas stream to a volume of approximately 2 mL and inserted into the *vial* bottle. The samples were then analyzed using Gas Chromatography Mass Spectrophotometry (GC-MS 2010 Plus Shimadzu).

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2.3 Analysis of phenanthrene in Sediment Samples

A total of 100 g sediment samples from Lae-Lae Island waters put into a 250-ml beaker. Added standard solution fena n trends 5 0 ppm 50 mL. Stir until evenly distributed and closed with *plastic wrap* then allowed to stand for 2 weeks. A total of 5 g sample of sediment that has been allowed to stand for 2 weeks weighed carefully and then extracted with 10 mL dichloromethane using an ultrasonic *Soniclean* 160 HT. The extraction was done 2 times each for 15 minutes. *Result of* extraction was centrifuged for 10 minutes at 2000 rpm to separate the solid phase and liquid phase. After phase of solid and liquid phase were separate, then the liquid phase is taken and put in a 50 mL Erlenmeyer, and evaporated using nitrogen gas stream to a volume of approximately 2 mL and inserted into the *vial* bottle. A total of 0.5 mL of sample and 1 ppm standard solution of phenanthrene pipetted into the *vial* which is different then added each 0.5 mL of 1 ppm standard internal of iso-octane and diluted to a volume of 4 mL. Samples and standards were analyzed using Gas Chromatography Mass Spectrophotometry (GC-MS Angilent 7890A).

2.4 Degradation of phenanthrene in Sediment Samples

A total of 15 mL of $KMnO_4$ with a concentration of each 0.05 M; 0.07 M; and 0.1 M was added to the 5 gram sample of sediment that has been mixed with a standard solution of phenanthrene. Sonicated using *Soniclean* 160 HT for 1 hour. Results sonication was then extracted with 10 mL dichloromethane using an ultrasonic *Soniclean* 160 HT. The extraction was done 2 times for 15 minutes. Result of extraction was centrifuged for 10 minutes at 2000 rpm to separate the solid phase and liquid phase. After a phase of solid and liquid phases were separated, then the liquid phase is taken and put in a 50 mL Erlenmeyer was then added 0.2 g Na_2SO_4 then allowed to stand for 1 day in the refrigerator. Samples were then evaporated using nitrogen gas stream to a volume of approximately 2 mL and inserted into the *vial* bottle. A total of 0.5 mL sample was put into different vial then added 0.5 mL of standard interrnal of iso-octane 1 ppm and diluted to a volume of 4 mL. Samples were then analyzed using gas Gas Chromatography Mass Spectrophotometry (GC-MS Angilent 7890A).

2.5 Analysis of PAH in the Sediments Water of Kayu Bangkoa Port by Gas Chromatography Mass Spectrophotometer (GC-MS)

Analysis PAH compounds performed by instruments Gas Chromatography with Mass Spectrophotometer detector (GC-MS 2010 Plus Shimadzu). GC conditions when the sample was injected to injector, temperature was set at 300 °C, with *splitless* mode, a capillary column type SH-Rxi-5Sil MS with a length of 30 m, diameter of 0.25 mm and a thickness of 0.25 μm film (5% diphenyl 95% dimethyl polycycloxan). The gas used is helium gas flow rate in the column of 1.32 mL/min. Column temperature was set at a temperature at150°C for 2 minutes than later the temperature was raised at a gradient of 150-300 °C is slowly interrupted for 5 minutes, and finally the temperature was raised to 300 °C for 7 min. After reaching the final temperature of 300 °C, instrument was left for 15 minutes. Temperature connect and the ion source was set at a temperature at 300 °C and 230 °C.

2.5 Analysis of PAH In Sediment Before and After Degradation by Gas Chromatography Mass Spectrophotometer (GC-MS)

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PAH analysis performed with instruments Gas Chromatography with Mass Spectrophotometer detector *(GC-MS Angilent 7890A)*. GC conditions when the sample is injected to injector temperature was set at 280 °C, with *splitless* mode, a capillary column HP-5MS types with a length of 60 m, diameter of 0.25 mm and the thickness of the film was 0, 25 μm (5% phenyl methylpolycyl). The gas used was helium gas flow rate in column 1 mL / min. Column temperature was set at 40 °C for 5 minutes and then the temperature was raised 10 °C / min up to 290 °C for 1 minute. After reaching the final temperature at 300 °C instrument left for 15 minutes. The temperature detector was set at 280 °C. The temperature of the transfer line was set at 280 °C.

2.6 Calculation of PAH Concentration

2.6.1 Response Factor Calculation [8]

$$R_f = \frac{A_{St} \times C_{[IS]}}{A_{[IS]} \times C_{St}} \quad .....(1)$$

Information :

R_f : The response factors of the standard analysis PAH and internal standards
A_{St} : Area of PAH on calibration standards
$A_{[IS]}$: Area of internal standard to standard calibration
C_{St} : Concentration of PAH by the calibration standard solution
$C_{[IS]}$: Concentration of internal standards for calibration standard solution

2.6.2 The calculation of PAH extraction results in sediment samples [8]

$$X_{HAP} = \frac{A_{HAP} \times X_{[IS]}}{A_{[IS]S} \times R_f} \quad .....(2)$$

Keterangan :

X_{PAH} : Amount of PAH by samples extraction
A_{PAH} : PAH area of sampel
$A_{[IS]S}$: Area of internal standard by samples
$X_{[IS]}$: Amount of internal standard which added to samples
R_f : Response factor

2.6.2 PAH concentrations in sediment samples (ng/g) [8]

$$C_{(ng/g)} = \frac{X_{HAP}}{m} \quad .....(3)$$

Keterangan :

C : Concentration of PAH in samples (ng/g)
X_{HAP} : Amount of PAH by samples extraction
m : Mass of samples (g)

3. RESULTS AND DISCUSSION

3.1 Conditions At The Sampling

Pollution of water conditions and activities in sea water can be affected by several factors such as temperature, pH and depth of seawater. Hydrological parameters are performed by in-situ method. Water conditions in the waters of the Kayu Bangkoa Port can be seen in Table 1.

Tabel 1. Water Conditions of Kayu Bangkoa Port

No.	Locations	Water Condition		
		Temp.	pH	Depth
1	Location 1	31 °C	7	120 cm
2	Location 2	30 °C	6	220 cm
3	Location 3	30,5 °C	6	180 cm

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3.2 Analysis PAH Compounds In Water Sediment of Kayu Bangkoa Port

The images presented chromatogram showed no PAH compounds that are not tied on three samples of sediment, but obtained compound 4H-1-Benzopyren-4-one,2-(3,4-dimethoxiphenyl)-3.5-dihydroxy-7-methoxy the retention time of 31.564 minutes with an area 304394 at location 1 and compound 4H-1-Benzopyren-4-one,5,7-dihydroxy-2-(3-hydroxy-4,5-dimethoxiphenyl)-6.8-dimethoxy at a retention time of 21.205 minutes with an area at locations 1702723. This indicates that PAH compounds contained in aquatic sediments of Kayu Bangkoa very small and difficult to isolate the compound that is not bound to do, so no quantitative analysis to determine levels of PAH compounds in sediment in the waters of the Kayu Bangkoa Port.

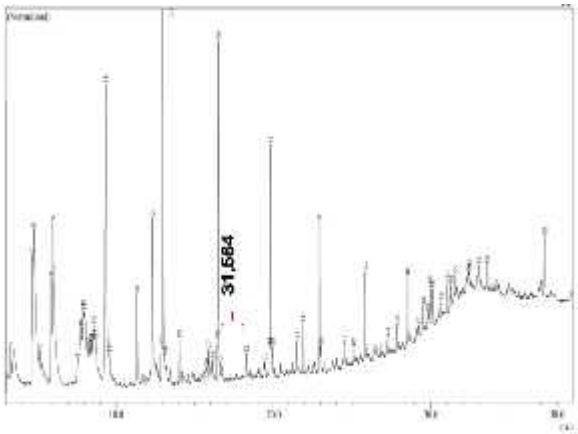

Figure 1. Chromatogram of PAH compounds in sediment taken on location 1

Pollution from PAH compounds likely to come from shipping activities that are around the port. Oil spill on the surface of the waters in the seas of Kayu Bangkoa Port gives pollution by PAH compounds. But the factor waves, winds and currents likely to cause the spread of the molecules of the oil spill, so as not to accumulate in the sediment sampling locations.

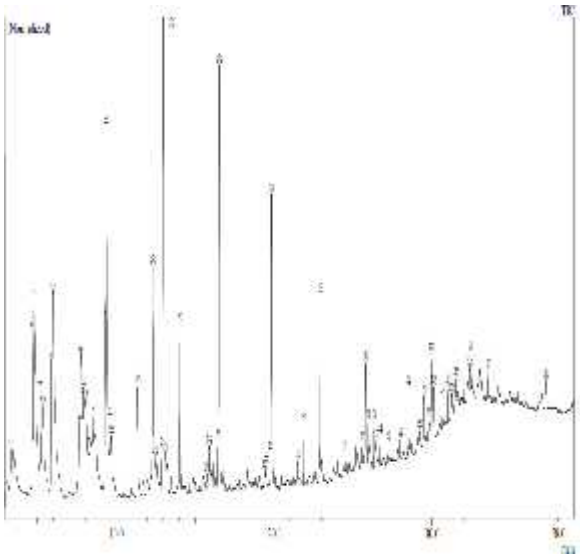

Figure 2. Chromatogram of PAH compounds in sediment taken on 2 locations

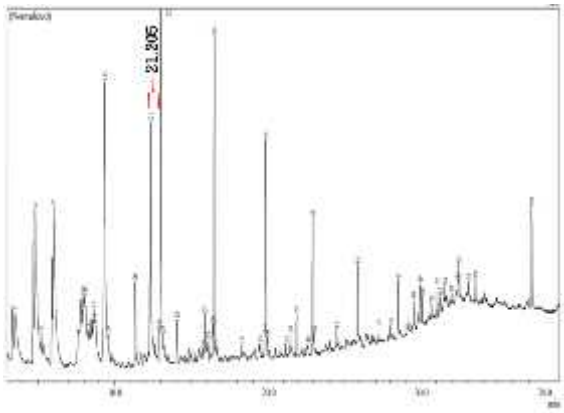

Figure 3. Chromatogram of PAH compounds in sediment taken on 3 locations

3.3 Analysis of phenanthrene in Sediment Samples

Sediment samples from the waters of Lae-Lae Island is used in the degradation of phenanthrene by using $KMnO_4$ because results of PAH analysis contained in the sediment samples in waters of Kayu Bangkoa Port very small and PAH compounds was obtained also as PAH compound which is bound so it is difficult to observe degradation products with $KMnO_4$.

Previously conducted was analysis to determine the compounds contained in the

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sediments in waters of Lae-Lae Island by used GC-MS. From the analysis results were not obtained PAH compounds in sediment samples from Lae-Lae Island so the sediment can be used in modeling degradation of phenanthrene by using the oxidizer $KMnO_4$.

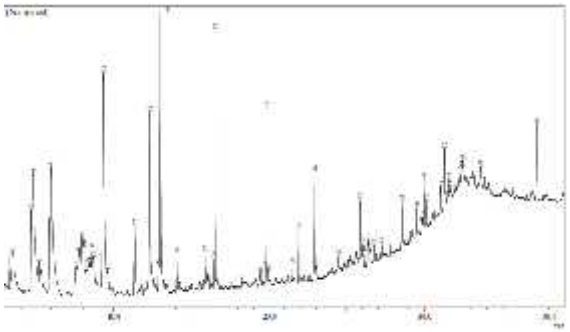

Figure 4. Chromatogram of compounds in sediment samples in the waters of Lae-Lae Island

After it was confirmed that there is no PAH compounds in the sediment of waters at the Lae-Lae Island then added phenanthrene 50 ppm in 100 gram samples of sediment and allowed to stand for 2 weeks and then analyzed using GC-MS. The results of the analysis of PAH compounds in the sediments showed phenanthrene was on the retention time of 21.49 minutes with area 79455. From the analysis using GC-MS also obtained internal retention time of the standard iso-octane at a retention time of 3.02 minutes with area 142270048.

Based on data were obtained from GC-MS analysis using the known concentration of phenanthrene in the sediment samples by calculation using an internal comparison of the standard iso-octane. The concentration of phenanthrene in sediments is 137.13 ng / g.

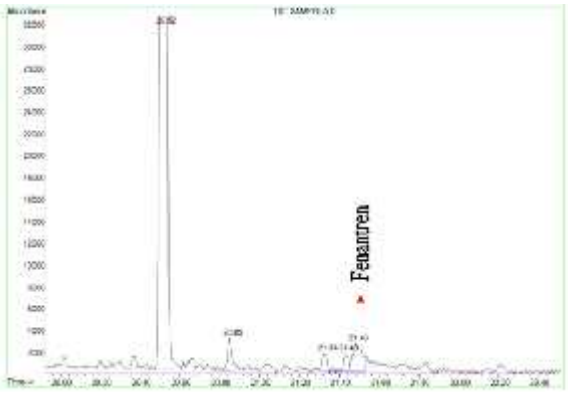

Figure 5. Chromatogram of phenanthrene in sediment samples after enlarged scale

3.4 Degradation Analysis of Polycyclic Aromatic Hidrokarbon (PAH) Compounds in Sediment Samples Using KMnO 4 oxidizing agents

Three samples of sediment that has been degraded by variations in the concentration of $KMnO_4$ was obtained that there is no phenanthrene. This indicated that phenanthrene in sampels might have been degraded or decomposition. The new compounds obtained allegedly were the result of degradation of phenanthrene. The absence of phenanthrene in sediment samples can also be caused by the ratio between the concentration of oxidizer $KMnO_4$ with phenanthrene in the sample was not balanced. The concentration of phenanthrene in the sample is very small compared to the concentration of oxidizing $KMnO_4$. The compound is a compound suspected as a result of a reaction between phenanthrene and $KMnO_4$. The perfect reaction of the degradation phenanthrene process is using oxidizer $KMnO_4$ should not produce other organic compounds but will produces CO_2 and H_2O which is not harmful to aquatic creatures [11].

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Figure 6. Chromatogram of phenanthrene in sediments after degradation with 0.05 M $KMnO_4$ after enlarged scale.

From the analysis using GC-MS can know the area and the structure of the compounds were obtained after the degraded using an oxidizer $KMnO_4$ 0.05 M. Based on the data was obtained, it is known internally retention time standard iso-octane was 3.01 minutes by area 86600803, also found that there is new compound in the sediment samples which have been degraded demonstrated by the chromatogram at the retention time of 27.87 minutes with area 84246. This compound is Dodekahidro-6H-pirido[1,2-b] Isoquinoline-6-one which allegedly as a result of the degradation of phenanthrene in sediments.

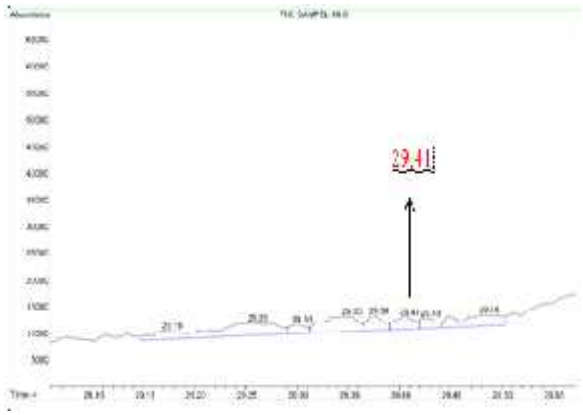

Figure 7. Chromatogram of phenanthrene in sediment samples after degradation with 0.07 M $KMnO_4$, after the enlarged scale

From the analysis using GC-MS instrument the area and the structure of the compound after the degradation by oxidizer $KMnO_4$ 0.07 M can be obtained. The data was obtained the retention time of iso-octane is 3.02 minutes with area 100997342.

From the analysis also showed that there are new compounds in sediment samples that have been degraded at a retention time of 29.41 minutes with area 30673. The compound is 2-Methyl-5-(4-morpholinyl)benzo-1,4-quinone that allegedly as a result of the degradation of phenanthrene in sediments.

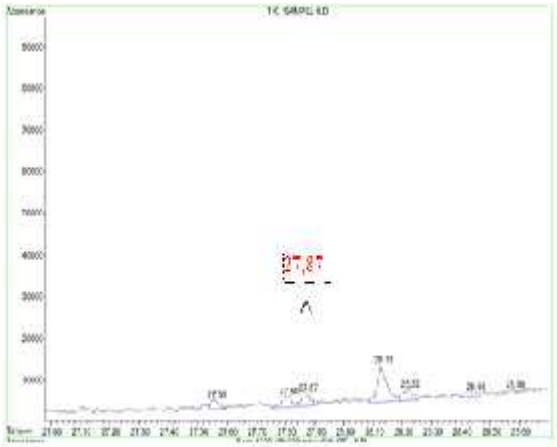

Figure 8. Chromatogram of phenanthrene in sediment samples after degradation with $KMnO_4$ 0.1 M, after enlarged scale

From the analysis using GC-MS can know the area and the structure of the compound was obtained after the degradad using an oxidizer $KMnO_4$ 0.1 M. Based on the data was obtained, it is known retention time of iso-octane was 3.00 minutes with area 108466180. From results of the analysis also found Dodekahydro-6H-pirido[1,2-b] Isoquinoline-6-one at retention time of 27.87 minutes with area of 4227369716, so that the compound allegedly the result of degradation of phenanthrene in sediments using $KMnO_4$ 0.1 M.

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The concentration of phenanthrene in sediment samples before the addition of oxidizer $KMnO_4$ was 137.13 ng/ g. After the process of degradation by oxidizer $KMnO_4$ 0.05 M; 0.07 M and 0.1 M is not obtained phenanthrene again but showed some new compounds are thought to be the degradation of phenanthrene result. By comparing the area of the compounds that were obtained after the degradation products with the compounds of the area before the degradation process, then allegedly phenanthrene was degraded into compounds Dodekahydro-6H-pirido[1,2-b] isoquinoline-6-one using oxidizer $KMnO_4$ 0.05M, while the compound 2-Methyl-5- (4-morpholinyl) benzo-1,4-quinon allegedly as a result of the degraded of phenanthrene in sediments using an oxidizer $KMnO_4$ 0.07 M, and compound Dodekahydro-6H-pirido[1,2-b] Isoquinoline-6-one allegedly as a result of the degraded of phenanthrene in sediment samples using an oxidizer $KMnO_4$ 0, 1 M.

Through the data analysis results by using GC-MS showed that the oxidizer $KMnO_4$ with a concentration 0.05 M; 0.07 M; and 0.1 M can degrade the overall concentration of phenanthrene with 137.13 ng /g. In a study by Silva, et al., [11], found that 7 g $KMnO_4$/kg of soil can degrade 87.5% of phenanthrene for 24 hours and 3 g $KMnO_4$ /kg of soil, can degrade 84.5% of phenanthrene for 72 hours. According to Pawar [10], $KMnO_4$ is indeed the most powerful oxidizer that degrade phenanthrene compound in particular PAH and antrasen.

4. CONCLUSION

Based on the research results can be summarized as follows:

1. There are polycyclic aromatic hydrocarbons (PAH) in the form of compound 4H-1-benzopiren-4-one, 2-(3,4-dimetoksifenil) -3.5-dihydroxy-7-methoxy and compound 4H-1-benzopiren-4- one, 5,7-dihydroxy-2-(3-hydroxy-4,5-dimetoksifenil) -6.8-dimethoxy in sediments in the waters of the Port of Wood Bangkoa.
2. $KMnO_4$ 0.1 M; 0.07 M; and 0.05 M is able to degrade the overall concentration of phenanthrene with 137.13 ng / g in sediments of waters in Lae-Lae Island.

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