



DETERMINATION AND DEGRADATION PYRENE FROM PAOTERE PORT SEDIMENTS WITH OXIDIZER KMnO_4

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ABSTRACT

Paotere port is one of port in Makassar which functions as a stopover place of ships, also serves as fish market and fishermen settlements. Various activities of transportation, commerce and households occurred in the Paotere port area can be a source of pollution of pyrene compounds to the surrounding environment. Pyrene compounds that accumulate and can not be degrade will impact the environment and marine life. Determination pyrene in sediment from Paotere Port have been carried out using GC-MS by sonication using dichloromethane as solvent. Result show that there was no PAH in sediment of the three sampling stations. Pyrene compound chemically degradation was conducted by sonication for 1 hour using an oxidant KMnO_4 concentration of 0.05 M, 0.07 M and 0.1 M. Results show that KMnO_4 as oxidizing agent could to degrade the whole pyrene with concentration of 87,8554 ng/g in sediment.

Key words: Paotere port, PAH, pyrene, dichloromethane, KMnO_4 , and GC-MS.

1. INTRODUCTION

Paotere port located in the district of Ujung Tanah, Makassar is one of the port in Makassar city earmarked for pilot ships and traditional ships^[1]. Besides as a ship stopover location, Paotere port which has a total area of ± 38 ha also functioned as a fish market and fishermen settlements.^[2] Various activities of transportation, commerce and households occurred in the area of Paotere port can be a pollution source to the surrounding environment. Especially the marine environment is a source of livelihood and the center of community activity in the port area Paotere^[3].

Mochtar^[4], marine pollution is defined as entry of a substance or energy by humans, either directly or indirectly into the marine environment that cause detrimental effect because of damage to biological resources, harm to human

health, inhibit the activity at sea, as well as lower quality sea water. One type of waste that is toxic to aquatic are compounds Polycyclic Aromatic Hydrocarbons (PAH). PAH compounds are organic compounds that are widespread in nature, consisting of some aromatic rings and hydrophobic.^[5] This compound is persistent because it is difficult to decompose and can survive in a very long time in the water. One compound known carcinogen PAH is pyrene.^[6] Pyrene is one of the PAH compounds that have a structure with four aromatic rings, more difficult degraded, persistent in the environment, hydrophobic, associated with soils and sediments, lipophilic, potentially accumulate through the food chain, endangering the environment and biotic components.^[7] Piren harmful to health and may increase the risk of skin cancer and lung damage. Piren often found as



pollutants in air, water and soil.^[8]

Contamination of pyrene that occur continuously will resulted the accumulation process. Pyrene that accumulates and if it can not be degraded will have an impact on the environment and marine life.^[1] Pyrene compound that accumulates takes a long time to degraded naturally in the environment.^[6] Pyrene degradation can occur biologically or chemically. In biology, degradation occurs with the help of microorganisms, while the chemical degradation occurs through photochemical processes (UV) and oxidation-reduction reactions.

The process of degradation of pyrene through oxidation-reduction reaction occurs with the help of a chemical oxidant. One oxidizer that is often used to degrade pyrene is oxidant KMnO_4 . The use of an oxidant is preferred because KMnO_4 has good efficacy in various ranges of pH, stable and highly efficient to decide carbon double bond in the structure of PAH compounds.^[9] Research conducted Choplin,^[10] and Silva^[11], showed that KMnO_4 oxidizing compound capable of degrading PAH well and have a longer persistence than other oxidizing agents.^[12]

2. METHODE

2.1 Sampling and Preparation Sample

A total of approximately 250 g sediment sample taken at each point. The sediment samples were placed in glass bottles that have been rinsed 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 Determination Pyren in Sediments from Paotere Port

A total of 5 g sample is weighed carefully and then extracted with 10 mL dichloromethane using a Soniclean 160 HT ultrasonic. The extraction was done 2 times respectively for 15 minutes. Extraction centrifuged for 10 minutes at a speed 2000 rpm to separate the solid phase and liquid phase. The liquid phase is taken and put in a 50 mL Erlenmeyer, and evaporated using nitrogen gas until the volume is 2 mL and put into vial bottle. Samples were then analyzed using gas chromatography mass spectrophotometry (GC-MS 2010 Plus Shimadzu).

2.3 Analysis of Compounds Piren In Sediment Samples

A total of 100 g sediment samples from Lae-Lae Island put into a 250 ml beaker. Added 50 mL of 50 ppm pyrene standard solution and stir until evenly distributed and closed with plastic wrap and 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 a Soniclean 160 HT ultrasonic. The extraction was done 2 times respectively for 15 minutes. Extraction centrifuged for 10 minutes at a speed 2000 rpm to separate the solid phase and liquid phase. The liquid phase is taken and put in a 50 mL Erlenmeyer, and evaporated using nitrogen gas until the volume is 2 mL and put into vial bottle. A total of 0.5 mL of sample and 1 ppm pyrene standard solution pipetted into another vial and then added to respectively 0.5 mL of the internal standard iso-octane 1 ppm and diluted with dichloromethane until the volume 4 mL. Samples and



standards were analyzed using gas chromatography mass spectrophotometry (GC-MS Angilent 7890A).

2.4 Degradation Pyren in Sediment Samples

A total of 15 mL KMnO₄ solution with each concentration of 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 pyrene standard solution. Sediments were sonicated using a Soniclean 160 HT ultrasonic for 1 hour. Results sonication was then extracted with 10 mL of dichloromethane using an ultrasonic Soniclean 160 HT. Extraction centrifuged for 10 minutes at a speed 2000 rpm to separate the solid phase and liquid phase. The liquid phase is taken and put in a 50 mL Erlenmeyer then added 0.2 g Na₂SO₄ and allowed to stand for 1 day in the refrigerator. Sample evaporated using nitrogen gas until the volume is 2 mL and put into vial bottle. A total of 0.5 mL of sample and 1 ppm pyrene standard solution pipetted into another vial and then added to respectively 0.5 mL of the internal standard iso-octane 1 ppm and diluted with dichloromethane until the volume 4 mL. Samples and standards were analyzed using gas chromatography mass spectrophotometry (GC-MS Angilent 7890A).

2.5 Determiation Pyren

1) Calculatuion of response factor

$$R_f = \frac{A_{St} \times C_{[IS]}}{A_{[IS]} \times C_{St}}$$

Information :

R_f : Response factor of pyrene standard analysis and standard internal

A_{St} : Pyrene Area in calibration standards

$A_{[IS]}$: Internal standards Area for calibration standards

C_{St} : Pyrene concentrations from the calibration standard solution

$C_{[IS]}$: Internal standard concentration for calibration standard solution

2) Calculation of Total Pyren Extraction on Sediment Samples

$$X_{Piren} = \frac{A_{Piren} \times X_{[IS]}}{A_{[IS]} \times R_f}$$

Information :

X_{Piren} : Total pyren extraction

A_{Piren} : Pyren Area from sample

$A_{[IS]}$: Internal standard area from sample

$X_{[IS]}$: Total internal standard added to sample

R_f : Response factor of pyrene standard analysis and standard internal

3) Pyren Concentration in Sediment sample

$$C_{(ng/g)} = \frac{X_{Piren}}{m}$$

Information :

C : Pyren concentration (ng/g)

M : Mass sample (g)

X_{Piren} : Total pyren extraction

3. RESULT AND DISCUSSION

3.1 Sampling Current Conditions

Port Paotere water conditions are shown in Table 1. The temperature and degree of acidity (pH) the waters can be one of the parameters pollution levels and water quality. Measurement of the temperature and the pH value of water Paotere performed in-situ.

Table 1. Water conditions Paotere Port

No.	Sampling Point	Temp	pH	Depth (m)
1.	Station 1	31 °C	6	3.8
2.	Station 2	30.5 °C	7	6.4
3.	Station 3	30 °C	6	7.5

The water temperature at the third station in Port Paotere is in the range 30-31 °C. The temperature is still around normal temperatures, where temperature of normal sea surface is between 25-32 °C, while the temperature in Indonesian sea ranging from 27-31 °C [13]. Temperature is a very important factor in regulating the process of life and spread of the organism. Atmospheric conditions, geographical factors, the dynamics of the flow and intensity of solar radiation entering the sea are several factors that affect the temperature in sea [14].

According to Ismail [13], the degree of acidity (pH) the waters is very important to know the quality of the waters because the pH value control type and rate of the reaction of some compounds in water. The results of the measurement of pH values at three stations in the waters of Port Paotere range between 6-7, this value can be considered normal when compared to pH values ranging from 6.0-8.5 Indonesian waters. Low pH value of the waters can be affected by a high content of organic compounds [14]. The depth of the waters has also become a determining factor for the accumulated value of a substance pollution of surface water to settle on the surface of the water.

3.2 Determination Pyren in Sediment

Pyrene in sediment in Port Paotere analyzed by GC-MS. From the results of the chromatogram in Figure 1, 2 and 3 there are no pyrene in three stations. It can be seen from the absence of peaks pyrene compounds that appear on the results of the three locations chromatogram.

The absence of the pyrene in sediment at some point sampling locations on the present study, can be caused by several factors, such as the activity of wind, waves and currents that may cause the spread of the molecules of the pyrene from the oil spill, so that the pyrene not to accumulate in sediment sampling point assigned [15].

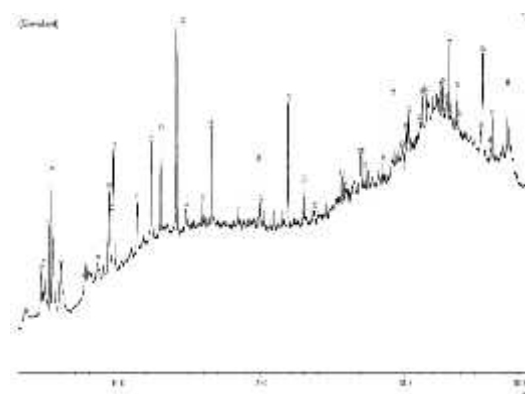


Figure 1. Chromatogram sediment at stasiun 1

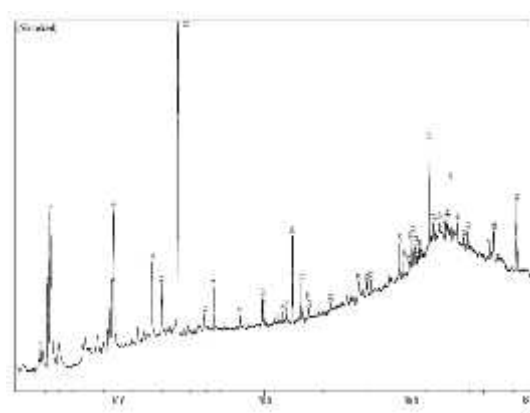


Figure 2. Chromatogram sediment at station 2

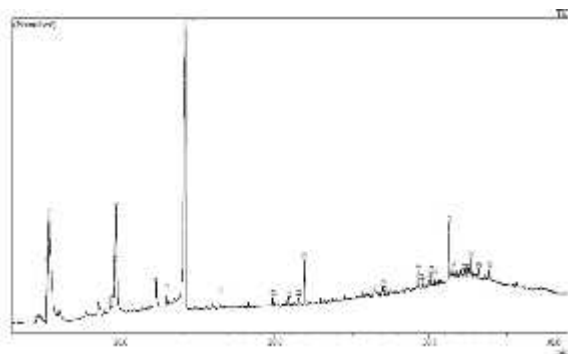


Figure 3. Chromatogram sediment at station 3

3.3 Piren degradation by oxidizing KMnO_4

Polycyclic aromatic hydrocarbon (PAH) is one of organic compounds that can cause pollution activities in the marine environment, even to produce toxicity. Pyrene which is one of PAH with carbon number 16 gives chronic toxicity to marine life, caused due to the low solubility of pyrene [16].

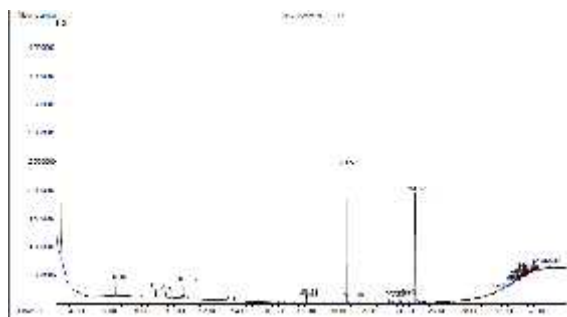


Figure 4. Pyren chromatogram before degradation

Figure 4 shows the chromatogram of a sample that has been added standard pyrene. Pyren contained at a retention time of 24.74 minutes with a peak area of 4101632. Concentration of pyrene in the sample can be calculated by using the internal standard method. Pyrene concentration before and after degradation by oxidant KMnO_4 are shown in Table 2.

Figures 5, 6 and 7 show the chromatogram of the sample after degradation by oxidant KMnO_4 each with concentration of 0.05 M, 0.07 M and 0.1

M in a row. From the results of the sample chromatograms showed that KMnO_4 with a concentration of 0.05 M, 0.07 M and 0.1 M able to degrade pyrene observed from the absence of the peak appearing at a retention time of 24.74 minutes.

In Figure 5 it can be seen the appearance of other compounds at a retention time of 25.01 minutes which dekadiaoat acid compound that is absent in the chromatogram before degradation. This compound is thought to be the result of degradation of pyrene compound with KMnO_4 0.05 M. Dekadioat acid is an aliphatic compounds that have 10 carbons. This compound has a lower toxicity than pyrene because they do not have any more aromatic rings, where the greater number of the aromatic ring of a compound, the more toxic the compound.

In Figure 6 and 7 compounds dekadiaoat acid compound is not formed, This could be because these compounds have also been degraded by KMnO_4 . However, in Figure 7 is formed other compounds that are not included in Figure 4, 5 and 6 are phenol compound at a retention time of 18.30 minutes. The phenol compound is also suspected as a result of the degradation of pyrene compound. Phenol compound has a lower toxicity than pyrene. Phenol compounds are classified by the EPA into Group D, which compounds are carcinogenic to humans [17].

Table 2. Concentration pyrene before and after degradation by oxidant KMnO_4

No.	Sample	Concentration (ng/g)
1.	Before degradation	87,8552
2.	After degradation with KMnO_4 0.05 M	-
3.	After degradation with KMnO_4 0.07 M	-
4.	After degradation with KMnO_4 0.1 M	-

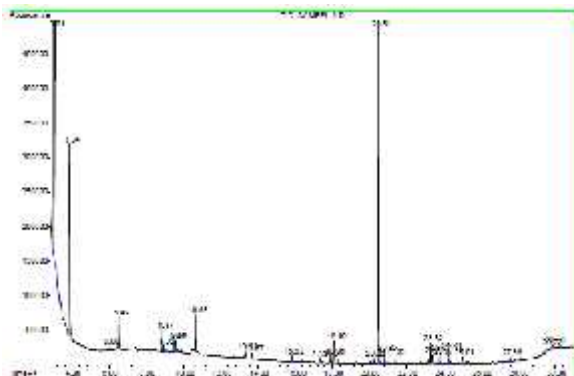


Figure 5. Pyren chromatograms results for Degradation with KMnO_4 0.05 M

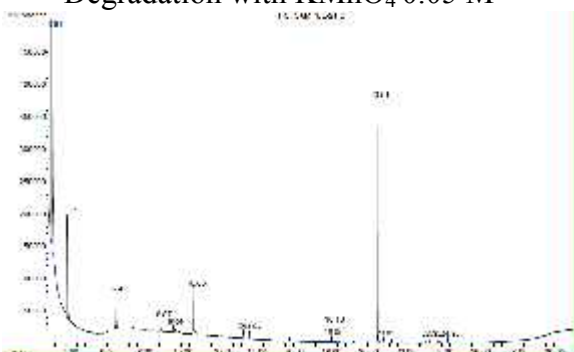


Figure 6. Pyren chromatograms results for Degradation with KMnO_4 0.07 M

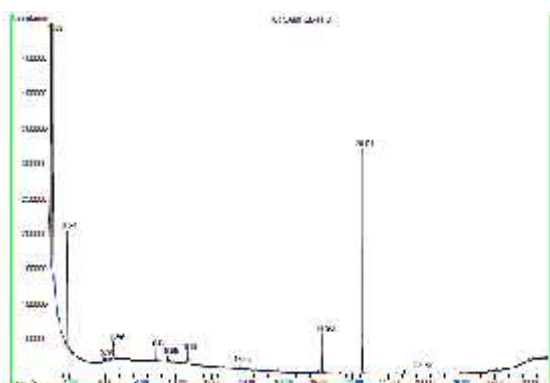


Figure 7. Pyren chromatograms results for Degradation with KMnO_4 0.07 M

Potassium permanganate is a strong oxidant with the oxidation potential of 1.7 eV. KMnO_4 oxidizing agents are very effective in degrading petroleum hydrocarbons [18]. Based on the results of the sample chromatograms before and after degradation, known oxidant KMnO_4 can not only degrade pyrene compounds but also some other compounds in the sample, as well as the ability KMnO_4 oxidant degradation increases with increasing concentration of oxidizing

agents. It can be seen from the chromatogram of the sample, where the increased concentration of oxidant the number of peaks that appear on the chromatogram diminishing indicating the decreasing of compounds contained in the sample.

4. CONCLUSION

Based on the research that has been done, it can be concluded that, pyrene is not found from the three station in the Paotere Port and the oxidant KMnO_4 with concentration of 0.05 M; 0.07 M; and 0.1 M able to degrade overall pyrene compound (87.8554 ng / g) in the sediment.

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