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Lead (Pb) Reduction Efficiency in Waste Lubricating Oil in Ship Using The Acid Clay Treatment Method: Perspective of Environmental Pollution Control at Paotere Port, South Sulawesi, Indonesia

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***Abstract**: The number of vehicles in the sea will have an impact on the amount of waste lubricant oil that is discharged into the sea, which ultimately results in pollution. The increasing level of hazardous and toxic materials (B3 waste) is concerned to have a wider impact on public health and environment quality. One of the B3 wastes that require special handling due to its high quantities is used lubricating oil. Utilization and processing of waste lubricant oil discharged from the ship is an alternative that can be applied to reach efficient consumption of petroleum which is shrinking from year to year. Therefore, we need a processing method that can reduce the pollutants generated from the waste, one of which is the Acid Clay Treatment method. This treatment aims to determine the best conditions for reducing heave metal lead (Pb) through Acid Clay Treatment method and to assess the decrease in Pb concentration contained in used lubricating oil from ship. The adsorbent used was clay that has been activated with sulphuric acid. The processing of waste lubricating oil was carried out using three variations, including adsorbent concentration, contact time, and acidity (pH). The test results of used oil lubricating oil processing were 15 gram of adsorbent concentration, 90 minutes of contact time, and pH 4. The Pb reduction efficiency obtained from Acid Clay Treatment method in the best conditions was 53.72%.*

***Keywords:** Lead, waste lubricant oil, Acid Clay Treatment.*

INTRODUCTION

The number of watercrafts on both land and sea influences the amount of waste lubricant oil that will be discharged and further burden the environment, which then will result in pollution. Therefore, utilization and processing of waste lubricant oil originated from motorcycles, cars, and ships is one alternative that can be applied to reach an efficient consumption of petroleum oil (Oladimeji, Sonibare, Omoleye, Emetere, & Elehinafe, 2018).

Over the years, lubricating oil is recycled for reuse and protecting the environment from the waste oil. If the lubricating oil is managed seriously, it is hoped to be able to save the oil usage every day. The recycling of lubricating oil can be performed in the industries specialized on waste lubricant oil treatment, which mainly focused on processing waste by using certain technologies to produce base oil for lubricants. The base lubricating oil is one of the main ingredients used as the raw material for the processing/manufacturing of lubricating oil (blending). This base lubricating oil is then mixed with additives according to a certain formula to produce new lubricating oils

(Mohammed, Ibrahim, Taha, & McKay, 2013; Sánchez-Alvarracín, Criollo-Bravo, Albuja-Arias, García-Ávila, & Raúl Pelaez-Samaniego, 2021).

In line with city development, the amount of lubricating oil continues to increase along with the increase in the number of motorized vehicles and ships in both land and sea. Even in rural areas, there are several small auto shops which generate waste from lubricating oils. In other words, the spread of waste lubricant oil is very wide as it can be found in both big cities and rural areas throughout Indonesia. One of the B3 wastes that require specific management due to its high quantities in the community is waste lubricating oil. Waste lubricating oil is the residue generated from an activity and/or production process. According to the waste criteria issued by the Ministry of Environment, waste lubricant oil is categorized as B3 waste (Toxic Hazardous Materials). Although waste lubricant oil can still be used, but if it is not managed properly, it can harm the environment (El-Mekkawi et al., 2020; Rustiah, Noor, Maming, Lukman, & Nurfadilah, 2020).

Waste lubricant oil contains heavy metal components, such as lead, Polychlorinated Byphenyls, and Polycyclic Aromatic Hydrocarbons, which have high toxic properties when released into the environment, especially in waters, as it can block sunlight and oxygen which then lead to harmful effects to living things in the water (Botas, Moreno, Espada, Serrano, & Dufour, 2017; Oladimeji et al., 2018). Heavy metal contamination, especially Pb, becomes one of the main problems in the environment in recent years. The accumulation of Pb in the nature can reach the food chain and causes pollution in soil, water, and even air (Ali, Ripin, & Ahmad, 2010; Waters, Sulawesi, Rustiah, Noor, & Lukman, 2019).

Refining is the refinement of waste oil. For example, used lubricating oil which has been processed through physical and chemical treatments in order to restore its base oil properties or through the addition of additive chemicals in the final process (El-Mekkawi et al., 2020). There are several processing methods for revining, one of which is acid clay treatment. Acid clay treatment is performed by adding acid and clay during the processing. Clay contains low iron content and is generally white or slightly whitish in color, which composed of Hydrous Alumunium Silicate ($2H_2O.Al_2O_3.2SiO_2$) and several additional minerals (Abdelwahab Emam, 2018; Riyanto, Ramadhan, & Wiyanti, 2018).

This research was carried out to contribute on possible treatments that can be applied to treat waste lubricant oil from ships. Hence, it is expected to be able to reduce the levels of pollutant substances contained in waste lubricant oil and prevent the spread of any harmful pollutant into the environment. The purpose of this study was to determine the best conditions for reducing Pb concentration in the processing of used lubricating oil using acid clay treatment, and to examine the Pb reduction efficiency of used lubricating oil from ships.

RESEARCH METHODS

Materials and Tools

The equipments used in this study were beaker glass, funnel glass, measuring cup, measuring pipette, Ohaus balance, oven (Memmert), magnetic stirrer and hot plate, Atomic Absorption Spectrophotometry (AAS), centrifuge, oven, jar test, 170 mesh sieve, and pH meters.The materials used were used lubricating oil directly collected from ships at the port of Paotere, clay, and 2 M of H_2SO_4.

Methods

Preparation of Lead Working Solution (Pb)

A total of 1000 mg Pb/L of Pb main solution was prepared first. 100 mg/L of standard solution was made by mixing 10 mL of Pb main solution into a 100 mL volumetric flask with the dissolvent until it reached the mark. Further, Pb working solutions with various concentrations (0,0 mg/L; 0,5 mg/L; 1,0 mg/L; 2,0 mg/L; 4,0 mg/L and 8,0 mg/L) were made from the standard solution.

Preparation of clay

Clay (kaolin) was baked in the oven until dry, then grounded and sieved using a 170-mesh sieve. The filtered clay was weighed as much as 25 g, mixed with 500 mL of distilled water, and stirred for 24 hours with a magnetic stirrer. Clay samples were then centrifuged at 6000 rpm for 10 minutes. The suspension was discarded, and the sediment was dried in an oven at a temperature of 170ºC for 7 hours. The dried clay samples were grounded and sieved using 170 mesh sieves (Abdelwahab Emam, 2018).

Clay's Activation

A total of 25 g of clay was dispersed into 100 mL of 0.2 M H_2SO_4 and stirred with a magnetic stirrer. Activation was carried out for 24 hours, then filtered and washed using warm distilled water. Washing was performed repeatedly until clay was free from sulfate ions which could be detected by dropping $BaCl_2$ solution on a filtrate. If there is no white precipitate of $BaSO_4$ was formed, then clay is considered as clean from sulfate ions. The washed clay was dried in an oven at a temperature of 100 - 110ºC. The dry clay was then grounded and sieved using a 120-mesh sieve. The solid clay was heated at 200ºC for 5 hours.

Processing of Used Lubricating Oil

A total of 10 mL of H_2SO_4 was added into 200 mL of used lubricating oil collected from ship, then stirred using a jar test at a speed of 150 rpm for 5 minutes. After stirring, a total of 150 mL filtrate was taken. Furthermore, the adsorbent, activated clay, was added into the filtrate and stirred using jar test. Adsorbent variants were created by adding various weight of adsorbent into the samples: (A1) 5 g of adsorbent; (A2) 10 g of adsorbent; (A3) 15 g of adsorbent. Samples were then stirred with a jar test at a speed of 150 rpm for 15 minutes. Meanwhile for contact time variation, after obtaining the maximum adsorbent that would be used in this experiment, the adsorbents were then placed into 3 different sample containers and stirred with jar test at a speed of 100 rpm with different time duration for each sample: (W1) 30 minutes; (W2) 60 minutes; and (W3) 90 minutes.

For experiments with variations in the level of acidity (pH), 1 mL of NaOH was added into the second sample (P2) and 2 mL was added into the third sample (P3). Meanwhile the first sample was not added with NaOH. After that, adsorbent was added into each sample, and then stirred with a jar test at 100 rpm for 15 minutes. Furthermore, a total of 100 mL of filtrate was taken from each sample that has been processed for testing its Pb concentration.

Optimization of atomic absorption spectrophotometry

The optimization was carried out before the usage of atomic absorption spectrophotometry. The optimum conditions were obtained by observing the maximum absorption at each change in flow rate, lamp current, ethylene flow rate, air flow rate, height, and combustion position (Kwasi Opoku, Ogbonna Friday, David Kofi, & Benson Osa, 2020).

The concentration of lead metal (Pb) in each sample was measured using atomic absorption spectrophotometry (AAS). The principles of AAS is started with the evaporation of sample solution, and the metal contained in it will be converted into free atoms. These atoms will absorb electromagnetic radiation from a light source emitted from a cathode lamp (hollow cathode lamp). The amount of absorbed radiation is measured at different wavelength which depends on the metal type (Fernández-Feal, Fernández-Feal, Sánchez-Fernández, & Pérez-Prado, 2018).

Determination of Pb reduction efficiency

The efficiency of Pb concentration reduction in used lubricating oil is determined by the following formula:

$$E = \frac{Co-C1}{Co}\ x\ 100\%$$

E : efficiency
C_0: initial concentration
C_1: final concentration.

RESULTS AND DISCUSSIONS

This study was carried out to determine the optimum conditions for reducing Pb concentration during the processing of waste lubricating oil from ships by using acid clay treatment, as well as to investigate the Pb reduction efficiency contained in waste lubricating oil. The efficiency of Pb reduction was measured by using atomic absorption spectrophotometry (AAS).

Variation of adsorbent concentration and efficiency of lead (Pb) reduction

Variation of adsorbent concentration

The method used to reduce the concentration of lead was the adsorption method, due to its easiness, high effectiveness, as well as its low cost. In this study, waste lubricant oil from ship with a concentration of 10 ppm and 5 g of clay as adsorbent were used for the measurement of the level of adsorbed lead. The level of lead metal adsorbed by clay is presented in Table 1.

Table 1. Lead metal adsorbed by clay in association with variation in adsorbent concentrations.

Samples	Adsorbent Concentration	Pb concentration (ppm)			
		Replicate 1	Replicate 2	Replicate 3	Average
A1	5 grams	4.5653	4.5213	4.5993	4.5619
A2	10 grams	4.5319	4.5197	4.5679	4.5398
A3	15 grams	4.5237	4.5144	4.5016	4.5132

The analysis of Pb concentration was carried out with 3 replicates in order to get more valid and precise data. Furthermore, based on the obtained data of Pb concentration, calculations were then carried out to determine the percentage decrease in the concentration of Pb waste (Figure 1).

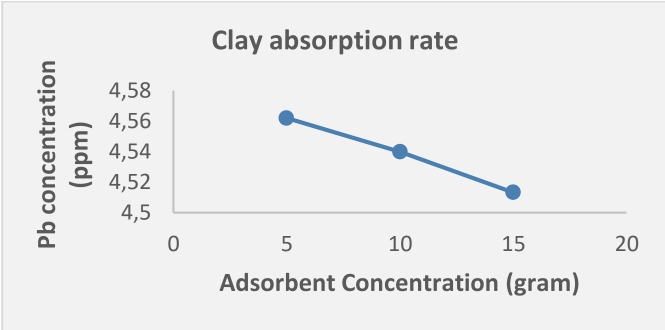

Figure 1. Graph of the decrease in Pb concentration against variations in adsorbent concentration

The analysis results showed that Pb concentration in waste lubricant oil from ships decreased after being adsorbed by clay (Figure 1). The decreasing concentration of Pb was detected in the treatment with 15 g of clay adsorbent. The higher the adsorbent concentration, the higher the Pb concentration that would be adsorbed by the adsorbent. The possible explanation is that the higher the adsorbent mass, the greater the contact surface area, which results in the higher adsorbance level. Therefore, the higher the adsorbent dose, the higher the dissolved metal removal rate (Fernández-Feal et al., 2018; Sánchez-Alvarracín et al., 2021).

Lead (Pb) Reduction Efficiency

The increase in efficiency (E) values against variations in adsorbent concentration in the processing of used lubricating oil from ships are presented in Table 2 and Figure 2.

Table 2. The Pb reduction efficiency in association with variations in adsorbent concentrations.

Samples name	Adsorbent concentration (gram)	*E* (%)
A1	5 grams	54.38
A2	10 grams	54.60
A3	15 grams	54.87

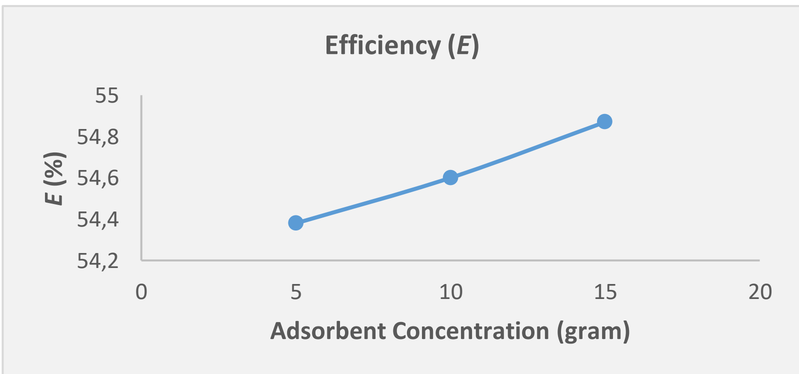

Figure 2. Efficiency graph againsts variation on adsorbent concentration

The association between variation of adsorbent contact time and lead (Pb) reduction efficiency.

Adsorbent contact time variations

The average trends of Pb concentrations obtained from replicate I, II and III are presented in Table 3 and Figure 3. The ability of adsorbent to adsorb Pb increased along with the increasing contact time as more adsorbates can be adsorbed, indicating more efficient adsorption. Therefore, the longer the contact time between lead and adsorbent, the more adsorption will occur.

Table 3. Pb concentration reduction in association with variation of contact time in the processing of used lubricating oil from ships.

Samples	Contact Time	Pb concentration (ppm)			
		Replicate I	Replicate II	Replicate III	Average
A1	30 menit	4.8133	4.8105	4.8009	4.8082
A2	60 menit	4.7382	4.7275	4.7351	4.7336
A3	90 menit	4.5589	4.5308	4.5415	4.5437

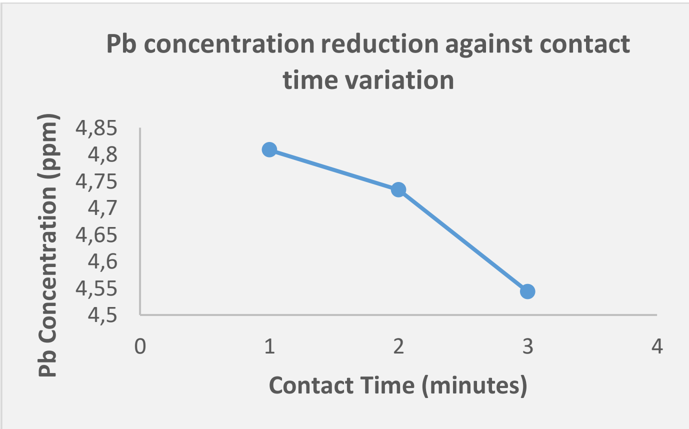

Figure 3. Graph of Pb concentration reduction against variation in contact time

Lead (Pb) Reduction Efficiency

The increased efficiency (E) against variations of contact time in the processing of waste lubricating oil obtained from ships is presented in Table 4 and Figure 4. These results indicated that contact time influences adsorption time, where there has been equilibrium between the adsorption and desorption rates.

Table 4. The efficiency of Pb concentration reduction against contact time variation.

Sample Name	Contact Time (minutes)	*E* (%)
A1	30	54,38
A2	60	54,60
A3	90	54,87

Figure 4. The relationship between adsorption efficiency (E) and contact time variations.

pH Variation and Efficiency of Lead (Pb) Concentration Reduction

pH Variation

The determination of optimum pH is one of the important parameters in the adsorption process that affects metal ions in solution. The objective of the pH determination towards adsorption capacity is to determine the pH value that supports maximum adsorption. pH value explaines the acidity of liquid waste as it describes the H^+ ions concentration in the liquid waste (pH = -log $[H^+]$. Highly acidic or alkaline liquid waste have damaging effects due to its corrosive nature, and furthermore may interfere the life of other organisms (Rustiah, 2021).

Table 5. The decrease in Pb concentration in relation with pH variations in the processing of waste lubricating oil obtained from ships.

Sample name	pH	Pb Concentration (ppm)			
		Replicate I	Replicate II	Replicate III	Mean
P1	4	4.8053	4.8055	4.8062	4.8056
P2	5	4.8112	4.8132	4.8149	4.8131
P3	6	4.8209	4.8258	4.8280	4.8249

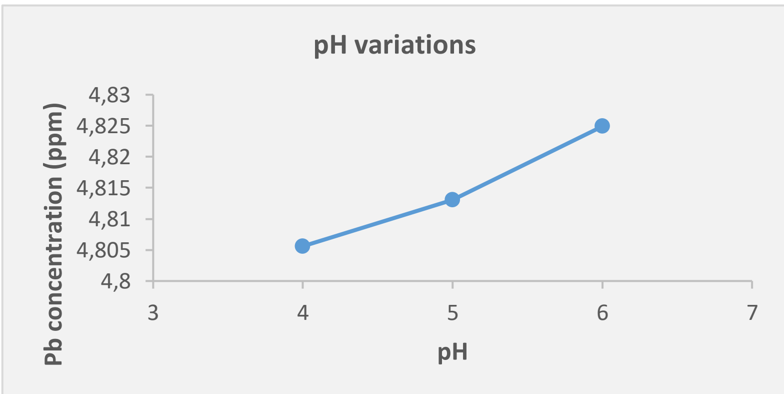

Figure 5. Graph of the decrease in Pb concentration against pH variations

The average trends of Pb reduced concentration are presented in table 5 and figure 5. The adsorbant ability to adsorb Pb metal was reduced along with the increasing pH values, indicating that pH values can influence the solubility of metal ions. Homagai, Ghimire, & Inoue (2011) explained that in a condition with low pH value, the Pb adsorption will be reduced due to the positive sites on the adsorbent surface tends to be high. At low pH environment, there is competition between Pb^{2+} and H_3O^+ ions to bind with the negative sites of adsorbent surface. Zhu, Zhu, Zhao, Liang, & Huang, (2015) added that high pH condition can cause a reaction between Pb^{2+} and OH^-, thus forming a precipitate of $Pb(OH)_2$. These precipitates can hinder the ongoing adsorption process. In addition, waste lubricant oil from ships with low pH has the potential to damage the environment.

Lead (Pb) Reduction Efficiency

The solubility of various metals is largely influenced by the solution pH. The general pattern of metal solubility is that it will decrease as the pH solution increases, because waste lubricant oil from ships formed a resistance against pH changes due to NaOH addition. However, after exceeding the buffer capacity, the addition of relatively small amounts of NaOH can significantly increase the pH of waste lubricant oil (Halnor, 2015; Jodeh et al., 2015). The data in Table 6 and Figure 6 showed reducing Pb concentration against pH variations in the processing of used lubricating oil from ships. These results indicated that increasing the pH solution affected the adsorption process.

Table 6. The efficiency of Pb concentration reduction against pH variation.

Sample name	pH	*E* (%)
P1	4	54.17
P2	5	54.09
P3	6	53.96

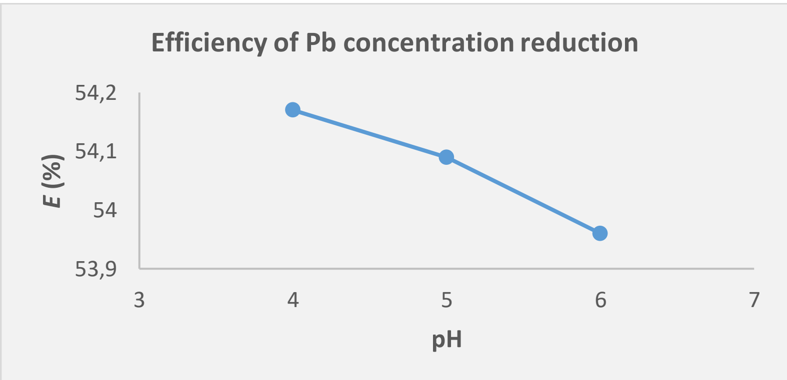

Figure 6. The efficiency graph against pH variations

CONCLUSION

The results of this study can be concluded that the best conditions to process 150 mL of used lubricating oil using Acid Clay Treatment method were at an adsorbent concentration of 15 grams, a contact time of 90 minutes, and an acidity (pH) level of 4. Then the efficiency of Pb concentration reduction obtained by using Acid Clay Treatment method is 53.72%.

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REFERENCES

Abdelwahab Emam, E. 2018. Clay Adsorption Perspective on Petroleum Refining Industry. *Industrial Engineering*, *2*(1), 19. https://doi.org/10.11648/j.ie.20180201.13

Ali, S. M. W., Ripin, A., & Ahmad, A. 2010. Adsorption of heavy metal from recovered base oil using zeolite. *Journal of Applied Sciences*, *10*(21), 2688–2692. https://doi.org/10.3923/jas.2010.2688.2692

Botas, J. A., Moreno, J., Espada, J. J., Serrano, D. P., & Dufour, J. 2017. Recycling of used lubricating oil: Evaluation of environmental and energy performance by LCA. *Resources, Conservation and Recycling*, *125*(January), 315–323. https://doi.org/10.1016/j.resconrec.2017.07.010

El-Mekkawi, S. A., El-Ibiari, N. N., Attia, N. K., El-Diwani, G. I., El-Ardy, O. A., & Morsi, A. K. E. 2020. Reducing the environmental impact of used lubricating oil through the production of fuels by pyrolysis. *Environmental Nanotechnology, Monitoring and Management*, *14*, 100308. https://doi.org/10.1016/j.enmm.2020.100308

Fernández-Feal, M., Fernández-Feal, M., Sánchez-Fernández, L., & Pérez-Prado, J. 2018. Study of Metal Concentration in Lubricating Oil with Predictive Purposes. *Current Journal of Applied Science and Technology*, *27*(6), 1–12. https://doi.org/10.9734/cjast/2018/41472

Halnor, S. 2015. Removal of Heavy Metals From Wastewater Effluents. *Mmerals Engineering*, *14*(10), 1–4.

Homagai, P. L., Ghimire, K. N., & Inoue, K. 2011. Preparation and characterization of charred xanthated sugarcane bagasse for the separation of heavy metals from aqueous solutions. *Separation Science and Technology*, *46*(2), 330–339. https://doi.org/10.1080/01496395.2010.506903

Jodeh, S., Odeh, R., Sawalha, M., Abu Obeid, A., Salghi, R., Hammouti, B., Warad, I. 2015. Adsorption of lead and zinc from used lubricant oil using agricultural soil: Equilibrium, kinetic and thermodynamic studies. *Journal of Materials and Environmental Science*, *6*(2), 580–591.

Kwasi Opoku, B., Ogbonna Friday, J., David Kofi, E., & Benson Osa, E. 2020. Adsorption of Heavy Metals Contaminants in Used Lubricating Oil Using Palm Kernel and Coconut Shells Activated Carbons. *American Journal of Chemical Engineering*, *8*(1), 11. https://doi.org/10.11648/j.ajche.20200801.13

Mohammed, R. R., Ibrahim, I. A. R., Taha, A. H., & McKay, G. 2013. Waste lubricating oil treatment by extraction and adsorption. *Chemical Engineering Journal*, *220*, 343–351. https://doi.org/10.1016/j.cej.2012.12.076

Oladimeji, T. E., Sonibare, J. A., Omoleye, J. A., Emetere, M. E., & Elehinafe, F. B. 2018. A review on treatment methods of used lubricating oil. *International Journal of Civil Engineering and Technology*, *9*(12), 506–514.

Riyanto, Ramadhan, B., & Wiyanti, D. 2018. Treatment of Waste Lubricating Oil by Chemical and Adsorption Process Using Butanol and Kaolin. *IOP Conference Series: Materials Science and Engineering*, *349*(1). https://doi.org/10.1088/1757-899X/349/1/012054

Rustiah, W. 2021. Determination of Zirconium(IV) Based on Flow Injection Analysis with The Xylenol Orange As A Complexing. *Al-Kimia*, *9*(2), 141–150. https://doi.org/10.24252/al-kimia.v9i2.23638

Rustiah, W., Noor, A., Maming, Lukman, M., & Nurfadilah. 2020. Recent analysis of carbon, nitrogen, and lignin phenol compositions in the suspended particulate matters at spermonde archipelago, South Sulawesi, Indonesia. *Environment and Natural Resources Journal*, *18*(2), 124–133. https://doi.org/10.32526/ennrj.18.2.2020.12

Sánchez-Alvarracín, C., Criollo-Bravo, J., Albuja-Arias, D., García-Ávila, F., & Raúl Pelaez-Samaniego, M. 2021. Characterization of used lubricant oil in a latin-american medium-size city and analysis of options for its regeneration. *Recycling*, *6*(1), 1–22. https://doi.org/10.3390/recycling6010010

Waters, S., Sulawesi, S., Rustiah, W., Noor, A., & Lukman, M. 2019. *Analisis Distribusi Logam Berat Timbal Dan Cadmium Dalam Sedimen Sepanjang Muara Sungai Dan Laut Perairan Spermonde , Sulawesi Selatan , Indonesia Distribution of Pb and Cd Heavy Metal Content in Sediments Along the River Estuary*. *7*(1), 1–8.

Zhu, Y., Zhu, Z., Zhao, X., Liang, Y., & Huang, Y. 2015. Characterization, dissolution, and solubility of lead hydroxypyromorphite [$Pb_5(PO_4)_3OH$] at 25-45°C. *Journal of Chemistry*, *2015*. https://doi.org/10.1155/2015/269387