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EFFECTIVENESS OF AMMONIUM POLYMER IN IMPROVING FLOATING TREATMENT WETLAND TO REDUCE COD OF PALM OIL MILL EFFLUENT

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ABSTRACT

Palm oil mill effluent (POME) is a liquid waste from the palm oil industry. This waste contains high levels of organic pollutants and can contribute to environmental pollution. Current technologies effectively degrade these pollutants but are often not environmentally friendly and expensive. Phytoremediation combined with an adsorption system using ammonium polymers is expected to address these challenges. Vetiver grass (Chrysopogon zizanioides) and ammonium polymers have been separately tested and proven capable of degrading pollutants in wastewater. The study began by modifying the planting medium for vetiver grass with gravel:polymer:soil ratio of 3:5:2. The modified net pot was then placed in a floating treatment wetland reactor for POME treatment over a remediation period of 7 days. For comparison, a control experiment was conducted using plants without polymers in the planting medium. The results showed a COD degradation of approximately 75% in POME after treatment. The reduction in COD continued to improve with increasing remediation time, reaching its peak on the seventh day. The modified planting medium also influenced plant growth, as the polymer adsorbed some phosphate and nitrate.

Efektivitas Polimer Amonium Dalam Peningkatan Pengolahan Lahan Basah Terapung Untuk Menurunkan COD Limbah Cair Kelapa Sawit

ABSTRAK

Palm oil mill effluent (POME) merupakan limbah cair yang dihasilkan dari industri minyak kelapa sawit. Limbah ini memiliki kandungan polutan organik yang tinggi dan dapat menjadi bahan pencemaran lingkungan. Teknologi yang digunakan saat ini cukup efektif untuk mendegradasi polutan tersebut namun teknologi tersebut tidak ramah lingkungan dan mahal. Fitoremediasi yang dikombinasikan dengan sistem adsorpsi menggunakan polimer ammonium diharapkan mampu menjawab tantangan ini. Tanaman akar wangi *(Vetiver grass)* dan polimer ammonium telah diuji terpisah mampu untuk mendegradasi polutan pada air limbah. Penelitian diawali dengan melakukan modifikasi pada media tanam akar wangi dengan perbandingan kerikil:polimer:tanah sebesar 3:5:2. Kemudian netpot tersebut selanjutnya diletakkan pada reaktor *floating treatment wetland* untuk proses pengolahan POME selama waktu remediasi 7 hari. Untuk perbandingan juga dilakukan control tanaman tanpa menggunakan polimer pada media tanamnya. Hasil degradasi COD pada POME setelah pengolahan adalah sekitar 75%. Penurunan COD terus ditunjukkan seiring dengan meningkatnya waktu remediasi hingga pada hari ketujuh. Modifikasi media tanam juga mempengaruhi pertumbuhan tanaman karena sebagian fosfat dan nitrat di adsorpsi oleh polimer tersebut.

Kata kunci: Adsorpsi; Polimer amonium; Pengolahan lahan basah terapung; Limbah cair kelapa sawit; Fitoremediasi

INTRODUCTION

Palm oil mill effluent (POME) is liquid waste produced by the palm oil industry. In the process of producing palm oil, a large amount of water is required. To process one ton of fresh fruit bunches, around 5-6 tons of water are needed, and from this processing process, 10-30% of palm oil is produced. In addition, this process produces around 50-79% of palm oil mill waste (Okereke & Ginikanwa, 2020). This waste is produced as much as 60% from the clarification process, 4%

from the fruit pressing process on the pressing machine, and around 35-45% from the sterilizer condensate from the fresh fruit bunch sterilization process (Irvan, 2018; Tan et al., 2022).

POME is a thick brownish liquid containing 95-96% water, 0.6-0.7% oil, and 2-4% suspended solids (Mohammad et al., 2021). Characteristically, POME contains oil and fat around 4,000 mg/L, COD around 50,000 mg/L, BOD around 25,000 mg/L, and total suspended solids around 40,500 mg/L (Kamyab et al., 2018; Meena R et al., 2023; Mohd Yusof et al., 2023). Meanwhile, the quality standards for palm oil liquid waste that can be discharged can be seen in Table 1.

Table 1. Palm Oil Industry Liquid Waste Quality Standards

No	Parameter	Standard	Unit
1	pH	6-9	-
2	BOD	100	mg/L
3	COD	350	mg/L
4	TSS	250	mg/L
5	Oil and Grease	25	mg/L
6	Nitrogen	50	mg/L

Source: (The Ministry of Environment and Forestry of Indonesia, 2014)

Based on Table 1, it can be concluded that POME (Palm Oil Mill Effluent) must undergo proper treatment to ensure it can be discharged into the environment in compliance with applicable standards without posing a hazard or potentially causing environmental pollution. The technology commonly used is the ponding system; this system is quite old and requires a large area and a fairly long retention time of around 100-120 days before it can be discharged into the environment (Lok et al., 2020; Zainal et al., 2018). Then, there is also processing using the principle of coagulation and flocculation, using chemicals, such as coagulants and flocculants. Then, there is a modern biological processing system consisting of anaerobic and aerobic systems. Then, there is also technology that uses a membrane filtration system. These methods effective for processing POME to meet quality standards. However, regarding operational costs, the chemical treatment method, membrane filtration, and modern biological processing require quite high costs. Then it also produces by-products of processing in the form of sludge from the flocs formed and also from the respiration of microorganisms during the pollutant degradation process in POME (Azmi & Yunos, 2014; Hakim et al., 2024; Mahmod et al., 2022; Saeed et al., 2016; Sari et al., 2022; Soo et al., 2022).

Phytoremediation is present as one of the alternative technologies that are environmentally friendly and economical because phytoremediation employs plants and microorganisms to absorb, degrade, or stabilize pollutants, leveraging natural biological processes. This reduces the need for chemical treatments or heavy machinery, minimizing ecological disruption and promoting biodiversity. Plants used in phytoremediation can sequester carbon dioxide from the atmosphere, contributing to climate change mitigation while simultaneously cleaning up contaminated sites (Bartucca et al., 2023; Islam et al., 2024). Many researchers have tested various types of plants to process POME as seen in Table 2.

Table 2. Phytoremediation Research for POME Treatment

No	Plant Species	Sample	Retention Time	Efficiency (%)	References
1	*Ipomoea aquatica*	Diluted POME	15 days	COD : 86.3 TP : 90.9 TN : 21.5	(Zulfahmi et al., 2021)
2	*Salvinia molesta*	POME (Facultative Pond)	16 days	COD : 39 TP : 95	(Ng & Chan, 2017)
3	*Scirpus grossus*	POME (Aerobic Pond)	18 days	COD : 88 TSS : 91 NH3-N : 96.3 TP : 45 TN : 92	(Sa'At et al., 2022)
4	*Napier grass*	POMSE	15 days	COD : 71.57 TSS : 83.59 NH3-N : 85.97	(Ujang et al., 2018)
5	*Vetiver grass*	POMSE	30 days	BOD : 92.8 COD : 94	(Darajeh et al., 2017)

Table 2 shows that several plant species are quite effective for processing POME but still depend on long retention times. So, to overcome this, phytoremediation must be combined with technology to obtain efficient processing. The addition of ammonium polymers in processing can be done to increase processing efficiency. According to Veranica et al. (2024), ammonium polymer as an adsorbent has been tested to be effective in degrading phosphate by 75% in vinasse wastewater. Then, research by Aini et al. (2023), found that adding quaternary ammonium to CH-T increased the effectiveness of phosphate ion removal by 96% and nitrate by 93%. This phenomenon indicates that polymers are effective tools for degrading pollutants in wastewater. This study examine the combination of phytoremediation and adsorption using ammonium polymer to treat POME with a one-pot approach method to create environmentally friendly POME treatment and prevent environmental pollution.

MATERIALS AND METHODS

Materials and Tools

The main material of this study is a monomer using a solution of [2-(Methacryloyloxy)ethyl]trimethylammonium chloride solution ($C_9H1_8ClNO_2$ from Sigma Aldrich, its crosslinker is ethylene dimethacrylate ($C_{10}H_{14}O_4$), isopropyl alcohol (C_3H_8O), polyethylene glycol/PEG 400 ($(C_2H_4O)nH_2O$), ethanol (C_2H_6O), trisodium phosphate (Na_3PO_4) and 2,2'-azobisisobutyronitrile/AIBN ($C_8H_{12}N_4$). Moreover, for analysis using methanol 99%, potassium dichromate ($K_2Cr_2O_7$) 0.25 N, Silver (I) Sulfate (Ag_2SO_4), sulfuric acid (H_2SO_4) 95%, mercury powder ($HgSO_4$), ferroin indicator, ferro ammonium sulfate solution ($(Fe(NH_4)_2(SO_4)_2.6H_2O)$ 0.25 N and distilled water and POME taken from one of the palm oil industries. Then, soil, gravel and liquid fertilizer were used for the plant media. The tools used in this study were phytoremediation reactors with dimensions of length, width, and height measuring 28:15:16 cm, respectively; it was equipped with a net pot at the top to serve as a container for the planting medium and vetiver plants, beakers, sample bottles, scales, magnetic stirrers, erlenmeyer, heating stoves, Whatmann 42 paper, thermometers, cuvettes, funnels, analytical balances, water baths.

Methods

Synthesis of Quaternary Ammonium Polymer

The ammonium-based polymer is first prepared by the composition of the research conducted by Rahayu et al. (2023). Several materials were prepared with 1.25 mL of META, 0.375 mL of EDMA, 1.75 mL of alcohol isopropyl, 0.35 mL of ethanol, 1.4 mL of PEG, and 2 mg of disgrace. Then, the solutions were mixed into the beaker until homogeneous using a stirrer. Homogeneous solutions were inserted into the cuvette and then the polymerization stage is carried out in the water bath of 70° C for 12 hours. Then, the polymer is rinsed with methanol and ready to use.

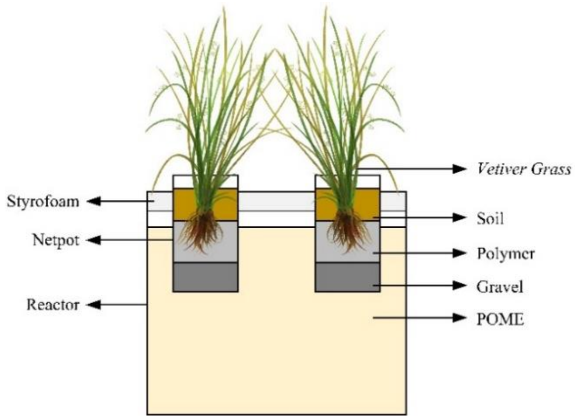

Figure 1. Experimental Setup Floating Treatment Wetlands

Experimental Setup

Aquadest 3L was filled into Phytoremediation reactors. Then, liquid fertilizer containing 2% P_2O_5, iron (Fe) 0.1% as Fe-EDTA, vitamin B1 (thiamine mononitrate) 0.10%, and NAA 0.04% for the acclimatization stage. Then, the vetiver grass was cleaned and washed. The plant was cut about 15 cm from the roots. In the net pot, plant media was filled in the form of gravel, polymers, and soils with a ratio of 3: 5: 2. Then the vetiver grass was put into the net pot (the reactor was six vetiver grass stems), and was placed in a reactor for an ache for 21 days. After the acclimatization stage, the water was replaced with POME and diluted 10 times with the initials COD 421 mg/L and the experimental stage was conducted for 7 days, using periodic analysis for COD and TSS during processing. The Experimental setup of floating treatment wetlands can be seen in Figure 1.

Data analysis

In this study, COD analysis was carried out using a method described in SNI 6989.73 2009, which discusses the COD test method with closed reflux titration (Environmental and Forestry Instrument Standardization Agency, 2023). As illustrated in equation (1) for calculating COD reduction efficiency, RE is Removal Efficiency (%), C0 is Initial Concentration (mg/L), and Ce is Final Concentration (mg/L).

$$RE = \frac{(C_0 - C_e)x\ 100\%}{C_0} \qquad (1)$$

RESULT AND DISCUSSION

Effect of Retention Time to COD Reduction

The optimum retention time is needed to test the ability of this combination of technologies. Increasing the retention time will increase the contact time between POME, ammonium polymer, and vetiver grass. Thus, the ability to degrade COD in the sample will also increase. The length of retention time shows a decrease in COD, which means that plants and polymers are still working to degrade pollutants. Specifically, the effect of retention time and COD reduction can be seen in Figure 2.

Figure 2 shows each reactor's significant effect on COD reduction in POME. The FK1 reactor or the reactor without treatment also experienced a decrease in COD until the third day of around 9% or equivalent to 385 mg/L. The decrease in COD in this reactor indicates the activity of microorganisms that utilize the substrate in POME, but this decrease only lasts until the third day. POME contains high organic matter that can be a growth medium for natural microorganisms. Over time, microorganisms such as aerobic and anaerobic bacteria break down organic matter in POME, reducing COD naturally through the biodegradation process. Based on research by Bala et al. (2018) and Ilyasu et al. (2024), bacteria such as *Bacillus sp, Micrococcus luteus, Stenotrophomonas maltophilia*, *Klebsiella pneumoniae,* and *Aspergillus fumigatus* found in POME and these bacteria are reported to have the potential to degrade carbon sources present in POME.

On the third day, the performance of pollutant degradation carried out by bacteria began to decline. It is predicted to be caused by the dissolved oxygen in POME being insufficient for the respiration of aerobic microorganisms; only anaerobic microorganisms are able to survive, and aerobic microorganisms will die, thus reducing the efficiency of pollutant degradation. Furthermore, the changes in environmental conditions due to bacterial metabolism can create stress for microbial communities. Factors such as temperature fluctuations, nutrient availability, and toxic byproducts from bacterial metabolism can also negatively impact microbial health and activity (Adegbola et al., 2020; David Bala et al., 2014; Periadnadi et al., 2024).

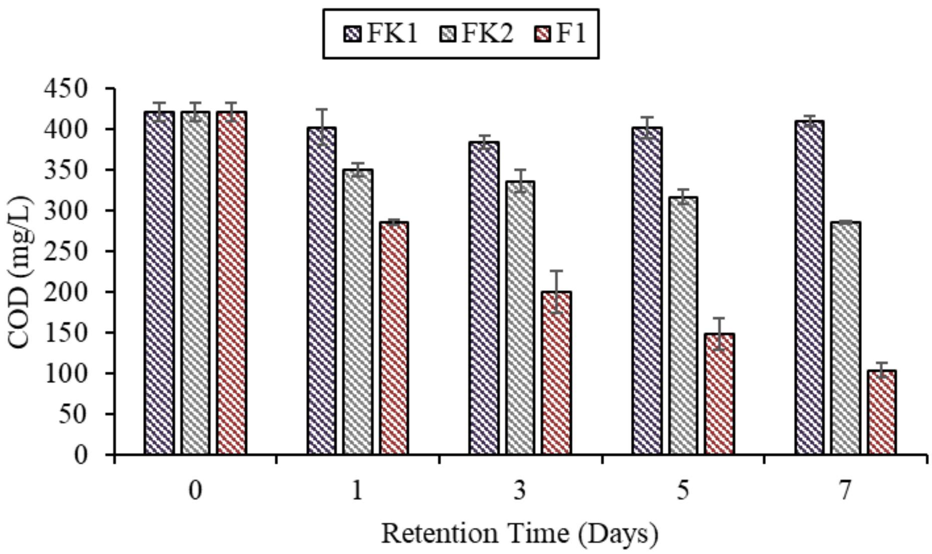

Figure 2. The Effect of Retention Time to COD Reduction. The different treatments were FK1 (Wastewater only), FK2 (Vegetated control), F1 (Vetiver grass + Ammonium Polymer)

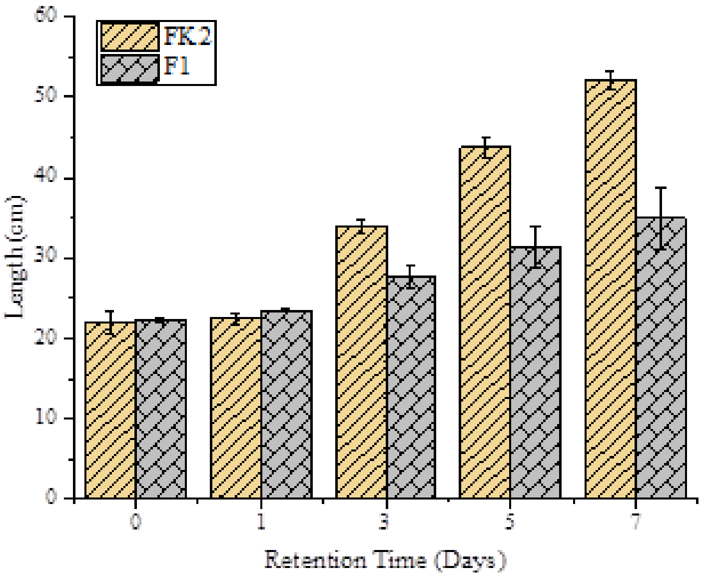

Figure 3. The Growth Rate of Vetiver Grass. The different treatments were FK2 (Vegetated control), F1 (Vetiver grass + Ammonium Polymer)

In the FK2 reactor, the processing of vetiver grass successfully reduced COD in POME to 286 mg/L. Until the seventh day, the COD reduction rate was around 32%. According to Mahmoudpour et al. (2021), The ability of vetiver grass to degrade pollutants is called phytoextraction. Phytoextraction is the process of plants absorbing contaminants from pollutant sources through their root systems. Vetiver grass has a strong root system that allows it to access and extract pollutants effectively. The results of this study are in accordance with research conducted by Darajeh et al. (2014), which shows that vetiver grass can achieve a COD reduction of up to 39% in a retention time of 14 days with an initial COD of 721 mg/L. Then Tan et al. (2019) conducted phytoremediation using *eichhornia crassipes* on POME for 21 days. On the fifth day, a COD reduction of around 25% was obtained. So, the COD reduction range for several types of macrophytes in processing POME for up to 7 days is around 25 - 39%.

The main reactor tested this time (F1) showed a COD figure after 7 days of processing of 104 mg/L with a reduction rate of 75%, higher than FK2. Ammonium polymer is an amine-based polymer that can be used to adsorb organic compounds, especially those containing polar groups or those that can interact with amine groups in the polymer (Aini et al., 2023). COD is related to the organic compounds present in POME, and many organic compounds contributing to the COD value have polar groups in their structure. These organic compounds may contain polar groups such as hydroxyl (-OH), carbonyl (C=O), amine (-NH_2), or carboxylate (-COOH), all of which have polar properties and can interact with polymers or adsorbents that also possess polar groups (Emilia Agustina et al., 2016; Stefany et al., 2022).

With the addition of adsorption technology using ammonium polymers, the phytoremediation capability will increase. This capability is in accordance with the research Fajri et al. (2024) who conducted a combined study of augmentation and phytoremediation to process textile waste. The study increased in COD reduction from 12% using only vetiver grass to 87% with a combination of augmentation and vetiver grass. Ammonium polymers with active groups can act as suitable anion exchangers to bind pollutant anions contained in POME (Rahayu et al., 2021). According to Hakim et al. (2025), the combination of ammonium polymer and vetiver grass can increase the COD reduction capacity in waste by up to 77% and phosphate by around 60%.

From all reactors, it is shown that retention time would significantly affect the sample contact process with the treatment system used for optimal pollutant degradation. Retention time is a key factor in the COD degradation process in liquid waste. Research shows that increasing retention time generally increases the efficiency of COD reduction. Therefore, choosing the right retention time according to the treatment method and wastewater characteristics is very important to achieve optimal results in wastewater management (Khan et al., 2024; Ting et al., 2020).

Growth Rate of Vetiver Grass

The growth rate in phytoremediation refers to the growth rate of plants used in the process. It is an important parameter that shows how fast the plants grow during remediation. The effect of vetiver grass growth rate on phytoremediation modification was observed to determine the relationship between planting media and pollutants that are sources of nutrients and plant growth. The growth rate of vetiver grass can be seen in Figure 3.

Figure 3 shows a significant difference in plant height between vetiver grass, whose planting medium was not using polymer, and vetiver grass, whose planting medium was modified using polymer. Until the seventh day of processing, there was a difference in plant height between FK2 and F1 of around 17 cm or around 33%. This difference is predicted because F1 contains ammonium polymers, which have been proven effective in degrading phosphate and nitrate. According to Rahayu et al. (2023), ammonium polymer can absorb phosphate and nitrate around 89, and 92% in sugar industry wastewater samples and synthetic waste containing nitrate and phosphate. In phytoremediation, When phosphate and nitrate are limited, plants face complex growth challenges. Plants may exhibit poor root and shoot development, reduced nutrient uptake, slower growth rates, and reduced productivity. Nitrate and phosphate compounds are nutrients plants need. The availability of nutrients that are important for plant growth can be reduced so that they have the potential to inhibit plant development (Razaq et al., 2017).

CONCLUSION

The research concluded that retention time was significantly impact on the efficiency of COD degradation in POME. The highest COD reduction efficiency was around 75% in the phytoremediation reactor modified using ammonium polymers. Daily observations showed an increase in COD reduction efficiency until the seventh day. Furthermore, modifying phytoremediation using polymer-based planting media affected plant growth because the adsorbent reduced phosphate and nitrate content in POME. There was a difference of about 33% in plant height between treatments with and without polymers, which is beneficial in controlling post-harvest phytoremediation time. However, modification of phytoremediation improves the COD degradation ability in POME and has the potential for implementation. Further research on this modification should include testing with pure POME and several types of diluted POME to determine the concentration at which this technology modification works effectively.

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