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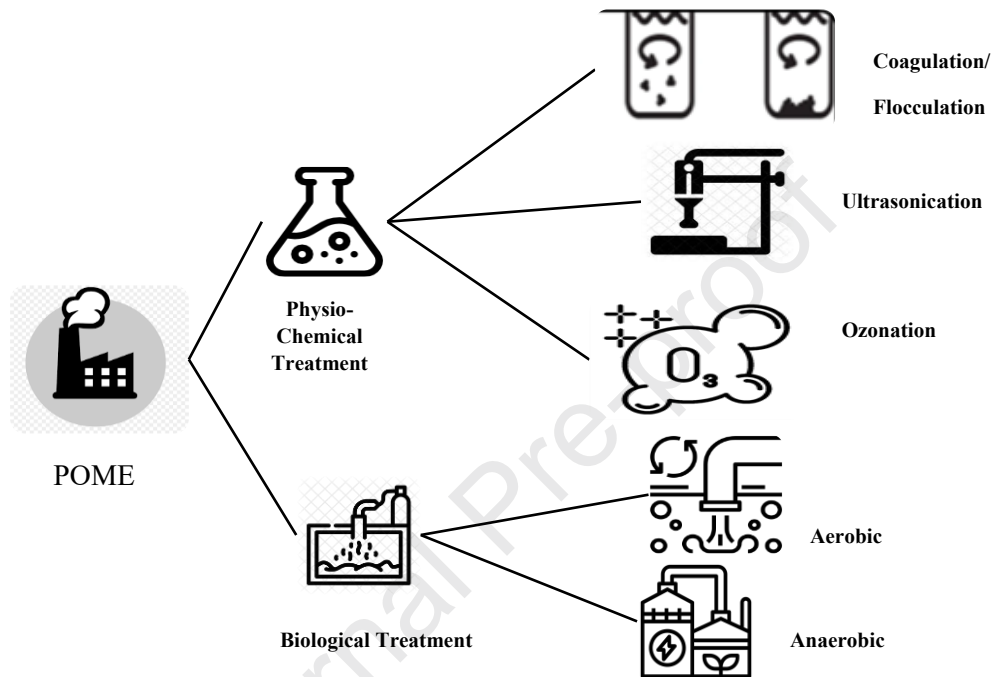
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Graphical Abstract



A review on the pollution assessment of hazardous materials and the resultant biorefinery products in Palm Oil Mill Effluent

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Abstract

The voluminous nature of POME is directly associated with environmental hazards and could be turned into biorefinery products. The POME, rich in BOD, COD, and oil and grease, with few hazardous materials such as siloxanes, fatty acid methyl ester, and phenolic compounds may significantly increase the risk of violating the effluent quality standards. Recently, the application of chemical and biological risk assessment that can use electrochemical sensors and microalgae-like species has gained paramount attention towards its remediation. This review describes the existing risk assessment for POME and recommends a novel assessment approach using fish species including invasive ones as suitable for identifying the toxicants. Various physico-chemical and biological treatments such as adsorption, coagulation-flocculation, photo-oxidation, solar-assisted extraction, anaerobic digestion, integrated anaerobic-aerobic, and microalgae cultivation has been investigated. This paper offers an overview of anaerobic technologies, with particular emphasis on advanced bioreactors and their prospects for industrial-level applications. To illustrate, palmitic acid and oleic acid, the precursors of fatty acid methyl ester found in POME pave the way to produce biodiesel with 91.45 %. Although there are some challenges in attaining production at an economic scale, this review offers some opportunities that could help in overcoming these challenges.

Keywords: siloxanes, fatty acid methyl ester, chemical sensors, biological indicators, photo-oxidation, biodiesel.

1. Introduction

Having a high share in fulfilling the need for oils and fats at the global level, palm oil ups the economic growth through more than half of the annual production. However, it leads to an increase in waste volume and a bigger amount of liquid matter in waste, thereby reducing the advantages of the recovered palm oil (Ahmad et al., 2003; Dominic and Baidurah, 2022). These liquid wastes are otherwise known as palm oil mill effluent (POME) (Abdullah et al., 2020). A total volume of 5-7.5 m³ of water has turned the fresh fruit bunches (FFB) into crude palm oil of approximately 1 tonne and more than half of the water was converted to POME (Aljuboori et al., 2014). The characteristics of POME often differ, and researchers are identifying extraction methods, the geology of the palm oil mills, and the sampling time that influences it (Rupani et al., 2015). In addition, in palm oil mills, the number of batches and days can also determine the quality of POME and may also depend on the nature of the palm (Madaki and Seng, 2013). POME is a mixture in the form of colloidal suspension that contains mostly water (95% - 96%) and a small amount of total solids (4%-5%) and suspended solids (2%-4%). It also contains a negligible amount of oil (0.6% to 0.7%) Moreover, the studies confirm that a high amount of BOD (26.3 gL⁻¹), COD (65.5 gL⁻¹), and carbohydrates (cellulose, hemicellulose, and lignin) exists within POME along with minerals, proteins, and lipids (Ahmad et al., 2011). The general characteristics of POME are given in Table 1. To be more concise, one volume of POME is posing as much environmental threat as three volumes of crude palm oil made and the presence of pigments and not the chemicals could turn the POME brown in color (Wu et al., 2010). Excess BOD and COD raise pollution levels which can affect peripheral water courses like canals and rivers, and aquatic life and cause highly polluted water (Abdurrahman et al., 2011; Nur et al., 2021). Also in the case of soil, POME can affect physico-chemical properties response to pH and can thus contribute to an increase in salinity (Islam et al., 2018). It is also stated by Hemming (1997), that the acidity of soil increases when POME is discharged but after biodegradation the pH of the soil decreases. The ability of plants to intake optimum amount of nutrients is affected by the pH of soil. Even with the presence of nutrients such as nitrogen, phosphorus and potassium does not increase the crop yield if the pH of the soil is more acidic. Hence, treatment of POME before discharge could cut the risk of water pollution.

The assessment of pollutants is mandatory before the planning of remediation methods through biorefining aspect. Regular environmental assessment can determine the quality of the ecosystem- which is associated with the level of degradation (Ajab et al., 2014). Various chemical and biological-based monitoring are more likely to take their preference and are fueling the accurate detection of pollutants in POME. In chemical-based systems, the electrochemical sensors are created by novel electrodes with chemically modified materials (Ajab et al., 2018). Novel electrodes such as boron doped diamond is known to produce high levels of hydroxyl radicals and able to oxidise organic compounds with more than 90% COD (Muharam et al., 2019); treatment of POME with platinum as anode and graphite as cathode results in 84% of COD reduction (Rakhmania et al., 2022); usage of iron and aluminum electrodes results in 95% and 90% of COD reduction respectively (Darmadi et al., 2018); a unique steel wool electrode that was employed in the investigation performed by Nasrullah et al., 2017 thereby eliminating the contaminants quickly, effectively, and affordably. Though the usage of electrodes to treat POME is advantageous, a shift from chemical electrode-to-cellulose electrode has just gotten a step closer to green chemistry. Thus, the cellulose-hydroxyapatite carbon electrode estimates the presence of heavy metals in POME (Ajab et al., 2019). In addition, while final discharge, pollutants in POME are having a profound impact on the water courses that extend to the entire aquatic ecosystem. Increased levels of heavy metals and an acidic pH (5.4 – 6.2) were caused by POME when discharged into waterbodies. These alterations are injurious to both humans and aquatic life (Ideriah et al., 2007). Hence, pollution monitoring with biological species which do not have a higher incidence of risk can make the analysis meaningful (Zulfahmi et al., 2018). Firstly, the whole effluent toxicity (WET) test may make *Daphnia magna* more able to detect the pollutants in POME and secondly, toxicity identification evaluation (TIE) is using bioassays and physic-chemical parameters on planktonic crustacean *D. magna* to detect the hazardous pollutants in POME (USEPA, 1991; Hashiguchi et al., 2020). In addition, researchers have developed an effective mixed culture of microalgae that can allow POME to measure the organic and inorganic substances present in them (Jasni et al., 2020). Decoding of an effective protocol has used POME to analyze phenolic acids, an approach that may be used to cost-effectively make 3,4,5-trihydroxycinnamic acid (THCA) (Pinthong et al., 2017). Finally, the results of Sharuddin et al. (2017) revealed that the bacterial community found in river water may act as bioindicators to represent the contaminations resulting

from POME. The hazardous materials used in the various risk assessment methods are tabulated in Table 2.

A sharp increase in the rate of effluent-linked BOD, COD, carbohydrates, organic acids, proteins, nutrients, and oil and grease among the components in POME could foreshadow a reversal in the overall decline in pristine quality of watercourse, even in a small river (Ganapathy et al., 2019). The above said hazardous materials in POME may not only lead to a higher risk of depletion of oxygen in watercourses but also have lasting effects on photosynthesis, respiration, and enzymatic activity in the microalgae (Yan and Pan, 2002). Various types of siloxanes including cyclotetrasiloxane, hexadecanoic acid belonging to fatty acid methyl ester (FAME), gallic acid, and caffeic acid of phenolic compounds, toxic heavy metals such as lead, chromium, cadmium, copper, and aluminium are the hazardous materials present in POME whose LC₅₀ values are 202 mg, 3g, 5g, 44 mg and 3600 mg.

Watercourses which receive a lot of untreated POME may be more likely to have water pollution in their inland environment and higher risk on aquatic species (Abdurrahman et al., 2011). Enormous production has made POME more voluminous and untreated conditions more destructive (Bashir et al., 2017). The lack of efficiency of treatment plants in processing mills is believed to be behind the existence of harmful substances in POME final discharge, which records a considerable leap in environmental disastrous activities in aquatic ecosystems worldwide (Garcia-Nunez et al., 2016). Hence, proper treatment methods such as pre-treatment and advanced treatments may be a signal for effective remediation of contaminants and therefore moving into a position to focus on maintaining the well-being of the environment (Alhaji et al., 2016).

In the biorefinery approach, abandoned agricultural wastes could be saved from either landfill or watercourses and turned into biobased products, including energy, chemicals, and materials (Dahiya et al., 2018). Biorefinery could reveal a circular bioeconomy-like greener approach is possible with POME. Redefining the valuation and cheaper rate of POME is linked to a lower burden of the treatment process that ups the chances of generating biofuels like hydrogen and value-added products like fertilizers, etc (Foo and Hameed., 2010; Sasongko et al., 2018). The presence of lipids in POME, which are linked to the production of biodiesel may replace fossil fuel usage (Islam et al., 2018). Likewise, the presence of carbohydrates, nitrogenous compounds,

and minerals in POME is a key to the production of bio-flocculants, biopolymers, biofertilizers, and more.

In addition to pollution assessment, the profile of hazardous materials, mitigation strategies and biorefinery platform, energy, and economic aspects of POME treatment have been discussed in this article. Moreover, the challenges faced in the process of POME treatment and economic-friendly opportunities that have been made to overcome the challenges have also been reviewed.

2. Pollution assessment methods for POME

2.1. Chemical-based monitoring

Initial monitoring and further detection of pollutants in POME, which exerts its presence in water and soil to make pollution control and remediation strategies are explained in this section. The real-time sample's crisis is of the sensitivity and selectivity of the pollutants in POME. Hence, chemical methods especially, analytical chemistry may hold key in analyzing the concentration of pollutants and the existence of interfering substances. In analytical chemistry, atomic adsorption or emission methods may not be better for on-site analysis, the electroanalytical approaches thus respond to environmental samples and can thus contribute to real-time analysis.

2.1.1. Cellulose-hydroxyapatite chemically modified electrodes

In electroanalytical methods, the use of electrochemical sensors helps in monitoring pollutants in POME with its robustness, ultra-trace level detectability, shorter duration of time for analysis, and ease of handling (Ajab et al., 2014). However, the sensors are altered during the analysis by the toxic nature of electrode materials. Hence replacing the electrode with plant-based cellulose may reverse the toxicity by binding to the various metal ions. When these plant based cellulose are chemically modified, they display higher adsorption capacity than the unmodified forms (Ajab et al., 2018). Thus, in addition to cellulose, hydroxyapatite (HAp) has been used to develop a better ability of ion exchange that could be used as a detector of heavy metal ions. Combining the sorption capabilities of HAp with the hydrophilic groups of cellulose, which are highly accessible for trapping the heavy metal ions, results in the possibility of effective cellulose/HAp composites for the removal of heavy metals from POME. Ajab et al. (2019) found that lead (Pb) ion is associated with adsorption on the rise in HAp-made electrodes and this could reverse the overall decline in cadmium (Cd) accumulation. The results further show that the

electrode is getting used to analyze POME samples with a limit of detection of $0.11 \pm 0.37 \mu\text{g L}^{-1}$ and with a limit of quantification of $0.37 \pm 0.37 \mu\text{g L}^{-1}$. Moreover, this technique overtakes conventional techniques as it explores good reproducibility ($\pm 3.11\%$), repeatability (2.73%), and stability period of >3 months against untreated POME while on-site. In addition to Pb and Cd, this technique simultaneously detects metals such as zinc and copper. Thus, the developed electrodes can be powered by the ability of cellulose and HAp and successfully tested in POME. Increased exposure to plant materials at electrodes not only raises environmental concerns for analytical chemistry but is also significantly helpful in building green chemistry concepts.

2.2. Biological-based monitoring

Monitoring with biological species outperforms chemical methods in analyzing the real-time samples in a natural ecosystem (Sharuddin et al., 2017). Because they exhibit more response when it comes to their living environment and thus is a sign of ecological consequences against the variation in environmental parameters. There are various methods with biological species such as *D. magna*, *Chlorella* sp, *Scenedesmus* sp, *Chromatiaceae*, and *Alcaligenaceae* equipped to measure the quality and quantity of pollutants in POME and can monitor the activity of bacterial cells and its nucleic acid ratio (Sharuddin et al., 2018; Hariz et al., 2019). These methods are giving satisfactory results even then fish species could be involved in a WET test using POME discharge as a testing material in the future.

2.2.1. Whole effluent toxicity (WET)

U.S. Environmental Protection Agency (USEPA, 1991) has devised an innovative method (WET) that has to be used to analyze the presence of hazardous materials in biological species from wastewater discharge. The bioassay-based WET test hints at surprising evaluation abilities in algal species, invertebrates, and fish. However, none other than Hashiguchi et al. (2020) applied the WET test on POME using planktonic crustacean *D.magna*. The toxicity level made by POME mills are varied and the study reveals that mills A and C produced a toxicity unit (TU) of 4.9 and 5.0 and a TU of 11 and 3.4 during 1st and 2nd sampling respectively. The results suggest that the TU values from the WET test reverse with chemical assessment values. To explain more, mill C had a lower TU value during 2nd sampling against its higher BOD and COD. Moreover, the study concluded that the analysis of POME to detect pollutants from chemical methods could not be a complete one. Hence, this test can be used as a tool to help ease the continuous discharge of

wastewater as well as toxicants and thus is having profound impacts on analysis that extend to be one of the best management practices. However, this test drove the identification of causing factors away from the analysis.

2.2.2. Toxicity identification evaluation (TIE)

TIE test developed by USEPA (1991) has been identified as a major chemical as well as a biological-based assessment method for the analysis of toxicants in wastewater. Prior to and during a range of physical and chemical changes, materials are submitted to TIE, which analyses the reactions of test organisms to identify the presence of toxicants. This makes it possible to separate and later identify the toxicants which are responsible. A variety of freshwater aquatic creatures can be used to test for toxicity, but the most popular ones include fish bioassay, macro-invertebrate survival, bacterial test, and algal growth (*Pseudokirschneriella subcapitata*). Environment Canada advises using this set of aquatic tests to detect acute lethality or short-term toxicity for evaluating water quality. It has phases I, II, and III to monitor the characterization, identification, and confirmation of the toxicants respectively. This test may help in identifying various types of wastewater including landfill leachate (Budi et al., 2016). According to Hashiguchi et al. (2020), phase I holds the clue to characterize the source of toxicants such as SS, and organic compounds, phase II identifies the presence of toxicants that may negatively impact the growth of *D.magna* and finally phase III confirmed the presence of toxicants exert low toxicity on *D.magna* and even low level of toxicants has turned the effluent into a problem for aquatic organisms. In addition, pH adjustment is having a profound impact that extends to the toxicity of the effluents and ends in a decrease in the toxicity of the compounds present in POME. The results of the study concluded that phenolic compounds, heavy metals, and acid-sensitive compounds in POME can cause inhibition of growth and up the risk of toxicity to *D.magna* like planktonic crustaceans.

2.2.3. Microalgae-based toxicity

The presence of organic and inorganic compounds in POME has both positive and negative impacts on microalgae diversity which is linked with phytoremediation (Emparan et al., 2020). Aquatic macrophytes can respond to a range of toxicants and can thus play a role in inhibition tests. Moreover, microalgae have been identified as a major bioindicator of the POME toxicants as they help predict environmental changes over a short duration of time. The microalgae-based toxicity is using a mixed culture of species to resemble the real ecosystem conditions (Jasni et al.,

2020). Acetic acid, one of the major organic compounds in POME with the highest concentration of 4100 mgL⁻¹ is more likely to stimulate the growth of microalgae and ends up in the highest biomass. Whereas, assigning low concentrations to stimulate and high concentrations to inhibit the growth of microalgae was observed in the case of other organic compounds including butyric acid. Likewise, the presence of copper and oil, and grease in POME alters the growth of microalgae by reducing the cell division rate, nutrient, and air supply rate. Hence, the results of the study suggest that POME can affect how microbial cells respond to organic compounds on short and long-term exposure and thus contribute to enhanced growth. In addition, inorganic and some organic compounds on long-term exposure contribute to inhibition.

2.2.4. Biocatalytic protocol

This protocol approves the phenol-based compound for the biorefinery product. An enzyme named p-hydroxyphenylacetate 3-hydroxylase (HPAH) which is isolated from *Acinetobacter baumannii* is used to generate value added chemicals such as trihydroxyphenolic acids from the effluent POME. These chemicals are also used as medicinal agents. Firstly, the protocol analyzes and confirms the presence of phenolic acids (p-Coumaric acid and caffeic acid) in POME. Secondly, these phenolic acids as precursors may make enzymatic reactions more able to produce 3,4,5-Tri hydroxyl cinnamic acid (3,4,5 –THCA) (Pinthong et al., 2017). Recently, a more efficient genetically engineered enzyme namely Y398S was used to generate about 75% of 3,4,5 –THCA from p-Coumaric Acid. A bioactive substance known as 3,4,5-THCA has a number of biological characteristics, such as antibacterial, anti-inflammatory, and antivenom actions. Three hydroxyl group substituents on the 3,4,5-THCA's aromatic ring provide the substance with more antioxidant potential. Because of the erratic price of oil and the growing popularity of eco-friendly items among consumers, bio-based chemicals may also eventually replace fossil-based ones. Additionally, because they may be used to generate special chemicals and bio-based building blocks, manufacturer's view bio-based chemicals as cost-effective (Kahar et al., 2021).

2.2.5. Assessment through bacterial indicators

Nowadays, the pollution assessment method is using microbes, especially bacterial communities to find out the contamination caused by POME. The selection of bacteria as indicators is because they are more likely to stop multiplication when exposed to toxicants containing POME. According to Sharuddin et al. (2017), the detection of *Chromatiaceae* and

Alcaligenaceae in downstream and not upstream suggests the possibility of POME final discharge. Again, the redundancy analysis confirms that environmental variables made by POME put bacterial species at risk (Sharuddin et al., 2018). To explain more, an increase in BOD, COD, temperature, and TOC of POME has negative effects on bacterial cells by increasing the viable cells and total cell concentration which is linked with oxygen depletion. The effluents in POME turn out to be a threat to nucleic acid proportions of bacterial cells. Having a high level of the above toxicants in POME ups the risk of nucleic acid shift. A shift in low (LNA) to high nucleic acid (HNA) content in bacteria made dormant cells become active and hit the original high LNA levels. In addition to chemical methods, the biological assessment method, viz., community shift test hints at surprising detection abilities in bacteria against POME (Zolkefli et al., 2020).

2.2.6. Novel assessment using fish species.

The presence of heavy metals in the effluent can be also assessed through fish (*Danio rerio*) embryo toxicity (FET) test. The presence of heavy metals also inhibits the development of the fish embryos. These tests can detect the presence of heavy metals such as Copper, Zinc and Iron. Exposure to POME in lab conditions not only raises environmental concerns for fish species but also significantly explores its ecological characteristics including reproductive performance (Zulfahmi et al., 2018). However, to date, no research could be conducted on native fish species in real-time monitoring. Thus, this review presses the need for pollution assessment such as WET and TIE for fish species belonging to both native as well as invasive in real-time analysis against POME.

3. Profile of hazardous materials

3.1. Siloxanes

Siloxanes tied to the final discharge of POME were identified as cyclotetrasiloxane, octamethyl (D4), Cyclopentasiloxane, desmethyl (D5), and Cyclopentasiloxane, dodecamethyl (D6) have been confirmed as cyclic volatile methyl siloxanes (cVMS) (Howard and Muir 2013). D6 has existence and toxicity, but D4 and D5's toxicity is more concerning the environment (Lassen et al., 2005). The highly volatile nature of cVMS in POME may not only lead to direct release into the atmosphere but also have lasting solubility effects in the water (Wang et al., 2013a). cVMS can affect the biotic species by its persistence and can thus contribute to bioaccumulation (Borgais et al., 2013). In addition, being at a lower trophic level is directly associated with a higher risk of lipid-normalized concentrations of D4, D5, and D6 and higher trophic species may reverse

this condition (Powell et al., 2018). Moreover, the concentration of the D5 compound is having profound impacts on the species that extend to the entire ecosystem (Wang et al., 2013b). Hashiguchi et al. (2020) analyzed POME and found that cVMS exists within POME from mills A and B and D4 has a concentration of 0.0148-0.0357 mg L⁻¹. Similarly, Neoh et al. (2014) reported the presence of the D4 compound of cVMS in POME. Siloxane degrades in soil via several stages: initially, it undergoes ring-opening hydrolysis to produce silanol oligomers that are then subsequently hydrolyzed to produce dimethicone glycol (DMSD). When the molecular weight of cVMS is larger, the rate of breakdown is slower. cVMS's final byproduct, DMSD, which volatilizes to the atmosphere, can either be directly biodegraded or photodegraded. Silicon dioxide, carbon-di-oxide, and water are the final byproducts of DMSD breakdown (Xiang et al., 2021).

3.2. Fatty acid methyl ester (FAME)

Free fatty acids from crude palm oil found as FAME in POME and transesterification have helped in transforming into FAME at 87% (Boonrod et al., 2016). The chemical structure of FAME may pose an environmental risk while undergoing oxidative and thermal degradation (Lukasik and Lenyk, 2009). POME most likely received the bulk of palmitic and oleic acid methyl esters essential for the production of biodiesel from the crude palm oil that itself contained free fatty acids such as palmitic acid and oleic acid (Matinja et al., 2019). Hashiguchi et al. (2020) found hexadecanoic acid, methyl ester, and octadecanoic acid, methyl ester is amongst the FAME in POME. In addition, FAME may hold key to identifying various characters and classes of bacteria as biochemical markers (Sreenivasulu et al., 2017). FAME can react at higher temperatures and explains how lower temperatures respond to the high melting point and can thus contribute to poor flow property during cold seasons (Suwanno et al., 2017). FAMEs decompose in the presence of beta-proteobacteria that secrete esterase to produce methanol as well as free fatty acids that are discharged into the medium. The free fatty acids undergo beta-oxidation, which removes two carbon atoms per cycle to produce carbon di-oxide and water in the end (Khoury et al., 2011). As a result, additional b-oxidation cycles are required to finish oxidising longer fatty acid chains. Compared to their long-chain counterparts, shorter fatty acid chains biodegrade more swiftly and completely.

3.3. Phenols and phenolic compounds

The presence of phenol and other phenolic compounds including polyphenols made POME highly toxic on final discharge (Islam et al., 2018). The study has revealed that plants having shikimic acid and pentose phosphate are to blame for phenylpropanoid metabolism which results in phenolic compounds or phenolic acids, a group of secondary metabolites (Randhir et al., 2004). In addition, phenolic acids exist in free and bound forms in palm fruits. The outer pericarp layer and different plant components may host free and bound phenolic acids respectively and the bound form is more likely to respond to the cell wall structure (Jamal et al., 2011). Exposure to palm fruit sterilization and extraction processes at oil production not only raises phenol but also significantly generates phenolic compounds at a concentration higher than 1000 mg L⁻¹ (Adeleke et al., 2017; Ahmad et al., 2017). Wet oxidation of lignin is having profound impacts that extend to the further production of these compounds. Researchers have identified gallic acid at a concentration of 668 mg L⁻¹, p-hydroxybenzoic acid at a concentration of 86 mg L⁻¹, p-coumaric acid at a concentration of 20 mg L⁻¹, as major phenolic compounds from POME (Chantho et al., 2016). The above results revealed that gallic acid overtakes other phenolic compounds as highly concentrated in POME. The study concluded that treatment processes like anaerobic digestion may not be able to wipe out phenol and other two phenolic compounds such as gallic acid and protocatechuic acid from POME. According to Hashiguchi et al. (2020), a phenolic compound, phenol, 2,6-bis (1,1-dimethyl ethyl)- was more likely to present in all samples of POME at a concentration of 0.03-0.04 mg L⁻¹. Moreover, the calculated pK_a value for this compound stands at 11.91, which could be a sign of a faster response to pH changes. In particular, the toxicity of this compound tied to short-term tests on *D.magna* exhibits an EC 50 value of 0.45 mg L⁻¹. The discharge of phenolics turns out to be the biggest threat to plants concerning phytotoxicity and microbial inhibitory effect (Jarujareet et al., 2019). And finally, the biocalcitrant nature of phenolics in the aquatic system may make species less able to involve in photosynthesis as well as in capturing dissolved oxygen (Kietkwanboot et al., 2015). Degradation of phenolics occur chemically. Chemically oxidising phenolic substances causes the cyclic ring to break into smaller molecules, which includes dicarboxylic acids, until the oxidation is eventually completed, and Carbon dioxide is produced (Krishnan et al., 2022).

3.4. Heavy metals

The increasing amount of heavy metals such as lead (Pb), cadmium (Cd), nickel (Ni), iron (Fe), copper (Cu), zinc (Zn), chromium (Cr), and aluminium (Al) is causing toxicity to the POME final discharge (Muhrizal et al., 2006; Ahmed et al., 2015). Leaching action in metal pipes, containers, and usage of paints and glazing materials tied to the release of heavy metals, at least in wastewater, POME (Ajab et al., 2019). Madaki and Seng (2013) revealed the fact that heavy metals including Fe can be a threat to the POME as it may be teeming with a concentration of (46.5 mg L⁻¹). The processes involved in palm oil production in every mill influence the heavy metal content in POME. A recent study by Hashiguchi et al. (2020) reported that palm oil mills A, B, and C fuelling the rise of heavy metals in POME; however, the analysis give mixed results on their concentration when compared Fe, Ni, Cu, and Zn between mills. Toxic heavy metals in POME, are a cause of worry for aquaculture (Adeleke et al., 2017). Exposure to higher levels of heavy metals in POME may cause a decline in the metabolic pathway, and lead to the inhibition of growth in crustaceans and microalgae (Jasni et al., 2020).

4. Mitigation strategies

4.1. Pome treatments

The final discharge of POME turns black or brown when the organic content in it is higher than usual (Bello et al., 2013). The phenomenon is exacerbated by low pH, lots of colloidal particles, and a lack of effective degradation (Budiman et al., 2015). It's in these conditions that either conventional or advanced treatment influences the degradation of toxicants in POME. Both physicochemical and biological approaches are coming under conventional as well as advanced treatments (Alhaji et al., 2016). POME running out of conventional methods (physico-chemical and biological approaches) to treat as it raises concerns for space allocation and its inefficiency in complete degradation (Alhaji et al., 2018). Thus, a pre-treatment followed by an advanced treatment may make POME more able to degrade its pollutants which may replace a single or common treatment against POME (Chan et al., 2010).

4.2. Physico-chemical treatments

One of the important conventional physico-chemical treatments, coagulation/flocculation (C/F) has proceeded as a pre-treatment approach, then it will be more beneficial and reduce the risk of degradation of solid particles at a later level. POME is a mixture of colloidal suspended

particles with a negative charge that has turned the settling of particles into a problem. Hence, a C/F technique is a key to better stabilization of charged particles to become neutralized. Hossain et al. (2019) selected ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) as a coagulant generated from titanium industrial waste that has negative effects on BOD, COD, and TSS of POME which is linked with single-stage treatment. However, exposure to chemical agents at C/F treatment of POME not only raises health concerns for humans but also significantly harms the ecosystem. On the other hand, biological agents are having profound impacts on biodegradability that extend to the avoidance of concomitant pollution risks (Aljuboori et al., 2014). Researchers have produced a bio-based coagulant/flocculant from chickpea powder that can speed up mixing and can thus improve the removal of COD and TSS at 56% and 87% respectively (Lek et al., 2018). In addition, in the focus on mitigation, Hassimi et al. (2020) revealed that POME itself outperforms other biological materials in the production of flocculants with the highest bio flocculant yield of 2.03 g L^{-1} . Similar to bio coagulants/flocculants, plant/animal materials are used as adsorbents for better treatment of POME. Abandoned banana peel and cow bone could be turned into activated carbon and applied as biosorbent and in the removal of color, tannin-lignin, BOD, COD, TSS, and $\text{NH}_3\text{-N}$ in POME treatment (Mohammed and Chong, 2014; Adeleke et al., 2017). In addition, researchers have used oil palm empty fruit bunches (EFB) coming from crude palm oil production to create biosorbent in the adsorption of phenol from POME (Alam et al., 2009). However, these conventional methods in POME treatment fail to keep up with the complete removal of organics and membrane fouling. Hence, researchers are more likely to take advanced methods for the complete mineralization of organics to save secondary pollutants formation.

Firstly, calcium oxide can trigger the granulation of sludge in POME and can thus contribute to a COD removal of 82.4% (Ahmad et al., 2011). Secondly, titanium dioxide (TiO_2) most likely receives the bulk of UV (ultraviolet) light essential for photo-oxidation in the cylindrical column immobilized photoreactor that performs well in the removal of COD, BOD, and color (Alhaji et al., 2018). In contrast to the above study, visible light irradiation during photocatalysis in POME using CaFe_2O_4 photocatalyst may significantly increase the removal of COD to a maximum of 69.0 % (Charles et al., 2019). Diluting acid (HCl) via the hydrolysis process may help to transform POME- a big polluting chunk of the aquatic systems-through POME hydrolysate into hydrogen, the cleaner energy for the world (Azman et al., 2016). According to Bashir et al. (2017; 2019), electro-persulphate oxidation and electro-coagulation-peroxidation

respectively applied as post-treatment techniques pushing the biologically treated POME to a polished state towards the removal of COD, color, and SS. Equipped with commercial anion, the organic resin can be able to remove pigments from POME under the process of adsorption, and lower pH more likely to exhibit a higher uptake rate (Bello et al., 2013). An intermittent photofermentation, ultrasonication treatment lets POME swipe for the removal of total COD (TCOD). The optimized amplitude and duration of ultrasonication parameters at A₂₀T₁₀ have significantly increased the TCOD to 52.2 % (Budiman et al., 2017). Researchers have identified another major contributor to the removal of COD, ozonation, it turns out, is teeming with ozone that increased the digestibility rate and could help set the system for stability and higher TCOD removal (Chaiprapat and Laklam, 2011). Finally, Fenton's process is linked to an advanced oxidation process, and it is Fenton's reagent (ferrous ions and hydrogen peroxide) that is responsible for the removal of color and solid COD at 90% and 82% respectively (Kongnoo et al., 2012).

4.3. Biological treatments

Under biological treatment, conventional approaches such as anaerobic and aerobic methods promote bioremediation by removing organic contaminants (Kim et al., 2013). Most palm oil mills are adopting anaerobic ponds to make treatments easier, because, the ponding system has made both capital and operating costs more economic (Chan et al., 2010). However, this system turns into failure when the startup level in it is slower than usual and the phenomenon is exacerbated by prolonged retention time and lots of areas needed, and emission of greenhouse gas (GHG) (Loh et al., 2019). Hence, as an alternate, aerobic treatment has been applied to POME. The aerobic process is linked to a shorter retention period in POME that ups the chances of being treated (Ganapathy et al., 2019). Anyhow, similar to anaerobic, aerobic has its disadvantage in the sense that it fuels the rise of energy for aeration. Thus, this process is more likely to be costlier than an anaerobic one (Alhaji et al., 2016). However, in general, the complex nature of pollutants, their toxicity, and their recalcitrant nature pave the way for incomplete degradation believed to be behind the conventional methods' extinction (Alhaji et al., 2018). Hence, the advanced and hybrid methods become the new treatment option for POME.

The main reasons for advanced approaches are cost-effectiveness, capability to react to different strengths of wastes, overall better removal rate, minimal maintenance, and low-level

microbial contamination. Firstly, an integrated ultrasonic anaerobic membrane system helps retain methane gas (CH_4), which is coming default from POME and this new design may raise the COD removal rate to 98.5 % (Abdurrahman et al., 2017). Switching to high-rate anaerobic reactors, made up of one primary hybrid and two secondary filters can enhance the COD removal rate to a maximum of 95.6 % in the case of POME (Choi et al., 2013). Moreover, exposure to secondary reactors may positively trigger the performance and stability of the system. Hybrid treatment in the anaerobic-aerobic-wetland sequential system tends to remove > 80% of organic wastes along with sludge drying. This system leads to uninterrupted organic removal even after 360 days as well as returns to a steady state earlier than thought (Ahmad et al., 2019). According to Krishnan et al. (2016), assigning thermophilic condition to an up-flow anaerobic sludge blanket reactor (UASB) and mesophilic condition to a continuous stirred tank reactor (CSTR) ups the removal efficiency of COD to 94 % in POME fermentation. Using *Commelina nudiflora* plant-powered copper nanoparticle (CuNP) for POME treatment reduces both COD concentration and microbial population and researchers found a positive correlation between the concentration of CuNPs and COD removal efficiency (Kuppusamy et al., 2017). A sharp increase in the rate of two-stage fermentation with two types of reactors such as anaerobic sequencing batch reactor (ASBR) and UASB reactor among POME treatment could foreshadow an uplift in the overall decline in COD removal (90%) (Seengenyoun et al., 2018). Tan et al. (2017) revealed that the Polyvinylidene Fluoride ultrafiltration membrane (UF) can treat POME, and the POME responds to coupled zinc-iron oxide nanoparticles, which are embedded in UF and can thus contribute to the removal of color and COD. Fermentative and hydrolytic communities of bacteria including *Pseudomonas* are getting used to extreme anaerobic conditions fast as the reactors are composed of sludge and packed zones. This hybrid system could turn the POME free from COD, SS, and oil and grease (Meesap et al., 2012). Researchers have used solar radiation to develop solar panels that may be used as solar-assisted bioreactors in anaerobic digestion to enhance the removal of COD at 68 % (Khalid et al., 2019; Zaied et al., 2020).

5. Biorefinery platform

The various biorefined biofuels and other value added products are summarized in the further sections and depicted in Figure 1.

5.1. Biofuels production

Biorefinery of POME results in the production of both liquid and gaseous fuels such as biodiesel, biohydrogen, biomethane, biohythane, and biogas respectively. The various biofuels formed from POME are also tabulated in Table 3.

5.1.1. Biodiesel

The triacylglycerol and free fatty acids may have short-chain alcohols such as methanol and ethanol in POME helped in transesterification catalysis and produce biodiesel (Matinja et al., 2019). In order to explain more, 43.5 % w/w of palmitic acid and 40.0 % w/w of oleic acid present in POME lead to the production of fatty acid methyl esters, one of the components of biodiesel. Oil recovered from POME may not only help in the reduction of COD but also act as a precursor for the production of biorefinery materials (Islam et al., 2018). According to Rakkan et al. (2017), biodiesel production from POME residual oil may be powered by animal fat. In this study the enzyme lipase from white shrimp could be a potential alternative to a chemical catalyst. Similar to the above research findings, 96.5 % w/w of methyl esters formed from fatty acids of POME resulted in the production of biodiesel at a maximum of 91.45 %. In addition, this type of biodiesel is set to the standards of international specification. Similarly, researchers have produced high biodiesel (92.07 ± 1.04 %) yield from POME oil from the same oil palm fruit as substrate and catalyst of palm trees, using the soxhlet method (Suwanno et al., 2017). Conventional palm oil mills use opportunities to process fresh fruit bunches whose efficiency hints at the production of microalgae at 223 tons (Sasongko et al., 2018). In addition, this opportunity not only produces microalgae but also produces biodiesel of 26,471 tons and is responsible for the reduction of GHG emissions to 30.90 %.

5.1.2. Biohydrogen

Regulating the pH at 6 and HRT (hydraulic retention time) at 12 h in the fluidized bed reactor by using POME as a potential substrate and activated carbon as a supporting carrier aims to the production of hydrogen at $1.24 \text{ mol H}_2 \text{ mol sugar}^{-1}$ (Jamali et al., 2019). Moreover, the immobilized cells are getting good at the microbial attachment.

According to Abdullah et al. (2020), POME rich in organic carbon and minerals with additives such as ferric ions under treatment may significantly increase the production of

biohydrogen. POME in hydrolysate form may be used to produce hydrogen with a volume of 334.2 ml (Azman et al., 2016). Researchers have found an intermittent way-ultrasonication technique to treat effluents including POME and turn it into biohydrogen, an advance that could increase the efficiency of photofermentation using *Rhodobacter sphaeroides* (Budiman et al., 2017). Highly efficient production of biohydrogen is associated with two-stage dark fermentation and microbial electrolysis cell and in recent years has become a promising option for major classes of biorefinery products including biohydrogen (Khongkliang et al., 2019; Zainal et al., 2018). The study also found that the thermophilic condition can maximize the activity of fermentation, which helped POME turn into biohydrogen. Similiar studies were also carried out by Chen et al., 2019 in which the biohydrogen was synthesized from POME using steam reforming techniques.

5.1.3 Biomethane

Researchers have developed anaerobic pretreatment followed by an anaerobic digestive way to convert POME into biomethane that could be used as renewable energy (Abd et al., 2019; Chantho et al., 2016; Zainal et al., 2019). A good way to produce biomethane from POME is the pre-treatment with ozone, switching to POME with lower COD could increase the yield to 54 % (Tanikkul et al., 2019). A sharp fall in organic pollutants bodes well for POME treatment (Meesap et al., 2012, Muhammad et al., 2021). They revealed that exposure to the hybrid reactor with fixed-bed film may raise methane production to 0.30 LCH₄ g COD⁻¹_{removed}. The study by Chan et al. (2017) suggests that an integrated anaerobic-aerobic bioreactor effectively alters the POME quality and it could have complied with the discharge standard. Moreover, exhibit an exceptional role in the aerobic system when it comes to exploring more efficient options for solving POME contamination. Finally, the anaerobic system outperforms overall COD removal efficiency, which results in the maximum production of methane at 64 %. Zinatizadeh et al. (2017) reported that mass transfer of substrate may signal the 'biomass washout' risk and which can be prevented through internal packing, which is otherwise known as a fixed film reactor, and keeping the system under stable condition. The fixed film reactor is using the packing material to enhance the granulation process and it has proved to be one of the stages of the supplementing treatment during low HRTs and up-flow velocities.

5.1.4. Biohythane

Two-stage microbial fermentation helps form biohythane in POME treatment (Kongjan et al., 2018). Dark fermentation followed by anaerobic digestion plays an important role in producing initially biohydrogen and biomethane at a later stage. As well as, 2 days HRT and an OLR of 27.5 gCOD L d⁻¹ is good for biohydrogen, and 10 days HRT and an OLR of 5.5 gCOD L d⁻¹ is good for biomethane. Having both hydrogen and methane in digesters ups the significance of Biohythane at a production rate of 1.93 L-gas L d⁻¹ with the proportion of hydrogen (H₂), CH₄ and CO₂ at 11 %, 52 %, and 37 % of biogas respectively (Seengenyong et al., 2018). Finally, the study concluded that the two-stage process leads to energy recovery with a maximum of 14.68 kJ gCOD⁻¹. Mamimin et al. (2015) have also confirmed the previous results that more CH₄ (51 %) than H₂ (14%) is produced in the mixture of Biohythane with 35 % (CO₂), being used as a chemical and energy carrier. However, the high production of volatile fatty acids such as butyric acid and propionic acid has left digesters at record-low methane levels, causing chaos for Biohythane production (Mamimin et al., 2017).

5.1.5. Biogas

Biogas rich in CH₄ and CO₂ could help promote power generation by capturing and preventing the accumulation of GHG which otherwise leads to global warming and climate change (Chuen and Yusoff, 2012; Sharvini et al., 2020; Aziz et al., 2020). Compounds such as total carbon, total nitrogen, and total phosphorous found in POME and cattle manure at equivalent proportions have helped to produce biogas to a maximum level of 1567.00 mL in POME treatment, where solar-assisted bioreactor programmed to develop the mesophilic condition (Khalid et al., 2019). Direct hydrolysis may increase the possibility of producing biogas by raising the levels of xylanase enzyme to 20 unit mL⁻¹ in the POME treatment associated with thermophilic fermentation (Prasertsan et al., 2017). The usage of organic load at an integrated anaerobic-aerobic-wetland sequential system can influence biogas production using POME as a substrate (Ahmad et al., 2019). To explain more, the biogas with a maximum production of 11,028 kg d⁻¹ at an organic load of 2.2 kg m⁻³ d⁻¹ which positively correlates with the COD removal rate of 99 %. Recirculation of biomass has taken place periodically to boost biogas production. The researchers revealed that biomass recirculation from a settler tank into an anaerobic digester will keep the active sludge more alive and stable, contributing to more methanogens growth (Garcia-Nunez et al., 2016).

5.2. Value-added products

Biorefinery of POME results in the production of value-added products such as biopolymers, flocculants, biomass, animal feed, and fertilizer.

5.2.1. Biopolymers

Researchers have successfully used POME to produce biopolymers using microbes, minerals, and anaerobic conditions. Microbial populations such as *Comamonas* sp. EB.172 is triggered by bioconversion, which holds the key to producing polyhydroxyalkanoates (PHA), a thermoplastic of biodegradable origin (Mumtaz et al., 2010; Zakaria et al., 2010, Anwasha et al., 2022) Assigning neutral pH to digesters and the aerodynamic feeding process to microbes ups the productivity of PHA (Lee et al., 2015). Moreover, microbes such as beta proteobacteria, alphaproteobacteria, and gammaproteobacteria in activated sludge may speed up the production of PHA such as 3-hydroxybutyrate and 3-hydroxy valerate to a maximum of 64 % weight compared to the pure substrate. Switching to optimizing conditions such as regulating pH, while fermentation of POME and mixed culture can lead to maximum PHA at 8 hours and may thus reduce the production costs with the use of less expensive POME. However, this method may take a toll on TCOD removal. In other words, 850 mg L⁻¹ scored in the PHA production reactor, triggering the advancement in the process including efficient COD removal, which will stop the accumulation of organic wastes. Taking a halogen-free method as an extraction procedure can help POME treatment by increasing the PHA content through the amount of polymer in the cell (Mohammadi et al., 2012). Overall, the components present in VFAs determine the type of PHAs such as 3-hydroxybutyrate, 3-hydroxy valerate, and 3-hydroxy-2 methyl valerate formed from POME (Gobi and Vadivelu, 2013).

5.2.2. Bioflocculant

In previous studies on the treatment of POME, Aljuboori et al. (2014), and Nilanjana et al (2022), developed a system that used microbes to produce bioflocculant, known as microbial bioflocculant capable of treating river water from colloids and removing turbidity- a significant improvement on existing synthetic polymers. *Aspergillus niger* is using POME as a source to produce a bio-flocculant named PM-5 with a flocculating rate of 76.8 % to kaolin suspension and overall good flocculating properties. The major component of PM-5 lies in the combination of carbohydrates and protein with 66.8 % and 31.4 % respectively. Similarly, *Bacillus velezensis*

also is a significant contributor to bioflocculant production to a maximum of 2.03 g L⁻¹ (Hassimi et al., 2020). They explored the mechanism of flocculation such as charge neutralization and interparticle bridging by observing interactions between the bioflocculant polymer and the lake water particles. Finally, the study revealed that the increased temperature of 40° C and increased incubation encourages the production of bioflocculant, an advance that may pave the way for POME powered by the fermented medium.

5.2.3. Biomass

External supplementation triggers the growth of microalgae on POME can lead to biomass production. To explain more, a combination of glucose, urea, and glycerol at 200mg L⁻¹ during *Chlorella sorokiniana* CY-1 growth was tied to a maximum production of 1.68 gL⁻¹ biomass in POME medium (Cheah et al., 2018a). On the contrary, the same research group focused on the strategy that pre-treatment conditions could save POME from supplement addition and turn it into biofuel. In addition, the research has been focused on the breakdown of lignin into simple, high-valued industrial chemical feedstocks such as biomass and lipid (Cheah et al., 2018b). Likewise, a novel biocompatible polymeric carrier derived from sodium alginate beads could help treat POME, which is a source of microalgae growth, a study has found (Emparan et al., 2020). In addition, microalgae such as *Nanno chloropsis* sp. whose growth in POME medium with a supportive carrier produce more biomass than those in POME medium without a carrier.

5.2.4. Animal feed

Adopt a microalgae cultivation system in a palm oil mill in Indonesia, as it not only deters GHG accumulation but also leads to the production of animal feed, suggests a new study (Sasongko et al., 2018, Farah et al., 2019a). They concluded that POME has been identified as a major alternative nutrient source to the microalgae traversing the 10 ha production system and feeding on organic compounds and resulting in the production of animal feed at 520.33 tons year. Researchers have made an effective formulation that allows the mixing of various types of wastes including palm acid oil from POME to convert into animal feed (Amalina et al., 2019). In addition, they seem to be very good at growth performance as well as at production cost. The researchers have found that the presence of surplus nutrients in the formulation of animal feed than the requirement of cattle, an advance that sheds more light on the potential role played by palm acid oil in the formulation of animal feed.

5.2.5. Fertilizer

Hasanudin et al. (2015) as well as Soh et al., (2019) have used anaerobic digestion to derive liquid fertilizer from POME that has in turn increased the production of FFBs. Plant nutrients from POME can enter the oil palm plantation through the land application and promotes growth that could lead to a reduction in the usage of commercial fertilizers, according to Hasanudin et al., 2015, which may pave the way for a sound economical method to accelerate the productivity of oil plantation. The developed liquid fertilizer mimics the composition of chemical fertilizers and may have real-world applications such as maintaining the microclimate condition of oil palm mills. Moreover, Loh et al. (2019) have developed a new integrated treatment system in palm oil mills that sheds light on how the POME transition from raw state to treated state-an advance that may lead to the development of organic fertilizer production. Sasongko et al. (2018) confirmed the fact that biofertilizer is one the most common additional co-product in POME. In addition, it's just been a fascinating treasure trove of benefits that the researchers have covered in recent times. The recent advances in the biorefinery of POME is tabulated in Table 3.

6. Energy and economic aspects of POME biorefinery

POME as a low-cost substrate reduces negative environmental impacts from direct letting into water courses without treatment or partial treatment. However, it could be a low-cost solution against costly raw materials and can have a measurable effect on the biorefinery concept (Azman et al., 2016). Hence, ponding systems like traditional methods of POME treatment are on the rise in every palm oil mill and could cost a low capital and operating value. However, this low-cost conservative method has left POME remediation and biorefinery at record poor outcome levels, causing chaos for the inland aquatic streams, environmental damage, and billions of money losses-a scenario that could portend the future as global temperature rises. (Abdurrahman et al., 2011, Wen et al., 2020). Thus, physico-chemical methods that keep POME treatment not only favorable but also economical are identified. Firstly, TiO_2 may contribute low-level electrical energy in the degradation of POME among catalysts, according to a study (Alhaji et al., 2018). The study also found that the presence of UV light in the photooxidation of POME has positive effects on energy consumption which is linked with low operational and maintenance costs. However, visible light is more economical in treating POME than UV light according to Charles et al. (2019), who studied photocatalysis, using a novel, visible-light active calcium ferrite catalyst. Secondly, adsorption

using banana peel aims to highlight the effect of natural coagulation in the POME treatment (Mohammed and Chong, 2014). It can make the process more economically viable on POME against the use of synthetic coagulants such as activated carbon. Likewise, in addition to coagulant, chickpea powder can also act as a natural flocculant, most likely receiving the bulk of organic pollutants from POME and making the treatment economically stronger (Lek et al., 2018). Moreover, the mixing speed influences the operating cost in POME in such a way that the optimum mixing speed (140 rpm) makes the breaking of flocs more effective, which leads to the production of sludge recovered from the POME with a calorific value of 19,584.86 Jg⁻¹. From an economic point of view, the usage of EFB as an adsorbent, which itself lies in the process of palm oil production and evolved as waste is meaningful, at least in POME treatment (Alam et al., 2009). The research reveals the EFB is believed to be behind the adsorption of phenol, which thus reduces the total cost of the process. Though physico-chemical methods fuel the rise of effluent quality positively, the problem has to do with most of the physico-chemical agents have made treatments more effective and economic aspects more destructive. Hence, smaller and cheaper biological methods bring a new economic revolution. Having an anaerobic follow-up can make the aerobic treatment of POME more economical (Chan et al., 2012, Yoke et al., 2021). This activated sludge phenomenon is exacerbated by simple design, single vessel, and flexibility in operation. However, anaerobic methods hint at surprising cost reduction abilities in POME treatment compared to aerobic ones. The researchers develop a pilot-scale wet anaerobic digester that will capture methane once it uses EFB (Hasanudin et al., 2015). A methane capturing system that may produce renewable energy of about 25.4-40.7 KWh ton⁻¹ of EFB. According to Hoo et al. (2017), anaerobic digestion can speed up biomethane production by 500kt. The produced POME as a whole is responsible for this highest share of biomethane. Not only POME but also its biogas (one m³) leads to the generation of a 2.62-kilowatt hour, as it has a nature to behave as a clean fuel (Hosseini and Wahid., 2015). Lee et al. (2015) have found a significant link between the activated sludge and anaerobic treatment of POME, which resulted in the production of PHA. They added that the risk of following a conservative method such as pure culture leads to a market value of \$4.4-6.0 kg⁻¹ which will give a green light for mixed culture, to be used for high production of PHA, paving the way for the economical way of production by reducing the total cost by 31%.

7. Challenges of POME biorefinery

An effluent enormous in volume on post-production of crude raw material like POME that fills up with complex nature of wastes but lacks simple compounds has left the treatment process uneconomical and highly difficult. In addition, oil and grease exhibit more accumulation ability than other organic contents of POME, when it comes into contact with sludge surface, and exploring more foaming and scum formation leads to a problem in digestion efficiency, according to a study (Chan et al., 2012, Farah et al., 2019b). Initially, treatment of POME through physical methods such as adsorption could be a sign that the system more likely needs high pressure, and maintenance and thus paves the way for the high cost (Adeleke et al., 2017). The presence of pigments that left POME unable to respond to membrane separation triggered the blockage in pores and thus ends up in membrane fouling (Tan et al., 2017). Secondly, rising chemical inputs and resultant sludge production are reducing the interest focus on chemical treatments such as photo-oxidation, Fenton's and ozonation protocols, the most efficient methods for POME treatment (Chan et al., 2012; Islam et al., 2018; Tanikkul et al., 2019). In addition, the application of coagulation-flocculation has kept some of the pollutants remaining in POME could reverse the shift in the effluent quality which reduces the potentiality of chemical treatments (Alhaji et al., 2016; Huzir et al., 2019). About biological methods, the ponding system, a conservative method, known to increase the risk for large land area, lengthier HRT, and uninterrupted release of CH₄ and hydrogen sulfide to the atmosphere have also been linked to an increased risk of inefficient separation between treated effluent and biomass (Prihardi et al., 2022). Hence to overcome the problem of the release of CH₄, the biogas plants should be installed. However, the installation of biogas plants involves high investment which challenges the economic aspect. While anaerobic digestion in POME treatment often obscures the simplicity with the presence of various microorganisms, the important component witnessed the sensitivity due to the interaction of temperature and pH (Azmi and Yunus, 2014). Hence, it is essential to address the future research which may help to meet the challenges in POME treatment.

8. Future Research Opportunities of POME Biorefinery

Considering the opportunities in the pre-treatment scenario, thermal pre-treatment could soon spell the end of other types of pre-treatment in POME. It has the potential to enhance the solubilization and effluent quality and to replace the chemical and biological methods and their

side effects such as the demand for further polishing and the need for the high cost for commercialization respectively, and hence reshaping the future of POME treatment on the full scale (Khadaroo et al., 2019). In advanced oxidation processes, the economic crisis in the offing as TiO_2 has been used in UV light bioreactors, to treat POME, hence, usage of TiO_2 as a catalyst in visible light bioreactors will be focused as present research and it will be considered as an opportunity in cost-effective viewpoint (Bello et al., 2017). Likewise, usage of Fenton's reagent in Fenton's process leads to more consumption of H_2O_2 , thus application of solar irradiation is advisory for a cost-effective and simple treatment for POME. Though it is a complex process, the anaerobic treatment makes the degradation of recalcitrant compounds more possible (Aziz et al., 2020). To explain more, anaerobic reactors of either fixed film or batch reactor become the perfect destination for not only indigenous microbes but also a consortium of mixed microbes, which leads to the biodegradation of oil and grease (Jabeen and Shreevathsa., 2016). In the palm oil sector, the incentives will have been given by the government may assist the oil mills in installing the biogas plants as an opportunity to capture biogas, which is an environmental concern (Ratnasari et al., 2022). Finally, in the case of biopolymers, commercialization of the product at the expense of both government and private sectors will be more beneficial (Binma-ae et al., 2020).

9. Conclusions

Abandoned biomass finds use in biobased materials, chemicals, and renewable energy. Nowadays, an enormous amount of research is focused on the use of low-cost raw materials from various substrates. The utilization of various waste materials from palm oil mill as a source of biorefinery products develop the cost reduction strategy in the case of raw materials, and waste minimization and thus make a concern for environmental protection. Of the various wastes in palm oil mills, POME is one among and a leading pollutant to the environment, especially to nearby water courses. Over the past few decades, various assessment methods have been introduced, ultimately leading to the identification of hazardous materials. This review summarizes the existing assessment methods such as chemical and biological methods for POME and recommends a new method that promotes the use of fish species including invasive one. Siloxanes, FAME, phenol, phenolic compounds, and heavy metals are the hazardous materials present in POME that can increase the toxicity and pollution level of POME has been discussed. Through physico-

chemical and biological mitigation strategies, FAME has yielded 91.45 % of biodiesel. Finally, in addition to biodiesel, other biorefinery products produced from POME have been reviewed.

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Tables

Table 1: General characteristics of POME

Parameter	POME	Reference
pH	Acidic, 3.3–4.6	Saputera, W.H., 2021
Oil and grease	4,000 – 5000 mg/L	Ahmad et al., 2017
Biochemical oxygen demand (BOD)	25,000–54,000 mg/L	Rajani et al., 2019
Chemical oxygen demand (COD)	60,000 mg/l up to 90,000 mg/l	Pratiwi, et al., 2019
Total solids	40,500–75,000 mg/L	Kamyab, 2018
Suspended solids	20,000 to 35,000 mg/L	Bala et al., 2015
Total volatile solids	10,000 to 50,000 mg/L	Justus et al., 2018
Ammonical nitrogen (NH ₃ –N)	25 to 35 mg/L	Mohamad et al., 2020
Total nitrogen (T.N.)	180–800 mg/L	Mohamad et al., 2020
Pectin	3400 mg/L	Mohammad et al., 2021
Lignin	4700 mg/L	Mohammad et al., 2021
Carotene	8 mg/L	Mohammad et al., 2021
Phosphorous (P)	120-140 mg/L	Muzzammil et al., 2021
Potassium (K)	2200-3000mg/L	Pranolo et al., 2020
Magnesium (Mg)	600-700 mg/L	Muzzammil et al., 2021
Calcium (Ca)	400-500 mg/L	Hayawin., 2018
Boron (B)	7-8 mg/L	Amosa et al., 2013
Iron (Fe)	150-200 mg/L	Agida et al., 2020
Manganese (Mn)	8.139 mg/L	Agida et al., 2020
Copper (Cu)	3 – 4 mg/L	Agida et al., 2020
Zinc (Zn)	25 – 30 mg/L	Agida et al., 2020

Table 2: Risk assessment methods and hazardous materials

S.No	Risk assessment		Applied materials/organisms	Hazardous materials assessed	References
	Chemical based monitoring	Biological based monitoring			
1	Electroanalytical method-electrochemical sensors	-	Cellulose-hydroxyapatite	Heavy metals such as lead, zinc, copper and cadmium	Ajab et al. (2019)
2	-	Whole effluent toxicity (toxicity as TU)	<i>Daphnia magna</i>	Toxicants including phenols, acid-sensitive compounds and heavy metals	Hashiguchi et al. (2020)
3	-	Toxicity identification evaluation(toxicity as TU)	<i>D. magna</i>	Toxicants including phenols, acid-sensitive compounds and heavy metals	Hashiguchi et al. (2020)
4	-	Microalgae based toxicity	Native microalgae species such as <i>Coelastrellasp.</i> , <i>Chlorella sp.</i> and <i>Scenedesmus sp.</i>	Organic and inorganic compounds	Jasni et al. (2020)
5	-	Biocatalytic protocol	<i>Acinetobacter baumannii</i>	Phenolic compounds	Pinthong et al. (2017)
6	-	Bacterial indicators	<i>Chromatiaceae</i> and <i>Alcaligenaceae</i>	BOD ₅ , COD and TOC	Sharuddin et al. (2017)
7	-	Novel assessment using fish species	<i>Danio rerio</i>	Copper, Zinc and Iron	Hashiguchi et al., 2021

BOD-biochemical oxygen demand; COD-chemical oxygen demand; TOC-total organic carbon; TU-toxicity unit value

1372 **Table 3: Recent Advancements in the production of bioproducts from POME**

S.No	Bioproducts	Process Involved	Yield %	Reference
1	Biochar	Microwave Pyrolysis	57.82 wt%	Au, 2022
		Pyrolysis with top-lit updraft (TLUD) Gasifier	20% w/w	Nadia and Nurhanim 2022
2	Biojet or Green Kerosene	Enzymatic hydrolysis and thermochemical	Refined biofuel yield was 94% and the biojet selectivity was 57%	Muanruksa et al., 2021
3	Biodiesel	Esterification of POME using Microwave heating	89 %	Davies et al., 2022
4	Biohydrogen	Addition of 2.5% (w/v) of phosphoric acid at the optimum pretreatment conditions of pH 5.5 and thermophilic temperature (60 °C) followed by fermentation by Continuous Stirred Tank Reactor (CSTR)	2.5 mol H ₂ /mol of Total Carbohydrate consumed	Arisht et al., 2022
5	Biogas	Dielectric Barrier Discharge Integrated with the Aerated Condition	Increased production of CH ₄ , CO, and CO ₂ and reduced BOD and COD level	Desimiarti et al., 2022
6	Bio-oil	<i>Rhodotorula toruloides</i> cultivated in POME	4.5%	Justine et al., 2022
7	Bioelectricity	Laccase-producing bacterial consortium integrated with microbial fuel cell through degradation of Melanoidin	0.540 A/m ² (21.60 A/m ³) of maximal current density and 0.080 W/m ² (3.18 W/m ³) of maximal power density	Junjira et al., 2022

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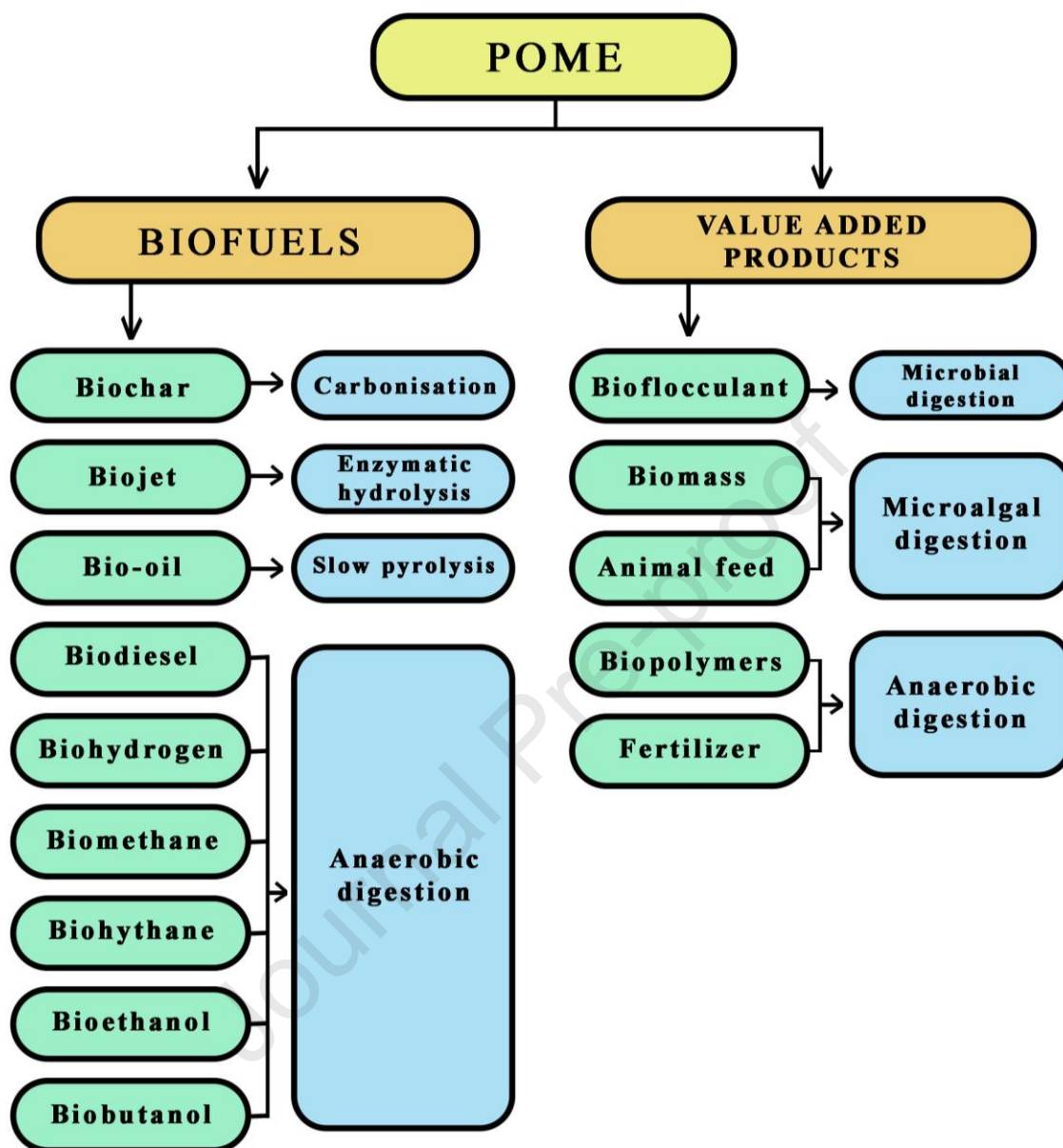


Figure 1: Biorefined Products from Palm Oil Mill Effluent and their respective technologies

Highlights

- This review emphasizes on POME biorefinery and its environmental hazards.
- Various treatment options of POME treatment and biorefinery schemes were discussed
- Different pollution assessment methods were highlighted
- Biological risk assessment with possible remediations was elaborated.

CRediT author statement

Anu Meena : Conceptualization, Methodology,, **Merrylin J**: Data curation, Writing- Original draft preparation , **Rajesh Banu J**: Data curation, Writing- Original draft preparation, Supervision **Shashi Bhatia**: Supervision, **Vinod Kumar**: Data curation, Writing- Original draft preparation **Gregorza Piechota**: Writing- Reviewing and Editing, **Gopalakrishnan Kumar**: Data curation, Writing- Original draft preparation, Resources

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



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