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A Short Review: Photocatalysis As An Alternative Method for POME Treatment

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Abstract - The liquid waste produced due to palm oil processing is called palm oil mill effluent (POME). It is challenging to manage because of its high production and inadequate treatment. The discharge of raw POME into the environment will result in multiple detrimental effects and environmental pollution. This short review compares the conventional treatment methods in Malaysia, which are the ponding system for the treatment of POME and the open or closed digesting tank. These systems are unable to achieve the standards set by the Department of Environment (DOE) of Malaysia. Photocatalysts, which are well-known as catalysts in the decomposition of organic contaminants, are suggested as an alternative method for POME treatment. The viability of using photocatalytic technology to remediate POME waste is discussed in this short review. The advancement and improvement of the nanoparticle system for POME treatment are identified based on past studies. It is aimed at providing readers with a clear comparison of conventional POME treatment methods and information on photocatalysis as an alternative POME treatment method.

Keywords— *Ponding system, Digesting tank, Photocatalysis, Wastewater treatment*

I. INTRODUCTION

Palm oil mill effluent, also known as POME, has been released in significant proportions as a result of the growth of the oil palm agricultural industry. It was estimated that 2.5 to 3.8 tonnes of POME were produced during industrial processing for each tonne of crude palm oil (CPO) [1]. Mainly POME waste is generated from sterilizer condensate stage (17%), clarification sludge stage (75%), and hydrocyclone waste stage (8%) in a ratio of 9:15:1 [2].

The process of clarifying wastewater from POME has a substantially higher solids concentration because of the presence of a larger proportion of soluble and insoluble carbohydrate elements compared to the wastewater coming from hydrocyclone and sterilization stages. Sterilized condensate is often produced by hot water and steam waste streams, and the wastewater from the clarification stage is normally separated and gathered in various oil pits to recover residual oil. Since the recovered sludge oil is of poor quality, it will not be used in the oil production process, especially since it is not qualified for food applications. Nevertheless, these oils will be sold as technical oils. Following oil recovery, the hydrocyclone wastewater is combined with sterilizer and clarification waste streams to create mixed wastewater, or POME [3]. Table I further describes the characteristics of POME sources.

POME contains different suspended materials, and it is said to be 100 times as polluting as domestic sewage. These wastes arise from the partial degradation of palm fruits [4]. POME is acidic in nature; the pH of POME was determined to be between 3.6 and 5.2 [3]. Because of the organic and free fatty acids, it has a low pH and is a high strength pollutant. Other properties include biochemical oxygen demand (BOD), chemical oxygen demand (COD), oil and grease (O, & G), volatile suspended solids (VSS), total nitrogen (TN), total solids (TS), volatile solids (VS), total phosphorus (TP), and volatile fatty acids (VFA) [1].

POME is a brownish, thick, viscous liquid as shown in Fig. 1, with a temperature of 80 °C and 100 °C [2]. The amount of water needed for 1 tonne of fresh fruit bunches

(FFB) to be processed is between 1-1.5 tonnes [5]. It is estimated that the manufacture of CPO results in producing about 3 billion pounds of POME annually. 5 to 7 tonnes of water will be needed to produce 1 tonne of CPO, with more than 50% of that water ending up as POME [6].

Table I: Characteristics of wastewater from sterilizer, clarification and hydrocyclone stages [3].

Parameters	Sterilizer condensate stage	Clarification sludge stage	Hydrocyclone waste stage
pH	5.0	4.5	-
O & G (mg/L)	4000	7000	300
BOD (mg/L)	23,000	29,000	5000
COD (mg/L)	47,000	64,000	15,000
Suspended solids (mg/L)	5000	23,000	7000
Dissolved solids (mg/L)	34,000	22,000	100
Total nitrogen (mg/L)	600	1200	100
Ammoniacal nitrogen (mg/L)	20	40	-



Fig. 1. Thick brownish POME [7].

POME is a heavily polluted waste that has an unpleasant odour. Carotene, pectin, tannin, phenolics, and lignin are the sources of the brownish colour, making this a nutrient-rich foodstuff. In the palm oil extracting process, chemicals are not used to take out the oil from the oil palm fruits, so there is no environmental harm from the waste that is created [8]. The main elements that make up POME include oxygen (O), carbon (C), nitrogen (N), hydrogen (H), phosphorus (P), sulphur (S), chlorine (Cl), potassium (K), calcium (Ca), aluminium (Al), magnesium (Mg), iron (Fe), and silicon (Si). However, other components such as cellulose, hemicellulose, and lignin only make up 11%, 7%, and 42% of POME, respectively. The absence of harmful heavy metals like mercury, lead, cadmium, chromium, or manganese in POME is advantageous [1].

Untreated POME discharge has a negative effect on the land, water, and environment because it will have a number of negative consequences for health, aquatic life, water quality, groundwater, and soil [1]. The high total solids content contributes to a rise in algal blooms in natural water sources because there is an overdose of nutrients accessible when untreated POME is released. These by-products must be treated using an effective management system to protect

the environment and reduce environmental pollution. The Department of Environment (DOE), Malaysia has set standard limits for the quality of treated effluent that can be discharged to the environment [4]. Table II describes the specifications of DOE, Malaysia. Researchers in many countries who are involved in the palm oil industries are still seeking alternative treatment methods in order to minimize environmental pollution while improving the treatment process in terms of cost, manpower, duration, and sustainability.

Table II: Characteristics of the POME and standard limits set by the Department of Environment, Malaysia [4, 9, 10].

Parameters	Average value concentration (Raw POME)	Standard limit
pH	4.2	5.0-9.0
Oil and grease (mg/L)	4000	50
BOD (mg/L)	25,000	100
COD (mg/L)	51,000	1000
Total solids (mg/L)	40500	1500
Suspended solids (mg/L)	18000	400
Total nitrogen (mg/L)	750	150
Temperature (°C)	80-100	45

II. CONVENTIONAL POME TREATMENT METHODS

Before undertaking the primary treatment, POME will go through a pre-treatment procedure involving the removal of grease and oil. An oil skimmer is used to remove extra grease and oil from the oil recovery pit. It will take 1 or 2 days for the MRE pre-treatment retention interval [5]. The oil palm industry uses a limited number of conventional POME treatment procedures, which are listed below:

- 1) Waste stabilization ponds / ponding systems
- 2) Closed or opened tank digester
- 3) Activated sludge system
- 4) Land application system

Among these methods, ponding systems and closed or open tank digester systems are thought to be the most desired conventional POME treatment options. In Malaysia, more than 85% of palm oil mills use ponding systems to treat POME, the remaining mills use closed or open tank digesters [4, 7, 11]. The ponding system consists of many stages of acidic, cooling, anaerobic, aeration (aerobic), facultative, and final polishing ponds as shown in Fig. 2. Prior to disposal to the environment, the overall hydraulic retention time (HRT) for this treatment technique is 100–120 days [8]. Raw POME was first added to the acidification pond. It was allowed to stay there for about 6 days. Then it was pumped into a cooling pond via a cooling tower, and the POME was then stored for an additional 6-7 days. The temperature of the POME was reduced to 35–38 °C and stabilized the pH at the cooling pond prior to the anaerobic stage [10].

Anaerobic treatment ponds were shown to be the most effective method for anaerobic decomposition treatment of high-strength wastewater. There are three basic steps in the

anaerobic process: hydrolysis, acidogenesis, and methanogenesis. In the hydrolysis process, complex polymers, including proteins, lipids, and carbohydrates, are broken down into their corresponding monomers [12]. POME that had undergone anaerobic treatment turned blackish brown and alkaline as a result of the partial conversion of lignin to phenolic [8, 13]. The four ponding series that made up the anaerobic treatment phases had an overall HRT of 54–60 days. Before being released into the facultative ponds, anaerobic POME was further treated for around 20 days in a series of aeration ponds that have floating aerators. Clarifying suspended microorganisms from the aerobically treated POME takes place in the final polishing pond. Three ponding series made up the hypothetical ponds, which are crucial for further lowering the organic matter content of the wastewater before releasing it into the river [10].

Waste stabilisation ponds/ponding systems were discovered to operate incredibly well in treating POME because of their high reduction of organic substances, cost-effectiveness [11], low maintenance costs, energy efficiency, system stability, and simplicity [10]. Drawbacks of this system are the frequently required long HRT (100–120 days), large pond areas [11], and the inability to achieve 100% decolorization. It also produces a significant amount of methane gas, which aids in the mitigation of serious environmental issues like the greenhouse effect. In addition, scum formation and solid sludge accumulation are creating problems in this treatment process and making it ineffective in some aspects [5, 8].

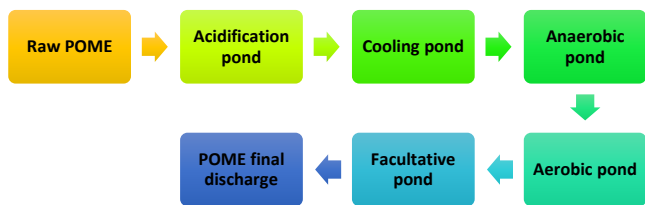


Fig. 2. Typical configuration of the ponding treatment system of POME.

Few companies in the palm oil industry use closed or open tank digesters to treat POME. This system combines a number of ponding systems with an open digester tank. This approach has the advantages of being available for a wide variety of volumetric capacities, low capital and operational expenses, shorter HRT (20–25 days), no need for mechanical mixing equipment to be put in the digesters, and a small amount of land being needed. The drawbacks of this system are the creation of a substantial quantity of biogas (about 5.5 kg of CH₄ per tonne), the accumulation of scum and solid sludge, and the corrosion of steel structures as a result of prolonged exposure to hydrogen sulphide [5, 8]. The comparison between ponding systems and closed or open tank digester systems is shown in Table III.

Furthermore, the typical conventional treatment is unable to meet the standards established by the DOE in Malaysia, with the level of BOD at 100 mg/L [4]. It is believed to be challenging to circumvent the POME processing incapability of the conventional system. Numerous studies have been

done to discover different approaches to these limitations of the traditional systems. Palm oil mills will not be interested in new technologies that have high operating costs. Because it is widely known that processing palm oil requires low costs to be competitive on the global stage. Therefore, using photocatalysts is one of the most appealing ways to decompose organic contaminants. This is due to the pollutants' promising, efficient, and effective degrading activity; it happens as a result of optimising the entire process by allowing both spontaneous and non-spontaneous responses. The reaction will be regulated using light or other photon sources; consequently, the procedure is described as a series of advanced oxidation processes (AOPs) [15].

Table III: Comparison between ponding systems and closed or open tank digester systems.

Conventional treatment method	Advantages	Disadvantages	References
Ponding system	Cost-effectiveness, Low maintenance cost, System reliability, energy efficiency, simple design	Long retention time (100-120 days), large treatment areas, produce much sludge, not 100% decolorization, methane gas generation that causes the greenhouse impact	[2, 4, 8, 14]
Closed or opened tank digester	Low capital, low operating costs, shorter retention time (20–25 days), limited land area	Significant amount of harmful biogas, accumulation of scum & solid sludge, corrosion of steel structure	[5, 8]

III. POME TREATMENT USING THE PHOTOCATALYTIC ACTIVITY OF NANOPARTICLES

The catalysts and photochemical reactions are combined in photocatalytic technology. The photocatalytic technique is based on the application of a material that stimulates the reaction without altering the amount or composition of the reactants. A material that accelerates the procedure by improving the necessary activation energy and reaction rate without directly contributing to the reaction is called a catalyst [16]. Materials with an energy band gap can be employed as photocatalysts. The band gap is the energy between the conduction band and the valence band that produces a current carrier. The valence band is the energy level at which low energy electrons can be found. This is called the highest occupied molecular orbital (HOMO). The energy level that is not filled with electrons is called the conduction band. It is known as the lowest unoccupied molecular orbital (LUMO). The electron transition from the valence band to the conduction band can be influenced by light energy if it is equal to or greater than the energy band gap. It helps to produce the positive holes (h⁺) in the valence band. Conductivity is obtained and produced when the electrode potential is sufficient due to the transfer of electrons (e⁻) [17]. Then it is called the electron-hole pair [18].

The photocatalytic procedure can be divided into two parts based on the type of catalyst. Both homogeneous and heterogeneous photocatalysis fall under this category. When reactants and photocatalysts are in the same phase, homogeneous photocatalysis occurs. Heterogeneous photocatalysis takes place between two phases or more [19]. Semiconductor-based transition metal oxides are the most commonly used photocatalysts (TiO₂, ZnO, WO₃, CeO₂, ZrO₂, etc.) [20]. The semiconductors employed as photocatalysts benefit from the narrow energy difference between the valence and conduction bands [16]. Visible light-active semiconductors are those that can perform photoexcitation in the visible light regime and have a band gap between 1.7 eV and 3.1 eV. In contrast, a semiconductor would be UV-active if its bandgap was higher than 3.1 eV [21].

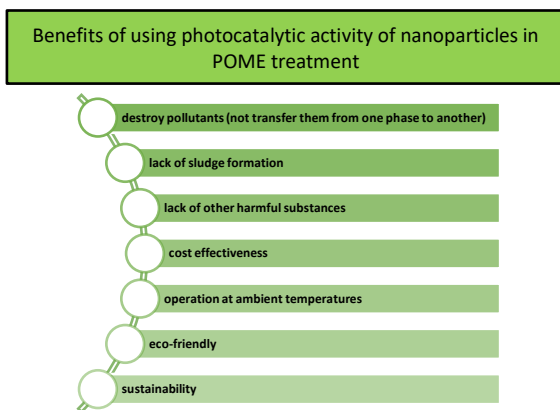


Fig. 3. Benefits of using photocatalytic activity of nanoparticles in POME treatment.

The photocatalytic method of POME treatment has recently attracted a lot of attention because of its characteristics, which include outstanding performance, eco-friendliness, operation at ambient pressure and temperature, cost effectiveness, a lack of secondary waste and other harmful substances production and sustainability [16, 22]. Additionally, it addresses the problems of environmental remediation and energy usage [23]. It is important to emphasise once more that one of the key benefits of this is the ability to destroy the contaminants rather than move them from one phase to another. These benefits are listed in Fig. 3 [10].

The heterogeneous photocatalysis process is used in POME treatment. This is a green pathway for POME treatment. The process will begin as a result of photoexcitation, which is the result of light hitting the semiconductor material [15]. The electron-hole pair that is produced by photosynthesis may combine again or take part in the redox process. The electron-hole pair that hasn't been merged will go to the catalyst's surface and start the redox process [24].

The positive hole in the valence band reacts with the electron donor, and the electron in the conduction band reacts with the electron acceptor. During the electron transfer, electron donors will go through an oxidation process, and electron acceptors (often oxygen (O₂)) will be reduced to various molecules. The reduction and oxidation processes

(redox) are used to suppress pollutants that come into contact with the photocatalyst surface. Reactive radicals, which can be exploited in the pollutant degradation process and are produced by both e⁻ and h⁺. Small molecules like CO₂, H₂O, and mineral acids will be produced as a result of the degradation of polluting substances by these radicals (superoxide radicals (•O₂⁻), hydroxyl radicals (OH•), and hydroperoxyl radicals (•OOH)) [25]. This process can be schematized as in Fig. 4, and the chemical reactions are summarised as follows [26]:

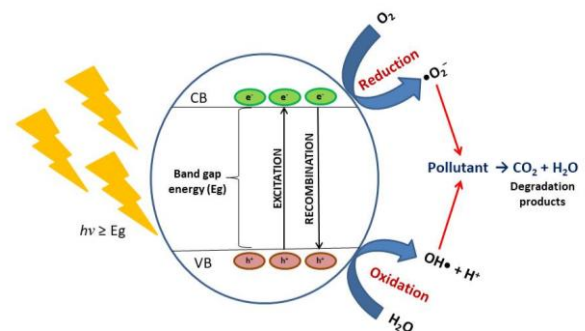
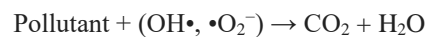
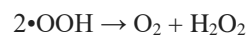
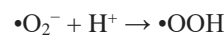
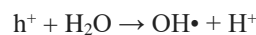
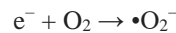
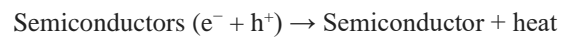


Fig. 4. Photocatalytic mechanisms for organic pollutant degradation.

In this short review of photocatalysis as an alternative method for POME treatment, we discuss the photocatalytic activity of certain semiconductors used in POME treatment. These are titanium dioxide (TiO₂), zinc oxide (ZnO), and copper (II) oxide (CuO). Tan [27] described CuO, TiO₂, and ZnO as having the ability to perform photocatalytic degradation of contaminants in wastewater.

A. Photocatalytic Activity of TiO₂ in POME Treatments

For photocatalytic activity of TiO₂ sewage treatment based on environmental protection, numerous organic contaminants can be successfully degraded by TiO₂ photocatalytic technology [25]. A naturally occurring oxide of the element titanium (Ti) is TiO₂. Three different crystalline forms of TiO₂ are anatase, rutile, and brookite [28]. Anatase and rutile are two of these three types that are most frequently employed. Compared to the rutile phase, the anatase form is more thermodynamically stable and offers superior physical and chemical qualities for waste treatment [29]. High band gap forms of rutile and anatase measure 3.0 eV and 3.2 eV, respectively [30]. As a result of this, to activate TiO₂, it required high-energy UV light radiation with a wavelength no greater than 387.5 nm.

The abundance of UV light in nature is required to increase the photocatalytic activity of TiO_2 in wastewater treatment. The electron-hole pair of TiO_2 can be easily reintegrated (recombination) and has relatively low adsorption capacity [2]. TiO_2 is by far the most widely used photocatalyst because of its advantages, such as corrosion resistance, inert properties, requiring less preparation than other semiconductors, low toxicity, inexpensiveness, commercial availability, and ability to absorb UV rays from the sun or any other ultraviolet-emitting light source under conditions of normal pressure and temperature [16]. The main drawback of TiO_2 is its broad band gap, which can only respond to light in the UV area (3.2 eV) [31].

B. Photocatalytic Activity of ZnO in POME Treatments

Based on its equivalent performance to TiO_2 and the same band gap energy (3.2 eV), ZnO has been suggested as an alternate photocatalyst [32]. ZnO is an inorganic compound. It is a white powder that is not soluble in water and is widely used as an additive in abundant materials. ZnO comes in two types of crystals. These have cubic zinc blende and hexagonal wurtzite crystal structures, respectively. Its stability at room temperature is a result of this; the wurtzite structure is the most prevalent structure [33].

There are many advantages to using ZnO. It is insoluble in water, an environmentally safe material with extremely high exciting stability, and also relatively cheaper than TiO_2 [33,34]. The reason is that TiO_2 is quite uneconomical for wide-ranging water treatments. ZnO semiconductors still have significant issues, such as the fact that they respond mostly to ultraviolet light and little to visible light [34], low photocatalytic quantum efficiency, immediate recombination of photo-generated carriers, and photocorrosion, which are significant drawbacks of ZnO semiconductors [33]. The two photocatalysts that are currently being researched the most are ZnO and TiO_2 . However, they experience electron and hole recombination, which is thought to be the main problem with these materials [15].

C. Photocatalytic Activity of CuO in POME Treatments

Copper compounds may remove a wide range of harmful organisms from biowaste and provide a more cost-effective alternative to employing waste-water treatment [35]. CuO is a type-p semiconductor with a 1.2 eV narrow band gap energy that belongs to the group of nanostructured oxides. It also has good optical, electrical, magnetic, catalytic, and biological capabilities [27, 36]. Table IV describes the comparison between TiO_2 , ZnO, and CuO.

D. Other Potential Nanoparticles Can Be Used for POME Treatment

Oxygen and tungsten transition metals are found in the yellow chemical compound known as tungsten trioxide (WO_3). Its crystal structure changes depending on the temperature; it is monoclinic at ambient temperature. Benefits of WO_3 include a semiconductor with a narrow band gap, strong adsorption power, excellent thermal and physicochemical stability, and strong photocatalytic activity in non-toxic acidic conditions [2, 37].

A photocatalyst with a narrower band gap likes to absorb more photons from visible light [18]. This has a band gap between 2.7 eV and 2.8 eV when compared with TiO_2 at 3.0 eV – 3.2 eV. It has a wider solar spectrum and can absorb light from UV to visible. The possibility exists for WO_3 to act as a visible photocatalyst. These materials have the drawback of being expensive and scarce. Additionally, the surface area of pure WO_3 is rather small and exhibits low photoactivity due to strong electron-hole recombination [2]. WO_3 has inorganic properties, so it does not have a strong affinity for the organic substrates; thus, only weak adsorption occurred [27].

BiVO_4 is a less expensive photocatalyst that can harvest visible light for photocatalytic processes and has a lower band gap (2.4 eV) than TiO_2 . BiVO_4 has been shown to successfully breakdown and decrease organic contaminants in wastewater by using methylene blue, methyl orange, and rhodamine blue as model chemicals [14].

IV. POST-PROCESSING RECOVERY OF PHOTOCATALYST IN POME TREATMENT

Post-processing recovery of photocatalyst is important because treated POME should be released into the environment without any harm to the environment. It is necessary to prepare a system that is able to separate the nano-sized particles from the treated aqueous system [26]. At the final stage of treatment, which involves recycling and releasing the treated POME, the critical step is the recovery and separation of photocatalysts from POME waste. Throughout the photocatalytic process, it is still challenging to effectively immobilise or separate photocatalyst particles. Magnetic separation and immobilisation on supports have generally been investigated as two effective methods to handle recovery and separation issues [2].

Evyan *et al.* [26] suggested that the degradation system or structure can be developed as nanoparticle composites such as nanocellulose, polymer, ceramic, or other materials incorporated with nanoparticles. These systems or models are recyclable, reusable, cost-effective, and environmentally friendly and can achieve sustainability [41, 42].

The polymer matrix can preserve the inorganic nanoparticles' electrical, magnetic, and optical characteristics. This has encouraged the concept of developing an efficient catalyst out of an inorganic nanoparticle/polymer composite. These are further stable under UV exposure, as are their oxidative environment, porous structure, and high absorption ability. These composites help to proceed with photocatalytic decomposition under stable conditions and can be easily removed after usage [26]. Nanoparticle composites can be made by using natural polymers such as collagen, polysaccharides, gelatine and synthetic polymers such as poly(lactic acid) (PLA), poly(lacti-co-glycolic acid) (PLGA), and poly(glycolic acid) (PGA) [42].

Table IV: Comparison between TiO₂, ZnO and CuO.

Photocatalysts	Advantages	Disadvantages	Applications	References
TiO ₂	Great oxidizing capacity, high efficacy against organic molecules, inexpensive, non-toxic, insoluble in water, good photocatalytic activity, widely available, high thermal and chemical stability, corrosion resistance, less processing and preparation than other semiconductors, inert properties, commercial availability	Low adsorption capacity, broad band gap (responds mostly to ultraviolet light and little to visible light), recombination of electrons and holes	Wastewater treatment, coating, cosmetic industry (sunscreen), pharmaceuticals, inks, papers, food products, textiles	[2, 14, 15, 16, 27, 37, 38]
ZnO	Insoluble in water, environmentally safe material, extremely high exciting stability, relatively cheaper than TiO ₂	Broad band gap (responds mostly to ultraviolet light and little to visible light), photo-corrosion, low photocatalytic efficiency, recombination of electrons and holes	Use in the waste-water treatment, additive in a plethora of materials and products including glass, ceramics, ointments, plastics, rubber, lubricants, paints, cement, foods, adhesives, sealants, pigments, batteries, ferrites and fire retardants	[15, 33-35, 39]
CuO	Excellent optical, electrical, magnetic, catalytic, biological capabilities	Toxicity	Fungicides, cosmetics, electronics, pharmaceutical, solar cell, magnetic storage media, lithium battery, bio & gas sensors, antimicrobial agents in the agriculture use in health sectors	[27, 35, 36, 40]

V. CONCLUSION AND FUTURE ASPECTS

POME waste from the palm oil industry has high amounts of COD and BOD, which can pollute the environment and harm aquatic life owing to low oxygen levels. Conventional POME treatment technology, such as ponding systems and closed or open tank digester systems, currently cannot completely achieve the standards set by the DOE in Malaysia. An affordable alternative is photocatalytic technology. On a lab scale, the use of photocatalytic technology to degrade the waste from the POME has shown good potential because it is highly effective at removing harmful microbes from wastewater and mineralizing organic substances [43, 44].

There are a few photocatalysts that have recently been developed and presented, particularly for water treatment technologies. This is a result of their low cost, effectiveness, and environmental friendliness. TiO₂ has gained interest as a photocatalyst due to its efficient photocatalytic activity. There are many researchers interested in ZnO. Numerous scientists are working to overcome the limitations of TiO₂ and ZnO photocatalysts by improving efficiency. These studies are directed at harvesting a greater spectrum of sunlight by producing more electron-hole pairs and lengthening the lifespan of the photo-generated electron-hole pair after improving the efficiency of photon-electron conversion [45].

To improve these steps, various researchers suggested the hybridization procedure. Doping, coupling heterojunction, and supporting materials are a few examples of such methods [15]. Through these efforts, TiO₂ and ZnO photocatalysts are being incorporated into smaller energy band gaps with slow recombination rates and accelerated interfacial charge transfer. The end result of all these efforts is better photocatalytic activity. One method of photocatalyst modification is doping. By introducing a few dopants, or impurity atoms, the semiconductor's band gap structure can be altered [2, 46].

A semiconductor coupled to another semiconductor is referred to as a coupling heterojunction. The supporting material can be inert or active during the photocatalytic process and could act as a co-catalyst or secondary catalyst [15]. Some researchers further studied the photocatalysts, which absorb light in the visible spectrum because of the narrow band gap. CuO is an example of such a material compared to photocatalysts like TiO₂ [47]. The use of nanoparticles in POME treatment will definitely improve the system by reducing the period of treatment and the formation of sludge and harmful substances. In addition, the factors of eco-friendliness, cost effectiveness, operation at ambient temperatures and pressure, and sustainability should be

considered to improve the existing POME treatment technology [9, 22, 23].

In conclusion, photocatalysis is certainly an alternative treatment method for POME towards sustainability. There are people against palm oil production due to its enormous pollution of the environment. However, an improved and enhanced system is more important to develop in order to continue enjoying the benefits and nutrients of palm oil.

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