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Advances in pretreatment technology for handling the palm oil mill effluent: Challenges and prospects

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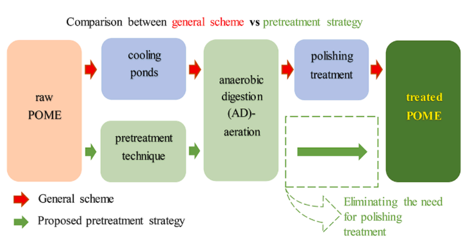
HIGHLIGHTS

- Advances in pretreatment technologies for handling POME are reviewed.
- Current pretreatment technologies can handle POME but with certain limitations.
- The use of magnetic composite adsorbents is promising to treat POME.
- Future studies should focus on nitrogenous matter, oil, and grease removal in POME.

GRAPHICAL ABSTRACT



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ABSTRACT

The palm oil mill effluent (POME) from palm milling oil activities is discharged into various water bodies which poses several environmental problems including turbidity, increases COD and BOD, adds oil and grease, increases total nitrogen, and other pollutants. Therefore, it requires effective treatment to remove the pollutants before disposal. The objective was to critically discuss the performance of POME pretreatments along with their limitations. To offer a coverage on the present less efficient technologies, the opportunities and challenges of advanced pretreatments that combine magnetic materials and natural composites as adsorbents are comprehensively reviewed here. Moreover, potential of various magnetic materials for POME pretreatment has been described. Several existing pretreatment methods such as physical pretreatments, chemical pretreatments, coagulation-flocculation, and adsorption can remove pollutant content from POME with certain limitations and the use of magnetic composite adsorbents can enhance the treatment efficiency.

1. Introduction

The development of oil palm agribusiness has resulted in the release of substantial amounts of liquid waste which is called palm oil mill effluent (POME) (Wajdi et al., 2021). It is estimated that about 2.5–3.8 tons of POME waste can be produced during the industrial processing of

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every ton of the crude palm oil (CPO) (Cheng et al., 2019). In 2018, global crude palm oil production was 71.47 million tons which means that 178.68 to 268.01 million tons of POME were generated where most of it is discharged into the environment without a proper treatment. The presence of POME in environment exerts numerous negative impacts to aquatic life, water quality, ground water, soil, and human health (Jasni et al., 2020, Zulfahmi et al., 2021). POME has a thick brownish viscous appearance, unpleasant odor, and high colloidal suspension (Syahin et al., 2020) and is considered among the leading hazardous pollutants. POME adversely affects the water, environment, and soil.

In water, POME has shown significant decrease in plankton diversity and the reproduction of fish caused by acid-sensitive compounds (Hashiguchi et al., 2020). For example, the toxicity of POME final discharge on *Daphnia magna* ranged from 1.1 to 11 (toxicity unit) evaluated based on whole effluent toxicity (WET). The study also detected the presence of octamethyl- (D4) in the range of 0.0148–0.0357 mg L^{-1}, which could be potentially toxic to *Daphnia magna*. In addition, POME can induce lethality and sub-lethality of fish embryo affected by chemical oxygen demand (COD) contain and heavy metals commonly detected in untreated POME (Hashiguchi et al., 2021). Moreover, several malformations of Nile tilapia larvae including lordosis, kyphosis, and curved tail were observed because of exposure to POME concentrations of 1.565 mg L^{-1}, 2.347 mg L^{-1}, and 3.130 mg L^{-1}, respectively (Muliari et al., 2020).

POME comprises 90.0% of water, 0.6–0.7% of residual oil, 2.0–4.0% of suspended solids, and 4.0–5.0% soil particles (Dashti et al., 2020, Onyla et al., 2001). The values for physicochemical properties of POME is shown in Table 1. Several studies have reported the physicochemical properties of raw POME (Sani et al., 2021, Suksong et al., 2020). It was found that pH of POME ranged from 3.6 to 5.2, indicating that POME has an acidic in nature. Other properties include biochemical oxygen demand (BOD), COD, oil and grease (O & G), volatile solids (VS), volatile suspended solids (VSS), volatile fatty acids (VFA), total solids (TS), total nitrogen (TN), and total phosphorus (TP). The BOD, COD, and O & G of the POME usually range between 15600 and 64440 mg L^{-1}, 25000–78290 mg L^{-1}, and 800 mg L^{-1}, respectively. In addition, VS, VSS, and VFA often range between 4260 and 42 200 mg L^{-1}, 4500 mg L^{-1}, and 1 273–2980 mg L^{-1}, respectively. While TS, TN, and TP range between 4980 and 50910 mg kg^{-1}, 800 mg L^{-1}, and 90 mg L^{-1}, respectively. These properties result in a decreased dissolved oxygen in the water which adversely affects the aquatic organisms.

Existing treatment techniques employ complicated methods that include applying cooling ponds before sending the POME waste to the next anaerobic digestion-aeration treatments and uses polishing treatment at the end of treatment (Norhan et al., 2021, Zainal et al., 2017). To simplify the remediation techniques, several pretreatment strategies had been proposed such as physical (Suksaroj et al., 2020, Wong et al., 2019), chemical (Abidin et al., 2021, Gamaralalage et al., 2020), and biological pretreatment (Khangkhachit et al., 2021, Naidua et al., 2021). These pretreatments have been applied to reduce the POME characteristics such as COD, BOD, TSS, O & G, and TN (Kietkwanboot et al., 2020, Saifuddin and Dinara, 2011).

The objective of the current study is to critically discuss current advances of various pretreatment techniques for handling POME. It highlights several appropriate aspects such as the limitations of several pretreatment techniques performances, magnetic material opportunities, and challenge of advance magnetic material. In general, this may contribute to the enhancement of knowledge for designing advanced and effective POME treatment in the future.

Table 1
Physicochemical properties of POME.

Parameters	Physicochemical properties of Raw POME				
	References				
	Nasrullah et al. (2017)	Suksong et al. (2020)	Wadchasit et al. (2021)	Sani et al. (2021)	Mishra et al. (2021)
pH	3.6	4.4	4.3	4.1	5.2
BOD	15,600	N/A	N/A	N/A	64 440
COD (mg L^{-1})	25,000	63,692	72,500	78 290	72 500
O & G (mg L^{-1})	2000	N/A	N/A	14 110	N/A
VS (mg kg^{-1})	N/A	4260	42,200	40 060	14 300
VSS (mg L^{-1})	4 500	N/A	N/A	N/A	N/A
VFA (mg L^{-1})	N/A	1273	2980	N/A	N/A
TS (mg kg^{-1})	20,000	4980	50,200	50 910	N/A
TN (mg L^{-1})	800	N/A	N/A	N/A	N/A
TP (mg L^{-1})	90	N/A	N/A	N/A	N/A

*N/A is not available.

2. Current methods for POME pretreatment

Pretreatment is the fundamental step to achieve proper substrate size, required porosity, improved degradability, and solubility (Atelge et al., 2020). Pretreatment can eliminate toxic materials from POME. Pretreatment methods can be selected based on physical and chemical characteristics of the POME. These methods can be classified into five groups namely physical methods, chemical methods, biological methods, coagulation-flocculation-based methods, and adsorption-based methods (Fig. 1).

Physical pretreatments do not need additional compounds such as chemicals, enzymes, or microorganisms (Roda et al., 2016). Physical pretreatments are further classified as thermal, ozone, and ultrasonic methods. Thermal pretreatment of POME which is commonly designed to improve thermophilic anaerobic digestion has been investigated on various solid–liquid ratios (Khadaroo et al., 2020). The method proposed 40S:60L solid loading as the best performing condition which resulted in the considerable removal efficiencies of COD (80.6%), BOD (81.0%), TSS (80.7%), and O&G (80.0%). These removal efficiencies showed that thermal pretreatment was able to enhance anaerobic digestion performance.

Another physical method for POME pretreatment is the use of ozone. Ozone technology has been widely reported to diminish organic content in POME. Ozone plays as an oxidizing agent that could breakdown organic content and complex structure in POME. Therefore, ozone can enhance the biodegradability of organic content and complex structures in POME. Study on long-term effect of ozone pretreatment in POME was reported at low and high ozone dosage (Al-Amshawee et al., 2021). The low and high ozone dosages were 15 mg L^{-1} and 30 mg L^{-1}. Ozone oxidation was applied for a long duration until 144 h. After 24 h ozone exposure, high ozone dosage achieved 79.0% COD removal, while low ozone dosage achieved 56.2%. During 24–96 h of ozone treatment high ozone dosage exhibited 83.0% of COD removal rate, while low ozone dosage failed to stabilize the removal rate, which was decreased to 33.0% at 84 h. After 84 h, the removal rate for high ozone dosage was unstable, decreasing up to 74.0%. It proved that ozone was effective for high dosage, although the performance decrease at 84 h but still above 70.0% removal (Al-Amshawee et al., 2021). A similar study explored the contact time of 110 h for ozone application on POME with the ozone dosages of 2.0, 5.0, and 10 g L^{-1} (Ahmad, 2019). Accordingly, a COD removal efficiency of 90.3% was achieved when 5.0 g L^{-1}ozone dosage was used for 70 h. Another study investigated the ozone performance for POME under mesophilic (37 °C), thermophilic (55 °C), and extreme-thermophilic (70 °C) conditions (Tanikkul et al., 2019). Under mesophilic conditions, the removal efficiency of total and soluble COD reached up to 44.0% and 37.0%, respectively, followed by thermophilic (24. 0% and 25.0%) and extreme-thermophilic condition (32.0% and 20.0%). The thermophilic and extreme-thermophilic conditions were

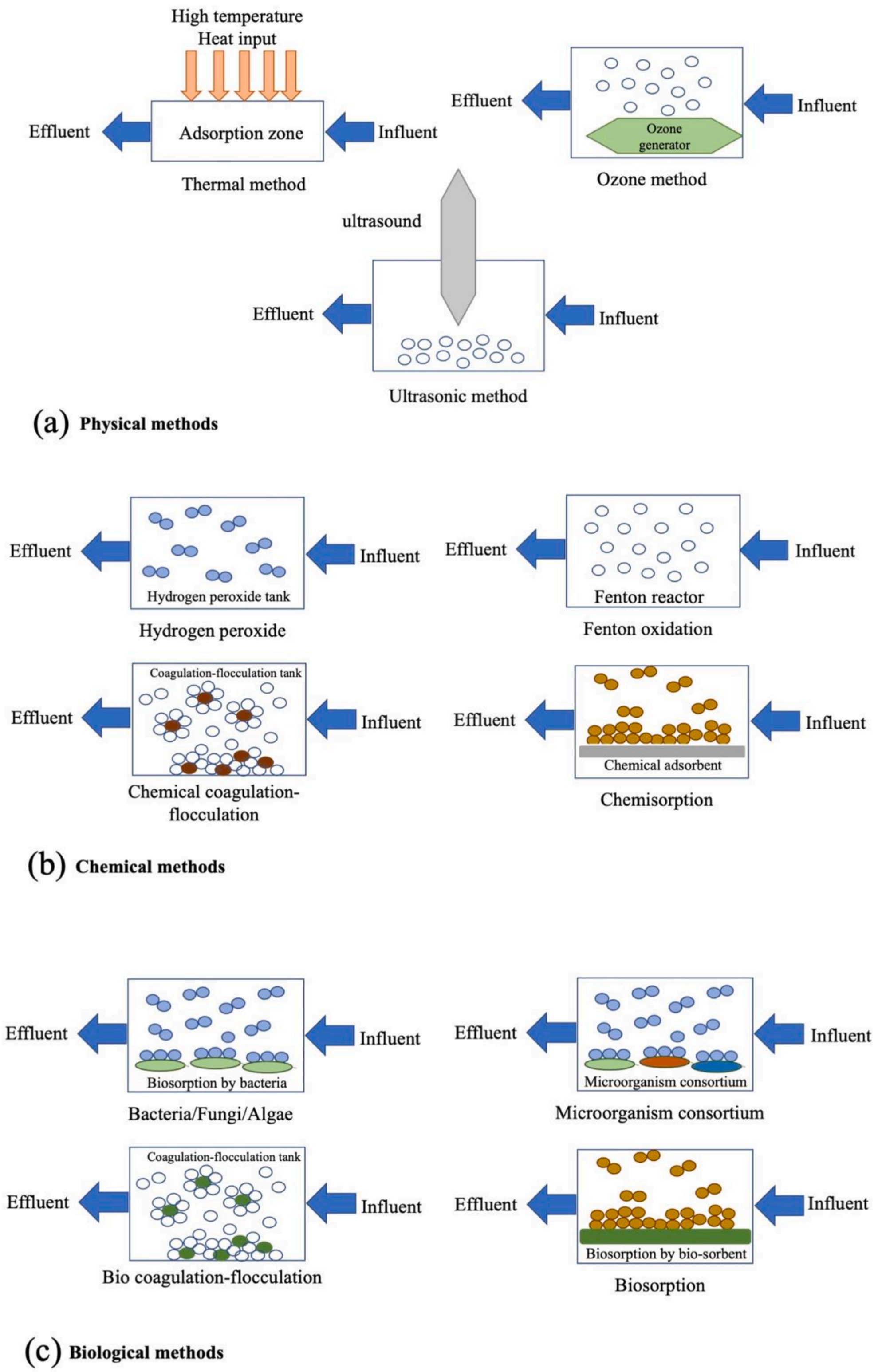

Fig. 1. Existing methods for POME pretreatment (a) physical methods, (b) chemical methods, (c) biological methods.

not favorable conditions although under mesophilic condition, the removal efficiencies were less than 50.0%.The ozone pretreatment also removed organic content from POME. Al-Amshawee et al. (2021) achieved 83.0% COD removal efficiency by using 30 mg L^{-1} of ozone while Ahmad (2019) used 5.0 g L^{-1} of ozone to achieve 90.3% of COD. See (Table 2).

By using ultrasonic waves is another popular pretreatment that is currently being employed for the pretreatment of POME. Usually, ultrasonic is utilized for organic content removal in POME. It decomposes macrostructures of the organic matter into microstructures which subsequently improves specific surface area of POME. Therefore, it leads to an accessible degradation and digestion. Ultrasonic pretreatment was applied to digest POME under anaerobic condition (Isa et al., 2020). The study was operated between 25 °C and 45 °C in anaerobic sequencing

Table 2
Comparison of treatment potential of existing methods.

Existing Methods	Type of method	Removal efficiencies	References
Thermal	Physical	COD (80.6%), BOD (81.0%), TSS (80.7%), and O&G (80.0%)	(Khadaroo et al., 2020)
Ozone	Physical	COD (37.0–44.0%)	(Tanikkul et al., 2019)
Ozone	Physical	COD (56.2–79.0%)	(Al-Amshawee et al., 2021)
Ozone	Physical	COD (90.3%)	(Ahmad, 2019)
Ultrasonic	Physical	COD (96. 0%)	(Isa et al., 2020)
Ultrasonic	Physical	TSS (31 0.0%)	(Wong et al., 2019)
Ultrasonic microwave	Physical	COD (75.6%)	(Mishra et al., 2021)
Ultrasound cavitation, $FeCl_3$ coagulation and activated carbon adsorption	Physical	BOD (89.7%), COD (88.1%), color (99.9%), and TSS (99.5%)	(King et al., 2019)
Hydrogen Peroxide	Chemical	COD (33.8%) and TOC (28.3%)	(Zaied et al., 2020)
Fenton Oxidation	Chemical	COD (37.0%) and color (85.0%)	(Affam and Bin Bistar, 2020)
Fenton Oxidation	Chemical	TN (27.0%), TOC (89.0%)	(Gamaralalage et al., 2020)
Fenton Oxidation	Chemical	TOC (91.0%)	(Gamaralalage et al., 2019)
Fenton Oxidation	Chemical	COD (85.0%)	(Saeed et al., 2016)
Fenton Oxidation	Chemical	COD (48.0%)	(Kaman et al., 2017)
Fenton Oxidation	Chemical	COD (93.0%)	(Ibrahim et al., 2015)
Thermoanaerobacterium	Biological	COD (62.2%) SS (93.6%) Oil recovery (80.0%)	(O-Thong et al., 2007)
Bacteria *Bacillus Thermoleovorans* strain A2	Biological	Phenol (61.1%)	(Chantho et al., 2016)
Klebsiella Pneumonia ABZ1	Biological	Color (80.4%)	(Abdulsalam et al., 2020)
Ochrobactrum sp. strain SZ1	Biological	COD (71.0%)	(Neoh et al., 2016)
Meyerozyma guilliermondii	Biological	COD (72.0%), TN (49.2%), TOC (46.6%), and O&G (92.4%)	(Ganapathy et al., 2019)
Scenedesmus sp. strain UKM9	Biological	COD (57.0%)	(Mohd Udaiyappan et al., 2021)
Chlorella vulgaris was co-cultured with a bacteria strain *Azospirillum brasilense*	Biological	COD (51.8%)	(Halim et al., 2019)
Microbial consortium AB-101	Biological	COD (91.3%)	(Abidi et al., 2020)
Aerobic Indigenous Mixed Microbial consortium	Biological	BOD (90.2%), COD (91.1%), and TSS (92.2%)	(Bala et al., 2018)
Rice Husk Ash (RHA) coagulant-flocculant	coagulation-flocculation	COD (52.4–52.4%) and TS (83.9–84.9%)	(Huzir et al., 2019)
peanut–okra and wheat germ–okra coagulant-flocculant	coagulation-flocculation	peanut–okra = turbidity (92.5%), TSS (86.6%) and COD (34.8%) wheat germ–okra= turbidity (86.6%), TSS (87.5%) and COD (43.6%)	(Chung et al., 2018)
Fenugreek (*Trigonella foenum-graecum*) and okra (*Abelmoschus esculentus*) coagulant-flocculant	coagulation-flocculation	Turbidity (95.0%), TSS (92.7%) and COD (63.1%)	(Lanan et al., 2021)
Moringa oleifera extract as green coagulant	coagulation-flocculation	Turbidity (51.0%), color (50.0%), and COD (65.0%)	(Mohamed Noor et al., 2021)
Tannin as a Polymeric Coagulant	coagulation-flocculation	BOD (97.6%), COD (88.9%), turbidity (93.0%), and SS (90.2%)	(Mat Yasin et al., 2020)
Mucuna seed shell as coagulant	coagulation-flocculation	SDP (suspended and dissolved particles) (95.0%)	(Nwabanne et al., 2018)
chickpea (*Cicer arietinum*) as a natural coagulant and flocculant	coagulation-flocculation	turbidity, TSS and COD are 86.0%, 87.0% and 56.0%	(Choong Lek et al., 2018)
Polyacrylamide	coagulation-flocculation	TSS (96.4%) and COD (70.9%)	(Zinatizadeh et al., 2017)
Activated carbon from palm kernel shell, iron oxide and zeolite	Adsorption	zeolite-Fe/AC = color (83.1%) and COD (67.2%) Fe/AC = color (86.8%) and COD (65.6%)	(Jun et al., 2020)
Activated carbon from palm kernel shell	Adsorption	TSS (90.0%), COD (68.0%), color (97.0%), and BOD (83.0%)	(Nahrul Hayawin et al., 2020)
biochar from oil palm frond	Adsorption	phenol (90.0%)	(Lawal et al., 2020)
FeSO4⋅.7H2O waste from titanium oxide industry	Adsorption	COD (70.0%), BOD (>80.0%), and TSS (>85.0%)	(Hossain et al., 2019)
Banana and orange sundried peels were pyrolyzed to produce value-added biochar	Adsorption	BOD (46.0%), COD (52.0%), TSS (18.0%), O&G (57.0%)	(Lam et al., 2018)
natural composite adsorbent composed of activated coconut shell carbon, cow bones and zeolite	Adsorption	COD (89.6%)	(Adeleke et al., 2017)
acid-washed coconut shell activated carbon (CSAC)	Adsorption	Color (61.0%), TSS (39.0%), and COD (66.0%)	(Sia et al., 2017)

batch reactors (AnSBR). The maximum removal efficiency of COD achieved was 96.0% at 30 °C. Ultrasonic confers a synergistic effect on thermal decomposition and free radical-induced reaction. The water is heated from the cavity implosion. Then, the heat breaks down the water into free radicals. These radicals then invade into water and degrade the organic compounds into soluble organic matter. The physical and mechanical effects reduce the particle size followed by an easier disintegration. After ultrasonic pretreatment, POME is easier to digest by anaerobes. Another study reported that ultrasonic pretreatment could remove 31.0% of TSS and improved 31.5% of COD solubilization (Wong et al., 2019). Other studies combined ultrasonic with activated carbon, ultrasonic-microwave, and ultrasonic-coagulation-activated carbon. Combination of ultrasonic and microwave could remove 75.6% COD (Mishra et al., 2021). Ultrasound cavitation, $FeCl_3$ coagulation, and activated carbon could remove BOD (89.7%), COD (88.1%), color (99.9%), and TSS (99.5%) (King et al., 2019). These studies showed that combination of ultrasonic with other methods performed better than ultrasonic alone. The additional methods possibly require additional operational cost. However, the ultrasonic pretreatment provides advantages for the maximum conversion of complex organic waste into H_2. Moreover, it has shown a considerable impact on cumulative H_2 production and organic compound reduction from POME.

Chemical pretreatment is effective to break down complex structures into simple structures. It requires chemical compounds, such as hydrogen peroxide, Fenton, alkalis, and/or acids. It improves biodegradability and digestibility of the substrate. Chemical methods are differentiated into hydrogen peroxide, Fenton oxidation, chemical coagulation-flocculation, and chemisorption or synthetic adsorption pretreatment. Hydrogen peroxide is one of the popular pretreatments in wastewater. Hydrogen peroxide is also feasible to combine with other techniques. For instance, Zaied et al. (2020) oxidated POME using hydrogen peroxide and catalyzed by UV light/zinc oxide. For UV/ZnO, pH was adjusted to 11.0, shaking was set at 200 rpm, ZnO concentration was 0.1–0.5 g, and the reaction duration was 2–5 h. With these conditions, COD removal and decolorization efficiencies were achieved by 37.0% and 85.0%, respectively. For UV/H_2O_2/ZnO treatment, the pH was adjusted to 11.0, shaking speed was set at 200 rpm, molar ratio of COD/H_2O_2 was 5.0, ZnO concentrations used were 0.1–0.5 g, and the reaction time used was 1 to 5 h. With these conditions, removal of COD and decolorization efficiencies were 60.2% and 91.6%, respectively. It indicated that hydrogen peroxide can improve degradation process. However, performance of the hydrogen peroxide could not be compared with the combined techniques.

Hydrogen peroxide in water generates hydroxy radical. The radicals disintegrate complex organic substrates including POME into simple composition. Therefore, hydrogen peroxide can enhance biodegradability of POME organic contents. Application of hydrogen peroxide and ferrous iron mixture is established as Fenton oxidation pretreatment where ferrous iron acts a catalyst. It is a simple method which does not involve any device and save energy. It is relatively affordable in cost. A study reported that POME was oxidized using Fenton reaction (Affam and Bin Bistar, 2020). During 2.5 h of oxidation at 298°K, Fenton oxidation enhanced biodegradability by 59.0%, removed COD 33.8%, and reduced TOC by 28.3%, respectively.

Several studies evaluated POME using Fenton oxidation. For instance, the highest removals of TOC, COD, and nitrogen by 89.0%, 91.0%, and 27.0%, respectively, were achieved by continuous addition of Fe^{2+} (Gamaralalage et al., 2019). The COD removal efficiency depends on the type of reagents used, reagent concentration, pH, and additional equipment. For instance, Saeed et al. (2016) achieved 85.0% of COD removal efficiency in the range of pH 3.0–3.5. While, Kaman et al. (2017) used conventional treatment and obtained 48.0% of COD removal efficiency, meanwhile using electrolysis addition attained 94.0% of COD removal efficiency. Ibrahim et al. (2015) applied aerated heterogeneous sono-Fenton to achieve 93.0% of COD removal. However, these results proved that conventional Fenton oxidation has low organic removal efficiency. It indicated that Fenton oxidation pretreatment is required to combine with other pretreatments to obtain better performance.

Besides, other chemical techniques including coagulation-flocculation and chemical adsorption method have also been used. For instance, use of polymer addition approach employed tannin and polyacrylamide for coagulation-flocculation process. Using tannin, the removal efficiencies of BOD (97.6%), COD (88.9%), turbidity (93.0%), and SS (90.2%) were obtained (Mat Yasin et al., 2020). Using polyacrylamide, removal efficiencies of TSS and COD were 96.4% and 70.9%, respectively (Zinatizadeh et al., 2017). These studies showed that tannin had better removal efficiency of COD when compared to polyacrylamide.

For chemical adsorption, a mass transfer phenomenon of the adsorbate was found onto adsorbents (Wang and Guo, 2020a). Adsorption is widely used due to its advantages, such as simple design, low cost, easy operation, high efficiency and eco-friendliness (Wang and Guo, 2020b). It can be classified into physical adsorption called physisorption and chemical adsorption called chemisorption. The mechanism of adsorption process that include physisorption and chemisorption is shown in Fig. 2.

Fig. 2(a) describes strong attractions between the adsorbate and the adsorbent surface. In the process explained in the Fig. 2(b), a driving force exists which prevents the sorbate to stay in the bulk aqueous medium. Then, the interaction between donor and acceptor molecules generates an increase in specific sorbate-surface attractions as seen in Fig. 2(c). In Fig. 2(d), the complementary charges on both pairs lead a specific sorbate surface attraction to arise. These mechanisms are defined as physisorption since there are no covalent bonding in the sorbate-surface interaction. Meanwhile, Fig. 2(e) describes the process of chemisorption since the bonding is present between the adsorbate and adsorbent surface (Al-Ghouti and Da'ana, 2020).

Besides, based on its mechanism, adsorption process needs an adsorbent surface. The efficiency of adsorption process depends on the efficiency of the adsorbent material. Based on the nature of the material, adsorbents can be either synthetic or natural adsorbents. In this section, synthetic adsorbents are discussed. For synthetic adsorbents, $FeSO_4{\cdot}7H_2O$ waste from titanium oxide industry was assessed to remove COD, BOD, and TSS content from POME (Hossain et al., 2019). Using this adsorbent, COD, BOD, and TSS removals of 70.0%, 80.0%, and 85.0% were achieved. Generally, this removal efficiency is considered as low. However, this study indicated that $FeSO_4{\cdot}7H_2O$ could be used as synthetic adsorbent. It needs further detailed investigations for the large-scale use of $FeSO_4{\cdot}7H_2O$ as an adsorbent to achieve better performance.

Biological methods of pretreatment are generally regarded as safe, affordable, environmentally friendly, and have lower energy demands. Commonly, biological methods utilize microorganisms and/or their enzymes. In this section, the potential of microorganisms such as bacteria, fungi, algae, and microbial consortia to treat POME is discussed. In addition, bio coagulation-flocculation agents and bio-adsorbents are also described.

Several studies employed bacteria for the treatment of POME. For instance O-Thong et al. (2007) used *Thermoanaerobacterium* and achieved 62.2%, 93.6%, and 80.0% removal efficiencies of COD, SS, and oil recovery, respectively. Other studies utilized bacteria *Bacillus thermoleovorans* strain A2, *Klebsiella Pneumoniae* ABZ1, and *Ochrobactrum* sp. strain SZ1 to remove phenol (61.1%) (Chantho et al., 2016), color (80.4%) (Abdulsalam et al., 2020), and COD (71.0%) (Neoh et al., 2016). It seems that *Ochrobactrum* sp. strain SZ1 has better performance than *Bacillus thermoleovorans* strain A2. However, these studies projected that bacteria could remove COD, SS, oil, color, and phenolic compounds from POME.

Besides, fungi, algae, and microbial consortium have also been studied to remediate pollutants from POME. The fungus *Meyerozyma guilliermondii* was proven to remove COD (72.0%), TN (49.2%), TOC (46.6%), and oil & grease (92.4%) (Ganapathy et al., 2019) . Algae *Scenedesmus* sp. strain UKM9 and *Chlorella vulgaris* co-cultured with a bacterial strain *Azospirillum brasilense*, and Microbial consortium AB-101 showed COD removal efficiency of 57.0% (Mohd Udaiyappan et al., 2021), 51.8% (Halim et al., 2019), and 91.3% (Abidi et al., 2020), respectively. Another microbial consortium could remove BOD, COD, and TSS by 90.2%, 91.1%, and 92.2%, respectively (Bala et al., 2018). These studies reflected that microbial consortium AB-101 had a better

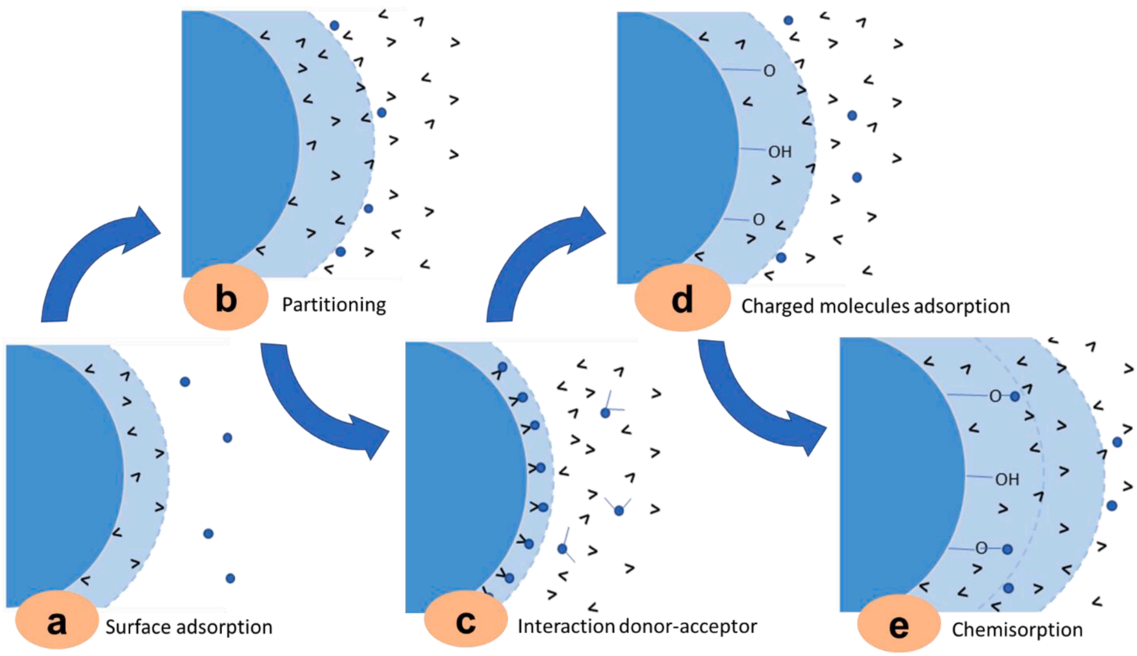

Fig. 2. Adsorption mechanism: (a) air to surface adsorption with limited water, (b) partitioning from aqueous solution to the adjacent layer (vicinal water) surface which serves as an adsorbent liquid, (c) adsorption from aqueous medium to certain surfaces sites due to the interactions between donor and acceptor, (d) charged molecules adsorption from aqueous medium for complementarily charged surfaces because of the electrostatic attraction, (e) chemisorption due to surface binding (Al-Ghouti and Da'ana, 2020).

ability when compared to fungi, algae, algae-bacteria co-culture, and aerobic indigenous mixed microbial consortium for COD removal from POME. Furthermore, its COD removal was higher when compared to *Ochrobactrum* sp. strain SZ. These studies prescribed that microbial consortium is highly recommended to achieve a higher COD removal from POME. These studies implied that microbial consortia performed better.

Another biological method is bio coagulation-flocculation and biosorption. Bio coagulation-flocculation agent destabilizes small particles in the suspension to form the flocs (Lebron et al., 2021). Several parts of plants are utilized for coagulation-flocculation technique as natural agents, such as peanut, germ, husk ash, seeds, and leaves extract. Two studies utilized okra to reduce turbidity, TSS, and COD using coagulation-flocculation process. Peanut–okra and wheat germ–okra were reported as coagulant and flocculant (Chung et al., 2018) while peanut–okra reduced turbidity by 92.5%, total suspended solids by 86.6%, and COD by 34.8%, whereas wheat germ–okra had removal efficiency of turbidity, total suspended solids, and COD by 86.6%, 87.5%, and 43.6%, respectively. Fenugreek (*Trigonella foenum-graecum*) and okra (*Abelmoschus esculentus*) coagulant-flocculant reduced turbidity, TSS, and COD by 95.0%, 92.7%, and 63.1% (Lanan et al., 2021). These studies demonstrated that fenugreek and okra combination had a better removal efficiency when compared to the each of them, separately.

Other studies operated rice husk ash (RHA), Mucuna seed shell, and chickpea as natural coagulant-flocculants. RHA remediated COD and TS by 52.4% and 83.9–84.9%, respectively (Huzir et al., 2019). *Moringa oleifera* extract could achieve a removal efficiency of turbidity, color, and COD by 51.0%, 50.0%, and 65.0%, respectively (Mohamed Noor et al., 2021). Mucuna seed shell had removal efficiency of SDP (suspended and dissolved particles) up to 95.0% (Nwabanne et al., 2018). Chickpea (*Cicer arietinum*) could remediate turbidity, TSS, and COD with removal efficiency 86.0%, 87.0% and 56.0% (Choong Lek et al., 2018). These studies showed that chickpea had better removal efficiencies of COD when compared to RHA and Mucuna seed. The studies also projected that combination of fenugreek and okra was better when compared to other natural coagulation-flocculation agents.

For biosorption process, natural adsorbents are studied to treat POME. Mostly, natural adsorbents are developed from biochar and activated carbon for POME remediation. Biochar from oil palm frond was employed to remove phenolic compound from POME by 90.0% (Lawal et al., 2020). Biochar derived from Banana and orange peels degraded POME contents, such as BOD, COD, TSS, and O&G with removal efficiencies 46.0%, 52.0%, 18.0%, and 57.0% (Lam et al., 2018). These studies showed that biochar has promising potential to treat POME.

Activated carbon has also been used to treat POME. Mostly, coconut and palm kernel shells have been used as activated carbon for POME. Activated carbon from coconut shell (CSAC) removed color, TSS, and COD by 61.0%, 39.0%, and 66.0%, respectively, from POME (Sia et al., 2017). Similar studies combined coconut shell with cow bones and zeolite to develop natural composites as activated carbon. This natural composite removed 89.6% of COD from POME (Adeleke et al., 2017). It seems that natural composite had better removal efficiency of COD than CSAC, nonetheless natural composite needed to be studied further for other pollutants degradation of POME. Activated carbon can also be developed from palm kernel shells. A study using activated carbon from palm kernel shell showed removal of TSS, COD, color, and BOD by 90.0%, 68.0%, 97.0%, and 83.0%, respectively (Nahrul Hayawin et al., 2020). Similarly, another study combined activated carbon with iron oxide and zeolite (Jun et al., 2020) which reduced color and COD of POME by 86.8% and 65.6%, respectively. Combination of activated carbon, iron oxide, and zeolite reduced color and COD of POME with removal efficiencies 83.1% and 67.2%, respectively. These studies demonstrated that activated carbon from palm kernel shell had better performance for COD removal than its combination. Moreover, activated carbon from palm kernel shell was proven to have high percentage efficiency for TSS and BOD removal from POME.

In addition, BOD and TSS removal efficiency of activated carbon from palm kernel shell was higher than synthetic adsorbents. Nonetheless, COD removal of synthetic adsorbent was higher than activated carbon from palm kernel shell even though it was insignificant. However, these studies indicated that activated carbon from palm kernel shell had better performance to degrade POME pollutants for adsorption technique.

3. Potential of magnetic materials for POME treatment

Existing pretreatment methods have shown a wide variation in their removal performances. Among others, adsorption process is seen as a method that can be easily modified to further improve its efficiency. Using magnetic materials in combination with adsorbents provides a new outlook that is of worth exploring. Magnetic materials for POME pretreatment have been employed using natural and poly composites. Several natural composites that have been utilized in combination with magnetic materials are activated carbon, chitosan, and cellulose; in addition, polymer material that was also added into natural composite. Commonly, the polymer material was polyacrylamide. An overview of applying magnetic materials for POME pretreatment along with their pollutant removal performances from POME is shown in Table 3.

Magnetically activated carbon composite prepared from palm shell was utilized which reduced oil content of the POME by 85.0% (Ngarmkam et al., 2011). Under optimum chitosan-magnetite dosage of 250 mg L^{-1}, the removal efficiencies for turbidity, TSS, and COD levels were 98.8%, 97.6%, and 62.5% at pH 6.0 (Saifuddin and Dinara, 2011). Similar study on magnetic-chitosan composite synthesized using *Fenneropenaeus indicus* sp. reported that the removal efficiencies of turbidity, TSS, ammoniacal nitrogen, and COD were up to 94.6%, 89.2%, 63.8%, and 90.6% under 4.0 g L^{-1} of magnetic chitosan composite dosage at pH 8.4 (Veknesh and Muhammad Heikal, 2020). Another study combined magnetic chitosan with activated carbon and ultrasound to remove POME content. The combined treatment removed 89.7% BOD, 88.1% COD, 99.9% color, and 99.5% TSS at pH 5.0 (Lee et al., 2020).

The oil removal efficiency using magnetic activated carbon composite was relatively low when compared to other natural adsorbents such as wood, kenaf, cotton, kapok, and milkweed. These studies reflected that higher magnetic chitosan dosage (under 4.0 g L^{-1}) could achieve higher COD levels (90.6%), significantly. Even though generally higher magnetic chitosan dosage decreased the removal efficiencies of turbidity, TSS, and COD, nonetheless its removal efficiencies were insignificant. Using combination treatment, study also found that the removal efficiency of COD was lower than magnetic chitosan under 4.0 g L^{-1} of adsorbent dosage. The studies indicate that magnetic chitosan composite is potentially employed as magnetic adsorbent for POME pretreatment since it is simple and no need additional equipment.

Beside activated carbon and chitosan composite, cellulose has also been employed as magnetic material composite. Magnetic cellulose degraded turbidity, color, TSS, and COD up to 74.6%, 63.9%, 77.2%, and 55.8% from POME (Noor et al., 2018). Another study used magnetic cellulose with polyacrylamide to degrade POME content. Polyacrylamide grafted onto magnetic cellulose (PAM-g-MagCell 1) was synthesized using microwave assisted method. It was proven to degrade TSS, turbidity, COD, color with removal efficiencies 83.0%, 88.6%, 53.2% and 91.8%, respectively (Mohamed Noor et al., 2020).

Table 3
Potential Magnetic Material for POME Pretreatment.

Magnetic Material	Operational Parameters for POME pretreatment	Treatment efficiencies	References
Magnetic composite prepared from palm shell-based carbon	Under CO_2 flow for 3 h	85.0% of oil	(Ngarmkam et al., 2011)
Magnetic chitosan	At pH 6.0, under dosage of 250 mg L^{-1}	Turbidity (98.8%), TSS (97.6%) and COD (62.5%)	(Saifuddin and Dinara, 2011)
Magnetic chitosan	under dosage of 4.0 g L^{-1}	Turbidity (94.6%), TSS (89.2%), ammoniacal nitrogen (63.8%), and COD (90.6%)	(Veknesh and Muhammad Heikal, 2020)
Magnetic chitosan with activated carbon and ultrasound bath	At pH 5.0	BOD (89.7%), COD (88.0%), color (99.9%), TSS (99.5%)	(Lee et al., 2020)
Magnetic cellulose (Magcell)	1.5 mL glutaraldehyde	turbidity (74.6%), color (63.9%), TSS (77.2%), and COD (55.8%)	(Noor et al., 2018)
Polyacrylamide grafted onto magnetic cellulose (PAM-g-MagCell 1)	-synthesized by microwave assisted -PAM-g-MagCell dosage 1.5 g/L, pH of 8.0 and settling time of 30 min	TSS (83.0%), turbidity (88.6%), COD (53.2%), and color (91.76 %)	(Mohamed Noor et al., 2020)

4. Challenges and prospects of advances in magnetic material for adsorption process

Most of the research up to now described the general scheme for POME treatment into three processes: cooling ponds, anaerobic digestion-aeration, and polishing treatment (Bashir et al., 2019, Ng et al., 2020). Cooling ponds cause a lot of heat loss and temperature is often dropped to 60 °C to mesophilic conditions which makes the treatment for oil content in POME extremely ineffective. Thus, the pretreatment technology is crucial to send treated POME into anaerobic digester at high temperature. It is noted that anaerobic digestion has been found to be effective not only for POME treatment but also for various pollutions (Ratnasari et al., 2021, Syafiuddin and Boopathy, 2021). Anaerobic digestion can produce bio-energy by utilizing volatile fatty acid (VFA) content as an ideal substrate for biogas production such as methane production (Aamer Mehmood et al., 2021, Syafiuddin et al., 2020). In addition, anaerobic open ponding system can also produce methane gas which can be generated from the conversion of COD (Chin et al., 2013). From this overview, it has the potential to apply biorefinery concept for bioenergy production during POME treatment. For instance, over 510 k tonnes of methane can be produced if all the POME was treated anaerobically and this is comparable with the 816 million litres of diesel (Sani et al., 2021). This suggests that the capture of biogas from POME treatment is promising and becomes new alternative energy source. The common technologies employed for biogas capture include covered lagoon and continuous stirred tank reactors (CSTRs) (Chia et al., 2020). Currently, the state-owned oil–gas company PT Pertamina in Indonesia is developing two biorefineries with 100% crude palm oil for developing new renewable energy (GAPKI, 2021). Through these projects, about 3000 to 20,000 barrels per day of biofuel are expected to be generated.

The recovery of POME in industry can result in gas emissions to environment. In Thailand, assessment of palm oil mill biorefinery reported that POME had 0.08 to 2.39 net carbon emissions (Beaudry et al., 2018). A case study in Malaysia found that 58.5 million tons of POME can produce 510 k tons of methane via anaerobic digestion (Chia et al., 2020). It is proportional to 816 million L of diesel. In addition, it can provide electricity generation over 1.8 MW (Tan and Lim, 2019). In Indonesia, a case study on POME assessed the ten sustainability factors including the presence of raw materials, profitability, greenhouse gasses emissions, energy efficacy, water utilization, manufacturing cost, investment, installed capacity, residentiary, and provision of employment (Septriana et al., 2022).

Several Asian countries have regulation and standard to eliminate negative effect of POME to environment. In 2010, Thailand monitored issues related to Thai palm by initiating Good Agricultural Practice Standard (Thai Gap) that regulates the application of pesticide, water, and fertilizer application. Thailand have a policy called as the Alternative Energy Development Plan 2015–2036 and have operated 12 palm oil refineries to improve biodiesel production. In Indonesia, Indonesian Sustainable Palm Oil (ISPO) had been implemented as standard monitoring issues of POME. This is issued to regulate palm oil production and its effluent for all palm oil industries in Indonesia. In Malaysia, the government produced the RM20 million Malaysia Palm Oil Conservation Fund (MPOC) to protect undomesticated creatures and preserve biological diversity in environment.

To remedy the negative effects of POME to environment, advance pretreatment technique is crucially needed to be implemented. Magnetic material pretreatment via coagulation-flocculation process or adsorption process is an advance promising method for POME pretreatment. It has potential to be developed since it does not require polishing treatment. Moreover, as pretreatment technology, it is affordable, saves times, and saves energy. In addition, it showed a better performance when compared to other pretreatment techniques.

When compared with other techniques, magnetic composite pretreatment represents a superior performance. Pretreatments using physical methods could remove COD by 37.0–96.0% (Khadaroo et al., 2020, Mishra et al., 2021). While, 96.0% of COD removal efficiency was accomplished using ultrasonic pretreatment (Isa et al., 2020). Pretreatment using hydrogen peroxide could remove COD by 33.8% (Zaied et al., 2020). In addition, pretreatment using magnetic composite material could remove by 55.8–90.6% of COD (Lee et al., 2020, Saifuddin and Dinara, 2011). Alternatively, a 90.6% of COD removal was achieved using chitosan-magnetic composite. It seems that ultrasonic pretreatment had a higher removal efficiency of COD than chitosan-magnetic composite. Nonetheless, chitosan-magnetic composite was proven to remove other contents, such as turbidity (94.6–98.8%), total suspended solids (89.2–97.6%), and ammoniacal nitrogen (63.8%) (Saifuddin and Dinara, 2011, Veknesh and Muhammad Heikal, 2020). In addition, magnetic composite such as chitosan-magnetic composite is simple and does not require additional equipment. Therefore, magnetic composites have been promising to be implemented for POME pretreatment. However, adsorption using magnetic composite is rather new to the POME pretreatment method. This technique requires magnetic method to separate adsorbent and adsorbate after adsorption. It indicates that magnetic composites potentially can be recycled. However, it would require more in-depth studies to find the optimum performances of magnetic composites after recycling.

Magnetic composites chemically combine the properties of conventional polymers and magnetic materials, such as ferromagnetic particles in a matrix (Lee et al., 2010). For POME pretreatment, it is also noted that mostly magnetic composites were produced using natural sources, such as chitosan, cellulose, and activated carbon. These natural magnetic composites are feasible not only via coagulation-flocculation process, but also via adsorption process. Using natural magnetic composites via adsorption is more affordable than via coagulation since coagulation-flocculation must achieve required flocculation level. Thus, the use of advance natural magnetic composites via adsorption process for POME pretreatment is strongly suggested.

Another crucial factor for POME remediation is POME substrate content. Up to now, the research has tended to focus on organic matter such as COD, BOD and TOC rather than on nitrogen matter and oil & grease. Based on previous investigations, the content of nitrogen matter and oil & grease in POME is approximately 670–780 mg L^{-1} and 5 614–8 812 mg L^{-1} (Loh et al., 2017). These contents can compromise aquatic organisms in water. Therefore, in future studies, advanced natural magnetic adsorbents should be developed having potential to remove not only the content of organic matter, but also nitrogenous matter, and oil & grease.

5. Conclusions

The currently employed pretreatment methods including physical pretreatments, chemical pretreatments, coagulation-flocculation, and adsorption can remove pollutant content from POME with several limitations. These limitations of pretreatments are also addressed here by proposing new approaches. Especially, the promising potential of magnetic composite adsorbents is highlighted as an opportunity to treat POME. The effective design of POME treatment is described. Challenges of advanced magnetic materials as adsorbents have been also highlighted.

CRediT authorship contribution statement

Anisa Ratnasari: Writing – original draft. **Achmad Syafiuddin:** Conceptualization, Writing – review & editing. **Raj Boopathy:** Conceptualization, Writing – review & editing. **Sana Malik:** Writing – review & editing. **Muhammad Aamer Mehmood:** Writing – review & editing. **Rizki Amalia:** Writing – review & editing. **Dedy Dwi Prastyo:** Writing – review & editing. **Nur Syamimi Zaidi:** Writing – review & editing.

Declaration of Competing Interest

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.

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