Principles and Mechanism of Adsorption for the Effective Treatment of Palm Oil Mill Effluent for Water Reuse

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1.1 Introduction

Wastewater is a general term used for the effluents generated from domestic, agricultural and industrial sources. The effluents contain organic and inorganic pollutants which are toxic to the ecosystem. Examples of organic pollutants are the volatile and chemical compounds with complex chain reactions. The discharge of volatile compounds and highly toxic chemical compounds have affected the quality of the water in some cases in Thailand, Vietnam and Columbia (Tran et al., 2015). The organic pollutants of palm oil-based waste can promote microbial growth affecting the flora and fauna of the water ways (Mukherjee and Sovacool, 2014). Example of the inorganic pollutants are the heavy metals deposit in water bodies due to the deposition of untreated waste from domestic, agricultural and industrial sectors into the water ways. Surface water degradation is caused by high toxicity of discharged waste pollutants into fresh water bodies (Essington, 2015). One of the most challenging problems of water pollution is the presence of organic pollutants and heavy metals in water bodies representing one of the greatest risks for the aquatic ecosystem (Galimberti et al., 2016). These pollutants are difficult to remove due to their low concentration in the effluent. When wastewater solutes are discharged into water ways, they are accumulated in

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sediments along the aquatic food chain (Mishra and Shukla, 2016). The toxic effects of the pollutants are not only limited to the water body but also on the environment without proper treatment before discharge (Guagliardi et al., 2013). The agro-based industries such as palm oil mill in Malaysia have become one of the largest contributors of water pollutants (Kamarudin et al., 2015). The palm oil mill effluent (POME) contains pollutant parameters such as chemical oxygen demand (COD), biological oxygen demand (BOD), oil and grease, suspended solids, ammonia-nitrogen and heavy metal concentration (Khemkhao et al., 2015).

Most countries in the world are developing regulations and strategies to ensure proper treatment of the water pollutants before discharge into the water bodies. Also, the level of awareness is on the increase to ensure that adequate protection and preservation of water is achieved. Wastewater management involves series of efforts that promotes effectiveness in the use of water (Cooper, 2016). There are three methods of wastewater treatment, which are the physical, chemical and biological methods. The physical methods include sedimentation, floatation, membrane filtration, and adsorption. Chemical methods include ozonation, advanced oxidation, electrolysis. Also, biological methods include the use of conventional activated sludge, anaerobic open ponding and anaerobic systems. However, some of the conventional techniques are costly and requires high maintenance to operate. For example the use of membrane have high potentials for the treatment of POME, but is expensive and have problems of membrane fouling (Azmi and Yunos, 2014). Some of the methods such as the anaerobic open ponding requires availability of large area for the treatment. Some other methods such as the anaerobic systems require routine maintenance of the reactors.

The method of adsorption is used for the removal of wastewater contaminant. Adsorption by solid reduces toxicity effect from industrial effluents (Haak et al., 2016). Adsorption has the advantage of low capital cost of adsorbents, easy to operate, minimum sludge generation and the ability of regeneration and reuse of spent adsorbents (Stawiński et al., 2017). Activated carbon adsorbent is applicable for wastewater treatment in the form of granular or powdered, it has been proven to be very effective for the removal of different types of contaminants in water ranging from industrial, municipal wastewater, landfill leachate and polluted groundwater. Activated carbon adsorption of pollutants of wastewater is recognized by USEPA (environmental protection agency) as one of the best methods of environmental control (Bautista-Toledo et al., 2014), this is due to large specific pore surface area which makes it a powerful adsorbent and has the ability to adsorb wide range of contaminants. The limitation of the use of commercial activated carbon as adsorbent is its high cost and problem of regeneration for reuse (Benhouria et al., 2015; Wei et al., 2012). However, the adsorptive capacity of activated carbon has necessitated low cost alternative adsorptive materials with similar composition as composite and the ability to have the potentials for regeneration. Activated carbon derived from cow bones have high potentials of both carbon and minerals composition, which is highly enriched in calcium and phosphorus, forming an insoluble precipitate known as hydroxyapatite (Medellin-Castillo et al., 2014). Adsorption on hydroxyapatite adsorbent material is effective for the treatment of both organic and inorganic pollutants (Patel et al., 2015). Activated carbon derived from cow bones have been processed for the treatment of POME (Adeleke et al., 2016). Waste materials from agriculture, domestic and industrial are synthesized to serve as replacement of commercial activated carbon for the treatment of wastewater. For example, coconut shell can be processed as activated carbon at elevated temperature and has been reported as a very good source of activated carbon because it contains cellulose, hemicellose and lignin. Materials containing lignocellulosic properties are a very good adsorbent material for the activation of carbonaceous materials. Adsorbent materials such as orange peel, mango waste have very good cellulose characteristics. However, the effectiveness of a prepared adsorbent material as activated carbon wholly depends on the ability of the adsorbent to reduce the pollutant of wastewater to a considerable low level.

1.2 Palm Oil Production and Processing

Oil palm is obtained from the fruit bunches which are sterilized by stripping and pressing at high pressure to separate the fruits from the bunch and to reduce the formation of free fatty acid. After the stripping of the bunch, the sterilized fruits are digested to loosen the mesocarp during pressing. The process is followed by the separation of the mesocarp and the nuts from the digester. The extracted crude oil contains both organic and dissolved matter in water. A centrifugation tank is used to separate the water from the crude oil. The crude oil refining process can be either physical or chemical as shown in Fig. 1-1 (www.google.com).

The process of degumming involves removing unwanted gums, such as phosphatide, which has the ability of affecting the stability of the processed crude oil. The crude palm oil is heated at between 90—110°C with phosphoric acid to decompose the phosphatides and making them to be easily removed by bleaching. The next stage is the bleaching which involves the treatment of the degummed oil which is usually achieved with bleaching earth at 100°C under continuous agitation with bleaching material until the contact time of 30 minutes is achieved. At this stage, the phosphatides are removed by the oxidative effect of the bleaching material (Rossi et al., 2003). The process of deodorization entails the removal of free fatty acid (FFA) in the form of palm fatty acid distillate (PFAD). In the chemical process, the phosphatides are removed by the addition of additives, the process is followed by naturalization with alkali for the removal of FFA. The naturalized oil is then bleached under vacuum using an agitator called bleacher at 90°C. The oil obtained after bleaching is heated at 200°C with the evolution of volatile materials to obtain a deodorized oil blend.

The waste from oil palm industries consist of oil palm trunks (OPT), oil palm fronds (OPF), empty fruit bunches (EFB), palm processed fibers (PPF), palm kernel shells, fresh fruit bunch (FFB) and POME discharge (Rupani et al., 2010). The wastewater from the sterilization process of the FFB is known as the sterilizer condensate. The process of sterilization results to high amount of condensate which has effect between the fruit and the wastewater. It contains 35%—45% of POME (Liew et al., 2015).

1.3 Palm Oil Mill Effluents and the Treatment Methods

The major source of wastewater of POME is the clarification water, which is the discharge from the clarification process of the crude oil. The produced crude oil is a mixture of palm

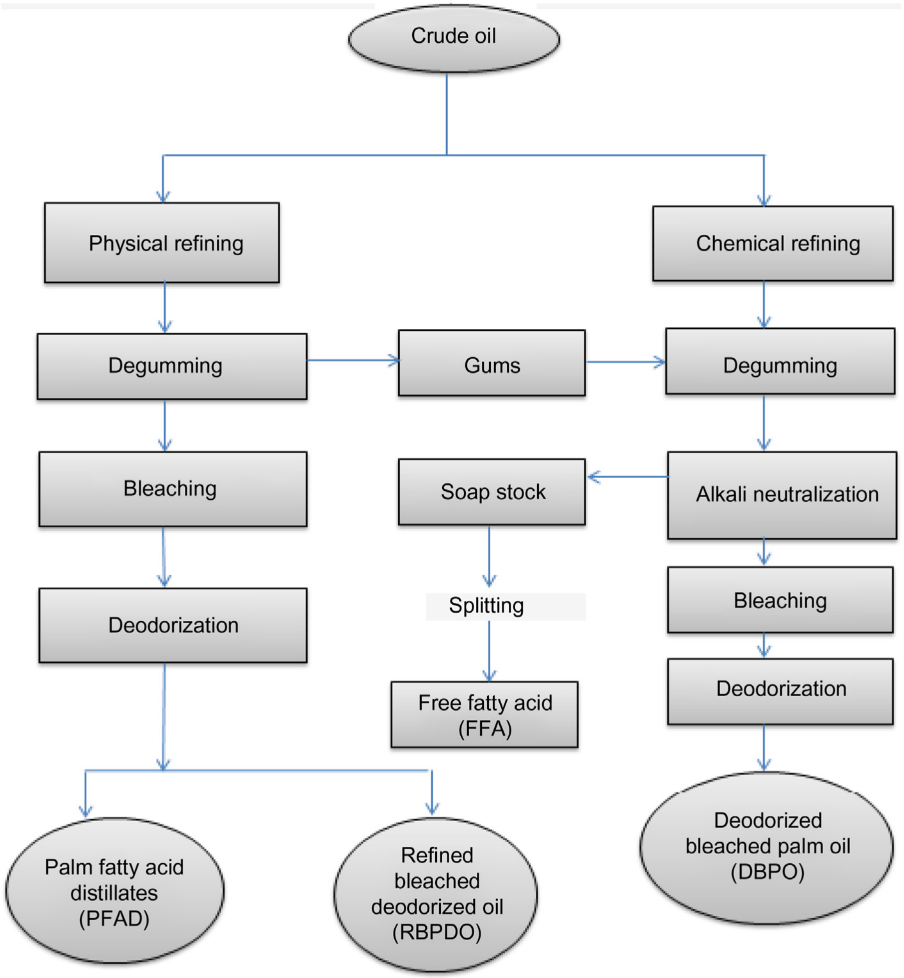

FIGURE 1-1 Palm oil processing.

oil, water and impurities comprising of organic matters (Ohimain and Izah, 2017) The wastewater from the clarification process contains about 60% of POME. The residual oil trapped in the press machine contains 4% of the POME and is known as the hydrocyclone wastewater (Liew et al., 2015). Palm oil mill effluent (POME) is a thick brownish colloidal slurry of water containing oil and fine cellulosic fruit residues. POME is usually generated from mill operation at a temperature ranging from 80 and 90 ^{o}C and is slightly acidic in nature. It has a pH of between 4 and 5 (Rupani et al., 2010). According to Ahmad (2016), POME is a very high strength industrial wastewater having 40,500 mg/L total solids, 4000 mg/L oil and grease, 50,000 mg/L COD and 25, 000 mg/L BOD. Detailed characteristics of the physicochemical parameters of POME are illustrated in Table 1-1.

Table 1-1 Characteristic of Palm Oil Mill Effluent

Parameters	Mean	Range
pH	4.2	3.5–5.2
Oil and grease	6000	150–18,000
Biochemical oxygen demand (BOD)	25,000	10,000–44,000
Chemical oxygen demand (COD)	50,000	16,000–100,000
Total solids (TS)	40,500	11,500–79,000
Suspended solids (SS)	18,000	5000–54,000
Total volatile solids (TVS)	34,000	9000–72,000
Ammonia nitrogen (AN)	35	4–80
Total nitrogen (TN)	750	80–1400
Phosphorus	180	
Magnesium	615	
Calcium	440	
Boron	7.6	
Iron	47	
Manganese	2.0	
Copper	0.9	
Zinc	2.3	

These physicochemical parameters must be reduced to appreciable low levels due to the danger they pose to human, animals and the ecosystem. The deposition of this effluent must comply with the prevailing effluent discharge standard for POME. The POME production per year increases sludge production and also high moisture content enriched with organic matter, which may constitute eutrophication effect. For this reason, it is considered one of the most harmful wastes for the environment if not properly treated. POME processing plant has increased over the years in Malaysia and Indonesia as a result of rapid industrialization, these has made both countries the two largest producers of oil palm. Consequently, POME produced in the oil palm processing mill has increased tremendously, thereby increasing the challenge of POME treatment before discharge.

Raw POME is colloidal in nature and contains 95%–96% water, 0.6%–0.7% oil, it also contains 4%–5% total solids and 2%–4% suspended solids having composition of solid matters from palm fruit mesocarp produced from sterilizer condensate, separator sludge and hydrocyclone wastewater (Ng and Cheng, 2017). POME is considered as the major contributor of water pollution by limiting the oxygen availability in water for aquatic respiration (Thangalazhy-Gopakumar et al., 2015), it contains elements like N, P, K, Mg, and Ca which are the major components of plant but the toxicity of this metals from effluents application in soil reduces the growth and developments of plants (Hossain et al., 2015). POME contains suspended solids and is acidic in nature with pH 4.5 (Khemkhao et al., 2015). According to Muhrizal et al. (2006), POME contains high concentration of Al and Pb at a concentration of >17.5 μg/g (Habib et al., 1997). Jameset al. (1996) stated that the presence of Pb in POME is as a result of pollution in pipes, tanks, and containers. The suspended particles and dissolved solids after the treatment of POME is known as palm oil mill sludge (POMS). The amount of POMS is dependent on the production of POME. It has high moisture content and pH of 8.4 and has elements such as nitrogen, phosphorus, and potassium in the concentration of 3.6, 0.9, and 2.1 mg/L respectively. The sludge, if not disposed, results in offensive odor and has the ability of polluting the surface and ground water. Therefore, it is very important for there to be effective technology at low cost for the disposal in order for the effluent to satisfy the prevailing discharge standard. According to (Chooi, 1984; James et al., 1996), POMS can be treated using open air drying and the dried product can be used as fertilizer because it has high nutrient value. However, the process is extremely difficult during the period of rainy season because of the slow drying rate and problem of over flow. Adsorption method is an effective method for the treatment of effluent; the method is applicable because it is less expensive compared to other treatment methods, in which the adsorbent materials are easily sourced and the treated effluent have no potential threat to the ecosystem.

1.3.1 Trends in POME Treatment Methods

The high amount of effluent generated in palm oil mill has increased research methods to minimize their effect of water pollution. Some of the methods that is applicable for the treatment of POME include the physical and chemical process such as filtration, floating sediment, coagulation, advanced oxidation precipitation and biological process which involves the use of either the conventional aerobic and anaerobic treatment systems as well as treatment using the anaerobic digestion. Some novel technologies are evolving for the treatment of raw POME such as biological digestion, membrane, Fenton technology and adsorption. The treatment efficiency of each method varies depending on the technology employed. The effectiveness of the treatment system is the ability of the treated effluent to satisfy the discharge standard. Some of the methods are classified into the physical-chemical methods and also the biological methods. The prevailing effluent discharge standard according to the Environmental Quality Act (EQA) Ministry of Environment (MOE) discharge limit Malaysia is illustrated in Table 1-1. It can be observed in Table 1-2, that the prevailing discharge of the physic-chemical parameters decreases over the years as the year increases except for pH and temperature from 1978 discharge standard to the present.

It was also observed that the prevailing discharge standard for the oil and grease deceases from 1978 and became constant from 1981 till present discharge standard. Similarly, the COD decreases as the year increases but as from 1982 onward, the concentration is not required in the effluent before discharge. This indicates that COD is a very important parameters that should be treated from the effluent before discharge. The concentration of BOD decreases from 1978 (5000 mg/L) to 100 (mg/L) since 1984. The reduction of the physic-chemical parameters especially the critical parameter is important in order to preserve the aquatic population and the water bodies.

Table 1-2 Environmental Quality Act 1974 for Palm Oil Mill Effluent Discharged

Parameters	DOE Discharged Limit (1986 Onwards)[a]	Environmental Quality Act[b]
BOD_3 (mg/L)	50	100
COD (mg/L)	1000	1000[c]
Suspended solids (mg/L)	1500	1500^3
Oil and grease (mg/L)	50	50
Ammoniacal nitrogen (mg/L)	100	150^3
Total nitrogen (mg/L)	200	200^3
pH	5.0	5.0–9.0
Temperature (°C)	45	45

[a] Malaysia Department of Environment (DOE).

[b] Parameters Limited of Environmental Quality (Prescribed premised) (crude Oil) Amendment.

[c] No new value stipulated since 1982.

1.3.2 Conventional Treatment Method

Biological treatment is the most common conventionally used method for the treatment of POME. The major principle of the biological method is to increase bacteria activities and other biodegradable organics to aid wastewater digestion. Biological treatment includes aerobic treatment making use of conventional activated sludge. It also includes the anaerobic open pond systems and the anaerobic treatment systems, known as the anaerobic digestion. The open ponding system is mostly used by palm oil mill operators around the world (Poh et al., 2015; Saswattecha et al., 2015). Some of the biological treatment methods is presented in Table 1-3.

The anaerobic pond is the most conventionally used POME treatment method. Open ponding system is the most popular treatment method of POME in Malaysia, utilized by more than 90% of the mills (Kuppusamy et al., 2017). It has a wide area of application because of its low cost of operation and capital. Anaerobic treatment has proven to be effective in reducing pollutants from high strength industrial wastewater. It involves biological reactions and sequences which enables one group of microorganism serving as substrate to another resulting in the conversion of organic matter to methane and CO_2. The treatment undergoes different stages of transformation of anaerobic microorganisms which produces CH_3 and CO_2. The anaerobic bacteria reduces the organic pollutants such as COD and BOD in the process of transformation. The open ponding system, also known as aerobic lagoons, are open shallow basin which treats wastewater with the use of bacteria and algae. It involves biological reactions and sequences which enables one group of microorganism serving as substrate to another resulting in the conversion of organic matter to methane and CO_2. A wide range of research efforts has been successfully conducted on reactor technology for industrial wastewater treatment such as food processing, textile industry, paper and pulp industry (Fiore et al., 2016).

Table 1-3 Treatment of Palm Oil Mill Effluent Using the Anaerobic System

Anaerobic Treatment System	Advantages	Disadvantages	Removal Efficiency (%)	Authors
Anaerobic pond	Higher emission of methane from tanks	Problem of land availability	97.8% removal of COD achieved before treatment in the facultative pond	Yacob et al. (2006)
Ultrasound membrane anaerobic system	High removal efficiency of COD at very short HRT	Expensive and requires routine maintenance	92.8%–98.3% COD removal achieved	Nour and Nour (2017)
Anaerobic palm oil mill effluent sludge	Pure culture bacteria for electricity generation	High rate of depletion of organic pollutant with increasing time, thereby reducing the generation of electricity in a batch system	High electricity generated and inversely proportional to the removal of COD	Nor et al. (2015)
Ponding system	High efficiency of the removal due to easy decomposition of microorganism	Longer HRT required	93.9% COD removal, 88.7% TSS removal achieved	Zahrim et al. (2014)
Sequencing batch reactor (SBR)	Very good settling ability and high biomass retention	POME samples used was from treated anaerobic pond	Total COD removal between 10–68% for total COD and 11%–94% soluble COD.	Fulazzaky et al. (2017)
Membrane bioreactor (MB)	Contains membrane fouling layer bio films which influences effluent quality by increasing bio-degradation	Prolonged retention time of POME in the MBR is needed for decolorization	30% COD removal rate achieved	Neoh et al. (2017)
Microbial fuel cell (MFC)-Adsorption hybrid system	The combustion catalytic oxidation can effectively analyze all organic compounds in the wastewater	Down flow mode results to clogging thereby minimizing organic removal	90 ± 0.3% COD removal achieved	Tee et al. (2016)
Ultrasound cavitation-adsorption hybrid system	Higher efficiency of COD removal achieved at shorter operational time	Breakdown of the granular activated carbon by the energy released during cavitation time increases the concentration of the suspended solids	73.08% COD 98.33% TSS	Parthasarathy et al. (2016)
Upflow anaerobic sludge blanket (UASB)	High hydraulic loading rate. Low quantity of sludge produced	Lower organic loading rate If pH is not controlled, acidenogenic biomass buffers itself to a pH which depends on other environmental conditions	90% removal of COD achieved at initial loading of 1.1 $gL^{-1}d^{-1}$	Borja et al. (1996)

(*Continued*)

Table 1-3 (Continued)

Anaerobic Treatment System	Advantages	Disadvantages	Removal Efficiency (%)	Authors
Upflow anaerobic sludge fixed film (UASFF)	Hybrid reactor which combines the advantages of UASB	Lower OLR for the treatment of suspended solids	97% removal of COD at 11.58m^3/day OLR, 3 day HRT achieved	Poh and Chong (2009)
Upflow anaerobic sludge blanket –hollow centered packed bed (UASB-HCPB)	Shorter hydraulic retention time (HRT)	A shorter HRT causes problem of sludge wash out due to high upflow shear force.	88% COD, 90% BOD at an OLR 28.12 g COD L day	Poh et al. (2014)
Extended granular sludge blanket (EGSB)	Higher loading rates enhances the efficiency of the reactor	Requires the granulation of the anaerobic sludge. Also, the surface of the scum may affect pipes of the system	0.44 m^3 biogas/kg COD produced. 65%–70% CH_4, 25.36% CO_2 and 800–1500 ppm of H_2S.	Wang et al. (2015)
Integrated anaerobic–aerobic bioreactor (IAAB)	Higher loading rate and shorter HRT	Constraints of availability of sufficient land for pond and the length of HRT	>99% removal of COD, BOD and TSS achieved at 10.5 g COD/day with methane yield of 0.24 L CH_4/g	Chan et al. (2012)
Upflow anaerobic sludge fixed film (UASFF)	Combines the function of UASB reactor and the immobilized cell called fixed film	Instability at prolonged retention time and high influent concentration of COD Sludge wash out occurrence due to the accumulation of TSS because of the inability of the fixed film bed to penetrate small size flocs	90% initial COD removal and at further increase, 82.4% COD removal achieved	Zinatizadeh et al. (2006)
Integrated baffled reactor inoculated with anaerobic pond sludge	High organic loading rate achieved	Increase in OLR results to the decrease in methane content	COD removal at 79% and 83% at HRT 4 and 6 days respectively	Malakahmad et al. (2014)
Upflow anaerobic sludge blanket reactor (UASBR)	It is very cheap and efficient at high OLR	The quality of sludge produced determines the stability of the treatment system	87% COD, 91% CH_3 achieved	Ahmad et al. (2005)
Continuous stirred tank reactor (CSTR)	Suitable for the treatment of substrates with high suspended solids	A deflector needs to be installed to promote the retention of suspended solids in the reactor	80% of COD removal achieved	Khemkhao et al. (2015)

Anaerobic systems are well acceptable technology because of its low construction and maintenance cost, low sludge production, small land requirements and biogas production as renewable energy. The treatment of POME undergoes different stages such as the sequences in the cooling pond, mixing pond, anaerobic pond and the facultative ponds. Yacob et al. (2006) treated POME using the anaerobic pond, in their findings, 97.8% removal of COD and between 35%–70% productions of CH_4/CH_2 was achieved. Also, Zahrim et al. (2014) achieved 93.9% removal of COD and 88.7% removal of TSS using the open ponding system. However, the limitation with the ponding system is the requirement of large land area for the treatment. Nowadays, 50% of mill operators treat POME using anaerobic digester systems (Ahmad, 2016). Nour and Nour (2017) treated POME using the ultra sound membrane anaerobic system. In their study, they achieved between 92.8%–98.3% removals of COD at short hydraulic retention time (HRT) between 8.2 and 500.8 days. High cost of setting up the membrane system makes the method not suitable for research.

Researches have demonstrated that anaerobic systems such as the sequencing batch reactor (SBR), membrane bioreactor (MB), up-flow anaerobic sludge blanket (UASB), up-flow anaerobic sludge fixed film (UASFF), up-flow anaerobic sludge blanket reactor (UASBR), continuous stirred tank reactor (CSTR) and extended granular sludge blanket (EGSB) can be used to treat high-strength industrial wastewater such as POME. Borja et al. (1996) were the foremost researchers who worked on UASB for the treatment of POME. In their findings, 90% COD removal was achieved at initial loading rate of $1.1\ g^{-1}d^{-1}$. This was obtained at high loading rate and low quantity of sludge was produced. The major challenge with the reactor was that if pH is not controlled, there is tendency for acidogenic biomass to buffer itself to a pH which is dependent on other environmental conditions. The UASBR was used by Ahmad et al. (2005) for the treatment of organic pollutants of POME. The reactor achieved 87% removal of COD and 91% production of CH_4. The method is cheap and very efficient at high OLR but the quality of sludge produced determines the stability of the reactor. The use of EGSB was reported by Wang et al. (2012) for the treatment of POME. It was observed that at high loading rate, $0.44\ m^3$ biogas/kg COD was produced. This contains 65%–70% CH_4, 25%–36% CO_2 and 800–1500 ppm of H_2S. Similarly, the CSTR was very suitable for the reduction of COD in the POME, even though there were high suspended solids, 80% removal of COD was achieved.

In some cases, reactors are combined and are used as hybrid system and have been reported in the literature for the treatment of POME. For example Poh et al. (2014) investigated the treatment of POME using the up-flow anaerobic blanket-hollow centered packed reactor (UASB-HCPB). The hybrid reactor achieved 88% COD removal and 90% BOD removal at an organic loading rate (OLR) of 28.12 g/COD. L.day. The result was achieved at a very short HRT. However, a reduced HRT may result to problem of sludge wash out due to high up-flow shear force. The use of integrated anaerobic-aerobic bioreactor (IAAB) achieved $>$99% removal of COD, BOD and TSS at 10.5 g/COD/day with methane yield of 0.24 L CH_4/g. The constraint with the method is the problem of availability of sufficient land and the length of HRT. Also, Malakahmad et al. (2014) reported the use of integrated baffled reactor inoculated with anaerobic pond sludge. In their findings, it was observed that high organic loading rate favoured 79% removal of COD at HRT of 4 days and 83% removal at HRT of 6 days. The UASFF was used as hybrid reactor with the functions of the UASB (Poh and Chong, 2009). The result of the hybrid system achieved lower loading rate for the treatment of suspended solids but achieved 97% removal of COD at 11.58m^3/day OLR which was achieved at 3 day HRT. The performance evaluation of up-flow anaerobic sludge fixed film (UASFF) was compared at mesophilic temperature for the treatment of POME with UASB and AF (Ohimain and Izah, 2017). The performance of the reactor has high organic loading rate (OLR) better than UASB and AF, the reactor could produce 71.90% methane under OLR of 11.58 kg COD m^3/day. The anaerobic hybrid reactor was used to remove 64% of total COD higher than the removal rate in the UASB reactors.

The anaerobic hybrid reactor was used to remove 64% of total COD higher than the removal rate in the UASB reactors. The membrane anaerobic system (MAS) was utilized for the treatment of POME (Nasrullah et al., 2017). The ultra sound membrane anaerobic system was used in the study of (Nour and Nour, 2017) for the investigation of the adsorption of COD from POME. The removal of COD (92.8%—98.3%) demonstrated the effectiveness of the system. The membrane bioreactor in Neoh et al. (2017) resulted to 30% of COD removal which indicated less suitability of the treatment system. The treatment effort was less effective due to the deterioration of membrane flux rate as a result of membrane fouling, which have the possibility of affecting the treatment process. Furthermore, the periodical replacement of membrane as a result of fouling is very expensive and not sustainable for research. The membrane fouling can be reduced with faster cross flow feed velocities and regular membrane flushing.

The conventional activated sludge requires a lot of energy for the purpose of aeration. It also produces a large quantity of sludge that makes the cost of treatment and disposal very expensive. In the study of (Nor et al., 2015) anaerobic palm oil, mill effluent resulted in high electricity generation, which is inversely proportional to the removal of COD. Aerobic treatment method involves the presence of oxygen for the stabilization of organic matter in wastewater. In the investigation of Fulazzaky et al. (2017), POME samples obtained from the treated anaerobic pond was further treated using the sequencing batch reactor, very good settling ability of the reactor was observed with high biomass retention time. In the investigation, 94% COD removal was observed in the treatment process. Aerobic treatment can be combined with physical method of treatment, such as adsorption in a hybrid system, for the improvement of the treatment process. In the study conducted by Tee et al. (2016), the investigation of microbial fuel cell —adsorption hybrid system for the treatment of POME was conducted. It was observed that the removal of COD was effective due to the combustion catalytic oxidation of the organic matter in the POME. About 90.5 ± 0.3% of COD removal was observed. Parthasarathy et al. (2016) conducted an experiment for the removal of COD and TSS from POME using a hybrid system that combines ultrasound cavitation-adsorption system. It was observed that the breakdown of granular activated carbon by the energy release at increase cavitation time during cavity increases the concentration of suspended solids. From the result of the investigation, 73.08% and 98.33% of COD and TSS was removed respectively.

1.3.3 Physical and Chemical Processes of POME Treatment

Physical processes involved in the treatment of POME includes process screening, sedimentation, and oil removal before secondary treatment in biological treatment plants. Some of the other methods in Table 1-4 are the ultrafiltration, solvent extraction, reverse osmosis coagulation, electrocoagulation, coagulation-flocculation, floatation.

Acidification of pond and flocculation treatments are advanced pretreatment processes, also includes the use of membrane (Hojjat, 2009). The researchers demonstrated that the centrifugation and coagulation methods gave better pretreatment quality than filtration method. The separation of effluent from activated sludge can be done at a low-pressure using either the microfiltration (MF) or ultrafiltration (UF). Ultrafiltration has been reported in the literature as a useful technology for the treatment of POME. The choice of the selection of membrane depends on the effect it has on the target pollutants. The hydrophobic membranes have high retention capacity than hydrophilic cellulose membrane for the treatment of protein compounds in POME (Wu et al., 2007).

Hydrophobic membranes have more inclination to retain hydrophobic solutes on the surface of the membrane better than hydrophilic membranes. The result of the ultrafiltration using polysulphone membrane was investigated in Wu et al. (2007). The result obtained showed 97.7% removal efficiency of TSS, 88.8% reduction of turbidity, 6.5% TDS removal and 57% removal of COD. In addition, the effectiveness of the ultrafiltration membrane achieved 71.26% removal of SS (Azmi and Yunos, 2014). Mixed matrix membrane was also used in the study for the treatment of POME. According to Ho et al. (2017), the POME used for the treatment was secondary effluent after undergoing pretreatment processes.

The constraint with the use of membrane is the problem of fouling, which increases process down time due to damage. A variety of chemicals can be used for flocculation treatment purposes. Flocculation is the addition of chemicals (coagulants) to destabilize and aggregate colloidal particles in wastewater. A flocculants are usually organic chemicals added to wastewater to enhance flocculation, such chemicals are alum, aluminium chlorohydrate, aluminium sulphate etc. Natural materials such as chitosan can also be used for flocculation purposes as a replacement for the expensive chemicals. Since suspended solids in POME are related with organic matter composition, therefore coagulants can be used effectively for the removal of colloidal and suspended organic solids but may not be very effective in the removal of dissolved organic matter (Rupani et al., 2010). In the study conducted by Zinatizadeh et al. (2017), coagulation was used for the pretreatment of POME, the result obtained showed the removal efficiency 96.4 and 70.9% of TSS and COD respectively.

The combination of coagulation and flocculation methods can improve on the reduction of the pollutants of POME. The use of coagulation-flocculation achieved 87% recovery of sludge in the study conducted by Bhatia et al. (2007), although high dosage of coagulant and flocculants were required in their investigation. Also the effect of the combined coagulation and flocculation was studied by Shak and Wu (2015) for the treatment of POME. The result of their findings revealed that 81.58% removal of TSS and 48.22% removal of COD was achieved which indicated the effectiveness of the treatment process for the reduction of

Table 1-4 Physical-Chemical Method of Treatment of Palm Oil Mill Effluent

Method	Parameter Investigated	Removal efficiency	Limitation	Author
Ultrafiltration membrane	TSS, turbidity, TDS, COD	97.7%TSS, 88.5% turbidity, 6.5% TDS, and 57% COD	Raw POME was pretreated and the result of the pretreatment was removal of 97.3% TSS, 88.5% turbidity, 6.5% TDS, and 46.9% COD	Wu et al. (2007)
Ultrafiltration membrane	SS	71.26%	Raw POME was pretreated using adsorption before further treatment using membrane	Azmi and Yunos (2014)
Ultrafiltration membrane	Color	58.9%	Aerobically treated used for the investigation	Subramaniam et al. (2017)
Solvent extraction	Oil and grease	71.1%	Higher temperature needed to evaporate *n*-hexane from the residual oil which may result to thermal decomposition of carotene pigment and as a result lower carotene concentration	Ahmad et al. (2005)
Mixed matrix membrane	Color, TSS, turbidity, COD, and chlorine	75.46%–88.52% color removal, 98.59%–100% TSS, 79.10%–89.30% turbidity, 62.91%–75.5% COD, and 64%–76% chlorine	Diluted effluent from the aerobic pond used for the investigation and also problem of fouling of membrane fluxes	Ho et al. (2017)
Coagulation	TSS and COD	96.4% and 70.9% respectively	Pretreatment using polymer induced coagulant and physical treatment methods	Zinatizadeh et al. (2017)
Electrocoagulation	pH, COD	Satisfactory pH of discharge (7.6), 75.4% COD removal	Treated secondary effluent used for the investigation	Bashir et al. (2016)
Coagulation-flocculation	SS	87% recovery of sludge	High dosage of coagulant and flocculants required	Bhatia et al. (2007)
Coagulation-Flocculation	TSS and COD	81.58% and 48.22% respectively	Not very effective for the removal of COD	Shak and Wu (2015)
Sedimentation and centrifugation	Oil and grease	80% of oil recovered with 27.67 ± 0.10 FFA	High temperature needed for evaporation after centrifugation and sedimentation	Suwanno et al. (2017)
Flotation	COD	53.7% COD removal at 12.5 minutes contact time	Secondary treated POME was investigated and treated effluent not satisfactory for discharge	Poh et al. (2015)
Combined air floatation and membrane	COD	36.1, 26.8 and 26.6% removal achieved	Removal lower than micro bubble floatation used in the study of Poh et al., (2015)	Faisal et al. (2016)

(*Continued*)

Table 1-4 (Continued)

Method	Parameter Investigated	Removal efficiency	Limitation	Author
Photocatalysis	COD	Ag/ TiO_2 achieved better photocatalytic degradation of POME better than TiO_2	Adsorption −desorption equilibrium achieved before photo catalytic reaction	Cheng et al. (2016)
Photocatalysis	COD	55% removal of COD was achieved	POME from the discharge pond used for the treatment	Ng and Cheng (2017)
Photocatalysis (Tungsten oxide photocatalyst)	COD, pH and color	51.15% COD removal and 96.21% color removal	Adsorption process is needed for the organic pollutants before photocatalytic process occur.	Cheng et al. (2016)
Electro persulphate oxidation	COD, color, and SS	77.7% of COD, 97.96% of color and 99.72% SS.	Combined the effect of electro-oxidation, electro-coagulation. Also, secondary effluent was used for the treatment	Bashir et al. (2017)
Fenton oxidation	COD and color	85.15% COD removal, 92.1% color removal	Secondary effluent treated before discharge	Saeed et al. (2015)
Sono-Fenton oxidation Fenton process	COD	80% removal	Combined ultrasound and Fenton process	Taha and Ibrahim (2014a)
Aerated heterogeneous	COD	75% removal achieved	Secondary effluent after anaerobic treatment investigated	Taha and Ibrahim (2014b)
Ambient Fenton oxidation	COD, Color	75.2% COD and 92.4% color	Biologically treated POME was used for the treatment	Aris et al. (2008)

suspended solutes. The use of electrocoagulation was used in the investigation of Bashir et al. (2016) for pH and COD concentration in POME. However, the result of the investigation revealed that the pH after treatment satisfied the discharge standard while 75.4% removal was achieved for COD removal. Evaporation process can also be used for the treatment of POME when POME containing 3%–4% total solid as feed, about 85% water composition in POME can be recovered by distillation. The limitation with the process of evaporation is the energy requirement where the energy consumption rate is very high (kg of stream required 1 kg of evaporated water) (Hazlan, 2006).

The gravity type oil separator can be used for oil separation in POME with low suspended solids. The trapped oil is usually designed for maximum flow rate at a permissible surface loading rate of 2–6 m^3/m^2h. To ensure effectiveness of the oil separator, an automatic skimming device is usually installed to help in the recovery of good quality oil. The efficiency of oil separation by the gravity type POME wastewater stream is in the range of 60%–90% (Wang et al., 2013). Solvents extraction was reported by Hammed (2003) as very effective for the removal of residual oil from POME with the percentage removal to increase with increase of mixing time, mixing ratio and mixing rate for all solvents. Ahmad et al. (2005) conducted experiments for the removal of oil and grease using solvent extraction. In their findings, 71.1% removal efficiency was achieved after the treatment process of the POME. However, high temperature was needed to evaporate *n*-hexane from the residual oil, which may result to thermal decomposition of carotene pigment in the POME. Similarly, Suwanno et al. (2017) studied the removal of oil and grease using sedimentation-centrifugation process. The result obtained revealed that 80% of oil was recovered with 27.67 ± 0.10%.

Chemical oxidation involves the use of oxidizing agent in the treatment of wastewater to oxidize the organic pollutants. The use of advanced oxidation is very common in the treatment of high strength wastewater such as POME. Some other advanced oxidation methods are photocatalysis, electro persulphate oxidation, Fenton oxidation, Sono-Fenton oxidation, Solar Fenton oxidation, aerated heterogeneous Fenton process, ambient Fenton oxidation.

The Fenton oxidation is a novel technology because of its simplicity and high removal efficiency of pollutant removal without any need for specialized equipment. The Fenton oxidation utilizes the principle of exchange of reactive hydroxyl radicals (. OH)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH \tag{1.1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{3+} + OOH + H^+ \tag{1.2}$$

A modified electron-Fenton process (EF) was developed to solve potential transportation risk ofH_2O_2, loss of reactivity and sludge production. The EF method effectively controls hydroxyl radical production and reduction of soluble Fe^{3+}cathodically toFe^{2+}. This principle is known as electrochemical catalysis (Barhoumi et al., 2016). The removal efficiency of EF is dependent on the production of H_2O_2 and Fe^{2+}cation, pH, density of current and concentration of electrolyte. Fenton oxidation consists of the reaction of the hydroxyl radicals on the alkyl chain of fatty acids of POME. The OH^-have strong affinity to destroy the aromatic ring attached with hydroxyl group in fatty acids. This results in the formation of water soluble compounds through removal of hydrogen and addition of oxygen atoms with the presence of ferric ions. An experiment using Fenton oxidation was conducted by Saeed et al. (2015) for the removal of COD and color from POME. The result obtained demonstrated that 85.1% COD and 92.1% color removal was achieved. However, the POME used for the study was obtained from the secondary treated effluent before discharge. Sono-Fenton method combines ultrasound and Fenton process for the treatment purposes. The combined process achieved 80% removal of COD (Taha and Ibrahim, 2014a). Aerated heterogeneous Fenton process also achieved 75% removal efficiency of COD from POME sample obtained from the treated effluent from the anaerobic pond (Taha and Ibrahim, 2014b). Ambient Fenton oxidation was used for the removal of COD and color using biologically treated POME for the investigation, the process reduced COD by 75.2% and color by 92.4%. The EF treatment process was used to study the changes in POME characteristics for 2 hours. It was observed that 46% removal efficiency of COD was obtained. Furthermore, the pH was observed to have increased from 5.3 to 7.4. This range of pH can be considered valuable for the effective reduction of COD, BOD, TOC, and TN (Babu et al., 2010).

The removal of organic pollutants from POME can be investigated under the influence of light by using conductor materials as catalyst. The process is known as photocatalysis. The photo catalytic degradation of POME for the reduction of COD was more effective using Ag/TiO_2 than with TiO_2 (Cheng et al., 2016). Also Ng and Cheng (2017) investigated COD removal from POME using photocatalysis. From their investigation, 55% removal of COD was achieved in the treatment process. The removal of COD, pH and color using Tungsten photo catalyst achieved 51.15% COD and 96.21% color removal in the study of Cheng et al. (2016).

The disadvantages of the conventional treatment methods include, large area required for the anaerobic ponds, high cost of routine maintenance is required for the reactors. Similarly, the methods are expensive and are not suitable for the treatment of POME at low concentration. In some other treatment processes using the physical and chemical methods such as coagulation and flocculation processes, there is the requirement of high dosage of adsorbent which may affect the pH of the treated POME and the use of membrane may be very expensive for the treatment of POME. Advanced oxidation such as Fenton oxidation and photocatalysis requires energy for the degradation of the POME.

However, the application of adsorption is a novel method of treatment of high strength wastewater such as POME, dyes and petrol chemical solutions. Adsorption process is affected by the nature of the adsorbate, adsorbent material, presence of other pollutants in solution and also atmospheric and experimental conditions.

1.4 Adsorption

Stability of emulsion is very important in terms of application and storage. Emulsion is an equilibrium system, but thermodynamically unfavorable systems, which tend to break down over time due to a number of physicochemical mechanisms, containing gravitational separation, flocculation, coalescence and Ostwald ripening (Dickinson, 1992; Friberg et al., 2004).

Adsorption is a valuable technology in the treatment of industrial wastewater. It is a very popular treatment method among other methods of industrial wastewater because of the simplicity of operation and efficiency of the treatment process. The method of adsorption has the capacity of treating high quality effluent with proper design consideration better than other chemical methods such as coagulation (Acero et al., 2016). Adsorption is the process through which substances present originally in one phase is removed from that phase by accumulation at the interface between the phase and a separate phase. Adsorption can take place at any solid liquid interface by the accumulation of a solute onto the adsorbent during the adsorption process. The adsorbate accumulates on the solid surface with interaction on the surface of the adsorbent. Such interaction is influenced by the pH of the medium, ion exchange, acid-base interactions, hydrogen bonding, hydrophobic and hydrophilic interactions and precipitation (Lalley et al., 2016).

Adsorption is used for the treatment of many industrial wastewaters because industrial wastewaters are toxic and difficult to remove through conventional secondary treatment methods. The substances are present in small concentrations and their removal becomes very difficult using other methods. The rate of adsorption is affected by the nature of the adsorbents, the concentration of adsorbate and the efficiency of the adsorption system. Adsorbents are materials that adsorbs wastewater pollutants while the adsorbate are the substances to be adsorbed. Pore structure of the adsorbate, pH of the solution, presence of inorganic salts, interacting solutes, temperature, pressure and the activation of the adsorbents are other factors that affect the adsorption of substances in water.

Adsorption can be classified into two types based on the nature and the interaction between the adsorbate molecules and the adsorbent surface. The classification could either be based on the process of physiosorption or chemisorption. Both types occur either in the gas–solid interface or liquid–solid interface due to the attractive forces at the surface adsorbent overcoming the activation energy of the adsorbent molecules (Ali, 2012).

1.4.1 Principles of Adsorption

Physiosorption is also called physical adsorption, which is a process whereby electronic arrangement of the molecules is affected by interactive forces called van der Waals forces. The van der Waals forces of the adsorption molecules occur as a result of the interaction between temporary and permanent electric dipoles. The adsorbed particles are very far from the surface plane but very active on the surface due to low binding energy. The desorption temperature is low as a result of the physiosorbates weak forces of interaction. In the process of physiosorption, single or multiple layers of the adsorbate molecules on the adsorbent surface occur as a result of low activation energy of adsorption (20–40 kJ) (Rouquerol et al., 2013). In the process of the interaction, there is spontaneous wetting of the surface of the adsorbent when in contact with the adsorbate, also there is tendency of the adsorbent material to dissolve in the adsorbate.

1.4.2 Chemisorption

The process of chemisorption of the adsorption system is otherwise referred to as chemical adsorption, which is defined as the process that occurs under the influence of chemical bond as forces of attraction between the adsorbed molecules and the adsorbent. Chemisorption occurs at very high temperature and the energy of adsorption exists between (200−400 kJ/mol) (Rouquerol et al., 2013). The activation energy is usually very high at high pressure. The result obtained is a monolayer of the adsorbate attached to the surface of the adsorbent. Both physiosorption and chemisorption are affected by adsorption parameters such as pH, contact time, agitation speed, particle sizes, initial concentration, temperature and cationic exchange capacity (CEC). These parameters each have effect on adsorption process and determines the rate of adsorption of solutes onto the adsorbent. In addition, the pH of both the adsorbent and adsorbate is very significant to the process of adsorption. On the surface of the adsorbent media, the condition when the electric charge density on the surface is equal to zero is referred to as the point of zero charge (pzc). It is the pH value when the number of cations and anions on the surface of the adsorbent are equal. The pH_{pzc} is described in terms of the concentration of the solution. In cases whereby the pH of the solution is lower than the pH_{pzc}, the acidic medium donates more protons than the hydroxide group. Hence, the adsorbent surface is positively charged. The surface favours the adsorption of anions from the solution. On the other hand, when the pH of the solution is above pH_{pzc}, the surface of the adsorbent is negatively charged, in this instance, adsorption of cations from the solution is more favorable. An example of pH_{pzc} can be obtained by plotting a graph of final concentration pH of adsorbent against the initial concentration by adjusting the solution using HNO_3^- and NaOH (Fig. 1-2).

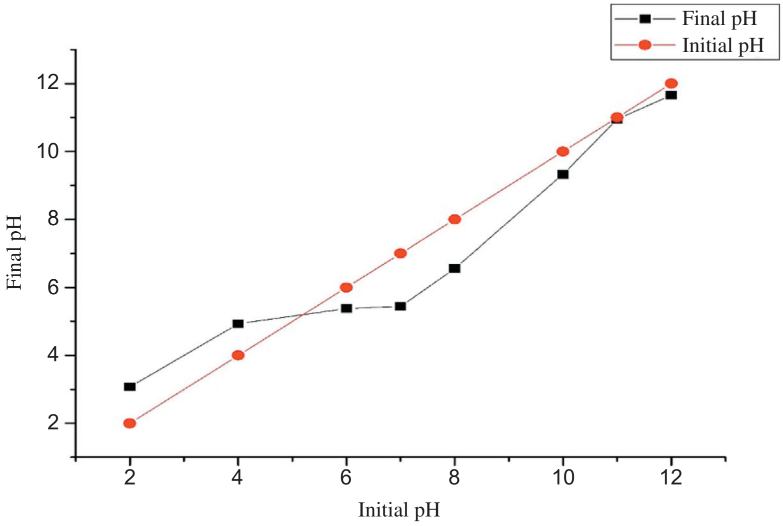

FIGURE 1-2 Point of zero charge.

The CEC is defined by the amount of negatively-charged sites that is available on the surface of the adsorbent, which has the capacity to retain positively charge ions, otherwise known as cations, such as Ca^{2+} Mg^{2+} and K^{+} by the process of electrostatic attraction. The cations retained as a result of the electrostatic force are easily exchangeable with the cations in the wastewater. Adsorbents with higher CEC has the potential to engage in cationic exchange in solution than those with lower CEC.

1.4.3 Wetting and Fluid Adsorption

The concept of wetting is the response observed when a liquid is in contact with a solid surface (Bormashenko, 2013). According to Bornashenko, the liquid could spread spontaneously resulting in a film dependent on the mass of liquid available. When a liquid drop rests on the horizontal solid surface, an angle is formed by the liquid—solid interaction and the liquid vapor interface. The inclination to the surface is called contact angle, which is observed as the interfacial coexistence of the solid, liquid, and vapor phase. A contact angle less than 90 degrees shows favorable wettability of the liquid on the solid surface. In a case of contact angle greater than 90 degrees, it indicates low wettability of the liquid on the solid surface. When the contact angle is greater than 90 degrees, it signifies low wettability and the result is an unfavorable wetting on the surface. For a contact angle less than 90 degrees, the liquids drifts spontaneously into smaller pore spaces in contact, such condition is referred to as hydrophilic behavior. At higher contact angle, the liquid requires energy to be in contact with the solid surface, thus the liquid minimizes its contact forming a well-rounded liquid droplet. This property is referred to as hydrophobic behavior. When the contact angle is zero, the condition is known as complete wetting case. The droplet becomes flat with the solid surface. The spreading of the liquid develops films spontaneously on the surface. The surface tension of a liquid is used to determine the shape of the droplet of the liquid. The mechanism involves the molecules being pulled equally in all direction by adjacent liquid molecules leading to resultant net force of zero. The effect of this is not limited to the molecules at the surface thereby causing no interaction between adjacent molecules to provide a balanced net force. They are pulled inwardly by the adjacent molecule; this results to an internal pressure. The liquid contacts its surface area to maintain lowest surface free energy. Surface tension and contact angles are the results of intermolecular forces. The application of contact angle is to have the description of the behavior of the adsorbent when in contact fluid. It gives valuable understanding whether the adsorbent material have affinity and interaction with water. In other words, they can easily be covered by film of water, the behavior of such material is known as hydrophilic properties of the media. The application of contact angle also gives the description of the adsorbent properties from resisting wetting by the adsorbate. The property of materials showing such behavior is hydrophobic in nature.

1.4.4 Hydrophobicity of Adsorbent Material

When hydrophobic particles are suspended in water, they have tendency to interact with particles of their kinds rather than with water. Typical example is the oil droplet, because of this trend, hydrophobic particles suspended in water has the physical nature of voids in the bulk solution. The consequence of such behavior results in the expansion and breaking of hydrogen bonds between water particles. The effect of the breaking of the hydrogen bonding as a result of expansion brings together the hydrophobic particles immersed in water. This can be achieved through the following mechanisms. When two hydrophobic particles immersed in water and cluster, the surface area of the coalesced particle is smaller than the sum of the surface areas of the combining particles. As a result of this, the energy leading to the breaking down of water particles proportional to the surface area of the particles decreases as a result of coalescence of the particles. This makes the process leading to coalesces thermodynamically spontaneous. The interaction of the molecules is achieved at a higher state of entropy and this is the reason causing nonpolar molecules such as oil and grease, hexane, and organic solutes to clump together. They readily dissolve in nonpolar solvent. The process of clumping together of the nonpolar molecules reduces the surface area exposed to water, hence decreases the entropy of the system (Davies, 2012).

When two hydrophobic particles move together and combine, the free energy of the system favours the attachment of the particle to the surface (Mitik-Dineva et al., 2009). The more the surfaces are hydrophobic, the more strongly they cluster together (Lewandowski and Beyenal, 2013). For two molecules to be in contact, the attraction energy is about six times greater in water than the interaction of van der Waals in vacuum. There is an assumption by researchers that the small hydrophobic areas available on the surfaces of microbial cells are mainly responsible for the adherence of microorganisms to hydrophobic surfaces (Ferrara et al., 2013). The dissolved organic matter in an effluent is characterized by the hydrophobicity of the medium (Xia et al., 2015). Adsorption of organic molecules was effective using hydrophobic nano-gel in oil-in- water emulsion study (Wang et al., 2012). Activated carbon is widely known for its hydrophobic properties and also very effective as a catalytic support for the reduction of organic pollutants such as COD mg/L and other toxic compounds in wastewater. Increased hydrophobicity of carbon surface improves adsorbate-adsorbent interactions. The effectiveness of the removal by sorption depends on the hydrophobic nature of the aqueous organics (Pradhan et al., 2016). The ability of microorganism to adhere can be determined by the effectiveness of interacting forces such as Vander Waals, Coulomb, electrostatic as well as hydrophobic interactions. Among the noncovalent forces, hydrophobic interactions at nano level at medium range is considered as the most relevant in water and also electrostatic interactions in the short range (Hannig and Hannig, 2009). Hydrophobicity of a material is also dependent on the interactions with the spaces that result to changes in the membrane structure and morphology. The material membrane can be wetted by nonpolar phase such as nonpolar organics where the aqueous polar phase cannot penetrate into the pores (Drioli et al., 2011). The two phases are immiscible because the operating pressure is controlled. However, the pressure of the polar phase must be equal or greater than the pressure of the wetting phase. This will avoid the possibility of dispersion of drops from one phase to another. The interfacial area is established as the pore mouth if the penetration of the polar phase into the membrane pore is avoided. Hydrophobicity of material is not an absolute guarantee for keeping the pore spaces.

1.4.5 Hydrophilicity of Adsorbent Materials

When hydrophilic materials combine with water, a thermodynamic interaction is more favorable than the interactions with oil or other hydrophobes. The particles are charged-polarized and have strong ability to engage in hydrogen-bonding. This results in the adsorbent material to be soluble in water and other polar solvents. In hydrophilic medium, solid–liquid interface is more favorable resulting in contact angle to be less than 90 degrees (Nguyen, 2016). In the process of hydrophilic interaction, the water drop on the substrate aligns with the topography which results in the decrease of the contact angle. The moisture also spreads within the substrate and coexists with the solid filled with liquid. In a situation of partial wetting, the Wenzel contact angle is decreased but greater than zero (Grundke et al., 2015). Zeolite is often classified as hydrophilic materials which may be spherical or granular in nature. The rate of diffusion of inorganic materials is slow because of smaller pores. For macroporous structure, diffusion rate within the pores are higher than the rate of diffusion of ion in water. As the pore becomes large, there is transportation of the molecular ions through the pores by convection and diffusion. The importance of short diffusion can be achieved by developing composite materials with small particles forming into large particles (Andaç and Denizli, 2014). Hydrophilic materials are soluble in polar and have contact angle <90 degrees, also materials soluble in nonpolar solvents are hydrophobic and have contact angle >90 degrees (Shirtcliffe et al., 2010). Adsorption is readily and rapidly reversible on hydrophilic materials than hydrophobic surfaces (Park et al., 2015).

1.5 Treatment of POME Using Adsorption

Many conventional methods such as the membrane system, open ponding, anaerobic reactors are used in the treatment of POME, recent advancement in research on the treatment of industrial wastewater such as POME using adsorption is a novel technology for the removal of heavy metals and other pollutants contained in low concentration in POME. Experimental data to predict the efficiency of the adsorbent for the adsorption of solutes in wastewater are often fitted to empirical models in order to predict the pattern of adsorption. A study was conducted to investigate the removal efficiency of residual oil from POME using powder and flake chitosan. (Ahmad et al., 2005). The initial concentration of residual oil was 2 g/L contained in POME. The weight dosage, contact time and pH of chitosan both in powder and flake form were investigated to obtain the optimum condition for the adsorption of the residual oil from POME. It was observed from results that chitosan powder at dosage of 0.5 g/L, 15 minutes of contact time and pH value of 5 represented the most optimum condition for the adsorption of residual oil with a removal efficiency of 99% achieved. The powdered form of chitosan demonstrated better adsorption rate compared to the flake chitosan. Igwe et al. (2013) also studied the removal rate of residual oil from POME using boiler fly ash. The percentage residual oil uptake reduced from 80% to 5% at an increased contact time from 10 to 120 minutes. As the initial concentration of the residual oil increased from 0.04812 to 0.2406 mg/L, the adsorption rate increased from 2.74% to 72.98%.

The maximum mono layer adsorption capacity was 0.3476 mg/g. The result revealed that boiler fly ash was a very good adsorbent for the removal of residual oil from POME. In addition, Ahmad et al. (2005), adsorbed residual oil of POME using synthetic rubber, from their investigation, there was effective removal of oil and grease up to 88% reduction was obtained. This was achieved at a contact time of 3 hours, agitation speed of 150 rpm obtained at pH of 7. It was observed that the adsorption process fit in properly to the Freundlich isotherm model with R^2 value of 0.9721.

Similarly, low cost adsorbent using waste activated sludge (WAS) from POME treatment plant was used to adsorb ammonium from aqueous solution (Muttalib, 2012). The investigation was done in a batch test to determine the effect of initial concentration, temperature, pH and adsorbent dosage on the aqueous solution. The result of the investigation showed that the ammonium removal increased with increasing pH, initial concentration of ammonium and adsorbent dosage but decreased with temperature. The adsorption of ammonium agrees with Langmuir and Freundlich isotherm, which are the most applied empirical isotherm models to predict the nature of the adsorption process. Langmuir model predicts the adsorption of pollutants from the adsorbate on a monolayer surface while the adsorption on heterogeneous surface is best described by fitting experimental data to the Freundlich isotherm model. Other forms of isotherm model such as the Temkin model describes the heat of adsorption between the adsorbent and the adsorbate. Low cost adsorbent media can also be effective for the reduction of heavy metals in the wastewater. In the study conducted by Adeleke et al. (2017), the reduction of zinc from POME was investigated using coconut shells and cow bones under fixed condition of pH 7, 105 minutes contact time and 150 rpm shaking speed, it was observed that more than 90% removal efficiency was achieved for each of the adsorbents used. The experimental data fitted to the isotherm model revealed that the BET model is more suitable for the adsorption of zinc on coconut shell while the Langmuir model better expressed the pattern of the uptake of zinc ion from the experimental data using the activated cow bone powder. Lau et al. (2013) prepared palm shell activated carbon (PSAC) by steam activation for the removal of H_2S from biogas studying the initial concentration, adsorption temperature and space velocity. The effect of the parameters was studied to determine the rate of adsorption of H_2S from aqueous solution. The effect of temperature on adsorption did not have major effect on the adsorptive capacity of H_2S onto palm shell activated carbon.

The adsorption of POME using banana peel was investigated by modifying the carbonyl group of the peel by the method of esterification using acidic methanol at a carbonized temperature of 500 °C for 1 hour (Mohammed and Chong, 2014), the result of the investigation showed that BET surface area of 24.2572 m^2/g was achieved. WAS from palm oil mill effluent was used for the adsorption of methylene blue (MB) in a batch study (Gobi et al., 2011), the maximum mono layer adsorption capacity of WAS was found to be 66.23 mg/g at 30°C, the adsorption kinetic fitted well to the pseudo-second—order kinetic with R^2 of more than 0.95 recorded. The application of batch adsorption study for the removal of Cd was investigated in the study of Adeleke et al (2016) using activated cow bone powder as adsorbent, the result obtained revealed that optimum condition of adsorbent dosage was recorded at an average of 97.37% reduction achieved for the duplicate sample. It was observed that the least uptake of Cd was achieved using 30 g adsorbent dosage at 95.1% removal efficiency for both samples. The effect of palm oil mill fly ash (POFA) for the adsorption of Cd (II) and Cu (II) ions from aqueous solution through column studies was investigated by Aziz et al. (2014), the effect of the column dynamics and the break through curve was analyzed from the study. The result of the investigation showed that the highest bed capacity was recorded as 34.91 mg Cd (II)/g and 21.93 mg Cu (II)/g of POFA at 20 mg/L of influent metal concentrations, column bed depth of 20 mm and flow rate of 5 mL/min. The break through curve for both Cd (II) and Cu (II) fit properly to Thomas and Yoon-Nelson models, the initial breakthrough region was better illustrated using the BDST model. However, the result revealed that POFA (palm oil fuel ash) can be effectively utilized for the adsorption of Cd (II) and Cu (II) ions from aqueous solution in a fixed bed column.

The adsorptive capacity of natural zeolite for heavy metal ions removal was investigated by (Shavandi et al., 2012). The metals studied were Zn (II), Manganese (II) and Iron Fe (III). The initial concentration of dosage on the adsorption of the heavy metals as well as the contact time, agitation time, speed, pH was studied. The optimum adsorption was achieved at equilibrium contact time of 180 minutes. The sorption increased with pH and the rate of adsorption was in the range of 0.015 and 1.157 mg/g of zeolite. More than 50% of Zn (II) and Mn (II) and 60 % of Fe (III) were removed. The removal of oil from raw POME can be effective by using hydrophobic adsorbent material that has the ability to adsorb pollutants in the nonpolar phase (Adeleke et al., 2017). In the study conducted by Wahi et al. (2017), 80.23% oil was recovered from raw POME immediately after the milling process at optimum pH 4.18 at 24 hour contact time at 30°C. Similarly, Abdullahi et al. (2015) achieved 96%—99% removal of oil using structurally modified raw kapok fiber (Ceiba Pentandra). A summary is illustrated in Table 1-5.

Adsorption technique for the treatment of wastewater has shown great potentials above other treatment methods for the removal of organic pollutants. Adsorption has advantage over other treatment methods because of the simplicity of the design, it is cost effective and saves problem of land availability. The adsorption technology has successfully been proven as an effective treatment method for POME. The application of adsorption for the treatment of industrial wastewater has received a lot of attention from researchers. However, the search for low-cost adsorbent material with pollutant-binding potentials has increased over the years. Materials sourced from industrial, agricultural wastes and natural materials can be used as adsorbents for the treatment of industrial wastewater. The effectiveness of the sourced materials should be applied based on the potentials for the treatment of target pollutants. For example, the adsorption of polar and nonpolar solutes can be effective on the nature of the adsorbent material with pollutant binding effect (Adeleke et al., 2016). The method of adsorption also can be widely applied with other methods for effective treatment of high strength industrial wastewater. The combination of magnetic field and adsorption process has been reported to enhance adsorption process (Mohammed and Chong, 2014). The result of their findings demonstrated that magnetization process could accelerate the removal of color, TSS and COD in adsorption process, the percentage reduction of color, TSS

Table 1-5 Adsorption of Palm Oil Mill Effluent Using Local Adsorbent Materials

Adsorbent	Removal Efficiency	Limitation	Authors
Rubber powder	88% removal of residual oil	Residual oil (0.6%–0.7%) is not considered critical parameter of POME	Ahmad et al. (2005)
Flake chitosan	99% removal of oil and grease	Residual oil not a critical parameter of POME	Ahmad et al. (2005)
Natural zeolite	66.638%, 58.575% and 61.51% of Fe, Zn and Mn respectively	Treated POME from aerobic pond (secondary treatment)	Shavandi et al. (2012)
Banana peel	Color, TSS, BOD, Tanin and Lignin (95.96, 100, 100, 97.41 and 76.74%)	Treatment was done before discharge after final stage of pond treatment	Mohammed and Chong (2014)
Activated Carbon	COD 10 mg/L and SS 2 mg/ L	After secondary stage before discharge	Othman et al. (2014)
Granular activated carbon	71.26% suspended solids	Adsorption was used for pretreatment before ultrafiltration membrane	Azmi and Yunos (2014)
Raw kapok fibers	BOD 74%–98%, Total organic carbon 72–94% and 66–80% total nitrogen	Modification of the adsorbent surface	Ahmad et al. (2005)
Montimorillonite	>95% of COD, TSS and color	Secondary effluent used for the treatment	Said et al. (2016)
Oil palm leaves (OPL) and oil palm fronds (OPF)	83.74% oil and grease removal using OPL and 39.84% of oil and grease using OPF	The modified OPL more hrdophobic surface than OPF	Jahi et al. (2015)
Activated carbon and ultrasound cavitation	73.08% COD removed 98.33% TSS removed	Treatment done after final stage before discharge	Parthasarathy et al. (2016)
Bioadsorbent	69% COD removal 96% removal of SS	Biologically treated palm oil mill effluent final discharge	Ibrahim et al. (2017)
Sago park fiber	80.23% oil removal achieved	Modification of surface through esterification process	Wahi et al. (2017)
Commelina Nudiflora	>40% COD removal after 9 h incubation	POME was investigated as secondary effluent before discharge	Kuppusamy et al. (2017)

and COD was observed as 39%, 61%, and 46% respectively. Membrane separator technology was combined with adsorption treatment method for the treatment of POME (Azmi and Yunos, 2014), the adsorption process was used as pretreatment and was achieved by stirring the raw POME with 0.20 g/L of palm kernel shell-based activated carbon at a contact time of 35.94 minutes and agitation speed of 39.82 rpm. There was a reduction of 71.26% of suspended solid, further treatment was achieved using the ultra-filtration technique. Adsorbent materials can also be combined with suitable adsorbent binder to form composite material. The combining adsorbent materials must be based on the target pollutants. In cases whereby the adsorption of polar solutes is required, hydrophilic adsorbent materials can be suitable (Adeleke et al., 2017). Activated carbon for adsorption of solutes are hydrophobic in nature and have the propensity of removing nonpolar solutes in the adsorbate. Hydrophobic particles have the tendency to interact with particles of the same kind rather than with water such as oil droplet. The process results in the breaking down of hydrogen bonding between the water particles. Similarly, hydrophilic adsorbents can be effective for the reduction of polar solutes in the wastewater. The combination of hydrophilic particles have a thermodynamic interaction which is more favorable than the interaction with hydrophobes such as oil. The degree of hydrophobic or hydrophilic particles is determined by the surface tension of the materials in the aqueous phase and the combination of the adsorbent materials can be very effective for the reduction of high strength waste water containing both polar and nonpolar solutes (Adeleke et al., 2016). The effectiveness of peat activated carbon composite adsorbent was applied for the reduction of SS, Color and Fe from landfill leachate (Rosli et al., 2017). At optimum condition of pH 7, 2 hours contact time and 200 rpm shaking speed, the optimum ratio of peat; activated carbon was achieved as 2:2 for color and 2.5:1.5 for Fe. A removal percentage 74.4% and 73.6% was achieved respectively. A batch adsorption study was conducted using composite adsorbent derived from activated coconut shell, activated cow bone and zeolite for the removal of COD and NH_3-N from POME using response surface methodology for the optimization of operational parameters (Adeleke et al., 2017). A central composite design (CCD) design expert 6.01 consisting of six independent variables was used in order to get the optimal conditions for the removal of COD and NH_3-N from POME. Eighty-five experimental design consisting of nine center points and eleven extra points were conducted in order to cover the possible effect of the combination of the operational factors. Batch adsorption experiments were performed in a random and with triplicate in order to reduce error percentage and the effects for the observed responses. The regression coefficients for reducing COD and NH_3-N in the POME at the end of the adsorption process were evaluated from the response surface quadratic model of the CCD to predict the reduction of COD and NH_3-N from POME on the composite. The result in Table 1-6 revealed that the regression model for the reduction of COD and NH_3-N was significant at a confidence level of 95% ($P < .05$) with determination coefficients

Table 1-6 Analysis of the Variance (ANOVA) of the Response Surface Quadratic Model for the Reduction of COD and NH_3-N from POME by Natural Composite

Source	Degree of Freedom	Sum of Squares		Mean Square		*F* Value		*P* Value	
		COD[a]	NH_3-N[b]	COD	NH_3-N	COD	NH_3-N	COD	NH_3-N
Model	53	5915.81	6647.89	111.62	125.43	14.09	6.50	< 0.0001	< 0.0001
Residual error	31	245.507	598.497	7.9195	19.3063				
Lack-of-fit	22	139.951	513.794	6.3614	23.3543	0.54	2.48	0.8836	0.0799
Pure error	9	105.555	84.7024	11.728	9.41138				
Total	84	6161.321	7246.391						

[a] $R^2 = 96.02\%$; R^2 (adj) $= 89.20\%$.

[b] $R^2 = 91.74\%$; R^2 (adj) $= 77.62\%$.

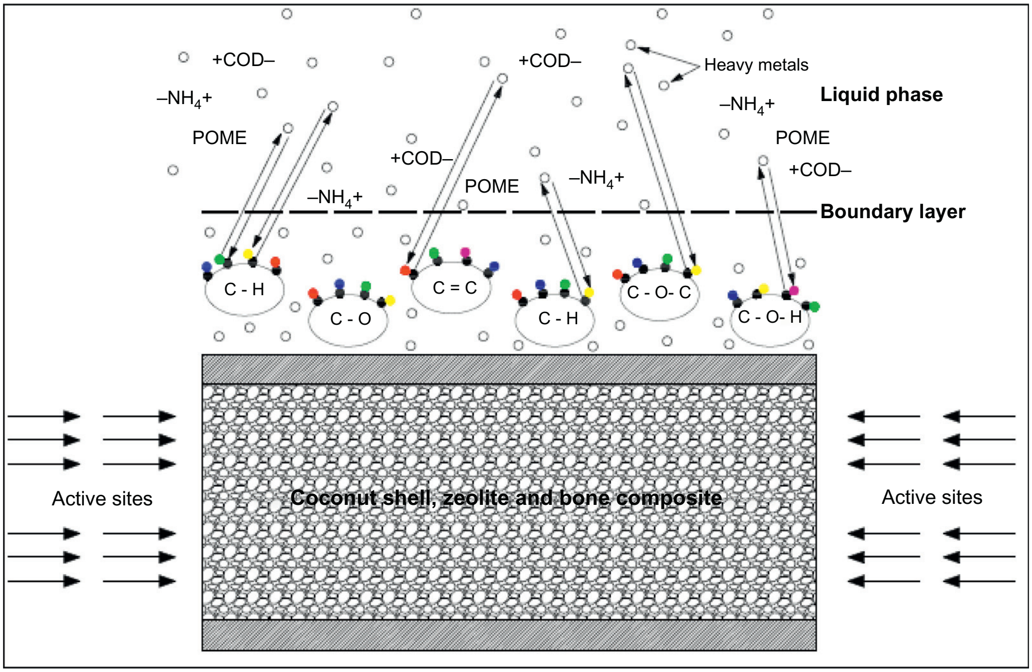

FIGURE 1-3 Ion exchange of pollutants and elements on the functional group on the active surface of the composite (Adeleke et al., 2017).

R^2 equal to 0.9602 and 0.9174 for COD and NH_3-N respectively, indicating the aptness of the model.

However, the application of composite adsorbent material from single adsorbent materials selected on the basis of target pollutants of wastewater has shown to have the potential and adsorption capacity than the individual adsorbent, although there could be the possibility of better removal capacity of pollutants using a single adsorbent material better than the use of composite depending on the nature of the adsorbent and the characteristics of the adsorbate. An illustration of the uptake of heavy metals from POME using composite adsorbent comprising of activated coconut shells activated cow bones and zeolite was illustrated in the works of Adeleke et al. (2017) is illustrated in Fig. 1-3.

The optimization of operational factors using regression model such as the central composite design can be more effective and more comprehensive optimization technique for the reduction of pollutants of wastewater than the conventional optimization method.

1.6 Conclusion

Open ponding systems, anaerobic reactors, membrane, and anaerobic systems are some of the conventional methods used for the treatment of palm oil mill effluent (POME). However, the major drawbacks of the conventional process is attributed to the cost of treatment, routine cost of maintenance and the effectiveness of the systems for the treatment of POME at low concentration. The future prospect of the effective treatment of high strength wastewater may not achieve the desired objective in terms of the reduction of pollutants of raw POME especially for critical parameters such as oil and grease and COD using conventional techniques. The application of locally-sourced adsorbent as activated carbon can be effective with respect to the target pollutants and has proven to be cost effective. Although, adsorption is effective as an alternative treatment method but the effectiveness of the treatment system is not wholly dependent on the nature of the adsorbent materials but also operational factors such as the pH, shaking speed, contact time, adsorbent dosage and initial concentration applicable to the adsorption system. The application low cost adsorbent is still a challenge due to the problem of the identification of proper adsorbent materials for the target pollutants. The combination of treatment methods such as membrane systems and adsorption has been applied for the reduction of the pollutants of POME. Additionally, the application of composite adsorbent has been applied and the optimization of the operational factors of POME using the composite adsorbent is still rare in the research phase for the treatment of POME.

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