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Performance of Chitosan as Natural Coagulant in Oil Palm Mill Effluent Treatment

Man Djun Lee and Pui San Lee

Abstract

This chapter presents the study on pollutant removal in palm oil mill effluent using chitosan as natural coagulant. Up until today, palm oil mill effluent (POME) considered one of the significant sources of environmental pollution. The characteristics of POME include contaminating the source of drinking water, which also harmful to the aquatic ecosystem by creating a highly acidic environment or causing eutrophication. With increasing public awareness of environmental pollution, it creates the need to address this issue. Chitosan is non-polluting food-based anionic and biodegradable biopolymer that are environmentally friendly useful in wastewater treatment. The critical parameter to determine the effectiveness of pollutants removal is chemical oxygen demand, color, and total suspended solids. This chapter also presents and discusses some of the significant findings to provide proper understandings and implications in this topic.

Keywords: wastewater treatment, oil palm industry, chemical oxygen demand, total suspended solids, color removal

1. Introduction

Palm oil industry is a significant industry sector and plays a significant role in Malaysia's economy as one of the largest palm oil producers in the entire world [1]. The palm oil industry in Malaysia contributes about 39% of the world palm oil production and also 44% of palm oil world export [2]. Due to this importance, a large area of land has been converted into oil palm plantation estate. At the same time more and more palm oil mill has been built to process the increasing amount of oil palm fresh fruit bunch (FFB) into crude palm oil [1]. The growth of the industry at the same time indicates the increase of wastewater or palm oil mill effluent (POME) produced and released into the watercourse, which will bring harm to the environment.

The process of extracting crude palm oil from the fresh fruit bunch consumes much water and therefore produces a large volume of wastewater. In Malaysia, a record of 0.67 cubic meters of POME generated in order to process one ton of FFB [1]. Approximately 5–7.5 tons of water is required to produce one ton of crude palm oil. Eventually, more than 50% of these water would become POME which is shown in **Figure 1** [2].

It is approximately 48–72 million tons, and 49–74 million tons of POME was generated in the year 2013 and 2014, respectively. In the year 2014, it estimated 19.66 million tons of crude palm oil produced with roughly 44 million cubic meters



Figure 1.
Palm oil mill effluent.

of POME generated [3]. In POME generated by processing 1 ton of FFB, it contains about 29-30 kg of 30°C, 3-days Biochemical Oxygen Demand (BOD₃) [1]. From the data of POME produced in the year 2014, if the raw POME discharged into the environment without any further treatment, the BOD discharged is equal to the waste generated by 75 million people which is the 2.5 times of current Malaysia's population [3]. POME is also said to be 100 times polluting than domestic sewage [1]. According to the Department of Environment (DOE) practice, there are two ways of discharging treated POME, which are into water course or land. For the discharge into the watercourse, there are seven contaminants contained in the POME regulated. The regulated parameters are BOD₃, suspended solids (SS), oil and grease (O&G), ammoniacal nitrogen (AN), total nitrogen (TN), pH and temperature. For the discharge onto the land, the only parameter is BOD₃ which set at 5000 mg/L. **Table 1** shows the characteristic of raw and treated POME obtained from the discharge point of the local palm oil mill in Malaysia and DOE discharge limit [2].

The most popular method to treat the POME in Malaysia is the ponding system due to low equipment cost and the system is easy to operate. In Malaysia, there are more than 85% of palm oil mills that are currently adopting this method to reduce the BOD of POME into an acceptable limit which is less than 100 mg/L in West Malaysia and 50 mg/L in East Malaysia. In the ponding system, the POME undergoes biological treatments which include anaerobic digestion process followed by aerobic ponding with the hydraulic retention time of 40 days or above. However, the ponding system also causes some drawbacks which are long hydraulic retention time (HRT), vast land needed and the release of greenhouse gases (methane). There are also many palm oil mills which are unable to achieve the discharge limit only by using the ponding system [3].

If untreated POME discharges into the watercourse, it will undergo biodegradation process and consume dissolved oxygen in the water which eventually

Parameters	Raw POME	DOE Discharge Limit
Temperature (°C)	85	45
pH	4.2	5.0–9.0
Oil & Grease (mg/L)	6000	50
BOD (mg/L)	25,000	100
COD (mg/L)	51,000	—
TS (mg/L)	40,000	1500
TSS (mg/L)	18,000	400
TVS (mg/L)	34,000	—
TN (mg/L)	750	200
Color (ADMI)	Above 500	200

Table 1.
 Characteristic of raw POME and DOE discharge limit [4].

will kill the marine animals, especially fish in the river. The untreated POME, which is acidic, will cause the watercourse to turn acidic and affect the aquatic life. Moreover, the oil content in untreated POME tends to form a thick layer on the water surface that will prevent the absorption of oxygen. The dark brown color and unpleasant smell of POME will turn the stream into brownish and unacceptable for public consumption [2]. Apart from that, the high concentration of suspended solids will remain at the bottom of the river and undergo biodegradation, which will produce sludge oxygen demand (SOD) and deplete the dissolved oxygen [4]. In order to protect the environment, DOE Malaysia establishes a standard where the final discharge of treated POME that came out from the mill must be less than 100 mg/L of COD. Hence, for POME to have the minimum or no impact on the environment when discharging and to comply with the discharge limits, the palm oil mill must have an effective POME wastewater treatment system. The cost of maintenance and operation of the POME wastewater treatment system, availability of land and location of mill greatly influencing the choice and selection of POME wastewater treatment systems in Malaysia. In return, it will stress the industry players, especially small and medium scale palm oil mill financially. Therefore, the central idea of this study is to provide an inexpensive and uncomplicated method for small and medium scale palm oil industries to process POME before discharging to the watercourse. This study provides insights into utilizing chitosan and polyglutamic acid in the POME treatment process to remove pollutants that contribute to high COD, color, and TSS of POME.

2. Palm oil mill effluent

2.1 Source of POME in palm oil mill

The most common way in extracting palm oil from fresh fruit bunches (FFB) is the wet palm oil milling process. Several stages of wet palm oil milling process required a tremendous amount of water and steam for washing and sterilizing. As a result, this generates a considerable quantity of wastewater or better known as POME from palm oil mill. **Figure 2** shows a simplified process flow diagram to produce palm oil.

In a palm oil mill operation using a conventional manufacturing process, there are three primary processing operations responsible for producing the

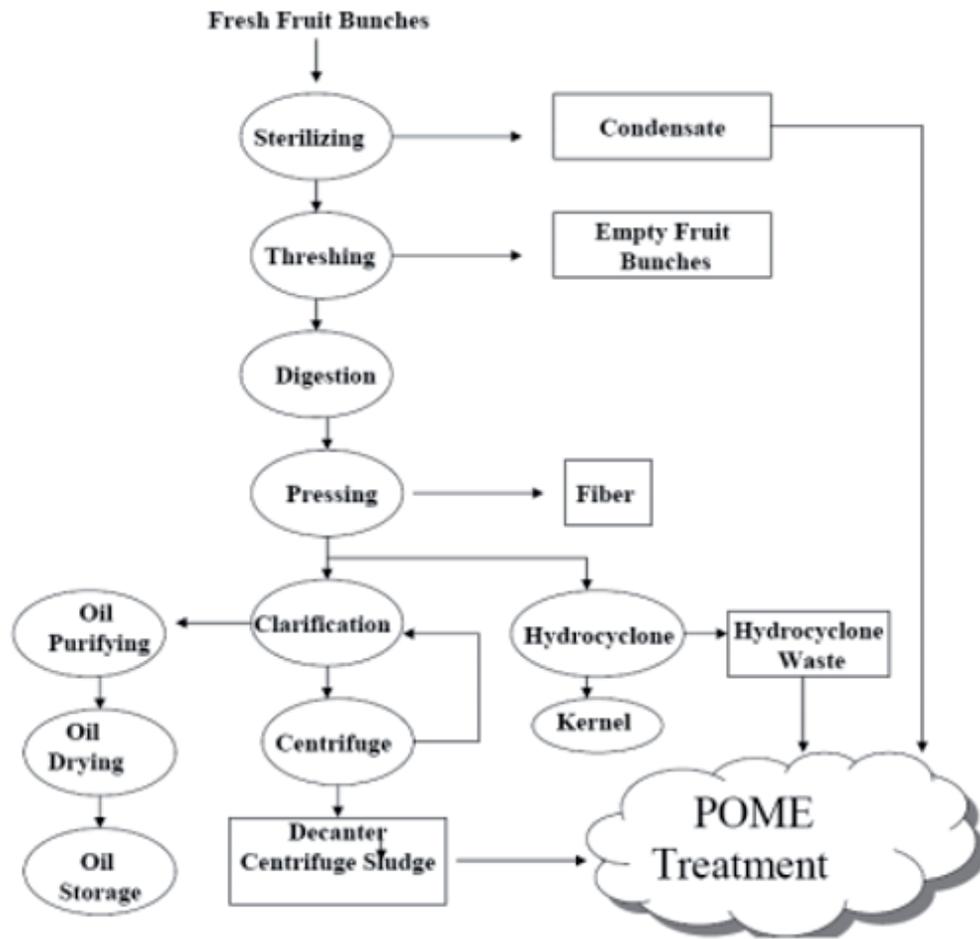


Figure 2. Typical palm oil process flowchart [5].

POME. These three primary processes are sterilization of FFB, clarification of the extracted crude palm oil and hydro-cyclone separation of the cracked mixture of kernel and shell. Sterilization process customarily carried out in horizontal cylindrical autoclaves known as sterilizers where the FFBs are cooked with steam at the pressure about 3 atm for 1 to 1.5 hours. The sterilization process aims to inactivate the natural enzymes in the fruits (lipases) and inhibit the splitting of fat into free fatty acid (FFA) and cause oil loss. Besides, the steam sterilization process loosens the fruits from the bunch and soften the mesocarp to ease the oil extraction. This station contributes approximately 36% of total POME [1]. The clarification process is to separate the oil produced from the press station, which is mixed with water and solid from the bunch fiber. The oil usually is separated from the mixture in the clarifier tank by using gravity, de-sander and also decanter. This station contributes the majority part of the POME, which is 60% [6]. The nuts from the nut silo will be cracked by nutcracker in the ripple mill. These cracked kernel and shell mixture are separated in air columns and by a water bath in hydrocyclone. This station only produces around 4% of POME. The POME generated from sterilizer condensate, clarification of oil and hydro-cyclone is in the ratio of 9:15:1 (36%:60%:4%). **Table 2** shows the characteristics of different source of wastewater in palm oil mill that combined to produce POME [1].

2.2 Characteristics of POME

The POME from different mills would have different characteristics due to different oil extraction technique, FFB quality, climate, condition of palm oil

processing and mill requirement on POME discharge limit [6]. POME is a mixture of water (up to 95%), oil and fine suspended solids [7]. The suspended solid (TSS) is the vegetative matter such as cell walls, organelles, short fibers, water-soluble carbohydrates (glucose, reducing sugar and pectin), nitrogenous compound (protein and amino acid), free organic acid, lipids and also combined small organic and mineral constituents [8]. POME is considered as non-toxic waste as the palm oil mills usually do not use any harmful chemical in the entire milling process [1]. The dark color of POME is usually caused by the decomposition of lignocellulosic materials; which produces lignin, tannin, humic acids, carotene and other organic matter that are recalcitrant to conventional treatment [9]. These suspended solids will eventually contribute to the high BOD of POME [1].

In term of organic content, based on the biochemical oxygen demand (BOD), raw POME has an average BOD of 25,000 mg/L. Raw POME is highly acidic. Biodegradability of effluent can be determined from the BOD/COD ratio. COD stands for chemical oxygen demand. BOD/COD ratio indicates the fraction of chemically oxidized organics which is eligible for biological degradation. In East Malaysia, the POME discharged when the BOD is less than 50 mg/L as required by Department of Environment (DOE). The pollution load of POME generated in a palm oil mill in a day can be calculated based on the following Eq. (1) and (2):

$$\text{Pollution Load, } \frac{\text{kg}}{\text{d}} = \frac{\text{POME Flow Rate, } \frac{\text{m}^3}{\text{d}} \times \text{Concentration, mg/L}}{1000} \quad (1)$$

$$\begin{aligned} \text{POME Flow Rate, } \frac{\text{m}^3}{\text{d}} = & \text{Process capacity } \frac{\text{ton FFB}}{\text{h}} \times \text{Process Efficiency, \%} \\ & \times \text{Operating Hours, } \frac{\text{h}}{\text{d}} \times \text{POME generated, } \frac{\text{m}^3}{\text{ton}} \end{aligned} \quad (2)$$

2.3 Biochemical oxygen demand (BOD)

Biochemical oxygen demand (BOD) is the measure of the amount of oxygen that bacteria will consume during the decomposition of organic matter content under aerobic conditions. BOD test should be carried out according to APHA Standard Method 5510B [10]. BOD is determined by incubating a sealed sample of water for five days and measuring the loss of oxygen from the beginning to the

Parameter	Sterilizer condensate	Clarification wastewater	Hydro-cyclone wastewater
pH	5.0	4.5	—
Oil and grease; mg/L	4000	7000	300
Biochemical oxygen demand (BOD) 3 days, 30°C; mg/L	23,000	29,000	5000
Chemical oxygen demand (COD); mg/L	47,000	64,000	15,000
Suspended solids; mg/L	5000	23,000	7000
Dissolved solids; mg/L	34,000	22,000	100
Total nitrogen; mg/L	600	1200	100
Ammoniacal-nitrogen; mg/L	20	40	—

Table 2.
 Characteristic of different sources of wastewater [1].

end of the test. The samples are usually diluted before the incubation because the bacteria could deplete all of the oxygen in the bottle before the test is complete [11]. It is essential to determine the sample size and dilution ratio before the BOD test, as this will ensure valid BOD results. The pH value of the samples should be in the range of 6.0–8.0, as alkalinity or acidity of samples can prevent bacteria from growing during the BOD test. pH can adjust by adding sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄) [10]. When the test carries out in this way, the BOD usually abbreviated as BOD₅. BOD is a severe problem in natural waters because the dissolved oxygen (DO) of the water can be stressed by BOD oxidation [12].

2.4 Chemical oxygen demand (COD)

Chemical oxygen demand is a measure of the amount of oxygen required to oxidize all organic material into carbon dioxide and water. COD values usually are higher than BOD values, but COD measurements can be obtained in a few hours while BOD measurements will take around five days [11]. Samples heated for 2 hours with sulfuric acid and strong oxidizing agent potassium dichromate. The reduction reaction is shown in Eq. (3).



The amount of Cr³⁺ produced is measured at wavelengths and reflected in mg/L of COD.

2.5 Total suspended solids (TSS)

Total suspended solids are a measure of suspended matter contained in the wastewater. Suspended solids contain BOD and can impair water quality by adding turbidity and reducing esthetics. Discharges of SS also caused deposits that developed at the bottom of waterways. In the laboratory, standard filtration and drying method used to measure SS, where the increase of weight of a container/filter is measured, for a known volume of wastewater filtered [12]. The TSS before and after the experiment measured according to Standard Methods Section 2540 D, and total solids dried from 103–105°C. The treated and the untreated POME samples were evaporated in a weighed dish and dried to a constant weight in an oven from 103–105°C. The increase in weight over the empty dish represents the total solids. TSS calculation is shown in Eq. (4).

$$\text{TSS} \left(\frac{\text{mg}}{\text{L}} \right) = \frac{(\text{Weight of dried residue} + \text{dish} - \text{weight of dish}) \text{ mg} \times 1000}{\text{sample volume, ml}} \quad (4)$$

2.6 Conventional method in POME treatment

The natural chemical properties of the POME make it easily treated by a biological approach. Currently, there are three biological processes employed in the palm oil industry which are anaerobic, facultative anaerobic, and aerobic treatments. The anaerobic treatment is the major part which is removing pollutant (BOD). It can remove BOD up to 95% [13]. There are four main stages which are hydrolytic, acidogenic, acetogenesis and methanogenic. The hydrolysis process begins with bacteria of insoluble organic polymers (carbohydrate) and complex organic compound (protein and lipid) to make them available for other bacteria. Hydrolytic microorganisms will secrete extracellular enzymes for hydrolysis. This process will convert organics into simpler molecule such as amino acids, glycerol, triglycerides,

sugar and fatty acids. Meanwhile, in acidogenesis process, the hydrolyzed or soluble products from the first stage are further broken down by acidogen into simpler organic compound such as volatile fatty acid (VFA), ammonia, carbon dioxide, hydrogen and hydrogen sulfide. In the acetogenesis process, the simple molecule from the previous stage is further digested by acetogens to produce carbon dioxide, hydrogen and acetic acid. For the methanogenesis process, the acetic acid, hydrogen and VFA are converted to methane, carbon dioxide and water by methanogens.

The ponding system is a combination of a series anaerobic, facultative, and algae (aerobic) ponds, as shown in **Figures 3** and **4**. Ponding system primarily anaerobic and facultative ponds require less energy as it does not need mechanical mixing, operation control or monitoring. The major drawback of the ponding system is a large area of land is needed to accommodate a series of ponds to achieve the discharge limit [13]. In constructing the ponds, depth is the primary consideration for different types of ponds. However, the optimum depth for the anaerobic pond is 5-7 m, the facultative anaerobic pond is 1–1.5 m and aerobic pond is 0.5-1 m. The sufficient hydraulic retention time (HRT) of anaerobic, facultative anaerobic and aerobic ponds are 45, 20 and 14 days, respectively [13]. The problems arise from the ponding system is the formation of scum. Scum form when the bubbles rise to the surface together with the fine suspended solids. It is caused by the presence of oil and grease in the POME. Another drawback of the ponding system is the solid



Figure 3.
Series of ponds for POME treatment.

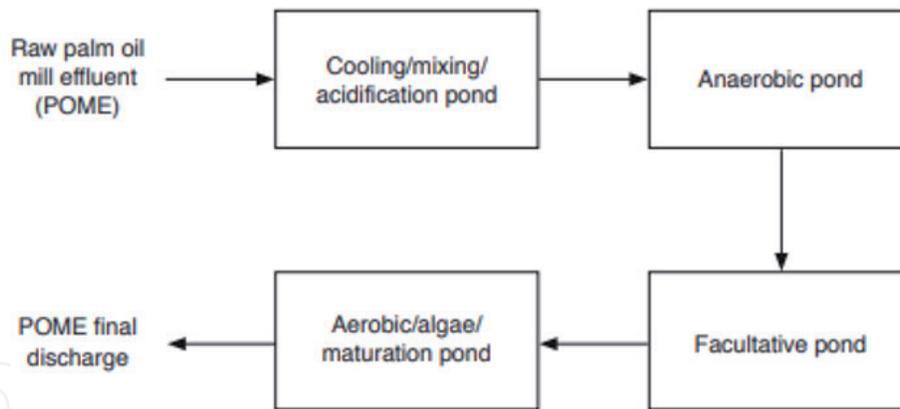


Figure 4.
Typical configuration for ponding treatment system for POME [14].

sludge accumulates at the bottom of the ponds. It will affect the effectiveness of the pond as it decreases the volumetric capacity and hydraulics retention time (HRT) [13]. Therefore, de-sludging is required when the sludge is more than one-third of the pond. About 85% of the palm oil mills that POME in Malaysia adopted ponding system because it is inexpensive, low capital, simple and easy to handle [14]. The palm oil industry is widely favored to the ponding system as only clay lining of ponds is needed and can be constructed easily by excavating hence low marginal cost [4].

The combination of open digester and ponding system is another type of conventional POME treatment system that combines an open digester tank with a series of ponds. **Figure 5** shows a typical open digester tank. Digester tank may build with various volumetric capacities ranging from 600 until 3600 m³. In this treatment method, digester has the same function as the anaerobic pond. It carries out the anaerobic digestion. The output of the POME from the digester will then enter facultative anaerobic ponds and then algae (aerobic) ponds. The digester can decrease the BOD in a shorter time than the pond. The HRT for digester is only 20–25 days which is a lot shorter than anaerobic ponding system. Although it is proven that the digester is more effective than anaerobic ponds, it brings some drawback to the operator. The disadvantages of digester include scum formation on the top, sludge accumulation at the bottom and the corrosion of the steel structure of the digesters due to prolonged exposure to hydrogen sulfide. There are incidents which reported that the digester burst and collapsed [13].



Figure 5.
Typical open digester tank.



Figure 6.
Surface aerator for POME ponds.

Extended aeration is to complement the previous conventional treatment system, which shown in **Figure 6**. In this treatment method, mechanical surface aerators are introduced at the aerobic ponds to supply more oxygen to the ponds. It can reduce the BOD in POME effectively by aerobic processes. Usually, the surface aerators are installed at the end of the ponds before discharging the POME. This treatment method is useful only used when the land area is a constraint and does not permit extensive wastewater treatment [13].

3. POME polishing technologies

In recent years, many studies conducted to investigate alternative POME treatment technologies, especially in secondary and tertiary treatment. The technologies that are widely investigated are adsorption, coagulation or flocculation, membrane filtration and advanced oxidation processes. Most of these investigations are in laboratory scale, but they show potential to overcome the drawback of conventional ponding system [2]. **Figure 7** shows an overview of recent POME polishing technologies.

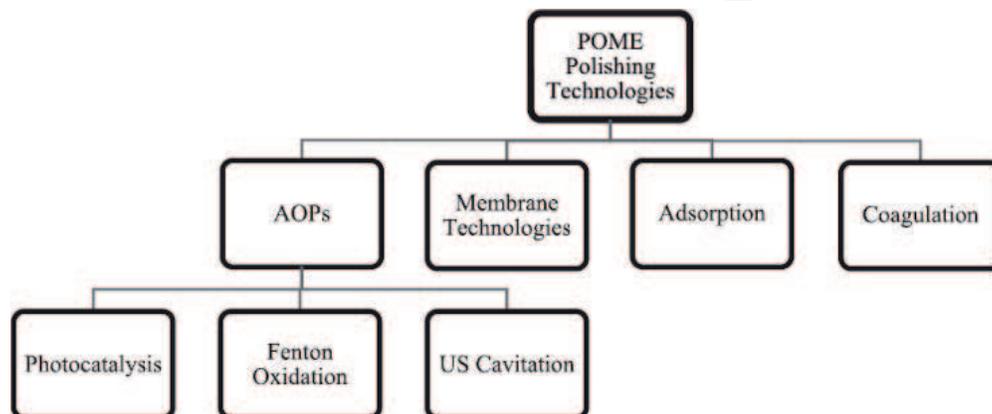


Figure 7.
Overview of recent POME polishing technologies [2].

3.1 Advanced oxidation process (AOP)

AOPs are the processes which degrade the organic pollutant by the powerful and reactive hydroxyl radical ($\text{OH}\cdot$). Hydroxyl radical ($\text{OH}\cdot$) generated would have an oxidation potential of 2.8 eV. $\text{OH}\cdot$ can generate through either one or a combined of chemical oxidation by using H_2O_2 , ozone, ultrasound and radiation assisted source (ultraviolet) [15]. During the treatment of wastewater, $\text{OH}\cdot$ will attack the organic pollutants and convert them to CO_2 , H_2O and inorganic salt [16]. AOPs can effectively degrade the pollutants and have its advantages of non-selectively, mineralization of pollutants and ease of operation compared to the conventional methods. The most popular AOPs are Fenton oxidation, photocatalysis, ultrasound cavitation and ozonation. Fenton oxidation uses the reaction between Fe^{2+} and H_2O_2 to produce $\text{OH}\cdot$ [17]. Photocatalysis applies metal oxide (such as TiO_2) in the presence of irradiation (UV and Vis) to produce $\text{OH}\cdot$ [18]. Ozonation uses the ozone, which is a powerful oxidant with high thermodynamic oxidation potential [19]. Ultrasound (US) cavitation uses ultrasound to oxidize the pollutants. AOPs are more effective when combined two or more AOPs due to more $\text{OH}\cdot$ is generated, lower catalyst consumption and shorter process time [20]. AOPs have successfully adopted as tertiary treatment of wastewater such as olive oil mill wastewater (OOWW), agrochemicals, pulp and paper, textile wastewater and pharmaceutical [2].

3.2 Membrane technologies

Besides advance oxidation processes (AOPs), membrane technology is also one of the popular polishing methods of POME. The advantages of membrane technologies are high removal rate, modularity, and ability to integrate with other water treatment method. However, the main drawback of membrane technologies is that the membrane fouling will cause significant reduction in permeate flow due to the surface and pore-blocking of the membrane. The high initial capital and maintenance costs have also limited the application of the membrane. The most commonly used membrane in membrane technologies are microfiltration (MF), ultrafiltration (UF), nano-filtration (NF) and reverse osmosis (RO) [2]. There is an argument about membrane technologies in removing COD from POME compared to other technology. Higher pressure might have provided higher treatment efficiency but at the same time also contributes to the increasing rate of membrane fouling. The effectiveness of membrane technologies in POME treatment depends on the properties of the membrane. Nano-filtration performs better than ultrafiltration, but it has a higher level of fouling compared to ultrafiltration. Membrane technologies can be combined with other technology such as coagulation and flocculation to increase their treatment effectiveness [2]. **Table 3** shows some of the application of membrane technologies used in POME polishing.

3.3 Adsorption technologies

For adsorption technologies, it is a physicochemical separation process involving inter-phase transfer between an adsorbent and a solution. The pollutant in the solution (adsorbate) absorb onto the surface of the adsorbent. Adsorption can be a reversible process which offers the possibility of adsorbent regeneration through desorption [28]. Adsorption mechanism mainly influenced by the physical forces (physisorption) or chemical interactions (chemisorption) between the adsorbent and adsorbate. The adsorption is also influenced by characteristics of the adsorbent such as specific surface area, porosity and surface charge. Chemical structure of

Process	Pressure (bar)	pH	Time (hr)	COD removal (%)	BOD removal (%)	Solids removal (%)	Color Removal (%)	Ref.
Membrane NF + UF	1-5	—	4	—	—	—	97.9	[21]
Membrane UF	5	9.05	4	88	—	80	—	[22]
Membrane UF	2	8	1.5	90	90	—	—	[23]
Membrane UF	—	6.6-7	—	95	—	79	—	[24]
Membrane UF	0.2-0.8	—	4.5	57	—	97.7	—	[25]
Membrane UF	1-7	1-14	—	60	60	—	97	[26]
Membrane UF + RO	UF: 0-7 RO: 0-60	5.5-6 0.5	—	98.8	99.4	—	—	[27]

Table 3.
The application of membrane technologies for POME polishing.

the adsorbate and environmental condition such as temperature, pH, solubility and ionic strength will influence the adsorption performance [29]. **Table 4** shows some of the application of adsorption process in POME polishing.

3.4 Coagulation and flocculation technologies

Coagulation process commonly used to remove the organic matter and suspended solids (SS) from the wastewater. During the coagulation process, the chemical is added into the wastewater to enhance the flocculation and sedimentation. It will help in removing dissolved solids and suspended solids from the wastewater. Aluminum and iron-based compounds coagulant are often used in water treatment, as they are simple, easy to handle, cheap, and have excellent removal efficiency [37].

Process/Adsorbent dosage	pH	Time (min)	COD removal (%)	Color removal (%)	TSS removal (%)	Ref.
BP/Natural clay: 5 g/L	7	90	95	95	95	[30]
BP/GAC: 150 g/L	4	87.9	—	90	—	[31]
BP/Fly ash: 90 g/L	4	60	89	97	96	[2]
FB/Resin: 0.3 mBH	9.28	—	88	98	—	[2]
BP/AC: 10 g/L	8.5	30	98	—	99	[32]
BP/Banana peel: 300 g/L	2	1800	100	95.96	100	[33]
BP/AC: 200 g/L	—	120	98.99	79.3	98.45	[34]
FB/Resin: 0.3 mBH	3	—	72	64	—	[35]
BP/Zeolite: 10 g/L	3	50	—	—	—	[36]

Table 4.
Application of adsorption for POME polishing.

Coagulant type/ dosage	pH	Mixing rate (rpm)	Time (min)	COD removal (%)	TSS removal (%)	Oil and Grease removal (%)	Ref.
Calcium lactate: 50 mg/L	—	258	23	58	58	—	[43]
Alum: 2124 mg/L	6	—	20	59	—	—	[44]
Chitosan: 0.5 g/L	4	100	15	—	95	95	[45]
Mango Pit: 50 g/L Fly ash: 90 g/L	4	200	60	89	96	—	[2]
PAC: 0.6 g/L + AC: 10 g/L	8.5	50	30	98	99	—	[32]
PAC: 2 g/L	—	150	5	93	—	—	[46]

Table 5.
Application of coagulation-flocculation in POME treatment.

Nevertheless, the residual aluminum and iron concentrations may inhibit the biological treatment process in wastewater due to the reduction of microorganism respiration rate and low organic matter elimination [38]. The drawbacks of these chemicals are high cost, non-biodegradable and possible adverse effect of the chemical. Recently, interests have shift to natural and biodegradable coagulants such as PGA, cotton, chitosan, natural seed gum, *Jatropha curcas* seeds, and *Moringa oleifera* [39–42]. It is because chemical coagulants are non-biodegradable, costly and not environmental-friendly. The coagulation technologies can also combine with other polishing technologies such as adsorption, membrane filtration and AOPs to achieve better pollutant removal. **Table 5** shows the application of coagulation-flocculation for POME polishing.

4. Chitosan

Chitosan is a biopolymer coagulant which is non-toxic, biodegradable, renewable and environmental friendly [47]. Chitosan is a type of marine polymer which has widely used in practical fields such as wastewater management, pharmacology, biochemistry and biomedical. Chitosan is a cellulose-like polyelectrolyte biopolymer which derived from de-acetylation of chitin, as shown in **Figure 8**. Chitin

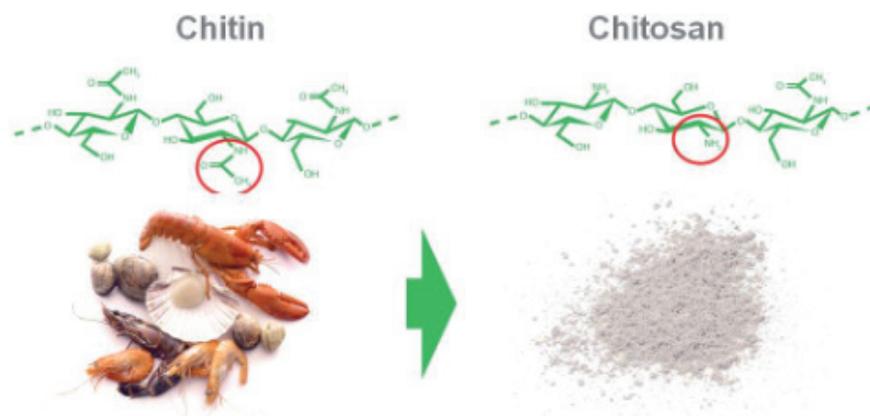


Figure 8.
Derivation of chitosan from chitin [47].

can easily found in marine nature, and it is occurring in the insects, yeast, fungi and exoskeletons of crustaceans [45]. Chitosan contains a high amount of amino functions that provide novel binding properties for heavy metals in wastewater [48]. Chitosan can coagulate effectively at pH less than 4.5 as strong acidic condition exaggerates POME to form unstable flocs [49]. The mechanisms involved in the coagulation can divide into two main categories which are charge neutralization or electrostatic interaction and sweep coagulation/co-precipitation [50]. The chitosan coagulation process is charge neutralization while synthetic coagulant such as ferric chloride (FeCl_3) is sweep coagulation as shown in **Figure 9** [51]. The flocs formed by charge neutralization are smaller than the flocs formed through sweep coagulation [52]. The smaller sized flocs could bring fouling risk to the membrane if membrane technologies are used.

4.1 Performance of chitosan in POME treatment

The optimum condition for coagulation treatment with chitosan as a coagulant is about 100 ppm (mg/L) of POME at pH 4.5. The removal percentage for the COD, the color and the TSS is 15.39%, 85.79 and 97%, respectively. The results are shown in **Figure 10**. The graph in **Figure 10** showed that any further increase in dosage does not increase the color and the TSS removal significantly. However, a further increase in dosage causes the COD to increase. The negative result of the COD

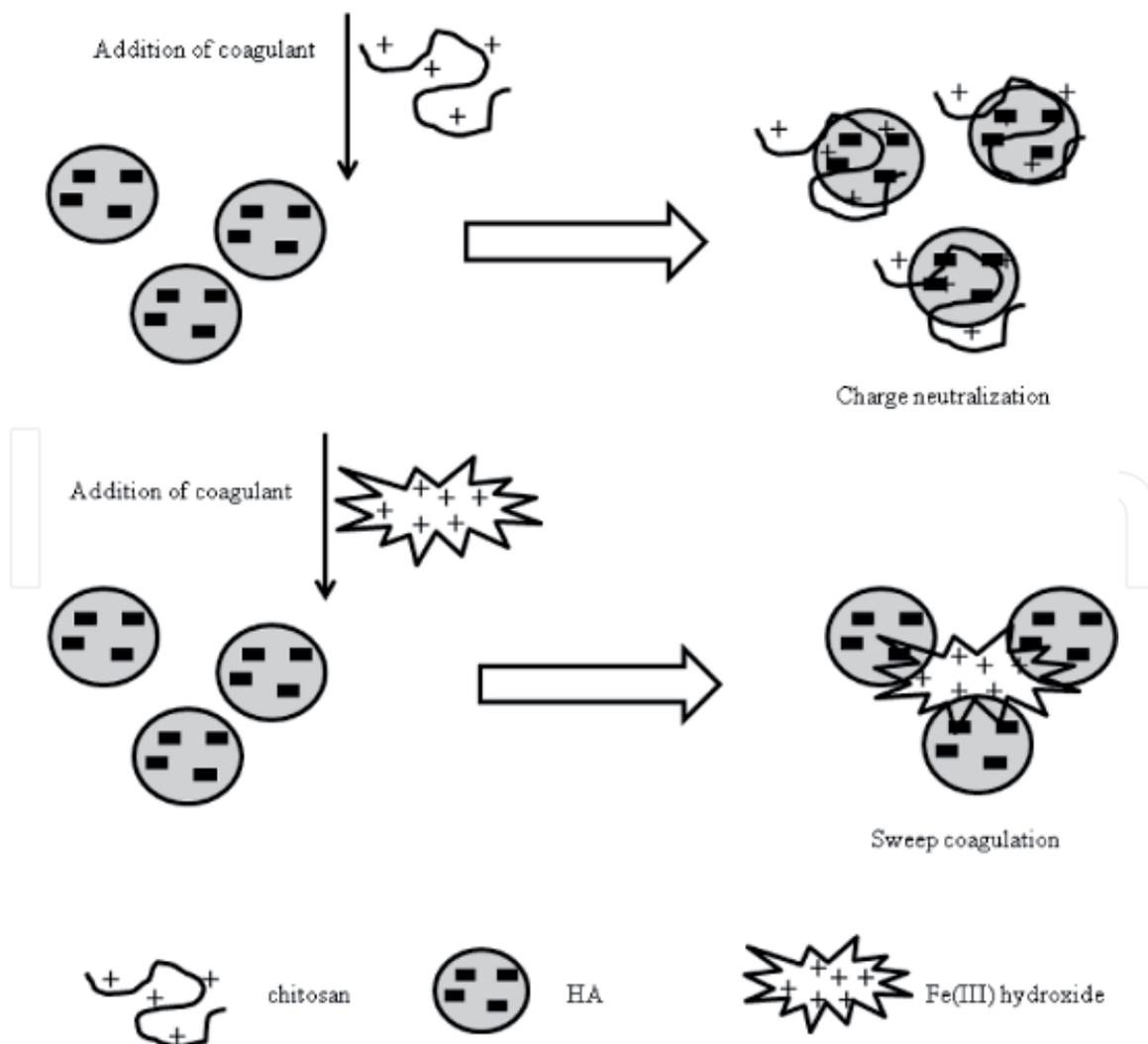


Figure 9.
Chitosan charge neutralization and FeCl_3 sweep coagulation.

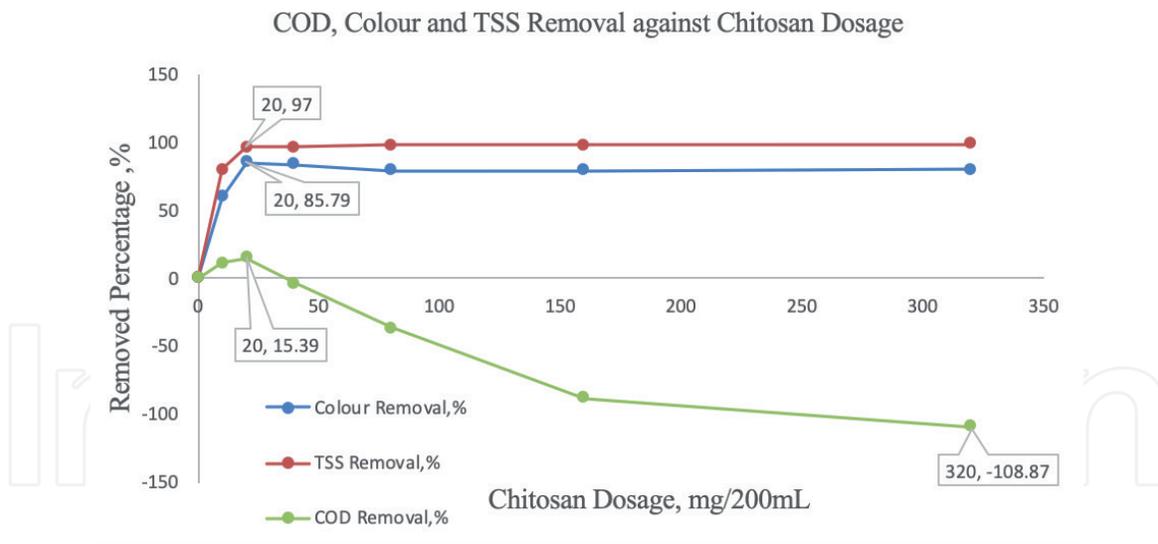


Figure 10. Effect of chitosan dosage in pollutant removal (COD, color and TSS).

removal observed with the addition of chitosan, which is a natural biopolymer coagulant (an impurity) that causes the COD to increase when the dosage exceeds its saturation point. In essence, the low COD removal was due to natural properties of POME as chitosan is not effective in removing dissolved solid [53]. Typical raw POME has a total solid of 40,000 mg/L, while 34,000 mg/L of it is dissolved solid [2]. Furthermore, TSS removal is very effective at low chitosan dosage [45]. However, chitosan is effective in removing suspended solids that contributes to the COD but not total dissolved solids (TDS).

4.2 Performance of chitosan paired with other method in POME treatment

This study was done by combining ultrasound (US) cavitation, chitosan and ferric chloride (FeCl_3) in different ways to determine the best combination and order of treatment. Every treatment method is conducted by following the result of optimum condition obtained from previous studies. The result is shown in **Figure 11**.

From the graph in **Figure 11**, the COD removal for the combination of ultrasound (US) cavitation, followed by ferric chloride coagulation treatment, is the highest, at

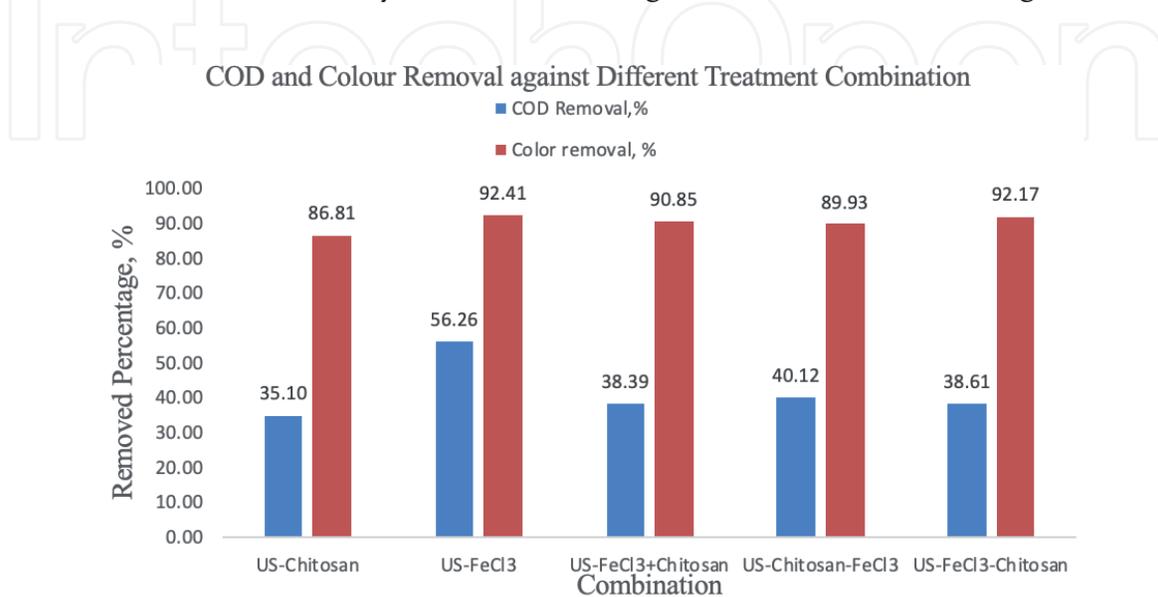


Figure 11. COD and color removal percentage with the different treatment combination.

56.26%. Besides, the color removal for this combination is the highest among other combinations, at 92.41%.

Furthermore, among all these combinations where chitosan is present, the COD removal percentage is less substantially, ranging from 35.1% to 40.12%, which can be observed at the combination of US- FeCl₃ (ultrasound and ferric chloride) that shows the COD removal at 56.26%. However, when chitosan added after it, the COD removal percentage drops to 38.61%, due to chitosan being a natural coagulant that is biodegradable [47]. Chitosan is not very useful in coagulating the organic pollutant (COD), which dissolved in the POME [53]. Therefore, chitosan will become the pollutant, contributing to COD and causing the COD removal percentage to decrease. Even though ferric chloride performs better when paired with other polishing methods, the dosage usage of chitosan in POME treatment is lesser and hence more superior in terms of cost-effectiveness and environmentally friendly method for palm oil mills in dealing with wastewaters.

5. Concluding remarks

This chapter presents the treatment performance of palm oil mill effluent by utilizing chitosan as natural coagulant. Chitosan is natural, food-based and environmentally friendly biopolymer which has enormous potential to be used to treat POME before discharged to watercourse. Some of the methods for combinations, as suggested in the study. The pollutant removal performance measure in terms of COD, color, and TSS removal percentage. The main contribution of this chapter is to provide a low cost and simple method to small and medium oil palm processing industry in processing their wastewater before discharge to the environment. For chitosan, the main advantage is that low dosage would contribute to high removal of suspended solids in POME. However, the disadvantage is that if paired with other methods such as ultrasound cavitation and ferric chloride, it would not have significant improvement in terms of pollutant removal percentage. On the other hand, ferric chloride could work with other methods to improve pollutant removal significantly. Nevertheless, utilizing chitosan would not contribute to significant increment in the overall treatment cost, which would encourage palm oil mill to adapt this method in treating their wastewater.

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