Performance of Polyglutamic Acid in Palm Oil Mill Effluent Treatment

Man Djun Lee, Mohd Shahril Osman, and Pui San Lee

***Abstract*—Up until today, palm oil mill effluent (POME) considered one of the significant sources of environmental pollution. The characteristics of POME include high acidity, temperature, and chemical oxygen demand (COD), which not only contaminate the source of drinking water but also harmful to the aquatic ecosystem by creating a highly acidic environment or causing eutrophication. With increasing public awareness of environmental pollution, this creates the need to address this issue. This study addresses this issue by performing a study on the pollutant removal performance of polyglutamic acid (PGA) in palm oil mill effluent (POME) treatment. PGA is a non-polluting food-based water-soluble anionic and biodegradable biopolymer that are more environmentally friendly in wastewater treatment. The critical parameter to determine the effectiveness of pollutants removal are COD, color, and total suspended solids (TSS). In this aspect, a series of experiments conducted to determine the optimum working conditions of PGA in POME treatment. It found that the optimum pH and dosage of PGA in POME for COD, color, and TSS removal are at pH 3 and 800 ppm. Findings revealed with this condition; the COD removal was up to 45.16%, color removal up to 77.6%, and 100% TSS removal. Results also showed that PGA is dosage-dependent, which works well in POME under room temperature, and no pH modification is needed. The findings indicated that PGA is significant in POME treatment to contribute to achieving environmental sustainability. For future studies, PGA could be paired with other wastewater treatment methods to achieve higher pollutant removal performance.**

***Index Terms*—Color removal, COD, TSS, polyglutamic acid, wastewater treatment.**

I. Introduction

In Malaysia, the most common way to extract palm oil from fresh fruit bunches (FFB) is through wet palm oil milling process. Several stages in wet palm oil milling process required a tremendous amount of water and steam for washing and sterilizing. This in return, this generates a considerable quantity of wastewater or better known as palm oil mill effluent (POME). In Malaysia, generally 0.67 cubic meters of POME is generated during the production of one ton FFB [1]. Apart from that, approximately 5-7.5 tons of water required to produce one ton of crude palm oil, and unfortunately more than 50% of these water would become POME [2]. Liew *et al.*, [1], identifies that during the processing of 1 ton FFB, the POME produced contains about 29-30kg of 30ºC, 3-days Chemical Oxygen Demand [1]. The previous study indicates that if the raw POME discharged into the environment without any further treatment, the COD discharged are equal to the waste generated by 75 million people, which is 2.5 times of current Malaysia's population [3]. Besides that, POME is also said to be 100 times polluting than domestic sewage [1]. The general properties of POME shown in Table I.

TABLE I: General Properties of POME [4]

Properties	Average	Range
pH	4.2	3.4-5.2
COD (ppm)	50 000	15 000-100 000
Oil and Grease (ppm)	6 000	150-18 000
Suspended Solid (ppm)	18 000	5000-54 000

The untreated POME if discharged into the watercourse, will undergo biodegradation and consume dissolved oxygen in water which eventually 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 prevents the absorption of oxygen. The dark brown color and unpleasant smell of POME will turn the stream into brownish and unacceptable for the 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].

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). Anaerobic treatment can remove BOD up to 95% [2]. Anaerobic treatment involved 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

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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. 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. In constructing the ponds, depth is the primary consideration for different types of ponds. The length and width are usually differ based on the availability of the land. However, the optimum depth for the anaerobic pond is 5-7m, the facultative anaerobic pond is 1-1.5m and aerobic pond is 0.5-1m [3]. The recommended time hydraulic retention time (HRT) of anaerobic, facultative anaerobic and aerobic ponds are 45, 20 and 14 days, respectively. 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 cause by the oil and grease presence in the POME. Another drawback of the ponding system is the solid 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) [1]. 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. 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 [2].

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. Aluminium and iron-based compounds coagulant are often used in water treatment, as they are simple, easy to handle, cheap, and have excellent removal efficiency. Nevertheless, the residual aluminium and iron concentrations may inhibit the biological treatment process in wastewater due to the reduction of microorganism respiration rate and low organic matter elimination. 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. 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 [5]. This study explores the potential of polyglutamic acid in the POME treatment process to remove pollutants that contributes to high COD, color, and TSS of POME. Poly-γ-glutamic acid (PGA) is a non-polluting food-based water-soluble anionic and biodegradable biopolymer that is a more environmentally friendly alternative in wastewater treatment.

In order to protect the environment, Department of Environment (DOE) Malaysia establish a standard where the final discharge of treated POME that came out from the mill must be less than 100mg/L of COD. Hence, for POME to have the minimum or no impact at all to the environment when discharging and to comply with the Department of Environment Malaysia's discharge limits, the palm oil mill required to 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 influenced the choice and selection of POME wastewater treatment systems in Malaysia. This is return 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.

II. Materials and Method

A. Palm Oil Mill Effluent

In a palm oil mill operation using a conventional manufacturing process, there are three primary processing operations responsible for producing the 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 fibre. The oil usually is separated from the mixture in the clarifier tank by using gravity, de-sander and decanter. This station contributes the majority part of the POME, which is 60%. The nuts from the nut silo cracked in a nutcracker called 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%) [4].

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. POME is a mixture of water (up to 95%), oil and fine suspended solids. The suspended solid (TSS) is the vegetative matter such as cell walls, organelles, short fibres, 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 [2]. POME is considered as non-toxic waste as the palm oil mills usually do not use any harmful chemical in the entire milling process.

The dark colour of POME caused by the decomposition of lignocellulosic materials which will produce lignin, tannin, humic acids, carotene and other organic matter which are recalcitrant to conventional treatment [1].

The POME samples collected from the local palm oil mills located in Sibu, Sarawak, Malaysia. The samples were refrigerated until being used. Samples were collected one-off in a drum of 20L from the palm oil mill to avoid fluctuations in its characteristics that might be due to the climate and condition of the palm oil processing. Both raw and treated POME were characterized by measuring COD, TSS, pH, and color. All the experiments were conducted at room temperature.

B. Poly-γ-Glutamic Acid

PGA is a water-soluble, biodegradable polymer that is produced by microbial fermentation. PGA is produced by several Bacillus species as an extracellular polymer and is completely biodegradable and non-toxic to humans. Due to its non-toxicity, PGA has appeared in many medical applications such as drug delivery, biological glues [5]. PGA' multi-functionality, biodegradability, nontoxicity, compatibility, and edibility have made it a promising biopolymer for application as health food, thickener, osteoporosis-preventing factor, and stabilizer in the food industry; as moisturizer in cosmetics; as chelating agent in waste-water treatment; as hydrogel (especially superabsorbent polymer, SAP) for environmental, agricultural, and biomedical product applications; as biodegradable packing material, and in many other possible applications including Liquid Crystal Displays (LCDs) and conductive display material, drug deliverer, gene vector, curative biological adhesive, dispersant, and enzyme-immobilizing material [6].

PGA samples obtained from Sigma-Aldrich Malaysia in the form of powder packaged in a 20kg bag. The 150mL of POME with pH to be determined prepared for polyglutamic acid coagulation treatment. Different dosages of polyglutamic acid were added to the POME to coagulate the pollutant. The COD, color, and TSS of each sample before and after treatment were measured and recorded.

C. Jar Testing Apparatus

The dosage of PGA used range from 100ppm to 1600ppm. The pHs of POME was adjusted to 3, 5, 7, 9 & 11 by adding sulphuric acid (H_2SO_4) and sodium hydroxide (NaOH). The optimum operating conditions for POME treatment determined by using the jar test procedure. The test was conducted using the jar test principle. Jar tester machine was used to stir the sample. The stirring speed is set at 120rpm for 1 minute and 30 rpm for 30 minutes [6]. The whole experiment was carried out at a room temperature of 25°C. The samples are then left to sediment for 90min and filtered with 9µm filter paper before measured for COD, color and TSS.

D. Chemical Oxygen Demand

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. Samples heated for 2 hours with sulfuric acid and strong oxidizing agent potassium dichromate.

The COD before and after the experiment measured according to the APHA method for Examination of Water and Wastewater using HACH reagent. The colorimetric determination of COD was carried out at 620 nm with a HACH spectrophotometer, DR 6000 [7]. Samples heated for 2 hours with sulfuric acid and strong oxidizing agent potassium dichromate. The reduction reaction is shown in (1).

$$6Cl^- + Cr_2O_7^{2-} + 14H^+ \rightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O \qquad (1)$$

E. Total Suspended Solid

Total suspended solids are a measure of suspended matter contained in the wastewater. Suspended solids contribute to COD and can impair water quality by adding turbidity and reducing aesthetics. Discharges of suspended solids also caused deposits that developed at the bottom of waterways. In the laboratory, standard filtration and drying method used to measure suspended solids, where the increase of weight of a container/filter is measured, for a known volume of wastewater filtered. The TSS before and after the experiment measured according to Standard Methods Section 2540 D, and total solids dried from 103°C to 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°C to 105°C. The increase in weight over the empty dish represents the total solids. TSS calculation is shown in (2).

$$TSS\left(\frac{mg}{L}\right) = \frac{(Weight\ of\ dried\ residue + dish - weight\ of\ dish)\ mg \cdot 1000}{sample\ volume, ml} \qquad (2)$$

F. pH

pH measured with pH meter (HACH SensION 4) with a pH electrode (HACH platinum series pH electrode model 51910, HACH Company, USA) used for pH measurement. The pH meter was calibrated with pH 4.0, 7.0 and 10.0 buffers.

G. Color

Color was measured according to the Hach method (Method 8025). Colorimetric determination of color was carried out at 620nm using a Hach spectrophotometer DR 6000. Color may be classified as apparent or real color. The apparent color is color from dissolved materials and suspended matter, while actual color determined by removal of the suspended materials with a filter or a centrifuge. The stored program is calibrated in color units based on the APHA recommended standard of 1 color unit is equal to 1 mg/L platinum as chloroplatinate ion [8].

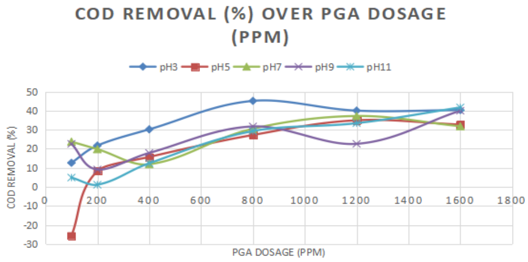

Fig. 1. COD removal percentage vs. PGA dosage under various pH.

III. Results and Discussion

A. Effect of PGA Dosage on COD Removal Percentage with Different pH

Fig. 1 presents the effect of PGA dosage on the removed percentage of COD under the medium of various pH. The removal of COD was optimum with a dosage of 800ppm at pH 3, where 45.16% of COD removed. As POME is produced in the pH range between 3 to 5, PGA is indeed useful in POME treatment without modifying its pH. This result further clarifies that PGA in wastewater treatment is dosage-dependent, and pH is not the critical parameter affecting its effectiveness [6].

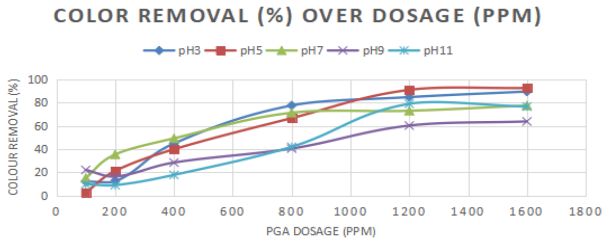

Fig. 2. Color removal percentage vs. PGA dosage under various pH.

B. Effect of PGA Dosage in Color Removal Percentage under Various pH

Fig. 2 reports the effect of PGA dosage on color removal percentage in POME treatment. The removal of color was the highest with a dosage of 1600ppm and a pH of 5, where 92.68% of color was removed. It is apparent from the figure that the effectiveness of PGA on color removal suggest better color removal with every increasing in PGA dosage. This finding is in line with Pan *et al.* [9], in which the color removal of polyglutamic acid is dosage-dependent. However, in industrial practice, increasing dosage means an increase in total production cost. Overall, the result suggests that the optimum dosage of PGA with 800ppm at 77.6% of color removal as any increase in dosage will not yield any significant results but would only contribute significantly to the total cost. There are similarities between the result from this study with a study conducted by Inbaraj [10] in which PGA (9.9 × 105 Da) is effective in the elimination of basic dyes from aqueous solution. On top of that, up to 98 % of the dye adsorbed on PGA could be recovered at pH 1, which promotes the reuse of spent PGA. By recycling the PGA, it would contribute to the environmental sustainability.

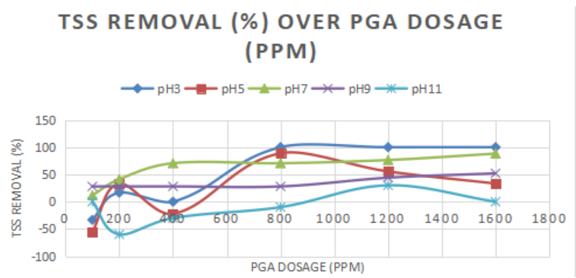

Fig. 3. TSS removal percentage vs. PGA dosage under various pH.

C. Effect of PGA Dosage in TSS Removal Percentage under Various pH

Fig. 3 shows the effect of PGA dosage on TSS removal. The optimum dosage found to be 800ppm under a pH of 3 in which TSS is 100% removed. Results showed that PGA works better with POME under acidic environment. In the case of TSS removal, pH found to be a critical parameter that contributes significantly. Results also revealed that there is a saturation point for TSS removal in every pH. Surprisingly, any increase in pH after the saturation point will not increase TSS removal but contributes directly to the increase in TSS in which will cause the PGA itself becomes a pollutant.

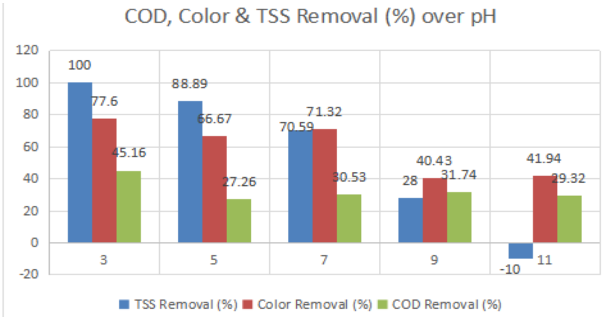

Fig. 4. COD, Color, TSS removal percentage under various pH.

The summary of all the result under various pH with dosage of 800ppm is recorded in Fig. 4. The best performance for 800ppm of PGA works best under pH of 3 with the highest removal of TSS (100%), color (77.6%) and COD (45.16%). Fig. 4 also shows that as pH increases, the pollutant removal efficiency reduces. Since most POME discharged at pH between 3 to 5, PGA is significant in pollutant removal for POME without the need of pH modification. This also contributes to environmental sustainability as no chemicals are needed in modifying the pH of the POME. The use of PGA contributes to save time as the pollutant removal process only take minutes and more superior compared to ponding method (bio-process) could take days to weeks to effectively remove pollutants that contributes to COD, colour and TSS.

IV. Conclusion and Recommendations

In this study, PGA, a natural, food-based, environmentally friendly biopolymer, used to treat POME and the performance measured in terms of COD, color, and TSS removal percentage. The main contribution of this study 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. This study demonstrated that PGA work best in an acidic environment which fits POME characteristics without the need for pH and temperature modification. This study found out that the optimum dosage for PGA in POME treatment found to be 800ppm with a pH of 3 that yields the results of 45.16% COD removal, 77.6% color removal, and 100% TSS removal. Future studies might explore the possibility of pairing PGA with other wastewater polishing methods such as ultrasound cavitation to increase pollutant removal.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Man Djun Lee conceived the original idea, planned and carried out the experiment. Pui San Lee wrote the manuscript with supervision from Man Djun Lee. Mohd Shahril Osman helped supervise the project.

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His greatest strengths are his research, and communication skills. He started teaching and working in technical work since 2009 in various background. He is currently working as lecturer in University College of Technology Sarawak. Man Djun Lee has written more than 20 papers and book chapters in his field of interests which are water treatment, waste management and renewable energy. Currently, Man Djun Lee is working on several projects including water treatment and renewable energy project.

Man Djun Lee had won several engineering design awards for his contribution in research project. Due to his interest in research, he has been appointed as journal reviewer and project consultant.