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Estimation of Melanoidin concentration in palm oil mill effluent ponding system and its treatment using Calcium Lactate

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Abstract. Colour removal from wastewater is among the major challenge in water and wastewater treatment. Among others, melanoidin could be the source of colour in wastewater. In this study, the estimation of melanoidin concentration in conventional palm oil mill effluent (POME) ponding system was investigated. Melanoidin was analyzed by detecting its absorption using double beam UV-Vis spectrophotometer. For melanoidin, the maximum absorption is 330nm. From the analysis, the melanoidin concentration decrease from anaerobic pond 1 to anaerobic pond 3 and slightly increase in anaerobic pond 4 and aerobic pond 1. After that, the melanoidin concentration decreased from aerobic pond 1 to final discharge. It is estimated that the anaerobic pond 1 had the highest melanoidin concentration which was 87.3 mg/L. Finally, the effectiveness of melanoidin removal using a coagulation/flocculation process was also studied. Calcium lactate was used as a coagulant and low molecular weight anionic polyacrylamide was used as a coagulant aid. The jar test experiment was carried out by using 0.3g/L calcium lactate solution and dosage of anionic polyacrylamide was altered in order to find out the best melanoidin removal. Experiments carried out by using sedimentation time of 20 minutes showed that the highest percentage removal of melanoidin was 80.93% at the dosage of 0.3g/L of calcium lactate without any anionic polyacrylamide being added. This result concluded that the addition of anionic polyacrylamide as coagulant aids is not significant when compared to the use of calcium lactate only.

1. Introduction

Melanoidins are dark brown to black coloured natural condensation products which are produced by non-enzymatic browning reactions called Maillard reactions [1]. Maillard reaction is a type of non-enzymatic browning reaction that formed between amino compounds and carbohydrates [2]. The Maillard reaction products are a particularly complex mix of different compounds of different molecular weight. They include a lot of functional groups such as aldehydes, ketones, dicarbonyls, acryl amides and heterocyclic amines and all of that will contribute to flavor, melanoidins and advanced glycation end products (AGEs), which are a polymeric product formed at the advanced steps of Maillard reaction [3]. Naturally, melanoidins are widely distributed in food and drinks. Besides that, melanoidins are also widely discharged in large amount by various agro-based industries especially from cane molasses based distilleries and fermentation industries as environmental pollutants [1]. Melanoidin is a main colour pollutant from molasses-based fermentation plants, alcohol distilleries, spent wash and sugar-based factories [4].

Melanoidin in the treated effluent brings threats. The dark brown characteristics can prevent the sunlight penetration to the water [2]. This will reduce the photosynthetic activity of the plants in the water and reduce the dissolved oxygen level of surface waters. This will then greatly affect the ecosystem in water. Besides, melanoidins also have such characteristics that it is a water-soluble recalcitrant colouring compound, which are highly resistant to the microbial attack. Therefore, conventional biological process and activated sludge treatment process are unable to treat these melanoidins containing wastewater. Therefore, such wastewaters require a proper pretreatment before it can be safely disposed into the environment [1].

Coagulation and flocculation is a vital process in water surface treatment which includes pre-treatment, post-treatment and main treatment. However, flocculants play an important role in affecting the flocculation effect during the process. There are a lot of flocculants commercially available in the market. However, some of them are believed to bring a lot of negative impacts to the environment and also human health [5].

Malaysia is one of the largest producers of palm oil in the world. Therefore, there is large amount of palm oil mill effluent (POME) being produced annually [6]. Palm oil mill effluent (POME) is a voluminous liquid waste. It has high biochemical oxygen demand (BOD) which normally discharged at 75-85°C. It is a colloidal dispersion of organics with an unpleasant odor. POME is a liquid waste that will bring harm to the environment. POME has total solids content of 5-7% of which more than half is dissolved solids and about the other half is mixture of various forms of organic and inorganic suspended solids [7].

Palm oil mill effluent contains amino acids, a mixture of carbohydrates such as hemicelluloses to simple sugars, organelles, free organic acids, nitrogenous constituents and inorganic nutrients such as sodium, potassium, magnesium, calcium and short fibers [8]. In 2009, Zahrim et al. has hypothesized that the anaerobic digested POME may contain melanoidin due to the existence of amino acid and carbohydrate compound in POME. Melanoidin which contribute to the colour of the POME should be treated before it is discharged into the river or seawater. By doing this, the ecosystem of the aquatic life can be preserved and protected.

There has been research done on the colour treatment of the melanoidins. Many types of conventional coagulants have been used to treat these melanoidins such as aluminium sulfate, ferric sulfate, aluminium chloride and ferric chloride and alum [9, 10]. In this research, calcium lactate is used instead of these kinds of conventional coagulant. This is because with the use of inorganic salts like aluminium chloride or aluminium sulfate, it can cause harm to human health by contributing to Alzheimer disease and produce a large scale of the sludge [5]. It is believed that calcium lactate with the combination of anionic polyacrylamide can be used to remove the melanoidin. The aims of this research are to estimate melanoidin concentration in palm oil mill effluent (POME) and analyze the usage of calcium lactate as a coagulant together with the help of anionic polyacrylamide (A-PAM) as coagulant aid in the coagulation/flocculation process of aerobic POME.

2. Experimental

2.1. Experimental materials

Raw material collection: Samples of palm oil mill effluent were collected from a palm oil mill in Beaufort, Sabah. The POME ponding system contained a cooling/grid pond, four stages of anaerobic ponds and four stages of aerobic ponds as shown in Figure 1. The collection bottles were rinsed with distilled water before samples were collected. Palm oil mill effluent samples were then stored less than 4°C in the refrigerator.

Standard melanoidin preparation: Standard solution of melanoidin was prepared by mixing 1M of glucose (Fluka) and 0.5M of glycine (Merck). After several processes of dilution and heating, the mixture will become hard solid objects. The solid will be left in the lab for drying for a day. The dried melanoidin was removed from the beaker and crushed into powder form.

Jar test: The coagulant that will be used is calcium lactate powder with Merck brand while the flocculent that will be used is low molecular weight of anionic polyacrylamide. The anionic polyacrylamide is supplied by Guang Xi Nanning Bonglin Business.

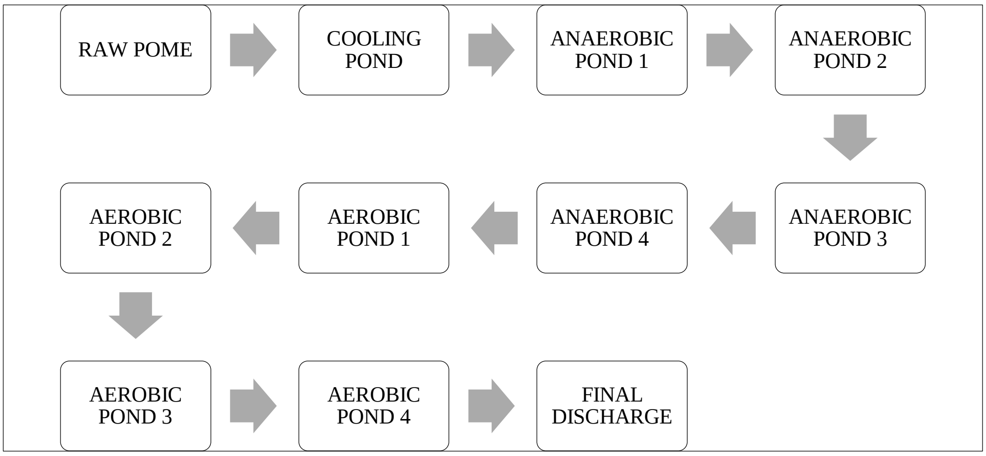

Figure 1. Flowchart of ponding treatment system of POME

2.2. Jar test
Melanoidin concentration in each samples taken from four anaerobic ponds, three aerobic ponds and final discharge were first estimated before the jar test was performed. The coagulation procedure started with adding pre-determined amount of calcium lactate stock solution into the POME. The mixture of POME and calcium lactate solution went through rapid mixing (258 rpm) for 3 minutes, followed by slow mixing (39 rpm) for 10 minutes. The stirrer will not be stopped during the changing of mixing speed. After that, low molecular mass of anionic polyacrylamide (if required) was added and the stirrer was stopped after 10 minutes passed. The total slow mixing period was 20 minutes. Then, the POME was allowed to settle for 20 minutes. The jar test was carried out for three times. For each run of test, the dosage of calcium lactate was made constant at 0.3 g/L while varying the dosage of anionic polyacrylamide at 0 ml, 0.025 ml, 0.05 ml, 0.25 ml, 0.5 ml and 1.0 ml.

2.3. UV-Vis test
After measuring the pH, a small portion of each of the melanoidin stock solution was transferred into the cuvette. The sample was placed in the UV-Vis beam and a graph of the transmittance or absorbance versus the wavelength was obtained. Alternatively, samples were prepared in known concentrations and their absorbance at the specific wavelength was read by the UV-Vis spectrophotometer. A standard graph for the melanoidin was made after the absorbance were obtained for the five different concentration of the melanoidin with pH 5, pH6, pH8 and pH9 as shown in Figure 2.

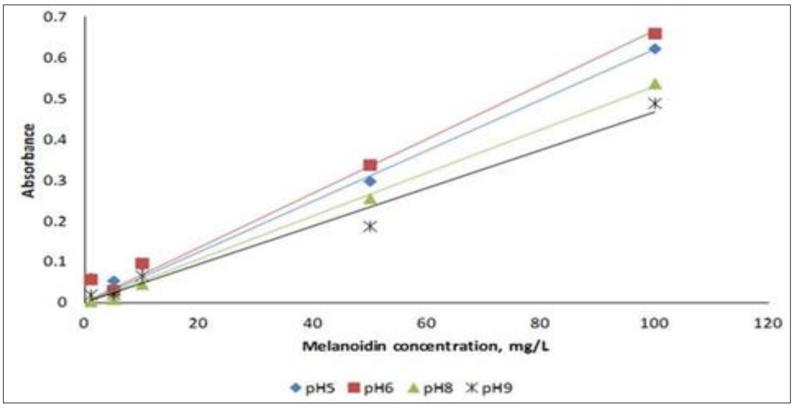

Figure 2. Standard graph of Melanoidin

3. Results and discussion

3.1. Melanoidin analysis

It can be seen from Figure 3 that the melanoidin concentration decreases from anaerobic pond 1 to anaerobic pond 3 and slightly increases in anaerobic pond 4 and aerobic pond 1. After that, the melanoidin concentration decreased from aerobic pond 1 to final discharge. It also can be seen that the anaerobic pond 1 had the highest melanoidin concentration which was 87.3 mg/L. This might be since the effluent from anaerobic pond has not undergone treatment yet. This was due to the higher colour intensity in the influent [11]. Therefore, it has the highest melanoidin concentration.

The melanoidin concentration is decreasing from the anaerobic pond 1 to pond 3. This indicated that the colour treatment efficiency is increasing from anaerobic pond 1 to pond 3. The sudden decrease of the melanoidin concentration from anaerobic pond 1 to pond 2 because of the lower pH operation in biological treatment in the POME (pH5) since melanoidin decolourisation had maximum decolourisation activity in optimum pH range of 5.0-6.0.12-13. During this pH range, the cleavage of the ethylinic C=C and azomethine C=N linkages might occurred where the presence of conjugated C=C and C=N bonds impart colour to the melanoidin [4]. Each microorganism had a specific pH for their microbial activity. All enzymes were protein in nature, therefore some proteins will denature at the unfavourable pH. This will inhibit the activity of the enzymes as well as its production [12]. It explained why the melanoidin decolourisation was so high from the anaerobic pond 1 to anaerobic pond 2.

However, the melanoidin concentration increased from anaerobic pond 4 to the aerobic pond 1. This phenomenon was due to the re-polymerization of colouring compounds after anaerobic treatment. For a palm oil mill, there was no chemical addition during the processing operation. Therefore, the colour from the palm oil mill effluent appeared from plant constituents such as lignin and phenolic while the colour of the sugar processing effluent were contributed by phenolic (tannic and humic acids) from the feedstock and melanoidins from Maillard reaction of sugars (carbohydrate) with proteins [13].

Aerobic treatment on the melanoidin was quite efficient from the aerobic pond 1 to the final discharge due to the decrease of the melanoidin concentration. However, the removal of melanoidin concentration was not very significant. This was due to melanoidin widely distributed in nature and was not readily susceptible to microbial degradation [14].

3.2. Melanoidin treatment

The standard melanoidin graph as shown in Figure 2 was used to determine the concentration of melanoidin at specific pH. Table 1 showed melanoidin concentration with varies anionic polyacrylamide concentration as performed via coagulation flocculation experiment.

Table 1. Melanoidin concentration with variation of anionic polyacrylamide concentration.

Calcium lactate concentration (g/L)	Anionic polyacrylamide concentration (mg/L)	Melanoidin concentration (mg/L)
0	0	46.98 (12.7573)
0.3	0	9.46 (6.1360)
0.3	0.05	19.79 (12.8740)
0.3	0.1	15.32 (1.8429)
0.3	0.5	26.98 (0.6343)
0.3	1	21.80 (0.8263)
0.3	2	19.02 (0.4417)

* ( ) value indicates the standard deviation of the melanoidin concentration

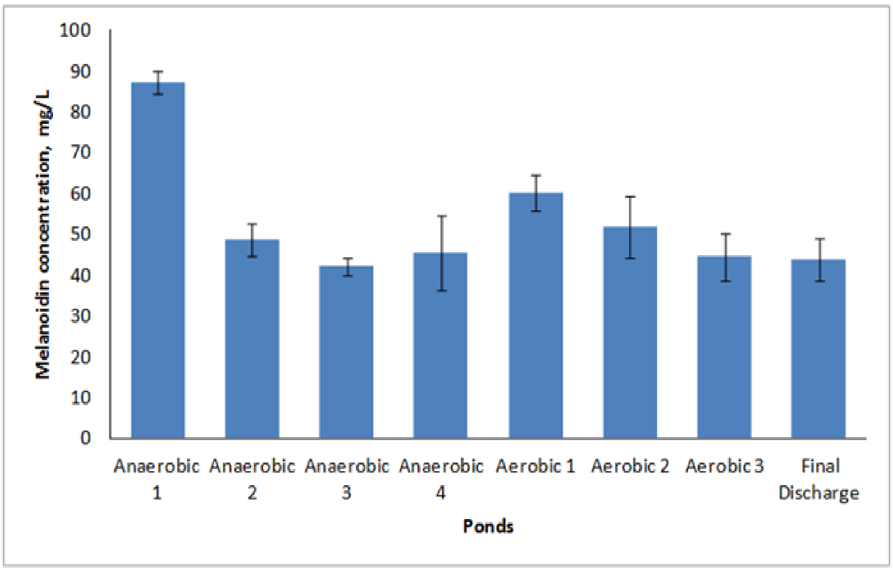

Figure 3. Melanoidin concentration against different ponds

The coagulation of the melanoidin colloid was done by the calcium lactate to reduce or neutralize the electrical repulsion between the colloids and causing them to aggregate to form microfloc. From Figure 4, it can be seen that the percentage removal of melanoidin is showing a decreasing trend from 0 mg/L to 2 mg/L of concentration of anionic polyacrylamide. It can also be seen that the highest percentage removal of melanoidin was 80.93% at the dosage of 0.3g/L of calcium lactate without any anionic polyacrylamide added. This phenomenon may be due to the formation of larger aggregates which were too hard for them to settle at the stated polymer doses [15]. This was because the sudden add-on of the anionic polyacrylamide at 0.05mg/L from none before and gradually increases of the polymer dosages from 0.1mg/L to 0.5mg/L might gave them some difficulty to settle down immediately. However, the density of the aggregates increased as the polymer doses increases [15]. This can be used to explain the better removal obtained for the polymer doses that are higher than 0.05 and 0.5mg/L.

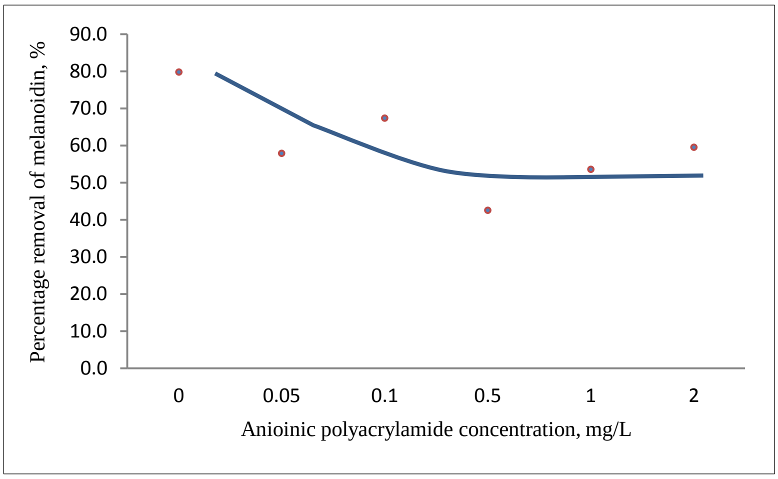

Figure 4. Graph of percentage removal of melanoidin concentration against anionic polyacrylamide concentration

The results show that there is only minor improvement in the removal of melanoidin by using anionic polyacrylamide (flocculants) as compared to the removal of melanoidin by using only calcium lactate (coagulant). This might be due to the molecular weight and charge density of the A-PAM led to the random coil rather than an extended conformation [9].

However, the melanoidin removal percentage was increasing at 0.5mg/L dosage of anionic polyacrylamide from 40.20% to 57.84% with the dosage of 2mg/L. This implied that the removal of melanoidin colloids increased with the increased in dosage of the anionic polyacrylamide. This was most probably because of the enlargement of flocs occurred. Enlargement of flocs can only occurred when there was enough adsorption affinity between the polymers and the flocs surfaces [15]. Polymers adsorbed onto the melanoidin colloid surface with the adequate amount of polymers. Besides that, the adequate amount of anionic polyacrylamide also produced sufficient long loops that can be attached to the surface of the melanoidin colloid that required for bridging flocculation [16]. By looking at the results obtained in this study, A-PAM may have disturbed the formation of flocs. Therefore, the main mechanism is believed to be charge neutralization-precipitation.

4. Conclusions

Treatment of aerobic palm oil mill effluent using combination of the calcium lactate and anionic polyacrylamide has been studied. It can be concluded that anionic polyacrylamide do not significantly assists the overall performance of the removal of melanoidin from palm oil mill effluent. Anionic polyacrylamide only showed some minor effect on the removal of melanoidin which is dark brown to black coloured natural condensation products of sugar and amino acid produced by non-enzymatic browning reactions called Maillard reaction. There are some further study that can be carried out on the POME such as a combined process that involving coagulation/flocculation and membrane filtration so that a complete removal can be achieved.

Acknowledgment

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