Performance of combined persulfate and tannin for the treatment of anaerobically treated palm oil mill effluent

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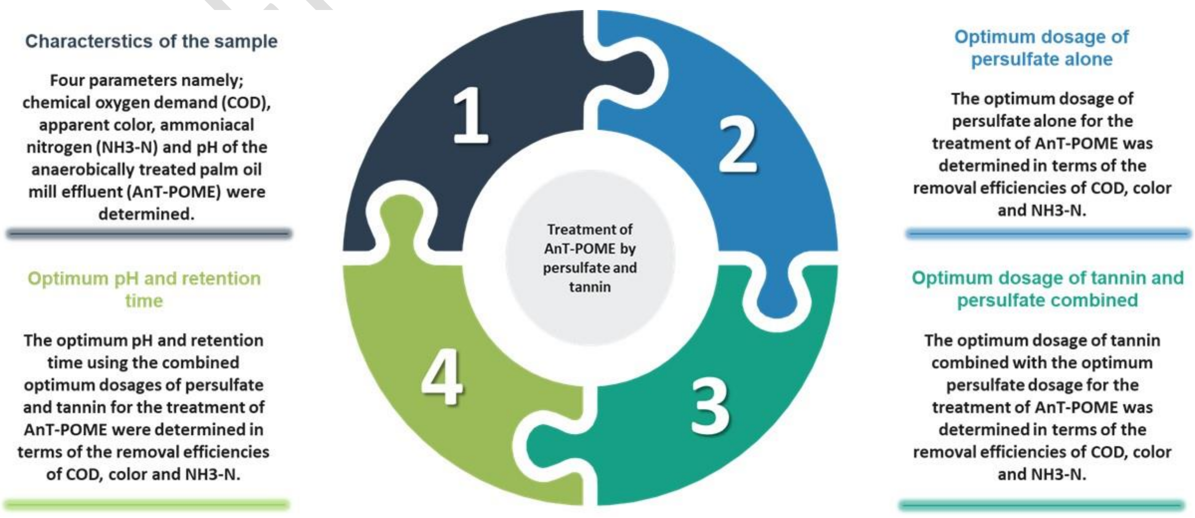
GRAPHICAL ABSTRACT



Abstract

The current research was aimed to investigate the performance of combined persulfate oxidation process and tannin via coagulation-flocculation processes as a post treatment of anaerobically treated palm oil mill effluent (AnT-POME). Different dosages of sodium persulfate ($Na_2S_2O_8$, 238 g/mol) 0.1 (w/v) and modified tannin were combined as a simultaneous reaction to treat AnT-POME. Different dosage of tannin ranged between 0.02g and 0.12g with pH variation ranged between 3 and 11 retention and retention time of (30, 90, 120 and 180) were evaluated. The performance of the treatment processes was evaluated based on the removal of three different parameters namely; chemical oxygen demand (COD), ammoniacal nitrogen (NH_3-N) and color under the following operational conditions: persulfate dosage, tannin dosage, pH and retention time (min). Using persulfate alone, the maximum removal efficiency of COD, color, and NH_3-N were 50%, 60% and 22%, respectively by using 4 mL of 0.1 (w/v) persulfate dosage at pH 7 and 60 min retention time. While the performance of simultaneous reaction improve the removal efficiencies of COD, color, and NH_3-N to 90%, 96% and 44%, respectively using 4 mL of 0.1 (w/v) persulfate and 0.06 g of tannin during 120 min retention time at pH 7. However, the maximum removal of NH_3-N (59%) was achieved at pH 11. The study revealed that the simultaneous persulfate/tannin reaction is a promising treatment method for industrial wastewater treatment.

Keywords: Persulfate, Tannin, Oxidation, Treatment, Removal, Effluent

1. **Introduction**

Elaeis Guineensis or African palm oil are recognized names for Oil palm trees. They originate from West Africa and have been introduced into Malaysia in 1910 by William Sime and Henry

Darby. Nowadays, Indonesia and Malaysia are the ultimate palm oil producers and the leading exporters worldwide. It is reported that the global palm oil production was more than 75 million MT in 2020/2021 as compared to approximately 73 million MT back in the marketing year of 2019/2020 (Statista, 2021). As a matter of fact, Malaysia is the second-largest producer of palm oil after Indonesia. Currently, Malaysia shares about 27% of the global production of palm oil (MPOC, 2019). Therefore; palm oil has become a significant source of revenue for Malaysia. The production processes of palm oil from fresh fruit bunch (FFB) generally produce three major commodities: Crude Palm Oil (CPO), Crude Palm Kernel Oil (CPKO) and Palm Kernel Expeller/Cake (PKE/C). These processes yield huge amount of solid and liquid wastes which play a role as the major source of environmental contamination. The high concentrations of Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Suspended Solids (SS), Ammoniacal-Nitrogen (NH3-N) pollutants, high color intensity and the acidity of POME produced by palm oil industries would pose critical threats to the environment if it was just released into the environment without/.partially treatment. Most critically; the water streams would deplete and result in the suffocation of the aquatic life in the water body that would even cause malodorous problems. Based on MPOB (2019 A and B), a typical POME in Malaysia, habitats an average COD and BOD of 51000 mg/L and 25000 mg/L; respectively. Thus; they have to be treated and controlled before discharged. Palm Oil Mill Effluent (POME) is identified as the most expensive and difficult waste to be controlled and managed by mill operators due to the enormous quantity of the effluent generated by the palm oil mill at a time. According to the Malaysian Palm Oil Board (MPOB), the production of CPO was more than 19 million MT by the end of 2020 (Malaysian Palm Oil Board , 2021). Consequently, the generation of POME is estimated to be more than 66 million m^3 per year. Palm oil industries are tremendously regulated and adhered to more than 15 laws and regulations on both solid and liquid wastes (MPOC, 2019A and B). Environmental Quality Act (EQA) 1974 is an example of the laws and regulations set by The Malaysian Ministry of Environment so as to govern a safe discharge of POME into water bodies. In Malaysia, POME is commonly treated biologically utilizing conventional oxidation ponds either anaerobically or aerobically (Bashir et al., 2019). Other processes involved for further treatment and degradation of contaminates in Anaerobically Treated Palm Oil Mill Effluent (AnT-POME) such as conventional anaerobic digestion treatment. In spite of the low operating cost, conventional anaerobic digestion treatment requires a high capital cost for a vast land area and long hydraulic retention time. Therefore, so many studies have been done in order to effectively treat POME such as coagulation-flocculation (Hameed et al, 2018), Electrocoagulation (Nasrullah et al., 2020 and Bashir et al., 2017), Electro-oxidation (Bashir et al., 2017), Adsorption and photo catalytic oxidation (Ng, 2021). Natural coagulants have recently received much attention for POME treatment application. Lim et al., (2021) used fenugreek as a natural plant coagulant for POME treatment. Lek et al., (2018) utilized chickpea (Cicer arietinum) as a natural coagulant for the treatment of POME. (Kim et al., 2020) used Fenugreek seeds and okra for POME treatment. Tannin has been introduced as an organic environment friendly alternative substituting those conventional inorganic chemicals. Tannin is recently used for wastewater treatment (Banch et al., 2019). Tannin is a complex polyphenolic compound whose molecular weight ranges from 500 up to more than 3000. It is found naturally in plants, especially pulses that have the ability to bind to and precipitate proteins and other macromolecules. Commercially speaking, it is known as modified condensed tannin which is an organic coagulant extracted from Acacia tree (Hameed et al., 2018). Accordingly, the performance of simultaneous oxidation and natural coagulant for POME treatment was not documented. The objective of this work is to determine the performances of combined Sodium Persulfate and tannin as a firs time for the treatment of pre-treated POME.

2. Methodology

2.1 Sampling

The sample used in this experiment was anaerobically treated palm oil mill effluent (AnT-POME) which was collected from SIME DARBY BERHAD at Ladang Kemuning, Melaka, 76460 in Malaysia, A sampling of 20L of AnT-POME was facilitated by the corresponding technician in charge. The collected sample was transferred to the laboratory characterized immediately, and then the sample was stored and refrigerated in order to prevent any further growth of microorganisms affecting its physical, biological and chemical characteristics. The general characteristics of AnT-POME are presented in (Table 1).

Table 1: Characteristics of AnT-POME and DoE discharge regulations 1977 and its subsequent amendments from 1978 to 1984 and thereafter.

Parameters	Range	Mean	Discharge Limit
COD (ppm)	2400-5400	**3900**	**1000**
NH_3-N (ppm)	320-380	**350**	**150**
Color (Pt-Co)	15600-22700	**19150**	**-**
pH	7.46-8.07	**7.77**	**5.0-9.0**

2.2 Experimental procedure

In this experimental investigation, persulfate stock solution was prepared based on preliminary experiments. The concentration of persulfate was 0.1 (w/v). The only operational condition studied here was the optimal dosage of persulfate for its performance of treating AnT-POME in removal of COD, color and NH_3-N at room temperature. Persulfate reagent ($Na_2S_2O_8$, 238 g/mol) was employed to treat AnT-POME. To determine the optimum conditions; a set of persulfate reagent dosage 0.1 (w/v) was immediately added (1 ml to 6 ml) into 250 ml conical flask reactor contains 50 ml of AnT-POME before each run to achieve the highest performance for the treatment. The solution was thoroughly shaken at 200 rpm for 1 hour. The mixture was allowed to be settled for up to an hour, then filtered. Maintaining the optimum dosage of persulfate 0.1 (w/v) determined, different tannin dosage was added gradually between 0.02g and 0.12g. Different pH and retention time were investigated; pH (1, 3, 5, 7, 9 and 11) including the average pH of the sample and retention time of (30, 90, 120 and 180) min including 60 min that was set as the basis for this research.

2.3 Analytical study

Leachate sample was shaken well prior to each analysis. COD, color and NH_3–N, were immediately tested before and after each experiment using HACH DR/2800. COD concentration was determined by the closed reflux, method 8000, a reactor digestion method at wavelength of 620-nm. Concentration of NH_3-N was tested by method 8155 and method 10031 used for high range (HR), a salicylate method at 655-nm. True color was determined by method 8025 at 455-nm. pH was measured using a portable digital pH/Mv meter. The tested values are presented as the average of three measurements, and the difference between the measurements of each value was less than 3%. The removal efficiencies of COD, color and NH_3–N were obtained using the following mathematical equation (1):

$$\text{Removal (\%)} = [(Ci - Cf) / Ci] \times 100 \qquad (1)$$

Where Ci and Cf refer to the initial and final COD, color and NH_3–N concentrations; respectively.

3. Results and Discussion

3.1 Persulfate Oxidation

Persulfate oxidation alone was used to treat the biologically treated POME. Several dosages of 0.1 (w/v) of persulfate namely; 1ml, 2ml, 3ml, 4ml, 5ml and 6ml were added to separate AnT-POME samples of 50mL. The pH of all six samples were initially measured and recorded as 7.96. The mixture-containing conical flasks were placed into in the incubator shaker at room temperature in which the retention time and agitation speed was fixed at 60 min and 200 rpm, respectively. The maximum removal efficiencies of the corresponding parameters, COD, color and NH_3-N were 50.00 %, 60 % and 22 %, respectively using 4 ml 0.1 (w/v) persulfate dosage (Figure 1). The pH of the samples was slightly decreased from 7.96 to 7.20 directly proportional to the amount of persulfate dosage added from 1ml up to 6ml. A slightly reduction was observed in the removal efficiencies of the related parameters when increasing the persulfate dosage more than 4ml. A higher amount of sulphate ions, which formed from the addition of persulfate at neutral medium as shown in the chemical equations (2 and 3) diverting the equilibrium to the right, may act as scavenger to inhibit the performance of oxidant (Liang et al. 2007).

$$S_2O_8^{2-} + 2H_2O \rightarrow H_2O_2 + 2HSO_4^- \quad (2)$$

$$2HSO_4^- \leftrightharpoons 2SO_4^{2-} + 2H^+ \quad (3)$$

Lim et al., (2021) reported reduction in COD removal for excessive amount of persulfate used for POME treatment.

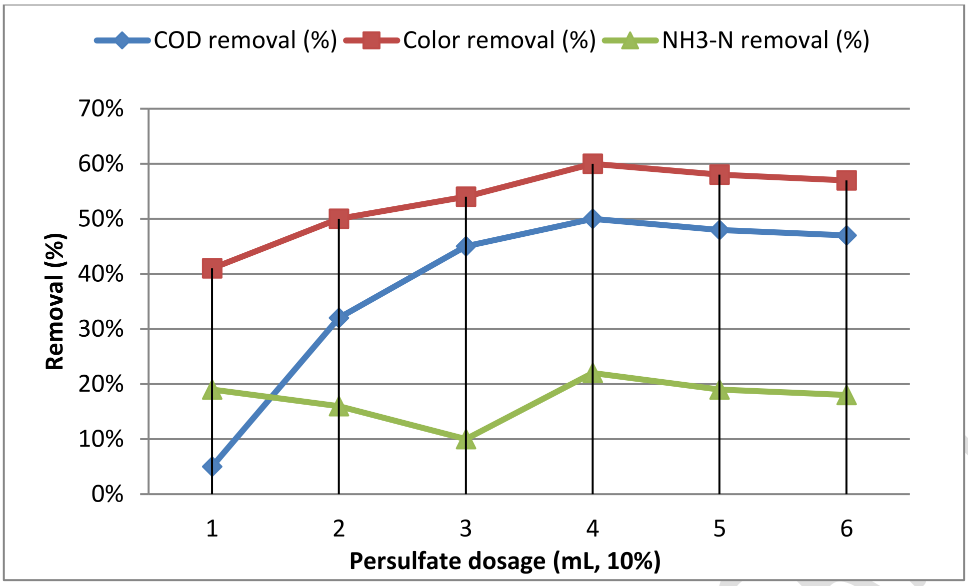


Figure 1: Effects of persulfate dosages on the COD, color and NH_3-N (Exp. Con.: 60 min retention time; pH_i= 7.96 and agitation speed= 200 rpm).

3.2 Effect of combined persulfate and tannin

In this section, varying dosages of tannin (0.02g, 0.04g, 0.06g, 0.08g, 0.10g and 0.12g) were each combined with persulfate to improve the removal of COD, color and NH_3-N from AnT-POME. The optimum dosage of 4 ml of 0.1 (w/v) persulfate was used for all runs. The initial pH of the samples was untouched and recorded as 8.07. Following the stipulated operating conditions of agitation speed and retention time used in this research, the maximum removal efficiency for COD, color and NH_3-N were 73 %, 77 % and 40 %, respectively using 0.06g dosage of tannin combined with the optimum dosage of persulfate. (Figure 2). After the treatment, the pH of the sample decreased from 8.07 up to 7.0 as tannin dosages increased. The removal efficiency was pointedly rising as the dosages of tannin increased from 0.02g up to 0.06g. It is illustrated that there was further degradation of organic matter when tannin was combined with persulfate. Since tannin has the ability to bind with macromolecules via hydrophobic and hydrogen bonding interactions when deprotonating and forming phenoxide ions in the solution (Hagerman, 2002), it is said that this is the reason why there was a great enhancement of the COD and color removals. The improvement in the removal of COD and color was due to the ability of polyphenols in tannin to absorb organics and metal ions (Palma et al., 2003). While, the enhancement in NH_3-N removal may attribute to the effect of electric double layers formed by phenolic and amino groups in the modified tannin (Schofield et al., 2001). Moreover, the primary amino groups in tannin with positive charge may improve the bridging mechanism of the particles and colloids in POME and enhanced the flocculation process (Mangrich et al.,2014). The removal was declined when the tannin dosage was higher than 0.06g. Condensed tannin is un-hydrolysed in the liquid and has a relatively high molecular weight. As a higher tannin dosage was used, a significant amount of tannin may clump together via hydrophobic interactions once added. In a result, it settled fast and led to inhibit the removal efficiency (Kim et al., 2020).

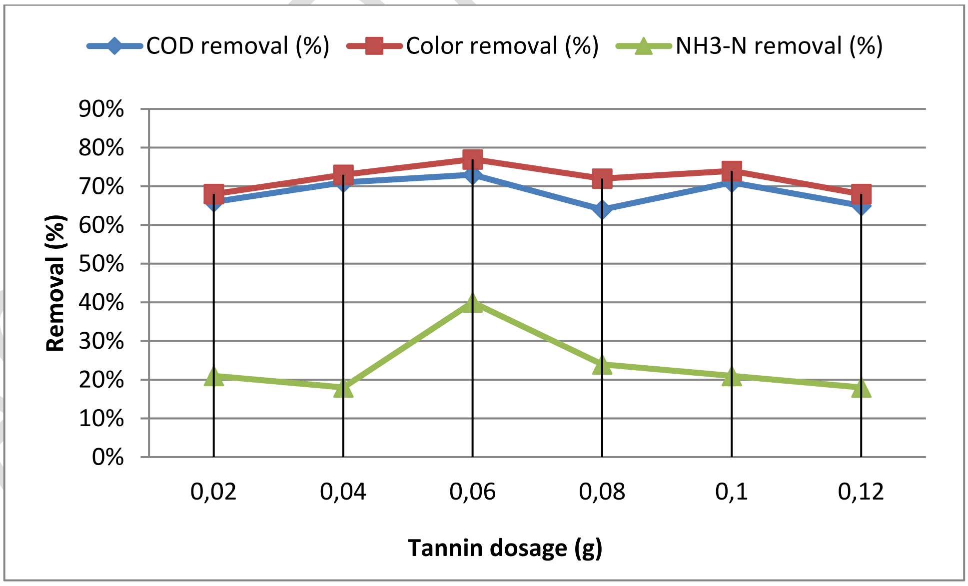


Figure 2: Effects of tannin dosages combined with persulfate on the removals of COD, color and NH_3-N (Exp. Con.: optimum 0.1 (w/v) persulfate dosage= 4 ml; 60 min retention time; pH_i= 8.07 and agitation speed= 200 rpm).

3.3 Effect of pH

Figure 3 illustrates the removal efficiency of COD, color and NH_3-N from AnT-POME with varying pH values (1, 3, 5, 7, 9 and 11) using combined optimum dosages of 4ml of 0.1 (w/v) persulfate and 0.06g of tannin. The retention time was fixed at 60 min at 200 rpm in the incubator shaker. As expected, after the treatment of the sample with the combined weak acids; persulfate and tannin, the final pH decreased. For instance, for the theoretical pH value of 7, the actual initial value of pH was 6.99 and then dropped after the treatment down to 6.77. The effect of the pH of the sample is essential and crucial for so many chemicals. Either to activate a given chemical or to de-activate it in order to get to the desired objective thru a related chemical reaction. In literature, optimal pH is needed for both persulfate and tannin to further boost the treatment of the sample. For persulfate, the optimum pH lies in between very acidic in which pH < 3 or very basic pH > 10. Sulfate radicals of a redox potential, E= 2.6V are produced and predominant at acidic medium as shown in the following chemical equation (4):

$$\boldsymbol{HS_2O_8^- \rightarrow SO_4^{\bullet-} + SO_4^{2-} + H^+ \ (Predominant)} \qquad (\mathbf{4})$$

Whereas, hydroxyl radicals of 2.8V are generated at basic medium as shown in the following chemical equation (5):

$$\boldsymbol{SO_4^{\bullet-} \rightarrow \ SO_4^{2-} + OH^{\bullet} \ (Predominant)} \qquad (\mathbf{5})$$

It is observed that the optimal theoretical pH value for treating the sample with the combined optimum dosages of persulfate and tannin was at neutral at a pH of 7. The COD, color and NH_3-N removal efficiencies were as the following, 85 %, 91 % and 39 %. Based on these figures upon the adjustment to the optimum pH of 7 compared to the initial pH of the sample, a significant increase in terms of the removal efficiencies of COD and color were observed. At a pH higher or lower than 7, hydroxyl and sulfate radicals could form and they would affect the treatment performances by interfering and competing with one another. However, a higher

NH_3-N removal was observed as the pH rises. The highest NH_3-N removal was accomplished at a pH of 11. It is believed that persulfate for being a strong oxidant, it has been playing a big role in oxidizing NH_3-N with additional removals by tannin. According to the chemical equation (5) in which hydroxyl radicals are formed at pH 11, the NH_3-N removal efficiency reached up to its peak at 59.46%. Simultaneously, hydroxyl radicals may oxidize some tannin and could cause a radical repulsion with some remaining sulfate radicals that were produced in an intermediate reaction at the basic medium as shown in the chemical equation (6) which results in the lowest removal of COD.

$$2S_2O_8^{2-} + OH^- \rightarrow 3SO_4^{\bullet -} + SO_4^{2-} + O_2^{\bullet -} + H^+ \qquad (6)$$

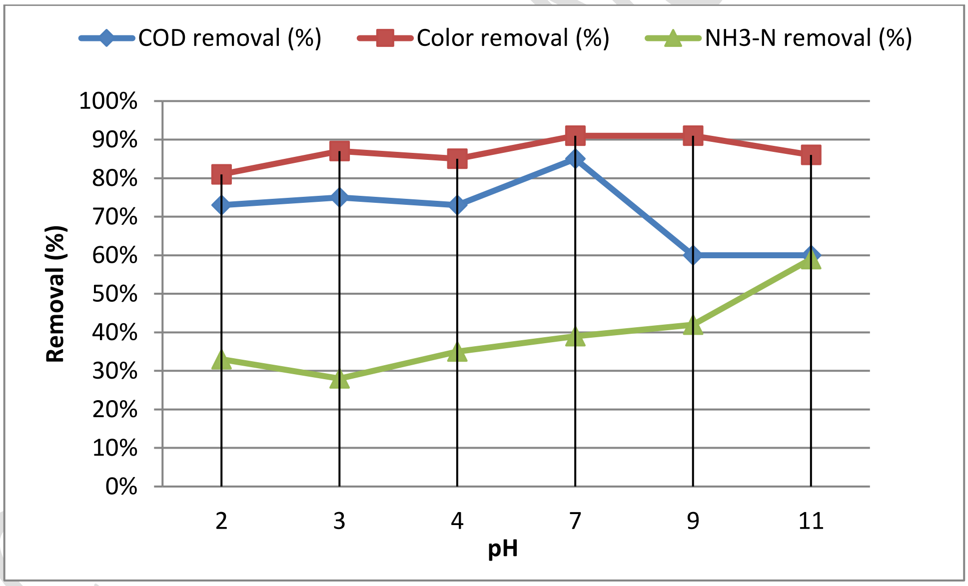


Figure 3: Effects of pH variations on the removals of COD, color and NH_3-N (Exp. Con.: combined optimum dosages of 4ml of 0.1 (w/v) persulfate and 0.06g of tannin; 60 min retention time and agitation speed= 200 rpm).

3.4 Effect of retention time

Figure 4 illustrates the removal efficiencies of COD, color and NH_3-N from AnT-POME with varying retention time in the incubator shaker (30, 60, 90, 120, and 150) minutes, with the optimum combined dosages of 4ml 0.1 (w/v) persulfate and 0.06g of tannin at the optimal pH of 7 and 200 rpm agitation time. All final pH values were decreased after the treatment has taken place by both weak acids persulfate and tannin. The removals of COD, color and NH_3-N were enhanced as the retention time increased until it reached to a steady state pool. The maximum removal efficiencies of COD, color and NH_3-N were found to be 90 %, 96 % and 44 %, respectively. Optimally speaking and pertaining to the time consumed for agitation, the removal efficiencies did not change substantially after 60 minutes of agitation in which the maximum removal efficiencies were observed at 120 minutes of retention time. Therefore, it is believed that after 60 minutes of retention time, good dispersion of persulfate and tannin throughout the sample to be treated has established and the necessary reaction has developed in which all colloidal particles and other organic and inorganic pollutants were oxidized by persulfate and coagulated by tannin.

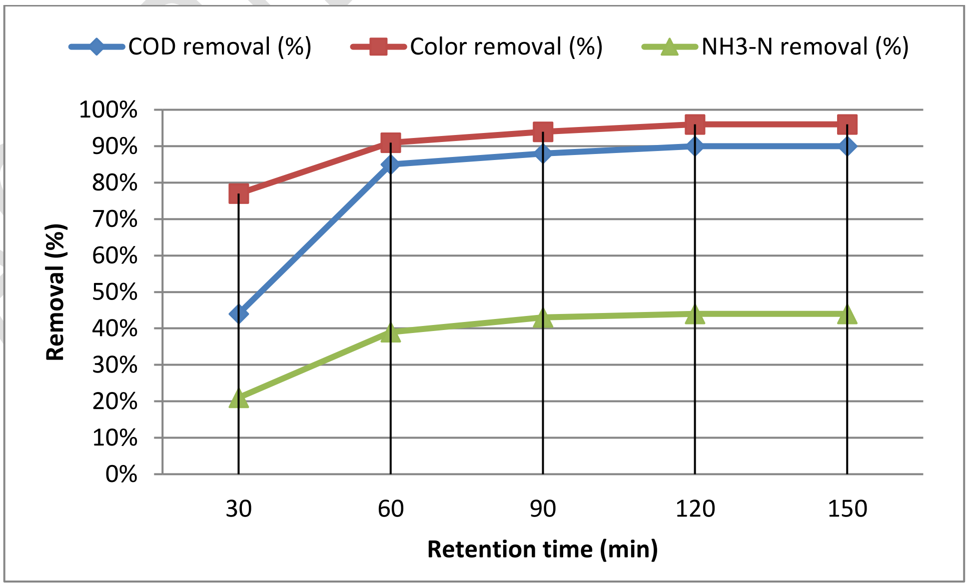


Figure 4: Effects of retention time variations on the removals of COD, color and NH_3-N (Exp. Con.: combined optimum dosages of 4ml of 0.1 (w/v) persulfate and 0.06g of tannin; optimum pH= 7 and agitation speed= 200 rpm).

4. Conclusion

The present research was designed to determine the operating conditions for the treatment of anaerobically treated palm oil mill effluent (AnT-POME) in terms of persulfate and tannin dosages, initial pH of the sample and retention time in response to the removal efficiencies of COD, color and NH_3-N. A combined dosages of 4ml of 0.1 (w/v) persulfate and 0.06g of tannin at pH 7 and retention time of 120 minutes achieved the maximum removal efficiencies for COD (90%), color (96%) and NH_3-N (44%). The performance of combined persulfate/tannin for the treatment of AnT-POME considerably showed significant removals of parameters compared with persulfate alone. The combined persulfate/tannin process can be recommended for organic removal from concentrated industrial wastewater.

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