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Sustainable Treatment of Palm Oil Mill Effluent (POME) by using Pectin and Chitosan in Jar Test Protocol – Sequential Comparison

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Abstract: Oil palm industry in Malaysia is developing as demand towards alternative and cheaper edible oil continuously received from the European Union. However, adverse environmental impacts from this activity coupled with laden recalcitrant effluent contribute to the water pollution pose risk to water body and human's health. The purpose of this research project is to compare the efficiency between Pectin (Heteropolysaccharide) and Chitosan (D-glucosamine) for tertiary treatment of anaerobic-aerobic treated palm oil mill effluent (POME). Factor that affecting the efficiency of the coagulation process such as dosage of coagulant used was studied by using jar-test protocol. From the experimental results, the ideal experimental conditions that remove turbidity, COD and colour were exceptional when using Chitosan. At this condition 83% of turbidity, 88% of TSS, 79% of colour and 53.1% of COD were removed. Nevertheless, it was observed that pH plays dominating factor that contribute to the overall removal efficiency. This research would give an idea on alternative way for tertiary wastewater treatment of POME

Keywords: POME, Pectin, Chitin, Coagulant, Sustainable, Treatment

1. Introduction

Palm oil mill effluent (POME) is a liquid pollutant that contain highly suspended and colloidal byproducts that exist in brown thick liquid form with a characteristic of strong-smelling [1]. The fresh produced POME has a waste characteristic of high biochemical oxygen demand (BOD), chemical oxygen demand (COD), colour and total suspended solid (TSS) which will cause severe effect to the aquatic ecosystem if discharge without treatment. However, POME has no toxic characteristic as there is no chemical substances were added during the palm oil extraction process [1]. Therefore, it is also important to avoid adding too much of chemicals during treatment of POME. POME is very acidic in nature which is in the range of 4.5 due to the presence of organic acid presence in the complex form that are acceptable to be the substrate of carbon sources.

The quality of raw material used during the extraction process will affect the quality of POME [2]. The brownish colour that is present in POME is due to the existence of lignin and some of its degraded substances like tannin and humic acid that is originated from crushed palm nut, lipid and fatty acid during the extraction of palm oil process [3].

Although most of the mils operator employed biological treatment process in minimizing the value of BOD and COD in the POME, some of the palm oil mills are still failed to comply the discharge standard that set by Department of Environment under Environmental Quality (Prescribed Premises) (Crude Palm-oil) Regulations, 1977 (amended by P.U. (A) 183/82). However, even though biological treatment have been employed, the problem of tea colour effluent remain unsolved even though the BOD and COD value meet the discharge standard [3].

The brownish effluent of treated POME is deemed as an indication of pollution by the public although colour is not included as one of the parameters in discharge

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standard [4]. On the other hand, the tea colour effluent will form a barrier that reduce the penetration of sunlight into the water bodies and thus it impaired the photosynthetic activity. In addition, some of the coloured elements that present in POME would have the characteristic of high affinity towards chelate metal ions. This will indirectly contribute to the formation of toxic and harm the aquatic life [5-7].

There are environmental pollution problems that caused by the industry sites such as a large amount of waste production, involving a large quantity of water usage in oil extraction process, and high organic content wastewater generation. In order to achieve more sustainable of the palm oil industry, the quality of discharged POME should be improved. In Malaysia, there is a lot of palm oil mill still fail to comply the standard before discharged and the final discharged POME with brown colour is not been reused due to the bad aesthetic. Therefore, it is important to have a tertiary treatment for a better discharge of POME that complying with permissible discharge limits enforced by DOE.

2. Materials

The POME used was anaerobic-aerobic treated POME which also the effluent after anaerobic – aerobic treatment. There were two types of anaerobic-aerobic treated POME that were collected, mesophilic anaerobic-aerobic treated POME (MPOME) and thermophilic anaerobic-aerobic treated POME (TPOME). The samples were collected from lab scale anaerobic-aerobic treatment system at lab 141, School of Technology Industry, Universiti Sains Malaysia, Penang. The sample were then stored in a tightly closed plastic container and keep in laboratory storage area at 4℃ in order to inhibit the microbiological activities that will bring to the composition in the sample according to (Malakahmad and Chuan, 2013).

2.1 Methods

(a)Preparation of Chitosan solution

Chitosan (D-glucosamine) with 85% of deacetylation degree (DD) form Sigma-Aldrich with medium molecular weight was used in this experiment. 200 mg of Chitosan was weighted and dissolved in 10 mL of 0.1M HCl. The mixture is then mixed with 90 mL of deionized water and agitate by magnetic stirrer until the Chitosan is fully soluble in the solution. Chitosan solution is always freshly prepared before the experiment start (Rizzo et al., 2008a).

(b) Preparation of Pectin solution

Pectin (Heteropolysaccharide) from Fluka with degree of esterification (70-75%) was used in this experiment. 200 mg of pectin was weighted and dissolved in 30 mL of deionized water. It is then being stir by using glass rod until fully dissolved in the deionized water. The mixture was poured into 100 mL volume of volumetric flask and top up by using distilled water to get 100 mL of pectin solution.

2.2 Analytical measurement

Turbidity was measured by using HACH 2100Q Turbidity meter. Calibration was done with standard solution of 10 NTU, 20 NTU, 100 NTU and 800 NTU prior measurement. COD was measured by using HACH DR 6000 Spectrophotometer with program number 435 (COD HR) at 620 nm wavelength. Method No 5220D (closed reflux, colorimetric method). Colour was measured by using similar spectrophotometer with program number 120 (True and apparent) at 455 nm and 640. The procedures of for all parameters measurement were carried out based on the recommendation by American Public Health Association (APHA) 2005 [8].

2.3 Experimental sequence

The overall experimental sequence is shown in Table 1.

Table 1: Experimental sequence

Coagulant/Flocculant	Dosage (mg/L)	Substrate
Chitosan	40,80,…..200	MPOME
Pectin	40,80,…..200	
Chitosan and Pectin	Combination of same dosage of Chitosan and Pectin (40 Chitosan + 40 Pectin; 80 Chitosan + 80 Pectin,…..200 Chitosan + Pectin)	

3. Results and Discussion

3.1 Removal efficiency of Chitosan and Pectin in MPOME

Effect of coagulant dosage in turbidity removal

Fig. 1 shows the removal trend for turbidity by using chitosan and pectin in MPOME. Generally, there is slight increase of turbidity removal with the increasing the dosage of chitosan. The lowest turbidity removal observed was 85.40% at the dosage of 40mg/L. The highest of removal is 90.32% when the chitosan dosage reach to 200mg/L. The p-value of the relationship between the dosage of chitosan and turbidity removal shows the value of 0.016 and the correlation coefficient show the value of 0.943. This indicate that the increment in dosage of chitosan show a significant relationship with turbidity removal.

On the other hand, the turbidity removal for pectin increase from 78.30 % at the dosage of 40mg/L to 79.51% at the dosage of 80mg/L before it continuously decreasing to 73.76% at the dosage of 200mg/L. Correlation coefficient value is 0.911 and p-value of the relationship between dosage of pectin and turbidity show the value of 0.031. This indicates that the increment in dosage of pectin will not decrease in turbidity.

Fig. 2 shows the combination of dosage of chitosan and pectin with the relation in turbidity removal. From the figure, the removal of the turbidity was fluctuated between 85-86% even in the increment of both dosage of chitosan and pectin and the highest turbidity removal is 87.81% at the dosage of 200 mg/L for both chitosan and pectin. However, the p-value for the correlation show a value of 0.320, which indicating the insignificant of higher turbidity removal when both of the dosage increase.

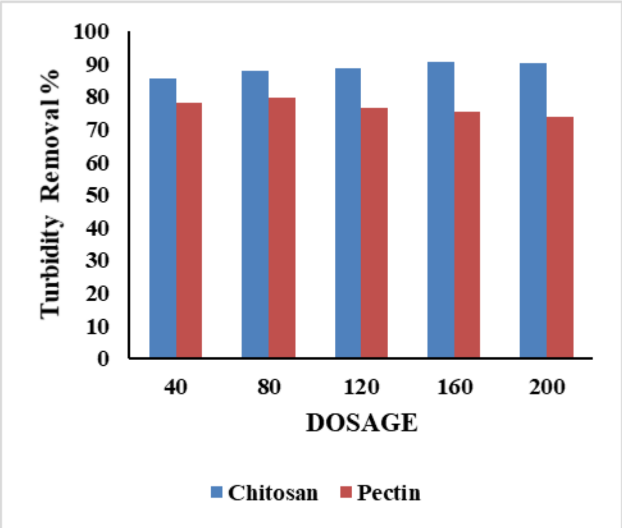

Fig. 1: Comparison between Chitosan and Pectin for turbidity removal under MPOME

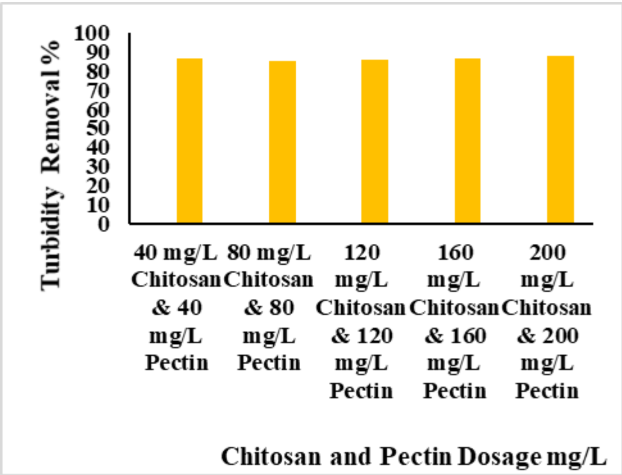

Fig. 2: Combination of Chitosan and Pectin for turbidity removal

Effect of coagulant dosage in COD removal

Based on Fig. 3, COD removal was slightly found to slightly increase with the respect in increasing the dosage of chitosan. The lowest COD was removed at 28.17% at the dosage of 40 mg/L of chitosan. The highest removal of COD at 35.41% when the chitosan dosage reachs to 200 mg/L. The correlation of the increment in dosage of Chitosan and COD removal shows the positive value of 0.951 and the p-value of the relationship shows the value of 0.013. This indicate that the increment in dosage of chitosan show a significant relationship with COD removal.

On the other hand, the COD removal for pectin increased gradually from the with 9.93% removal at the dosage of 40mg/L to the highest removal of 20.72% when the pectin dosage was fixed at 200 mg/L. The correlation coefficient and p-value of the relationship between dosage of pectin and COD show the value of 0.983 and 0.03 respectively. This p-value shows that the increment in dosage of pectin shows a positive significant effect with the respect of COD removal.

Fig. 4 shows the combination in dosage of chitosan and pectin with the relation of the COD removal. From the figure, the removal of the COD decreased fairly along with the increasing in dosage of both chitosan and pectin. The highest COD removal is 18.78% at both 40mg/L for chitosan and pectin and the lowest COD removal occur at 200 mg/L for both chitosan and pectin with the removal efficiency of 13.32%. The correlation coefficient of the relationship shows -0.951 the p-value of correlation show a value of 0.013, which indicating it is negative significant of lower COD removal when both of the dosage decreased.

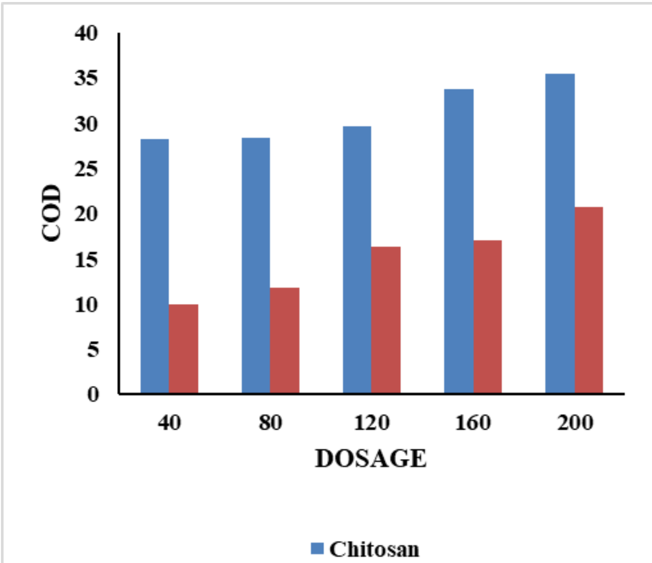

Fig. 3: Comparison between Chitosan and Pectin for COD removal under MPOME

Effect of coagulant dosage in colour removal

Fig. 5 shows the effect dosage in the colour removal of tertiary treatment of POME by 2 different type of coagulant, which is chitosan ad pectin. Based on the removal trend, the colour removal fluctuated between 19%-21% with the increasing in chitosan dosage from 40 mg/L to 160 mg/L before it reach the highest colour removal, 24.07% at 200 mg/L. However, the p-value of the correlation between the dosage of chitosan and colour removal is 0.123. This expresses that the addition in a dosage of chitosan is insignificant in colour removal.

Apart from that, the colour removal which was moderately increased when the dosage was increased. The colour removal increased from 17.68% at the dosage of 40 mg/L to the peak of 22.52% at 120 mg/L before the removal efficiency drop to 21.26% at the dosage of 200 mg/L. As specified by the p-value which is 0.162 in the correlation test, it shows that the gain in dosage of pectin have insignificant effect on the colour removal.

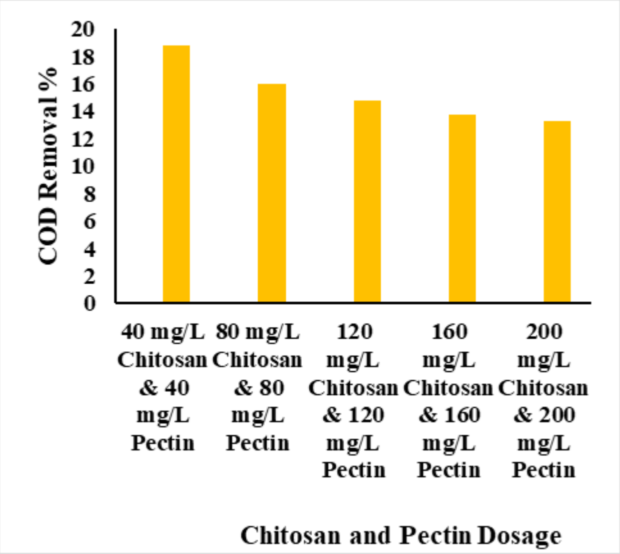

Fig. 4: Combination of Chitosan and Pectin for COD removal

Fig. 6 shows the mixture in dosage of chitosan and pectin with the relation of the colour removal. From the figure, the removal of the colour occurred from the highest removal of 23.84% at both 40mg/L for chitosan and pectin decreasing to a minimum of 18.57% at the 160mg/L for both dosage before further increased in dosage led to marginal colour removal to 20.61% at 200 mg/L for both chitosan and pectin. The p-value of correlation show a value of 0.152, which indicating the insignificant of higher colour removal when both of the dosage increase.

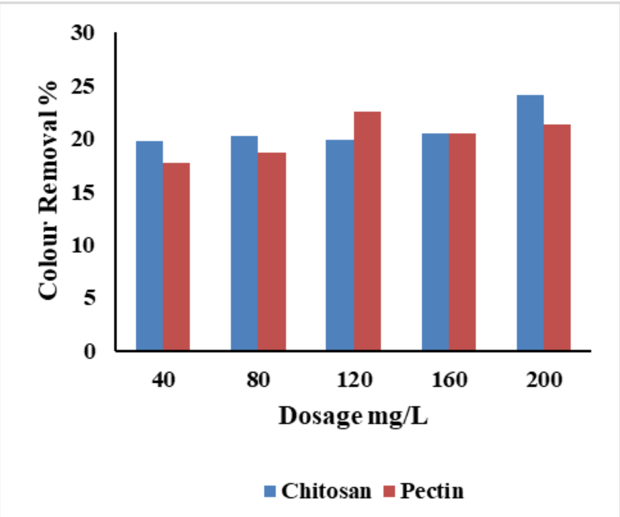

Fig. 5: Comparison between Chitosan and Pectin for colour removal under MPOME

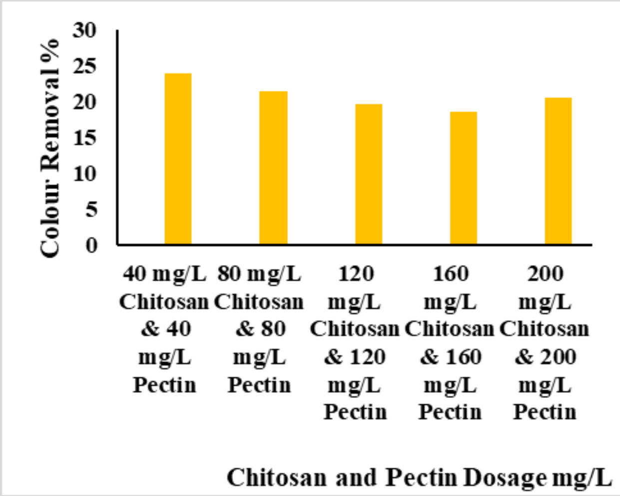

Fig. 6: Combination of Chitosan and Pectin for Color removal

Discussion

In general, the performance of chitosan alone is the best among all of the three in terms of turbidity removal, colour removal and also COD removal. POME poses negatively charge in nature. The waste particle had negative surface charge when it is alkaline condition [9]. The mechanism of chitosan involve 3 main mechanisms in removing colour, COD, and also turbidity ie. charged neutralization, patch flocculation and also bridging. When chitosan is introduced into POME which is negatively charged in nature, charge neutralization occurs between the negatively colloidal substances and the positively charged chitosan. The opposite charged ion attract to each other charged neutralization and lastly ease the formation of larger floc by Van der Waals force of attraction [10].

According to Hassan et al [11] and Ahmad et al [12] their removal in term of turbidity and total suspended solid for chitosan is more than 90% in pH 5 and pH 4 in both wastewater from manufacturing industry and palm oil mill effluent respectively. And for pectin, the removal efficiency in turbidity is more than 90% with the dosage of 30mg/L at pH 4 in kaolin suspension [13]. It shows that the usage of chitosan and pectin is restricted by a narrow range of pH due to their poor solubility in alkaline condition. Typically above 6.5, chitosan will lost its cationic characteristic [14]. This is because coagulant will not able to perform well in extreme pH [15]. It can deduced that when decreasing in pH, both pectin and chitosan would have a better performance in removal.

The performance of chitosan can be higher in acidic condition. However, in this project, pH adjustment is not done to avoid too many adding of chemical into the POME. The pH effect plays an important role in the degree of protonation of the amine group, the changes in the macromolecular chain's structure and also the floc density.

In low pH condition, chitosan protonated and become high charged density cationic polymer favour the binding mechanism between chitosan functional group and wastewater colloidal particles [9]. This is due to the H+ ion in acidic condition protonated with the active amino group in chitosan chain. A long cationic polyelectrolyte chain has formed and this chain poses characteristic of adsorption and static attraction [16].

Besides, the performance of the removal in turbidity, COD and also colour in the combination of chitosan and pectin is lower compare to the performance chitosan alone because when in alkaline condition, the concentration of H^+ is limited. At this level, the amount of OH^- and COO^- that own by the biopolymer play a significant role in reaction of the wastewater. A repulsive force will form between the negatively charged ion in the substrate and the negatively charged ion that found in the biopolymer. The repulsive force avoids formation of hydrogen bonding that favour the coagulation process [13].

Removal efficiencies for turbidity, COD and color when $FeSO_4$ added as main coagulant assisted with Chitosan

Previous discussions have shown that Chitosan removed higher turbidity, COD and color from MPOME. However, all parameters were found not complying to standard discharge limit by DOE. Therefore, main coagulant which was $FeSO_4$ was used assisted with coagulant aid which was the Chitosan. Fig. 6-8 show the combination of different $FeSO_4$ and chitosan dosage in turbidity (NTU), colour (PtCo), and suspended solid (mg/L) effect. Based on the graph, it was observed that the turbidity concentration level was accounted at 76.7 NTU, colour of 6420 PtCo and total suspended solid level at 152mg/L in original TPOME solution.

The effect of pH on turbidity graph indicated as the value of pH increased, the turbidity also increased. Consequently, all turbidity concentration when in pH 5 is lower than the original experiment sample. In pH 5, the least reading is 13 NTU in $FeSO_4$ and chitosan solution with the dosage of 1200 mg/L and 120 mg/L respectively. The turbidity was 39.40 NTU when the ratio of $FeSO_4$ and chitosan were 800 mg/L and 120 mg/L, then 68.63 NTU in 1200 mg/L of $FeSO_4$ and 160 mg/L combination and followed with 79.14 NTU in 800 mg/L $FeSO_4$ and 160 mg/L of chitosan.

For color removal efficiency, the usage of $FeSO_4$ contribute least colour removal at pH 5. Among of all the different kind of combination in pH 5, the dosage of $FeSO_4$ and chitosan in 1200 mg/L and 120 mg/L shows the best reading result of 1324.72 PtCo and the highest colour reading was 2443.88 PtCo in the condition of 800 mg/L $FeSO_4$ and 160 mg/L chitosan.

The effect of pH on total suspended solid indicated that lower pH level contributed to lower suspended solid reading. The lowest reading of total suspended solid was 18.272 mg/L in the combination of 1200mg/L of $FeSO_4$ and 120 mg/L of chitosan in pH 5. On the other hand, the highest reading show 81.08 mg/L in the condition of 800mg/L of $FeSO_4$ and 160 mg/L of chitosan in pH 5.

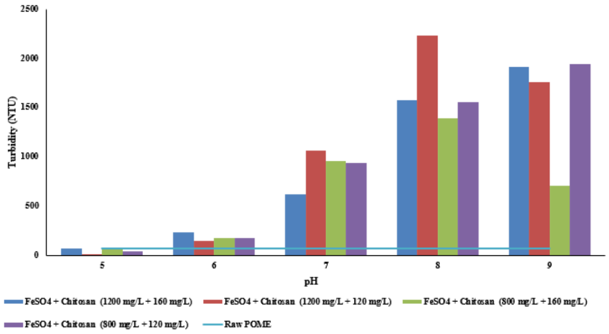

Fig. 6: Turbidity removal with combination of $FeSO_4$ and Chitosan

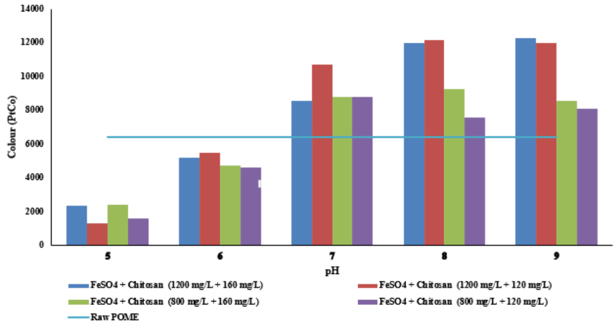

Fig. 7: Turbidity removal with combination of $FeSO_4$ and Chitosan

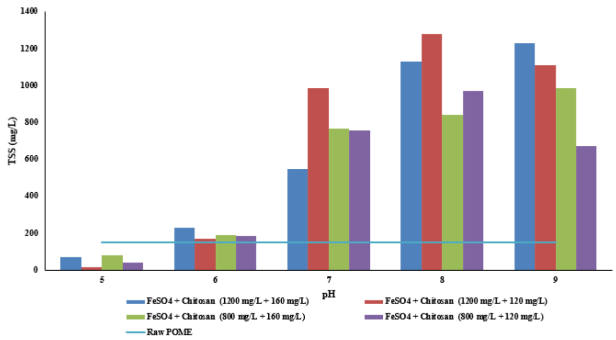

Fig. 8: TSS removal with combination of $FeSO_4$ and Chitosan

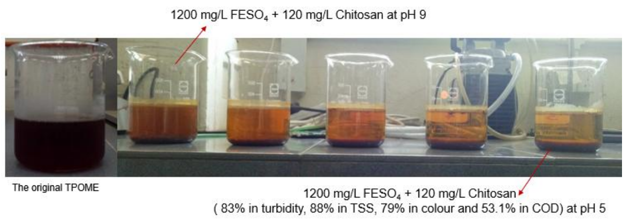

Fig. 9: Comparison between different ratio $FeSO_4$ dosage combined with Chitosan

4. Summary

From the experiment, it was observed that chitosan performed better than pectin for organics removal from POME. Chitosan shows better removal efficiency in terms of colour, TSS and turbidity removal in MPOME. Ferrous Sulphate with chitosan in the dosage of 1200 mg/L and 120 mg/L respectively works best that have a removal efficiency at pH 5 in TPOME.

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