

Synthesizing Green *Chitosan*-Magnetic Composite Particles From *Fenneropenaeus indicus sp.* for Palm Oil Mill Effluent (POME) Pre-Treatment

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ABSTRACT

Biodegradable materials have attracted the industry with the increasingly global trend of biopolymers of low toxicity and durability. *Chitosan* is a high molecular weight and charging density naturally organic polyelectrolyte (biopolymer), which is obtained from chitin's de-acetylation from the crustaceans shell. *Chitosan* allows improve its inhibition output through comprehensive processing and composite formation. *Chitosan* and magnetic particles are cross-links together via co-precipitation method to satisfy the needs of high adsorption, regeneration, fast separation, and cost-effective treatment of wastewater. This would best POME pre-treatment cost-effectively and sustainably. This study was laboratory-based using an actual POME. Optimal dosing of 4 g / L *chitosan*-magnetic composite particles has reduced turbidity, TSS, ammoniacal nitrogen and COD by 94.6%, 89.2%, 63.8%, and 90.6% respectively. The pH of POME has also changed to 8.35 which followed the discharge standard. In contrast, *chitosan* seems to need, a much higher dose of 5.5g / L to reach maximum reduction of turbidity, TSS, ammoniacal nitrogen, and COD about 88.7%, 84.7%, 52.2%, and 78.5%, with 8.92 pH value respectively. The synergistic effect of the *chitosan*-amino-group cationic character in the POME pre-treatment cycle results in increased agglomeration, adsorption, coagulation, and flocculation efficiency. Thus, the potential of *fenneropenaeus indicus sp* is relevant in POME pre-treatment.

Keywords: *Chitosan, chitosan-magnetic composite particles, biopolymer, biodegradable, palm oil mill effluent*

1. INTRODUCTION

For environmental engineers, it is difficult to develop efficiently and easily methods for processing POME. The common method used to treat POME is open ponding system, aerobic and anaerobic digestion, with the modern and alternative treatments. Taking into account the highly organic essence of POME, anaerobic is the safest way of treating it. A variety of studies have been conducted with different forms of coagulants and flocculants on the treatment of POME. Coagulation and flocculation are used in wastewater treatment to isolate suspended contaminants from water. Coagulation is a unit process where the mutual repulsion of the suspended particles using chemical substances (coagulants) is interrupted and brought together by a flocculation process [1].

In recent years, natural organic coagulants have been used as environmentally safe coagulants in wastewater treatment. Natural organic coagulants are environmental-friendly products that are biodegradable from either plants or animals and are made from organic waste such as prawn shell waste [2, 3]. The prawn waste is a rich pollutant of protein and chitin, which can be valued by developing and implementing a system for the extraction process.

Although the waste is biodegradable, large amounts of dumping delay the disposal process and waste additional time accumulates, a significant environmental concern.

Chitosan is a high molecular weight cellulose-like biopolymer obtained from chitin de-acetylation [4, 5]. After cellulose, chitin is the second richest organic material. The key applications of *chitosan* are the ability to make fiber and film, biodegradation, biocompatibility, organic operation, non-toxicity, and in-allergenic properties [6, 7].

Chitosan was used for wastewater treatment applications for the synthesis of the membrane as both an absorber and a coagulant or flocculant [8, 9]. It has a broad absorption capacity, higher than activated carbon, to extract toxins from wastewater with a high adsorption efficiency. At present, magnetic particles are widely studied in the area of water treatment. Magnetic particles are inorganic particles which, due to their magnetic fields, have been very widely formed in different studies and fields of application [10]. The finite-sized effect and high surface-to-volume ratio of magnetic particles result in increased adsorption capacity. Magnetic particles used to adsorb effluent pollutants and can be removed by the simple magnetic method after adsorption from the medium [11, 12]. *Chitosan* and magnetic particles are inter-linkable to satisfy the needs of high adsorption, regeneration, fast separation, and cost-effective treatment of wastewater. The chemical co-precipitation method recommended to be used to prepare *chitosan*-magnetic composite particles [13 – 17, 34]. Such composite particles are best treated for efficient agglomeration, adsorption, and coagulation in the pre-

treatment phase of POME. This would boost POME pre-treatment cost-effectively and sustainably.

This study has been conducted as it provides a greener environment to society in the long term. *Chitosan*-magnetic composite particles create greener energy and help develop an environmental-friendly waste management system to minimize environmental pollution. Besides as a very useful biomaterial, *chitosan* has demonstrated considerable potential and can be extracted from a very easily accessible source. This research is being performed with the use of green *chitosan*-magnetic composite particles as part of the palm oil mill effluent (POME) preliminary treatment (pre-treatment). *Chitosan-magnetic* composite particle has been effective in coagulating, eliminating the suspended solid from POME. *Chitosan*-magnetic composite particles are reinforced in the pre-treatment process for better agglomeration, adsorption, coagulation, and flocculation of POME. Analytical tests of chemical oxygen demand (COD), turbidity, ammoniacal nitrogen, total suspended solids, and pH should demonstrate treatment effectiveness and will define maximum reduction in the POME parameter.

2. MATERIALS AND METHODS

2.1 Chemicals and materials

Prawn shells were taken from the local supermarket (Econsave) at Semenyih, Selangor for this research. The length of the specific prawn shell was within the range of 2 – 3cm. 1.5 M of *Hydrochloric acid*, HCl was prepared for the demineralization process which was obtained from Evergreen Engineering & Resources from Semenyih, Selangor. 99.8% purity of *Acetic acid* and 98% of *Sulfuric acid* were also obtained from Evergreen Engineering & Resources from Semenyih, Selangor. *Sodium hydroxide*, NaOH was supplied from R&M Chemicals from Subang, Selangor and it was applied to extract *chitosan* (deproteinization and deacetylation) and synthesis composite particles via co-precipitation method. *Ferrous sulfate heptahydrate*, FeSO₄.7H₂O, and *Ferric chloride hexahydrate*, FeCl₃.6H₂O were obtained from R&M Chemicals from Subang Selangor for the synthesis of composite particles.

2.2 Synthesizing *chitosan-magnetic composite particles*

2.2.1 Extraction of *chitosan* from prawn shells

Chitosan was prepared from shells of white prawn, *Fenneropenaeus indicus* sp. The water washed and the shells dried under the sun for 7 hours. The extraction process started with the deproteinization. A total of 10 g of prawn shells was added to 3.5% w/v of *sodium hydroxide* for 60 minutes at 100°C (3.5 g NaOH per 100 mL of water).

The shell's tertiary protein structure has been compromised by this. Filtered the solution and washed with distilled water. To begin with, demineralize at room temperature for 1 hour by adding HCl (up to 100 ml HCL solution with distilled water) 1.5 M Hydrochloric acid for 100 ml solution stock.

The way inorganic carbonate from the shells is extracted has been enhanced. The chitin was crushed using porcelain mortar and pestle and washed with distilled water. *Chitosan* is made at 95°C at 1.5 hours by deacetylation of chitin with 40.0 percent w/v *sodium hydroxide*, NaOH (40 g of NaOH per 100 mL of distilled water). The acetyl group C₂H₃O and the amino group, NH₂, were generated by this technique. Upon deacetylation, the solvent had been drained and the traces were washed in distilled water thoroughly and dried for 2 hours in an oven dryer at 80°C. The product was finally pulverized and packed like *chitosan* [18 – 25].

The *chitosan* was analyzed based on a few parameters to obtain a good quality of *chitosan* such as solubility, degree of deacetylation, and moisture. First of all, 1.0% w/v of acetic acid was prepared (1 mL of acetic acid mixed with 99 mL of distilled water). 0.5g of *chitosan* was measured and added into 1.0% w/v of acetic acid solution. The solution was continuously stirred for 30minutes to dissolve the *chitosan*. Then, the solution was filtered to collect the residue left (*chitosan*) and measured the weight. The solubility of *chitosan* was calculated by equation 1. Drying *chitosan* at 80°C into an oven dryer was used to measure the moisture of *chitosan* up to constant weights achieved. *Chitosan* deacetylation (DD) was also tested for *chitosan* as one of the key parameters. Measurement and dissolution in 20 cm³ were performed for 0.2 g *chitosan*, 0.1 m hydrochloric acid, and 25cm³ distilled water. Thirty minutes continuously the solution was stirred. Apply 25cm³ of distilled water again and mix for 30minutes. The next step; make sure that the *chitosan* does not last up to 45 minutes in the atmosphere. After the full dissolution of the *chitosan*, the 0.1 mol dm³ sodium hydroxide solution was approved for office with 0.01 cm³ precision. The number of *chitosan* deacetylation has been determined in the following equation 2.

The solubility of chitosan =

$$\frac{\text{Initial weight of } chitosan \text{ (g)} - \text{Final weight of } chitosan \text{ (g)}}{\text{Initial weight of } chitosan \text{ (g)}} \quad (1)$$

$$DD [\%] = \frac{2.03 \times \Delta V}{m + 0.0042 (\Delta V)} \quad (2)$$

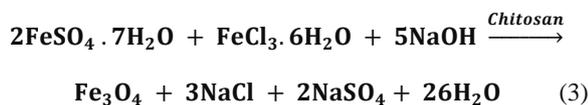
ΔV: Volume of 0.1 mol dm³ of sodium hydroxide solution used in titration (cm³)

m : Mass of *chitosan* (g)

2.2.2 Chitosan-magnetic composite particles synthesis

The chemical co-precipitation of Fe^{2+} and Fe^{3+} ions [32 – 34] formed *chitosan*-magnetic composite particles; in the presence of *chitosan sodium hydroxide* ions. In 100 ml of distilled water, 5.75 g *chitosan* has been dissolved. Distilled water was also processed in around 84 mL (Molar Ratio, $Fe^{2+}: Fe^{3+} = 0.0275: 0.0550$), $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$. NaOH was prepared separately for 30.0% w / v (30 g per 100 mL of distilled water) in combination with precipitation. NaOH was a co-precipitation of *sodium hydroxide* as shown in equation 3.

Along with the *chitosan* solution, $FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ solutions were mixed evenly using hot plate magnetic stirrer at 100rpm. Then the resulting solution was heated up (while mixing) to 90°C and chemically precipitated by adding 30.0% *sodium hydroxide* dropwise with constant stirring. The suspension was stirred continuously to finish the *sodium hydroxide*. The suspension cross-linking technique was used in this method for the preparation of *chitosan*-magnetic composite particles. The suspension was cut off from the heat supply once completely changed into the black. At the end of the experiment, the *chitosan*-magnetic composite particles were decanted from the reaction mixture by using a permanent magnet. The products were washed several times with distilled water and dried at 80 °C for 2.5 hours in the oven dryer. The moisture content of *chitosan*-magnetic composite particles was determined by measuring weight loss after drying for 2.5 hours.



2.3 POME pre-treatment

The POME pre-treatment method involved the coagulation and flocculation process by adding *chitosan* and *chitosan*-magnetic composite particles under the Jar test [26]. Jar test was carried out by adding the *chitosan*-magnetic composite and *chitosan* particles with a blending time of 30 minutes and a mixing rate of 100rpm. The mixing time is then 15min with a mixing speed of 25rpm. The POME sample is then given 1 hour to settle. Then, POME samples have analyzed the reduction of wastewater parameters which consists of pH, turbidity, chemical oxygen demand (COD), ammoniacal nitrogen (NH_3-N), and total suspended solids (TSS) to determine the optimal dose of *chitosan* and *chitosan*-magnetic composite particles for the pre-treatment. Firstly, in the turbidity meter, a POME sample (approximately 30mL) was placed and the lid was closed. The results have been read and recorded.

COD of POME samples was determined by filling 2.5mL of samples into three equal tubes. Then, 1.5mL of potassium dichromate was added inside each tube, followed by 3.5mL of sulfuric acid each. The tubes are tightly closed and held in a COD digester for two hours at 150°C. After two hours, the tubes were cooled down to room temperature and transferred into three different conical flasks. The burette was filled with freshly prepared ferrous ammonium sulfate and added 2 drops of the Ferro indicator inside each flask. Finally, the samples were titrated to ferrous ammonium sulfate and the amount of ferrous ammonium sulfate used was measured and recorded. The value of the COD was determined using equation 4 and 5.

Molarity of ferrous ammonium sulfate =

$$\frac{\text{Volume potassium dichromate titrated, mL}}{\text{Volume ferrous ammonium sulfate used in a titration, mL}} \times 0.1 \quad (4)$$

$$\text{COD (mg/L)} = \frac{(A-B) \times M \times 8000}{\text{Volume of sample (mL)}} \quad (5)$$

where,

A: Mark the titrant used in the mL sample

B: Mark the titrant used in the mL blank sample

M: Molality of the ferrous ammonium sulfate

For TSS, 100 mL of POME sample was filtered through a pre-weighed filter using a vacuum filter. Each filter paper was placed in its aluminum weight pan in the 105°C oven dryer for 30minutes. Then, the filter and paper were cooled down in a desiccator and the final weight was obtained. Then, each paper was placed again in its aluminum weight pan in the 105°C oven dryer for 1 hour. Afterward, the filter and paper were cooled down in a desiccator and the constant weight was obtained by repeating the drying (for 1hour) and desiccation step. The total suspended solids (TSS) were calculated using equation 6.

$$\text{TSS, } \frac{\text{mg}}{\text{L}} = \frac{\text{Initial weight (for 30min)} - \text{Final weight (for 1hour)}}{\text{Sample volume, L}} \times 1000 \frac{\text{mg}}{\text{L}} \quad (6)$$

For NH_3-N , 250mL of the POME sample was measured and poured inside a beaker, and 12.5mL of borate buffer solution was added into the beaker. Then, the solution was transferred into the round bottom flask and placed it on a heating mantle. 25mL of the plain boric acid solution was added into a 250mL flask, followed by 0.25mL of mixed indicator solution. A mixed indicator solution was a mixture of methylene blue and methyl red that dissolved in alcohol. The condenser was connected between the round bottom flask and a flask containing indicator solution, and the tap was open to allow water to flow inside the condenser. Then, the round bottom flask was heated to start the distillation

process and vapor of sample will condense, and run into the end receiver which is the flask with indicating solution. The distillation process was continued until the sample flowing into the indicating flask reach volume of about 100mL. Thus, the total volume in the receiving flask should be 125mL (100mL of sample + 25mL of plain boric acid). Then, the heating mantle was switched off and the tap was closed, and the receiving flask was removed from the distillation unit. Distilled water was added into receiving flask up to 250mL. The solution was titrated with 0.02M of the sulfuric acid solution and the pale lavender color was appear at the end of the titration. The amount of sulfuric acid used was recorded and ammoniacal nitrogen was calculated using equation 7.

Ammoniacal nitrogen, mg/L =

$$\frac{\text{The volume of sulfuric acid used} \times 280}{\text{Sample volume, mL}} \quad (7)$$

3. RESULTS AND DISCUSSION

3.1 Chitosan-magnetic composite particles synthesis

In this study, *chitosan*-magnetic composite particle synthesis was prepared in two stages: *chitosan* extraction from the prawn shell (including deproteinization, demineralization, and deacetylation) [4, 27 – 29] and the co-precipitation process in the presence of *chitosan*. *Chitosan* and magnetic particles (Fe_3O_4) were combined in an appropriate proportion in the cross-linked process (co-precipitation) to form a *chitosan*-magnetic composite particle. *Chitosan* existed in a form of pale pink flakes, which was converted to powders. The degree of deacetylation (DD) was tested for *chitosan* as one of the key parameters and the DD level of *chitosan* was 84.92%.

Besides, the *chitosan* solubility in 1percent of acetic acid was 88.2% with a pH level of 8.32. The moisture content found in extracted *chitosan* was 5.181% with a yield of 81.7%. Furthermore, *chitosan*-magnetic composite particles were synthesized in good quality of the range. The yield and moisture of *chitosan*-magnetic composite particles obtained were 92.63 % and 5.05% with a pH of 8.17. The principal advantages of using normal, water-treatment-based coagulants, such as *chitosan* and *chitosan*-magnetic composites, are sustainable and cost-effective, not likely to produce treated water with extreme pH.

3.2 Wastewater quality

3.2.1 Start-up period

POME is a nutrient abundant organic substance with varied value-added applications, although typical wastewater produced in the palm oil milling process with its polluting features. Nevertheless, its disposal is critical because it has

high BOD and COD values. To eliminate suspended solids and waste oil in the air flotation unit, the POME was usually coagulated and flocculated by dosing the organic substances or coagulants. Given Ng et al. (2019) [30], POME has a very high COD at the time of anaerobic digestion, which, since no chemical compounds are included to the extraction process, is non-toxic and has an acidic pH of about 5.5 because it contains organic acids in complex forms which can be used as carbon fuels.

Besides, the high COD of POME is mostly between 15,000 and 100,000 mg / L, and ammonia nitrogen in the 4–80 mg / L range. The following table (Table 1) displays the list of values for the POME test sample parameters of the anaerobic digestion pond before pre-treatment coagulation. By carrying out the analytical experiment, the value of parameters is obtained except the COD value. COD value from Zero Discharge treatment plant data set, analyzed based on DOE, Malaysia (1995) processes, was taken.

3.2.2 End-up period

POME is a nutrient-rich organic material with numerous value-added applications, although it is typical wastewater produced during palm oil milling processes. A jar tester was used as the best solution to evaluate POME's treatment capabilities and to define the optimum parameters (more efficient coagulant, appropriate dose levels, COD, etc.). It is the simplest and cheapest way to get accurate data on various coagulator and solid removal variables. Key parameters of POME such as COD, TSS, ammoniacal nitrogen, turbidity, and pH value were analyzed as shown in Table 2. The pre-treatment process involved the coagulation and flocculation process by adding *chitosan* and *chitosan*-magnetic composite particles.

3.3 Dosage of coagulants needed to optimize wastewater parameters reduction

Naturally, POME is an acidic effluent, with *chitosan*-magnetic composite particles and *chitosan*, which can settle suspended solids fast. The functional amine groups in *chitosan* and the magnetic particles which are positively charged help to coagulate the suspended solids and absorb them. As charges are neutralized, the small suspended particles can bind together by fast mixing; the suspended solids can be produced by slow mixing until the coagulation cycle is complete [3]. The wastewater was subjected to sedimentation when floc reached its optimum size and strength. Coagulation or flocculation processes were commonly used as pre-treatments for the extraction, in the primary application of suspended particles. In this analysis, the impact of various parameters was investigated. For the coagulant dose, sixteen analytical experiments were performed for both composite and *chitosan* particles. To increase the effectiveness in future procedures (aerobic digestion, ultrafiltration, and reverse osmosis), the coagulation and flocculation steps were aiming at

minimizing turbidity, total suspended solids (TSS), ammoniacal nitrogen (NH₃-N) and chemical oxygen demand (COD).

Chitosan and magnetic particle combinations display an improvement in productivity as the majority in organic compounds suspended in POME and the turbidity reduction at their original pH of 5.65 is reduced. The synergistic effect of the *chitosan*-amino-group cationic character in the POME pre-treatment cycle results in increased agglomeration, adsorption, coagulation, and flocculation efficiency [31]. The effect of different coagulant dosages on POME destabilization was analyzed for *chitosan*-magnetic

composite particles and *chitosan*. For POME coagulation *chitosan*-magnetic composite particles were far better than *chitosan*, as their parameter reductions were much greater. The findings for *chitosan* are consistent with Ahmad et al., (2006) [8] study which stated that *chitosan* is even better for extracting the suspended solids POME than alum and PAC, which require a far higher dose. For *chitosan*-magnetic composite particles, some recent studies have been declared for its use as an absorbent for the removal of heavy metal ions from industrial wastes. All have demonstrated increased adsorption in contrast with *chitosan* by *chitosan*-magnetic composite particles.

Table 1 Characteristics of Palm Oil Mill Effluent (POME) sample

Parameters	POME (anaerobic digestion)
pH	5.65
Turbidity	1840.1 NTU
Total suspended solids, TSS	21700 mg/L
Ammoniacal Nitrogen, NH ₃ -N	40.544 mg/L
Chemical oxygen demand, COD	43000 mg/L

Table 2 Characteristics of Palm Oil Mill Effluent (POME) at an optimum reduction by using both *chitosan* and *chitosan*-magnetic composite particles

Parameters	POME (anaerobic digestion)	
	<i>Chitosan</i>	<i>Chitosan</i> -Magnetic composite particles
pH	8.920	8.350
Turbidity	207.9 NTU	100.0 NTU
Total suspended solids, TSS	3320.0 mg/L	2340.0 mg/L
Ammoniacal Nitrogen, NH ₃ -N	19.38 mg/L	14.672 mg/L
Chemical oxygen demand, COD	9245 mg/L	4023.04 mg/L

In this experiment, the optimum dosage of *chitosan*-magnetic composite particles that needed to achieve the maximum reduction on wastewater parameters was 4.0g/L, whereas for *chitosan* was 5.5g/L. A study of the effect on POME destabilization of different coagulating dosages of pH, turbidity, ammoniacal nitrogen, COD and TSS was performed for *chitosan*-magnetic composites and *chitosan*. Tests were conducted at the POME sample initial pH, i.e. 5.65. The main coagulant used for destabilizing, coagulation, and further flocculating the suspension are *chitosan*-magnetic composite particles and *chitosan*. The results are shown in Figure 1 for *chitosan*-magnetic composite particles and *chitosan*, respectively. Those data show that changes in coagulant doses lead to improved coagulation efficiency for both *chitosan*-magnetic composite particles and *chitosan*. Therefore, patterns are nearly identical for all parameters. It was measured that 5.5g

of *chitosan* was required to reduce the turbidity (207.93NTU), TSS (3320.1 mg/L), ammoniacal nitrogen (19.38 mg/L) and COD (9245 mg/L) from a liter of POME. The reduction of the same amount for turbidity, TSS, ammoniacal nitrogen, and COD from one liter of POME just requires around 4.0g of *chitosan*-magnetic composite particles.

The highest reductions of parameters for applied 4 g / L, i.e. decreased by 94.6% for turbidity, 89.2% for TSS, 63.8% for ammonia nitrogen, and 90.6% for COD respectively, were recorded with *chitosan*-magnetic composite particles. *Chitosan*, on the other hand, seems to require a little more dose, i.e. 5.5 g / L, to achieve the maximum reduction in turbidity, TSS, ammoniacal nitrogen, and COD of 99.90%, 95.80%, 52.2%, and 47.70%. *Chitosan*-magnetic composite particles are better for POME coagulation than *chitosan* because the parameters are much lower with lower dosing

levels than *chitosan*. The combination of load neutralization and the process for polymer bridge resulted in *chitosan*-magnetic composite particle coagulation of POME. The *chitosan* amino group and the magnetite ion do indeed have a synergistic impact in the POME pre-treatment process, thereby enhancing the efficiency of coagulation.

In this study, co-precipitation with the involvement of *chitosan* without any cross-linking agent was used to prepare the *chitosan*-magnetic composite particles. Because the bond between *chitosan* and magnetic particles was thus helped to develop it. Nevertheless, the efficiency of pre-treatment may be undermined relative to previous studies. Given Saifuddin & Dinara (2011) [3], The obtained magnetic nanoparticle was protected by an ionotropic *chitosan* gelation layer using sodium tripolyphosphate (cross-linking agent) for the synthesis of *chitosan*-magnetite composite particles. Thus, the optimum dose of 4 mg / L *chitosan*-magnetic composite particles, decreased the levels of turbidity, TSS, and COD by 98.8%, 97.6%, and 62.5% respectively.

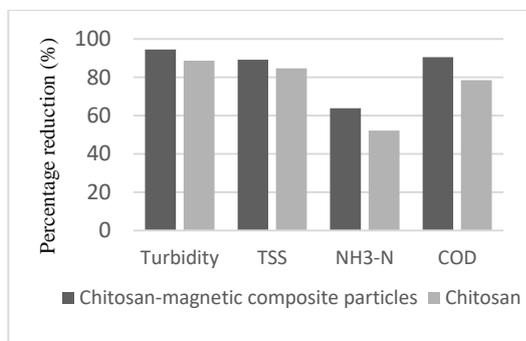


Figure 1 Percentage reduction of wastewater parameters using the optimum dose of *chitosan* and composite particles

3.4 Effect on pH

The pH analysis is critical if the treatment system is to determine the optimal dosing condition. The pH influences not just the surface load of the coagulant, but also the stability of the suspension. From this study, at the pH of 8.35, the reduction was optimal for *chitosan*-magnetic composite particles while at a pH of 8.92 for *chitosan*. The acidic situation of POME contributes to the removal of suspended solids. POME is compounded by the acidic conditions to destabilize the suspended solids.

In this way, suspended solids in POME are improved coagulated by neutralizing the alkaline coagulant (*chitosan* magnetic composite particles and *chitosan*) to process the solution according to the typical discharge criteria (8.23±0.2) [32]. Given Ahmad, Ibrahim, Ismail, & Bhatia., (2002) [1], the coagulant hydrolyzed the electrical charges on hanging solids, which continue to form agglomerations called floc which is extracted through the sedimentation and filtration. The coagulation method will modify the suspended particles to stay together and decrease the

POME's acidity. Throughout coagulation, the surface charge was decreased to the point that the particles were not repelled from each other with a positive metal ion from the magnet particles.

3.5 Effect on turbidity

The maximum reduction obtained in terms of turbidity was 100NTU (94.6%) when using *chitosan*-magnetic composite particles as shown in Figure 2. 4g of composite particles was enough to treat one litre of POME to achieve the maximum reduction on turbidity. The turbidity value decreases as the dosage of *chitosan*-magnetic composite particles increases. However, when the composite particles were added more than the optimum dosage level, the turbidity value slightly increases.

If the saturation of polymer bridging reaches the *chitosan*-magnetic composite particles or *chitosan* dose, the surplus *chitosan*-magnetic composites or the *chitosan* tends to disrupt bridging between particles and thus increases residual turbidity. The maximum reduction obtained in terms of turbidity was 100NTU (94.6%) when using *chitosan*-magnetic composite particles, whereas for *chitosan* was 207.9NTU (88.7%) as shown in Figure 1. 4g of composite particles was enough to treat one litre of POME to achieve the maximum reduction on turbidity. However, when the composite particles were added more than the optimum dosage level, the turbidity value slightly increases. Because the excess coagulant creates cloudiness as it achieves its maximum limitation on the coagulation process.

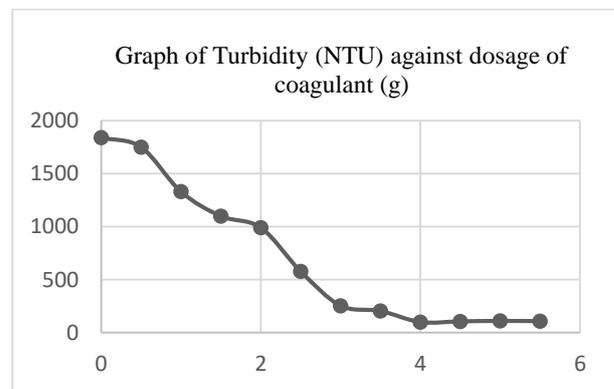


Figure 2 Effect on the turbidity of treated POME using *chitosan*-magnetic composite particles

3.6 Effect on chemical oxygen demand

Figure 3 shows the chemical oxygen demand value of treated POME using *chitosan*-magnetic composite particles. The maximum reduction obtained in terms of chemical oxygen demand when using *chitosan*-magnetic composite particles (4g/L) was 90.6% which is equivalent to 4023.04 mg/L. When used *chitosan*, the COD concentration was

reduced to 9245 mg/L which is equivalent to 78.5 %. Chemical oxygen demand values decrease as the dosage of chitosan-magnetic composite particles increases. There are no changes that occurred on COD reduction when using more than 4g of chitosan-magnetic composite particles, as the coagulant achieved its limitation on COD reduction.

An indicator of the water's ability to use oxygen in the decomposition of bio-materials and oxidation of inorganic chemicals such as ammonia and nitrites is the chemical oxygen demand (COD). COD is an important parameter in water quality, as it provides an index for the evaluation of the impact of wastewater on the recipient climate, similar to the Biological Oxygen Demand. Higher COD levels mean that the sample has a greater amount of organic, oxidizable content that decreases the dissolved concentration of oxygen (DO).

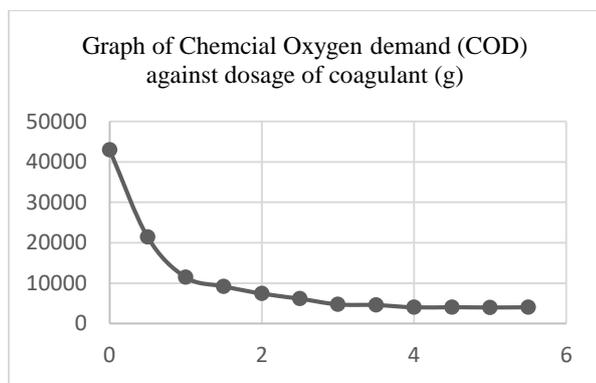


Figure 3 Effect on COD of treated POME using chitosan-magnetic composite particles

3.7 Effect on ammoniacal nitrogen

In this study, the maximum reduction obtained in terms of ammoniacal nitrogen when using chitosan-magnetic composite particles (4g/L) was 63.8% which is equivalent to 14.672 mg/L; whereas the maximum reduction obtained when using chitosan (5.5g/L) was 52.2% which is equivalent to 19.38 mg/L as shown in Figure 1.

Figure 4 shows the ammoniacal nitrogen value of treated POME using chitosan-magnetic composite particles. The maximum reduction obtained in terms of ammoniacal nitrogen when using chitosan-magnetic composite particles (4g/L) was 63.81% which is equivalent to 14.672 mg/L. Ammoniacal nitrogen values decreases as the dosage of chitosan-magnetic composite particles increases then the trend became a steady-state after reached optimum dosage. The efficiency of the ammoniacal nitrogen removal in the POME can be seen in Figure 4. If coagulant dosage increases, it does not affect the ammoniacal nitrogen reduction much; the reduction increase by 0.45%. This is because the coagulant achieved its limitation on ammoniacal nitrogen reduction. After the coagulation of

both composite particles and chitosan, ammoniacal nitrogen has been extracted from the supernatant liquid.

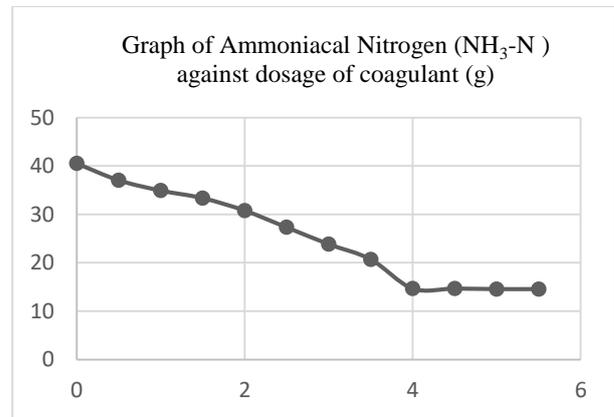


Figure 4 Effect on NH₃-N of treated POME using chitosan-magnetic composite particles

3.8 Effect on total suspended solids

The turbidity and color of the POME are due to the presence of solids and organic substances in the POME. Total suspended solids (TSS) in POME which may be trapped by a filter are known as solids. A wide variety of materials such as plant waste, industrial waste, and contaminants, can be included in the TSS [33]. Suspended solids at the bottom of POME may become sedimentary. While this solution increases the clarity of the water, the increased slit will smother benthic organisms after discharge into the water. From the experiment, figure 5 shows the total suspended solids value of treated POME using chitosan-magnetic composite particles. The maximum reduction obtained in terms of total suspended solids when using chitosan-magnetic composite particles (4g/L) was 89.2% which is equivalent to 2340 mg/L. Total suspended solids value decreases as the dosage of chitosan-magnetic composite particles increases. As turbidity, TSS slightly increases after added more composite particles than the optimum dosage level. Besides, the maximum reduction recorded when using chitosan (5.5g/L) was 84.7% which is equivalent to 3320 mg/L. Chitosan-magnetic composite particles have a high reduction in their performance for an efficient adsorption process, compared to chitosan.

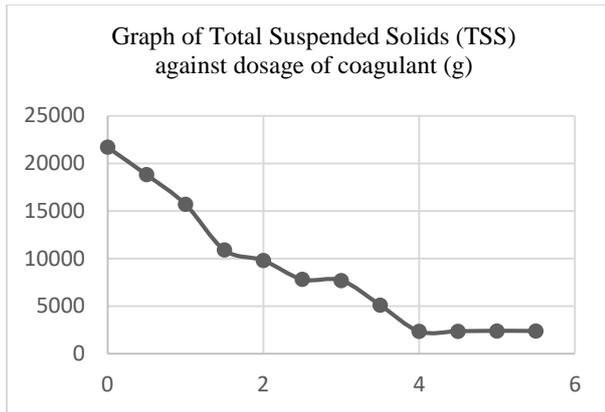


Figure 5 Effect on TSS of treated POME using chitosan-magnetic composite particles

4. CONCLUSION

As a fundamental and important treatment technique in water and wastewater treatment systems, coagulation and flocculation methods would thus be suitable for POME. Thus, in the presence of *chitosan*, the co-precipitation method of magnetic particles (Fe_3O_4) was used to synthesize *chitosan*-magnetic composite particles as a coagulant for the POME pre-treatment. The results have shown that *chitosan*-magnetic composite particles have been well performed for coagulation and removal from POME of suspended solids, ammoniacal nitrogen, turbidity, and COD, compared to *chitosan*. However, the pre-treatment procedure with both coagulants was environmentally sustainable. Optimal dosing of 4.0g/L *chitosan*-magnetic composite particles was reduced turbidity, TSS, ammoniacal nitrogen and COD by 94.6%, 89.2%, 63.8%, and 90.6% respectively. The pH of POME was also changed to 8.35 which followed the discharge standard. In contrast, *chitosan* seems to require, a much higher dose of 5.5g/L to achieve optimum turbidity, TSS, ammoniacal nitrogen, and COD about 88.7%, 84.7%, 52.2%, and 78.5%, with 8.92 pH value respectively. The synergistic effect of both amino groups in *chitosan* and magnetic ions on the cationic character in the POME pre-treatment cycle improves the efficiency of agglomeration, adsorption, coagulation, and flocculation.

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