High molecular chitosan-based seed shells (*Tachyleus gigas*) with silver nanoparticles as waste treatment of palm oil industry (pome)

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Abstract. The focus of this study is to Investigate, study and modification of chitosan molecules tow with nano silver particles as an adsorbent for absorbing oil industry palm oil mill effluent. Liquid waste palm oil industry (POME) from local palm oil mill is used as a sample of oily wastewater. High molecular chitosan from crab shells do crosslink raw materials has to Overcome the disadvantages as the adsorbent, the Appropriate crosslink is AgNO\textsubscript{3} used for this study. The controlled variable is the volume of the adsorbent, contact time and pH. A batch of detailed studies on high molecular chitosan and chitosan Als also nanoparticles and silver are conducted with respect to the adsorption capacity, isotherm. Characterization using Fourier Transform Infrared (FTIR) Spectrophotometer see changes in the functional groups of high molecular chitosan and chitosan -nanoparticle silver that has been crosslinked before and after the adsorption treatment to prove that the palm oil industry waste liquid has been absorbed by the adsorbent. The performance is assessed in terms of turbidity, total suspended solids (TSS) of chemical oxygen demand (COD), Biochemical Oxygen Demand (BOD), and Parameter metallic iron (Fe), copper (Cu) and Zinc (Zn). Using maximum adsorption capacity of the high molecular chitosan nanoparticles of silver is calculated. This research study Will Prove the high molecular chitosan and chitosan silver -nanoparticle high molecular adsorbent after cross section as expected very potential to absorb liquid palm oil mill waste industry.

1. Introduction
Production of palm oil industry is the main industry in Nusantara Forest, province of North Sumatra. Palm oil industry has been developing very rapidly and has become the most important agricultural based industry in this country. Indonesia is the largest producer of palm oil and crude palm oil with total production in 2010 and 2013, respectively 17,734,441 and 16,044,874 tons, export earnings from palm oil, palm kernel oil, and related products in 2000 amounted to nearly US $ 5, 6 billion, equivalent to 5.6%. Amount of plant palm in North Sumatra province has increased rapidly, from about 10 factories, 112 was operation factory in 2012. However, the rapid development of the industry has had serious consequences on the natural environment, which mainly relates to water pollution because large untreated or partially treated water is discharged to water bodies. In 2010, the palm oil
mills in Indonesia produce more than 58 million tons of liquid waste and the figure is expected to increase every year.

The palm oil industry's liquid waste (POME) is colloidal and brownish in suspension acid characterized by high organic content and solids of 80-90 °C. It is estimated that the palm oil industry's liquid waste contributes about 30% of the total biochemical oxygen demand (BOD). Wastewater treatment facility is one of the most important components in the palm oil industry [1]. This facility is commonly used for maintenance of large volumes. POME palm oil industry oil wastes generated during crude palm oil (CPO) production before it is safely discharged to the surrounding environment via water or river canals. In particular, the amount of POME produced is about 3.8 m3 for each ton of CPO production [2].

Chitosan offers a wide range of applications because it has unique properties of chitin and chitosan, such as biocompatibility, biodegradation, biological activity, non-toxicity, non-allergic and fiber and film forming capabilities [3]. In the wastewater treatment applications, chitosan have been used to synthesize the membrane, used as the absorber as well as the primary coagulant or flocculent. It has been proven that chitosan can agglomerate and flocculate various suspensions or wastewater including brewery wastewater. These products should be dissolved, for example, diacid acetate and therefore applied only in a small range of pH (up to about 7). Two types of modifications are usually applied in the preparation of chitosan-based adsorbents [4]. Cross to enhance the solubility and engineering properties and grafting functional groups to increase the adsorption capacity and selectivity [5]. With the rapid development of nanotechnology, magnetic nanoparticles are now widely studied in the field of water treatment and wastewater treatment. It is believed that magnetic nanoparticles (Fe3O4) have been able to demonstrate the ability-size, high rate and produce high adsorption capacity. In addition, the easy separation loaded magnetic nanoparticles from solutions and quick turn around speeds can be achieved using an external magnetic field. The magnetic particles can be used to absorb contaminants from wastewater or gas and after adsorption can be separated from the media by a simple magnetic process [6]. However, all these materials have the disadvantage of small surface area or small adsorption capacity, which limits their application. In this work, high surface area and high adsorption capacity and magnetic composite based on chitosan particles/iron oxide nanoparticles are made with a simple method and are used to remove contaminants from water.

There are many reports of Fe3O4 magnetic particle coating with organic materials as the adsorbent to pull back the metal. However, few studies have been done in composites magnetic nanoparticles and a solution of coagulant to improve coagulation by adsorption and the effect of Fe3O4 magnetic nanoparticles. In this paper, a new composite coagulant for pre-treatment of POME made by adding magnetic Fe3O4 nanoparticles of chitosan. The high content of amino groups in the chitosan also allows modifications chemistry in the polymer in order to increase the selectivity and adsorption capacity [7]. The nanocomposite beads can be removed easily from the water with the aid of external magnetic properties of the magnet due to their exceptional. Coagulation behavior of chitosan and chitosan-magnetite nanoparticles have studied under different initial pH conditions and coagulant dose [8].

In the design of this study, high molecular chitosan nanosilver particles have not been used for the treatment of liquid waste industry palm oil mill, prepared by the method of chemical conversion and effect coagulant for the treatment of liquid waste industry palm oil (POME). The experiments were carried out in a series of coagulation tests to obtain the optimal coagulant required to achieve maximum suspended solid total reduction (TSS), silver nanoparticles (AgNPs), raffinose and chitosan will be applied as absorbent materials for the palm oil mill industry wastewater [9].

2. Materials and Methods

2.1 Tool
Inductively Coupled Plasma (ICP) Spectrophotometer, Shimadzu FTIR spectrophotometer set, Beaker glass pyrex, ErlenmeyerPyrex, Glass Ukur Pyrex, Spatula, Funnels, Filter Paper Whatman no.1 / 41,
2.2 Material
Chitosan, NaOH pa (E.Merck), AgNO3 pa (E.Merck), Acetic Acid pa (E.Merck) HNO3p.a (E.Merck) Aquadest Waste CP.

2.3 Procedure and Preparations
2.3.1 Preparations Acetate Solution 1% (v/v)
A total of 10 mL of glacial acetic acid put in a 1000 mL volumetric flask, then diluted with aqua destilated until the line marking, and homogenized.

2.3.2 Preparation 2 M NaOH (w/v)
A total of 40 g NaOH pellets inserted into the glass beaker. Diluted with distilled water, was added to the 500 mL flask is then measured to mark the line in order to obtain NaOH 2 M.

2.3.3 Preparation solution of AgNO3 0.5M
A total of 42.4675 g AgNO3 crystals incorporated into the glass beaker. Diluted with distilled water, was added to the 500 mL then measured to mark the line in order to obtain a solution of 0.5 M AgNO3.

2.3.4 Preparation of Chitosan Solution
A total of 10 g of chitosan was dissolved in a solution of acetate 1% (w/v) of 1000 ml, and stir until homogeneous in order to obtain chitosan viscous solution.

2.3.5 Preparation Chitosan Nanoparticles Silver
Chitosan solution was added to Beaker glass, then added with a solution of 0.5 M AgNO3 with the ratio (2:1) to obtain a viscous solution. It was added to the injection pump and dropped into a solution of NaOH 2 M to form black granules. Subsequently, it soaked for a night, then filtered washed with distilled water and dried.

2.3.6 Provision of industrial waste Palm Oil
Wastewater from palm oil mill (POME) is obtained from PT Perkebunan in North Sumatra, were collected from the plant at a temperature ranging from 75 to 90 °C. It samples allowed to cool about 45-50 °C before being transferred into a plastic container. Tiɡht sealed containers and labeled before being transported laboratorium’s USU. In the laboratory, the samples were stored at 4 °C in a sealed plastic safe to use and to prevent wastewater biodegradation due to the inclusion of microbes need to be preserved before. Liquid wastes are suspensions brown, slightly acid and a part is consisted mainly of water. Its characteristics always vary depending on the time the sample is taken. This may be due to the processing method, the quality of fruits. In order to minimize the different effects, the treatment was repeated several times with different samples to obtain average results. The sample sections were analyzed because of the initial residual oil content, turbidity, TSS, COD, and BOD values.

2.3.7 Preparation CPO Waste Method with Wet
A total of 100 mL of CPO, added 50 mL of HNO3 is heated up to half the initial volume above the hotplate, then cooled and filtered with filter paper whatmann 42 and diluted into 1000 ml flask and metal analysis Zn, Fe, Cu by using ICP.

2.3.8 Analysis Suspended Solids (TSS) on Oil Results destruction
Whatmann filter paper no. 42 raised overall with distilled water, filter paper heated in the oven at a temperature of ± 105°C, for 1 hour. Cool in a desiccator for 15 minutes and then weighed, repeated
heating to obtain a constant weight. Then 100 mL samples removed with a pipette in a filtering device
existing filter paper to dry, then strain, then the filter paper is taken slowly to clamp a clean and then
placed on a porcelain dish and put into the oven to be heated at a temperature of 105°C, for 1 hour, cool
in a desiccator and then weigh it. Repeated Heating until a constant weight is obtained.

2.3.9 Analisa TSS, COD and BOD Oil Destruction Added Results Chitosan Nanoparticles Silver
A total 20 g of chitosan nanoparticles Silver put in a column that has been wrapped with filter paper,
then put a 100 mL sample and allowed to immersed for 1 hour, then open the faucet tool column and
detained with Beaker glass. further tested the value of TSS, COD, BOD and metal analysis Zn, Fe, Cu
by using ICP.

3. Results
3.1 Result
3.1.1 Data FT-IR
Results of analysis of the spectrum of functional groups for seed shell chitosan can be seen in figure 1.
below:

Figure 1. The FT-IR spectrum of chitosan Commercial

Data of the spectrum at the horseshoe crab shell chitosan can be seen in Table 1. below:
Table 1. FT-IR data Chitosan Commercial

| Wavelength (Cm⁻¹) | Functional groups     |
|-------------------|-----------------------|
| 3440.01           | OH overlap with NH    |
| 2879.28           | CH                    |
| 2360.64           | C = O                 |
| 1641.75           | C = C                 |
| 1423.79           | CH2                   |
| 1383.18           | CN                    |

Results of analysis of the functional group of chitosan nanoparticles spectrum Silver can be seen in
Figure 2. below:
Figure 2. FT-IR spectrum Chitosan Nanoparticles Silver

Data from the spectrum of the chitosan nanoparticles of silver can be seen in table 2 below:

Table 2. Data FT-IR Nanoparticles Silver

| Wavelength (Cm\(^{-1}\)) | Functional groups       |
|-------------------------|-------------------------|
| 3467.18                 | OH overlap with NH      |
| 2359.42                 | CH                      |
| 1694.27                 | C = N                   |
| 1459.67                 | NH3                     |
| 1384.78                 | CO                      |
| 866.17                  | CX                      |

3.1.2 Determination of Levels of Metals, Iron, Copper, and Zinc On CPO Waste
The results of the analysis of data metals Iron, Copper and Zinc in CPO waste before and after the addition of Silver Nanoparticles Chitosan can be seen in table 3. below.

Table 3. Metal On Waste CPO Before and After Addition of Chitosan Nanoparticles Silver

| Metal       | Concentration (mg / L) | Percentage |
|-------------|------------------------|------------|
|             | Chitosan (-)           | Chitosan (+) |          |
| Iron (Fe)   | 0.32                   | 0.02252     | 92.96%    |
| Copper (Cu) | 0.03                   | 0.00132     | 95.60%    |
| Zinc (Zn)   | 0.5                    | 0.11740     | 76.52%    |

3.1.3 Determination of total suspended solids (TSS) on waste CPO
Total Suspended Solids resulting data on waste CPO before and after the addition of Nanoparticles Silver Chitosan can be seen in Table 4. and 5. below:
Table 4. Mass Measurement Result filter paper before and after the addition of Chitosan Nanoparticles of silver.

| Treatment | Without Chitosan Nanoparticles Silver | addition of Chitosan Nanoparticles Silver |
|-----------|--------------------------------------|------------------------------------------|
|           | Initial filter paper mass | End mass filter paper | Initial filter paper mass | End mass filter paper |
| 1         | 1.1313 | 11.9637 | 1.1378 | 2.0896 |
| 2         | 1.1210 | 11.8518 | 1.1267 | 2.0889 |
| 3         | 1.1208 | 11.8430 | 1.1254 | 2.0857 |
| Average   | 1.1243 | 11.8761 | 1.1299 | 2.0880 |

Table 5. The percentage reduction in waste CPO TSS values without and added chitosan.

| Sample Volume | Concentration (mg / L) | Percentage reduction |
|---------------|------------------------|----------------------|
| 50 mL         | TSS without chitosan   | TSS added chitosan   |                         |
|               | 215.04                 | 19:16                | 91.09%                 |

3.1.4 Determination of COD and BOD in Waste CPO Before and After added Chitosan

The results of the data analysis of COD and BOD value on CPO waste before and after the addition of Silver Nanoparticles Chitosan can be seen in table 6. Below.

Table 6. Results of the determination COD in CPO waste without and added Chitosan

| Analysis | Concentration (mg / L) | Percentage |
|----------|------------------------|------------|
|          | without chitosan       | added chitosan |               |
| COD      | 23.4                   | 0.1000     | 99.57%       |
| BOD      | 1.36                   | 0.2700     | 80.14%       |

4. Conclusions

From the research conducted, it can be concluded: After absorption Percentage Added with Chitosan Nanoparticles Metal Silver on Metal Iron (Fe), copper (Cu), and zinc (Zn) By Streak is 92.96%, 95.60%, 76.52% while After absorption Percentage, TSS Value Added Chitosan Nanoparticles Silver is 91.09%. Percentage Impairment COD after Added Chitosan Nanoparticles Silver is 99.57%. Impairment percentage BOD After Added Chitosan Nanoparticles Silver is 80.14%.

Acknowledgement

The authors would like to show high gratitude for the financial support by Talenta Research of University of Sumatera Utara No. 6049/UN5.1.R/PPM/ 2016.
References

[1] Suryan et al 2017 *IOP Conference Series: Material Science and Engineering, IOP Conf. Ser.: Mater. Sci. Eng.* **222** 012008

[2] Abu Hassan et al 2007 *Malaysian Journal of Civil Engineering*, **19** 128

[3] Suryani et al 2018 *IOP Conf. Series: Journal of Physics: Conf. Series* **953** 012015

[4] Agusnar H et al 2013 *J. Advances in Environmental Biology* **7** 3857

[5] Satriananda et al 2018 *IOP Conf. Series: Journal of Physics: Conf. Series* **953** 012013

[6] Renault B 2009 *European Polymer Journal* **45** 1337

[7] Rihayat T et al 2017 *International Conference on Sustainable and Renewable Energy Engineering (ICSREE)* 10-13

[8] Hesami F et al 2014 *Int J Env Health Eng* **3** 8

[9] Masitah H et al 2011 *J. Applied Science*. **11** 2292