Use of Chitosan as Coagulant in Treatment of Oily Produced Water by Induced Air Flotation

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Abstract **Treatment of oily produced water (OPW) before reuse in injection process and remove to surrounding are necessary to reduce formation damage and pollution. This can be done using induced air flotation (IAF) method to minimize and separate oil from water. Chitosan act as coagulant in this process to enhance the efficiency of oil removal in this process. In this respect, these research objectives are to investigate the affect of pH when changed and to determine the dosage of chitosan required. It was found that the removal of oil by chitosan increase at pH 2 then others. The oil removal by chitosan reached 78.03% and 61.87% at pH 2 and pH 8 respectively. The ability of chitosan to remove oil also decreases after adding aluminium sulfate (alum). Data shows that the highest efficiency of oil removal by mixing chitosan and alum (40% chitosan: 60% alum) is 76.32%. Generally, chitosan has high ability to remove crude oil from OPW and can reduce the cost for water treatment.**

Keywords- Oily produced water (OPW), chitosan, induced air flotation (IAF)

I. INTRODUCTION

Oily produced water (OPW) can cause a lot of problems in many aspects such as technical, environmental, and economical in oil and gas production. The presence of OPW can limit the life production of oil and gas wells. OPW also cause other serious problems including fine migratatic loading and corrosion of tubular (Hosny et al., 2016). So, before the OPW being reused in production or remove to the surrounding, it must be treated. Produced water also can be known as salt water and brine. Oil reservoir is the source of OPW production. The reservoir can be included from above and below the hydrocarbon zone and inside the hydrocarbon zone. According to US National Energy Technology Laboratory (NETL), the total production of OPW is increasing about 10 million barrel per day for every 2 years. The ratio of water to oil production is 5:1 and 8:1 in US, and 2:1 and 3:1 for worldwide. The present of OPW can give a lot of problems to the production facility but it also can give a lot of support to the production facility after being treated. Why volume of OPW is important in oil and gas production? The reason is the managing cost of OPW is an important factor in the profitability of oil and gas production, treatment construction cost and disposal facility including the equipment and acquisitions, operation cost for those facilities, cost of managing any residues, and shipment cost. The total cost to manage this OPW will increase if the volume is too high. Furthermore, there are many factors that affecting the production of volume of OPW during the production process. The OPW depends on the technique of well drilling, well location, the types of well completion method, the water separation technologies used, water injection for Enhanced Oil Recovery (EOR), low mechanical study, and poor communications (Fakhru'l-Razi et al., 2009). So in this research, the focus is to reduce the volume of OPW by using a specific water separation or treatment technologies by the support from a selected coagulant. Induced air flotation (IAF) process is an effective technique for use with presence of coagulation of oil-water emulsion in which air bubbles can minimize the density droplets of oil and make the separation process more effective (Meyssami & Kasaeian, 2005). IAF is a process for water treatment that defines wastewaters or OPW by the removal of suspended matters. The removal of suspended matters is achieved by injecting gas bubbles into OPW in flotation tank. The small bubbles stick to the suspended solid and cause it to float to the surface of the water and then be removed by a skimming device. The IAF technology is widely used in the industry for water treatment such as in oil refineries, and natural gas processing plants. Furthermore, the usage of coagulant in this research has been finalized to enhance the efficiency in the IAF process. Process of small particles connected with other forming floc is large enough to be separate from solution in a specific time is called coagulation. So, in order to form flocs, the present of coagulant is must. Chitosan has been chosen as the coagulant in this research because it demonstrated good results in the flocculation experiments (Haufe et al., 2017). The first objective in this experiment was to investigate the affect of pH when changed to the concentration of oil in OPW. Then, the second objective was to determine the dosage of chitosan required in this research.

II. METHODOLOGY

A. Materials

Crude oil sample used in this research was kindly obtained from Bertam Crude Oil. The crude oil then was stored in a tin container and kept in laboratory in room temperature to avoid any changes happen until the treatment process.

For the preparation of OPW, seawater also needs in this process. Seawater was taken from Pantai Morib and stored in 5 tanks. Then, it was stored in laboratory in room temperature until treatment process.

Chitosan that was used in this experiment were extracted from shrimp shell. Shrimp shells were supplied in fresh condition from GL Marine Frozen Sdn. Bhd. The shells then were separated from the head and legs. The shrimp shells were washed with tap water and dried out under the sun for 8 hours. The dried shells were blend to fine powder.

B. Sample preparation

Synthetic produced water

Synthetic produced water contaminated with oil was prepared by mixing between seawater and crude oil. For preparation of 150 ppm of concentration of synthetic produced water, 0.09 g of crude oil had been weight and mix together with 600 mL of seawater. The solution then must be stir for about 30 minutes with 1000 rpm in order to become homogenous.

Chitosan

1. Sample collection and preparation

Chitosan was chosen as coagulant in this research. Chitosan being extracted from shrimp shell obtained in fresh condition from GL Marine Frozen Sdn Bhd, Jalan Kebun. This company produced large quantities of shrimp shell waste in Selangor. The sample was washed with distilled water to remove any contaminant material on the shell then dried under the sun for 8 hours.

2. Extraction of chitin by chemical method

- Deproteination (DP)

The research was conducted at a laboratory ratio by using 500 mL beaker. Sample of total 30 g raw shrimp shell was added with 2.0 NaOH in the ratio about 1:16 (w/v) and then left for 2 days at standard temperature 25^{o}C with pH range 11 to 13. Next, filter the solution and wash the samples with distilled water until the pH become neutral around 6.5-8.0. Before performing the demineralization process, water from the samples was removed (Ahing & Wid, 2016).

- Demineralization

Samples produced from deproteination then were added with 1.0 M HCl in the ratio about 1:16 (w/v) and allowed to be left for 1 day with pH value between pH 1.0-2.5 at standard temperature 25^{o}C. Then follow the step from the deproteination process above. The samples then dried for 6 hours and continued using an oven at 80^{o}C until constant weight was obtained. The dried sample of chitin is produced (Ahing & Wid, 2016).

3. Chitosan production

- Deacetylation (DA)

The deacetylation process was operated by soaking dried chitin in a 48% NaOH for 2 days at standard temperature 25 ^{o}C. The product is known as chitosan after 2 days (Ahing & Wid, 2016).

Figure 1 Chitin

Figure 2 Chitosan

UV-Vis calibration curve

In order to determine the value of concentration of oil in OPW before the research begin, UV-Vis calibration curve need to be tested. Calibration curve was a general method to determine the concentration of a substance in unknown sample by comparing to a set of known concentration. 200 mL of Hexane was mixed with 0.09 g of crude oil to prepared 150 ppm concentration and being stirred until become homogenous. The solution then was labeled as stock solution. 2.5 mL of stock solution then diluted with 7.5 mL of hexane to prepared 25 ppm concentration. The step above then repeated by preparing 50 ppm, 75 ppm, and 100 ppm concentration.

C. Experimental setup

Figure 3 Induced air flotation (IAF) setup

Chitosan as coagulant was used to remove oil from OPW using induced air flotation (IAF) method. Fig. 3 above showed the IAF setup before the research was began. One beaker was prepared with magnetic stirrer and vacuum pump. 200 mL of OPW were mixed homogenously before being switched into another beaker. The samples were measured for oil concentration for representing an initial concentration. After the desired amount of chitosan was added into the sample in the beaker, the beaker was agitated at various mixing time and speed (250 rpm) for 15 minutes and slows mixing (30 rpm) for 30 minutes with the present of air bubbles. The flowrate of the bubbles was set 1.0 L/min. after the agitation finished; the suspension was allowed to settle down undisturbed for 30 minutes. 100 mL of the sample was taken by using 25 mL syringe and placed into 100 mL beaker. The pH was controlled by adding either acid (1 M HCl) or base (1 M NaOH). All tests were performed at room temperature in the range 26-37 ^{o}C. The same steps repeated for different pH value and different value of dosage of chitosan.

D. Liquid- liquid extraction method

This method is a method for separating compounds or metal complexes in two different immiscible liquids, usually water (polar) and organic solvent (non-polar) based on their relative solubility. All glassware was rinsed twice with 100 mL Milli-Q water and 30 mL hexane. The pH of each OPW (100 mL) was then reduced to less than 2 by adding 1 M hydrochloric acid (HCl). 12 mL of hexane then was added to the OPW in 2 L reparatory funnel. The mixture was vigorously shaken for 1 minutes and left for settle for 5 minutes. The hexane then floated above the water line. The layers were separated by draining water from the bottom of the funnel. To dehydrate the water extract, it was filtered by sodium sulphate (Na_2SO_4) after which it was collected, stored and sealed in a 100 mL volumetric cylinder. The procedure was repeated by using another OPW sample. UV-Vis analysis was performed on a portion of this extract by filling it into the cuvette and placed in the UV-Vis spectrophometer.

III. RESULTS AND DISCUSSION

A. *Chitosan FTIR Analysis*

The FTIR test method was used to determine the functional groups exist in the chitosan. In Fig. 4 below, the infrared spectrum of chitosan that can be observed. A strong band in the region 3255.66 cm^{-1} corresponds to N-H stretching. The bands of absorption at 2876.4 cm^{-1} can be attributed to C-H symmetric stretching. This band was typical characteristics of polysaccharide and can be found in other polysaccharide spectra such as glucans. The presence of N-acetyl groups was found by the bands at 1619.46 cm^{-1} (C=O stretching of amide) to 1376.53 cm^{-1} (C-N stretching of amide III). The bending of CH2 and CH3 symmetrical deformations were confirmed by presence of bands around 1414.40 cm^{-1} and 1376.53 cm^{-1} respectively. The absorption band at 1153.56 cm^{-1} can be assuming to asymmetric stretching of the C-O-C bridge. The band at value 1069.10 cm^{-1} equal to C-O stretching.

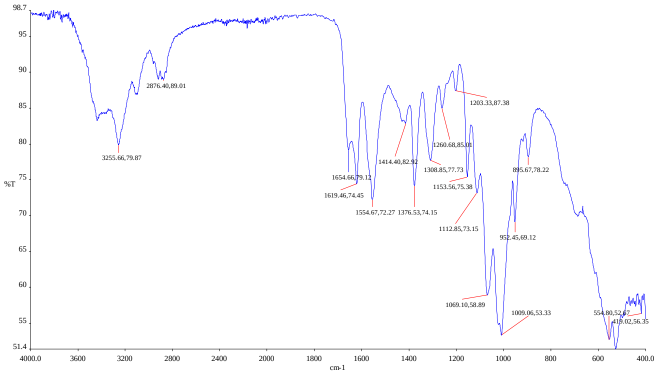

Figure 4 FTIR spectrum of chitosan and commercial chitosan

B. *UV-Vis calibration curve of oil concentration*

After being prepared the OPW, the concentration of oil was determine by using UV-Vis Spectrometry. The result of calibration curved was showed in Fig. 5 below.

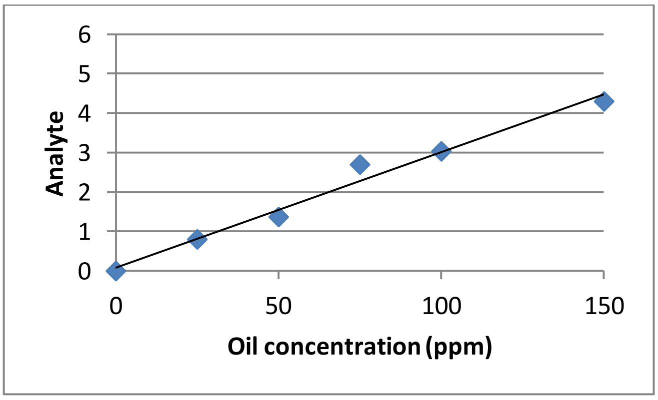

Figure 5 Oil concentration calibration curved

After finished the research, the sample of concentration of crude oil in OPW will be compared with above result to get the result. The higher the reading of the analyte signal, means that the concentration of oil still higher in the OPW.

C. *Effect of pH*

The different value of pH also affects the efficiency of OPW treatment. Because of that, pH adjusted to study the effect of adsorption of crude oil into the chitosan that acted as coagulant as shown in Fig. 6. The dosage of chitosan used in this study was 0.5 g/L. The results showed that the adsorption of crude oil reached 114.68 ppm at pH 2 that corresponds to 76.45% oil removal. The adsorption recorded at alkaline medium (pH 8) was 92.81 ppm corresponds to 61.87 % of oil removal. From this study, it can be conclude that acidic base was good in separation process because it can make the condition of OPW unstable and easy to separate.

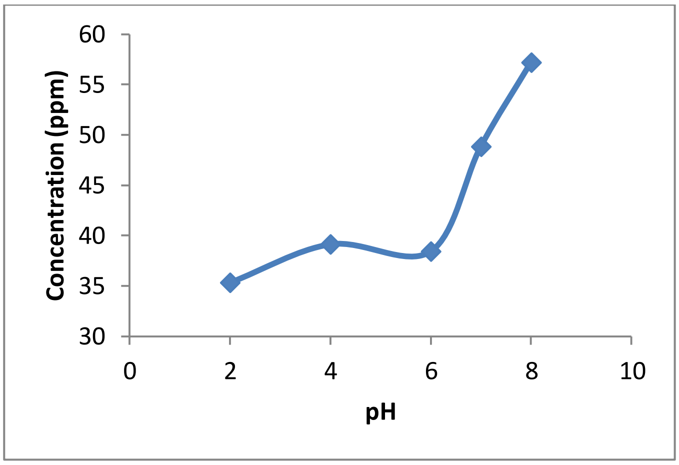

Figure 6 Effect of pH on the removal of oil from OPW using chitosan

In Fig. 7, the graph showed the amount of oil concentration left in OPW by using mixture of coagulant. The ratio 8:2 chitosan to aluminium sulfate (Alum) was used in different pH value of OPW. The result recorded that pH 2 remove more oil than other pH value that was 108.82 ppm equal to 72.54% greater than pH 8 that was 78.54 ppm of oil removal equal to 52.36%. Once again, pH 2 acts as best medium for separation process.

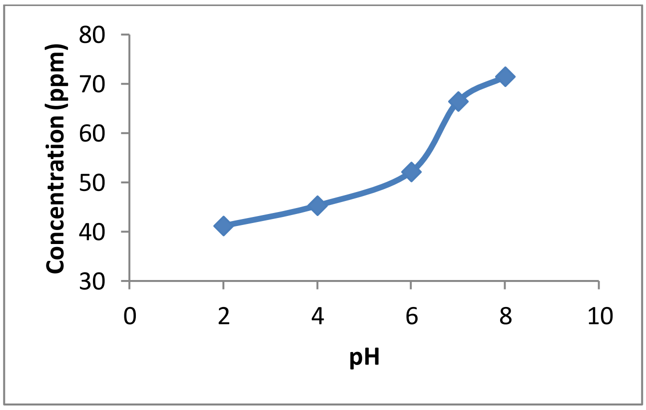

Figure 7 Effect of pH on the removal of oil from OPW using chitosan and aluminium sulfate

From the Fig. 6 and Fig. 7, it can be concluding that pH 2 was suitable and can be selected as optimum pH value to undergo another research objective. The hypothesis that can be made from the result is the higher the value of pH, the lower the amount of oil adsorption from chitosan.

D. *Effect of dosage*

The amount of dosage of coagulant also plays an important role in this study. The amount of dosage of chitosan showed in Table 1 below. The pH 2 value was used.

Table 1 Chitosan dosage

Dosage g/L	Dosage g/200mL
0.3	0.06
0.5	0.1
0.6	0.12
0.7	0.14
0.8	0.16

The chitosan weighed by using laboratory weighing scale. There were 5 different dosage used to compared the effectiveness of removing oil from OPW.

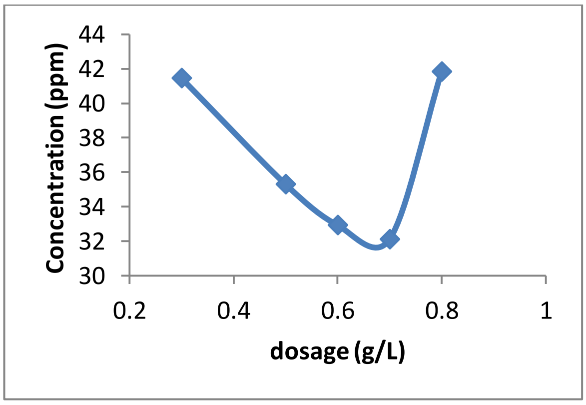

Figure 8 Chitosan dosage

From data shown in Fig. 8, OPW that used 0.7 g/L of chitosan as coagulant reduce more concentration than other dosage with 117.05 ppm equal to 78.03%. The sample that used 0.8 g/L chitosan is the lowest for oil reduction that was 108.15 ppm corresponds to 72.1%. Low volume of dosage not effective because it can't handle large amount of concentration while high volume still can't give a good result because the amount exceed the limit and make the OPW more polluted. It can be conclude, the optimum value of dosage required in this study was 0.7 g/L.

Table 2 Chitosan and Alum dosage

ratio		dosage		dosage 0.12 g/200mL		concentration
chitosan	alum	chitosan	alum	chitosan	alum	Ppm
1	0	0.6	0	0.12	0	32.95
0.8	0.2	0.48	0.12	0.096	0.024	47.98
0.6	0.4	0.36	0.24	0.072	0.048	38.79
0.5	0.5	0.3	0.3	0.06	0.06	37.31
0.4	0.6	0.24	0.36	0.048	0.072	35.52
0.2	0.8	0.12	0.48	0.024	0.096	40.26
0	1	0	0.6	0	0.12	59.5

The study continues with another variable by using 0.7 g/L of coagulant in pH 2 OPW. Chitosan and Alum mixed together with different ratio in order to compare the result at the final. The ratio of the mixture showed in Table 2.

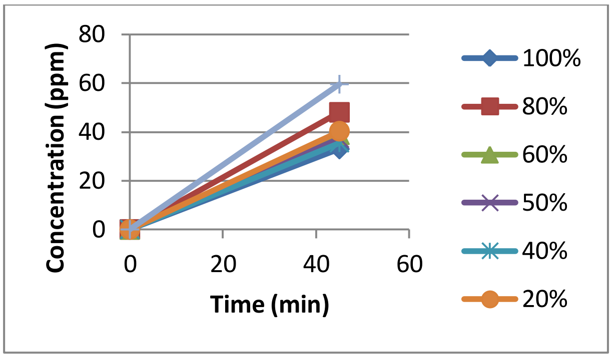

Figure 9 Percentage of chitosan

Data from Fig. 9 shows that the 100% of chitosan used reduced more oil concentration in OPW. The 100% chitosan reduced the concentration from 150 ppm to 32.95 ppm while 0% chitosan just can reduce the concentration to 59.5 ppm. But for the mixture of chitosan and alum, the ratio 4:6 provided a better result that reduces the concentration down to 35.52 ppm.

IV. CONCLUSION

The result of chitosan mix with aluminium sulfate clarifies that the ability to remove oil from OPW lowers than the chitosan only. The highest removal of oil from OPW by chitosan only is 78.03% while the highest removal efficiency by mixing chitosan and alum (40% chitosan: 60% alum) is 76.32%. This happen because chitosan have many hydrophilic groups that can make the surface area higher than alum. Conclusion, the optimum water pH value was pH 2 and dosage required was 0.7 g/L of chitosan.

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References

[1] Ahing, F. A., & Wid, N. (2016). Extraction and Characterization of Chitosan from Shrimp Shell Waste in Sabah, *3*(Figure 1), 227–237.

[2] Fakhru'l-Razi, A., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., & Abidin, Z. Z. (2009). Review of technologies for oil and gas produced water treatment. *Journal of Hazardous Materials*, *170*(2–3), 530–551. http://doi.org/10.1016/j.jhazmat.2009.05.044

[3] Haufe, S., Bohrisch, J., Schwarz, D., Yu, S., Steinbach, C., & Schwarz, S. (2017). Flocculation e ffi ciency of reacetylated water soluble chitosan versus commercial chitosan. *Colloids and Surfaces A*, *532*(February), 222–227. http://doi.org/10.1016/j.colsurfa.2017.05.013

[4] Hosny, R., Fathy, M., Ramzi, M., Abdel, T., Desouky, S. E. M., & Shama, S. A. (2016). Treatment of the oily produced water (OPW) using coagulant mixtures. *Egyptian Journal of Petroleum*, *25*(3), 391–396. http://doi.org/10.1016/j.ejpe.2015.09.006

[5] Meyssami, B., & Kasaeian, A. B. (2005). Use of coagulants in treatment of olive oil wastewater model solutions by induced air flotation. *Bioresource Technology*, *96*(3), 303–307. http://doi.org/10.1016/j.biortech.2004.04.014