Treatment of Oily Produced Water (OPW) using Mixture of Coagulant and Shrimp Shell

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***Abstract*— The large volume and complex composition of oily produced water (OPW) make its treatment not a simple matter. Coagulation is a common method to treat OPW. However, the health and cost issues regarding chemical coagulant had piqued interest in natural coagulant. In this study, the efficiency of the coagulant mixture consists of chitosan and alum to treat OPW is studied. The optimum pH value and the best ratio of chitosan and alum were determined using a standard jar test apparatus. It was found that the coagulant worked best in the acidic condition which was pH 2-4 and the optimum chitosan dosage was 0.6 g/L where the oil percentage removals were 69% and 64% respectively. The best ratio for coagulant mixture was at 6:4 of chitosan to alum. The oil percentage removal by coagulant mixture at the optimum condition was 69%. Generally, the mixture of chitosan and alum had the ability to treat OPW hence can reduce the alum usage.**

***Keywords*— Chitosan, coagulant, oily produced water.**

I. INTRODUCTION

Produced water is water that is byproduct during oil and gas extraction from the underground reservoir. It has a complex composition such as high oil and grease (O&G) content, high salinity, contain organic acids and many more. This is due to its contact with a reservoir for centuries [1]. Besides that, its volume is large which is approximately 250 million per day and it is believed the volume is increasing due to maturing of formation [2]. The greatest concern is O&G concentration in produced water. Normally upstream OPW contains approximately 500 mg/L O&G and to satisfy the discharge oil concentration limit which is 30 mg/L, a polishing method to treat OPW is needed [3]. Coagulation is widely used for water treatment and alum as a coagulant is commonly used. However, issues about a large amount of dosage and aluminium residual in the treated water which leads to Alzheimer's disease increase the interest about natural coagulant [4].

Chitosan is a linear polysaccharide that is resulted from deacetylation of chitin. Chitin is the second most abundant natural polymer that exists in green algae and exoskeleton of crustacean [5]. The best source for preparation of chitosan is shrimp shell due to its high average molecular weight and a high degree of deacetylation [6]. Fig. 1 shows the structures of chitosan. Chitosan has the functional group of amine and amide which have a high potential for adsorbing oil. Chitosan also has a high positive charge that can interact strongly with negative groups to obtain electrical neutrality [7].

Recently, there are many studies about chitosan as coagulant or coagulant aid to reduce turbidity, remove dye, and to remove E. coli [8]. However, the study about the ability of chitosan to remove O&G in produce water treatment is still rare. In this study, the effectiveness of a mixture of chitosan and alum at different ratio and the optimum pH value to treat OPW was examined. Assuming that it is polishing treatment for produced water, synthetic produced water (SPW) with an initial concentration of 150 mg/L with no presence of suspended solid is used in this experiment.

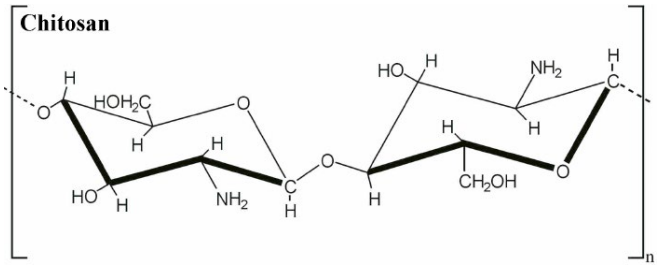

Fig.1: Chemical structure of chitosan.

II. METHODOLOGY

A. Materials

Fresh local red shrimp shell (Metapenaeus lysianassa) were received by GL Marine Sdn. Bhd., Klang. The heads were removed and the shells were washed then dried under the sun for 8 hours.

Crude oil with 34^{O} API and density of 855 kg/m^3 was received from Bertam oilfield. Seawater was collected from Morib beach, Banting.

Sodium hydroxide (pellet) and aluminium sulphate (from R&M Chemicals), hydrochloric acid (37% from Fisher Scientific (M) Sdn. Bhd.), and *n*-Hexane (from Schmidt BioMedTech Sdn Bhd.) were used as received.

B. Extraction of chitosan from shrimp shell

The dried shrimp shell was treated with 2M NaOH in a ratio of 1:16 (w/v) and left for 48 hours. Next, the samples were filtered and washed then treated with 1M HCl with the same ratio and left for 24 hours. Lastly, the sample was soaked in 48% NaOH for 48 hours then dried under the sun for 8 hours. All of the procedures were done at room temperature 25-30^{O}C [9]. After that, chitosan was ground to 300 microns to increase its surface area.

C. Characterization of chitosan

The solubility of chitosan in acid solution was determined by dissolving chitosan in 1% acetic acid. Then, it was stirred until homogeneous solution was obtained. The dried insoluble chitosan in acid solution was weighted and solubility (%) was calculated.

Chitosan was scanned by Fourier Transform Infrared (FTIR) spectrometer with a frequency range of 400 to 4000 cm^{-1}. The degree of deacetylation (DD) was calculated using the equation below [10].

$$DD\ (\%) = 100 - \left[\left(\frac{A_{1320}}{A_{1420}} - 0.03822\right)/0.03133\right] \quad (1)$$

Where A_{1320} and A_{1420} are the value of absorbance at the band of 1320 cm^{-1} and 1420 cm^{-1}. The equation below was used to convert transmittance (%T) to absorbance.

$$Absorbance = 2 - \log(\%T) \quad (2)$$

D. Preparation of SPW

The seawater was filtered before added to crude oil to produce SPW at 150 mg/L. It was stirred at 1000 rpm at room temperature until the solution becomes completely homogeneous [11].

E. Experimental procedure

A conventional jar test apparatus accommodating six beakers together with six spindle steel paddles were used to carry out the experiment. Prior to the experiment, the SPW were mixed homogeneously and fractionated to 200 ml in each beaker. The pH was varied (2-8) and controlled by adding 1M HCl or 1M NaOH. pH was checked by pH meter (Mettler Toledo). After the desired amount of chitosan and alum was added into the sample, the beakers were rapidly mixed at 250 rpm for 15 minutes then 30 rpm for 30 minutes. Then, the suspension is allowed to settle for 30 minutes [12]. After that, a sample was withdrawn with a pipette in the middle of solution for oil concentration measurement. All tests were carried out at room temperature 25-30^{O}C and repeated three times.

The collected sample was extracted following the liquid-liquid extraction method. The sample was acidified to pH below 2 and *n*-hexane was used as solvent with a ratio of 3:25 solvent to sample. The solution was transferred to separatory funnel and vigorously shaken for two minutes then left to settle until two layers can be visually seen. After that, the water which was at the bottom layer was removed and the upper layer was collected. Then, it was dried using anhydrous sodium sulphate. After that, a portion of this extract was analysed using UV-vis spectrophotometer at wavelength 226 nm to determine the concentration of residual oil [13].

III. RESULTS AND DISCUSSION

A. Characterization of chitosan

The chitosan extraction yield (%) was calculated by dividing the weight of dried extracted chitosan (g) with the weight of dried shrimp shell (g). This study had a chitosan extraction yield of 15.7% on average. This value agrees with the previous study from Southeast Asia where the range was 15-30% [14].

Next, the solubility of chitosan is one of an important character to classified the quality of chitosan. High solubility indicates high deacetylation degree which means better quality chitosan produced [6]. Chitosan is insoluble in water and alkaline solution but can be dissolved to some extent in dilute aqueous acid solutions. The presence of the amino group in chitosan will result in protonation of chitosan in the aqueous acid solution then lead to its solubility [15]. The chitosan produced from this experiment had the solubility of 20% at an average which in agreement with a study done by Patria (2013). The study was done in Indonesia and the solubility was 17-95.29% [16].

Next, characterization of chitosan by infrared spectroscopy was done to determine its functional group. Fig. 2 shows the comparison between FTIR spectra of chitosan produced from this study and commercial chitosan from Maya Reagent with purity of 95%. The spectrum for produced chitosan showed peaks at 3255 cm^{-1} for aliphatic primary amine and the commercial chitosan had this peak at 3359 cm^{-1}. 2876 cm^{-1} peak in extracted chitosan indicated C-H stretching and commercial chitosan had this peak at 2863 cm^{-1}. Peaks at 1619 cm^{-1} for produced chitosan and 1590 cm^{-1} for commercial chitosan showed the presence of N-H amine. For C-H bending, peaks were observed at 1414 cm^{-1} and 1376 cm^{-1} for produced chitosan and 1377 cm^{-1} for commercial chitosan. Peaks at 1153 cm^{-1} for produced chitosan and 1150 cm^{-1} for commercial chitosan indicated C-O stretching. Peaks for produced chitosan at 1308 cm^{-1} and 1203 cm^{-1} showed the presence of C-N stretching. Peaks for produced chitosan at 1112 cm^{-1} indicated C-O stretching in secondary alcohol group and at 1069 cm^{-1} showed C-O stretching in the primary alcohol group. The peaks showed similar trend with previous study by Varun (2017) which were at 3418 cm^{-1}, 2920 cm^{-1}, 1580 cm^{-1}, 1422 cm^{-1}, 1380 cm^{-1}, 1320 cm^{-1}, 1075 cm^{-1}, and 1029 cm^{-1}. [17]. Table 1 summarized the wavelength obtained by FTIR. The spectrum of produced chitosan had a similar trend with commercial chitosan and the previous study by Varun (2017). The variance could be due to age and type of shrimp from which the sample was taken [17]. The extraction method of chitosan could also be one of the factors that affect the variance of peaks obtained by FTIR [16].

Next, the degree of deacetylation (DD) of chitosan is one of the important criteria to determine the quality of chitosan. DD affect the physical, chemical, and biological properties of chitosan such as its biodegradability and sorption properties [18]. DD also differentiate between chitin and chitosan and indicate the content of free amino groups in chitosan [18]. The DD obtained from this study was 63% on average and within range with previous studies. Other works of literature had DD within 40% to 90% [18]. However, the DD of produced chitosan was slightly lower than the majority of commercial chitosan which had DD of 70-90% [18]. This may be due to the different method during the deacetylation process. Deacetylation in an autoclave or using microwave method had higher DD in the range 70-90%[9].

B. Effect of pH

The pH of the solution affects the surface charge of coagulant and stabilization of the suspension [19]. Emulsion breakage also related to the pH value of the sample [7], [12]. Therefore, the optimum pH for chitosan and mixture of chitosan and alum to treat OPW was studied by adjusting pH from 2 to 8 with 0.5 g/L dosage and a ratio of chitosan to alum 8:2 following the optimum dosage

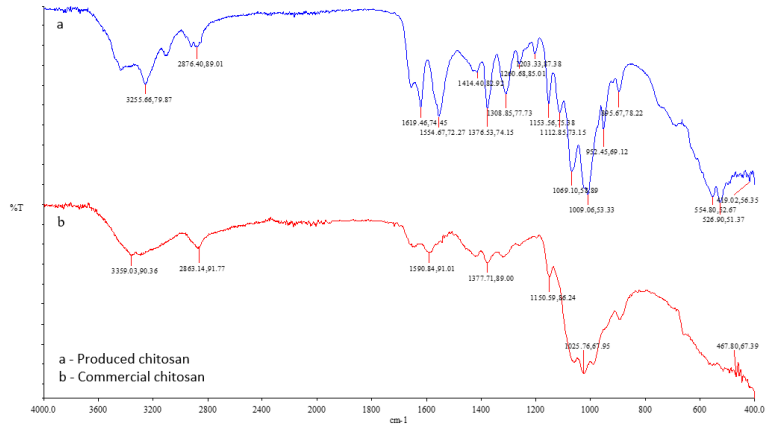

Fig. 2: FTIR spectra of produced chitosan and commercial chitosan.

Table 1: Wavelength of the bands obtained by FTIR of produced chitosan.

Functional group and bonds in the compound	Produced chitosan (cm^{-1})	Commercial chitosan (cm^{-1})	Chitosan from Varun (2017) (cm^{-1})
N-H stretching, aliphatic primary amine	3255	3359	3418
C-H stretching	2876	2863	2920
N-H bending, amine	1619	1590	1594
C-H bending	1414 1376	1377	1421 1381
C-N stretching	1308 1203	-	1322
C-O stretching	1153	1150	1151
C-O stretching in the secondary alcohol group	1112	-	1071
C-O stretching in the primary alcohol group	1069	-	1020

and ratio from the previous study [7], [12]. Fig. 3 illustrate the relationship of pH value and percentage of oil removal. pH 2 showed the highest percentage of oil removal for chitosan which was 69%. As for the mixture of chitosan and alum, the highest percentage oil removal was at pH 4 which was 62%. When pH was adjusted towards basic values which were pH 6 and above, the oil removal become poorer compared to the acidic condition. This showed that both the coagulants work best in the acidic condition which was pH 2-4. This is due to strong acidic condition enhance oil droplets to break. The acidic condition also stimulates physicochemical effect of chitosan that leads to demulsify and increase the droplet size and enhance adsorption of oil. More protons will be available to protonate amine groups (-NH_2 group) which is the adsorption site of chitosan [7], [12]. The result showed that the mixture of chitosan and alum had lower oil removal percentage than chitosan. This could indicate that ratio 8:2 of chitosan and alum was not the best for this experiment.

C. Effect of coagulant mixture at the different ratio

The optimum dosage of chitosan to treat OPW was determined before determining the most effective ratio of chitosan to alum. It is important to determine the optimum dosage to avoid overdosing and obtain optimum performance in treatment. The effect of chitosan dosage was studied by varying the weight dosage 0.3-1 g/L at pH 2. Fig. 4 shows the oil removal percentage at the different dosage of chitosan. It was noticed that the optimum dosage of chitosan to treat OPW was 0.6 g/L which can remove 64% of the oil. Initially, the removal efficiency improved steadily as the dosage of chitosan increased until reaching the optimum dosage which was 0.6 g/L. When the dosage exceeded the optimum dosage the removal efficiency decrease. This is because of the overall surface area of adsorbent increase by increasing the amount of adsorbent which provides more active binding sites [20]. The amine functional group in chitosan attracts anionic ions which led to binding of residue oil with chitosan. Chitosan is positively charged biopolymer that capable of adsorbing residue oil and destabilizing negatively charged colloids of residue oil and emulsion [7].

Next, using the optimum dosage which was 0.6 g/L, chitosan was mixed at the different ratio of alum (0-100%) to determine the best mixture that gives the highest removal efficiency. Fig. 5 illustrate the oil percentage removal using coagulant mixture at the different ratio of chitosan and alum. It can be noted that at coagulant mixture of 100% alum, the removal of oil is 61%. However, usage of alum as coagulant could result in residuals of Al^{+3} in treated water and alum is costly than chitosan [21]. Coagulant mixture at the ratio of 6:4 of chitosan to alum gave the highest oil removal which was 69%. As the ratio of chitosan increase, the treatment efficiency also increases steadily. This trend agrees with the previous study by Hosny (2016) where the increase of chitosan dosage in coagulant mixture leads to better coagulation performance. The highest oil removal percentage was 69% which had 46 mg/L of residual oil after treatment. This value did not meet with the discharge limit of oily water where the oil content must be below 30 mg/L [3]. The study by Hosny (2016) had 85% of oil removal from OPW using coagulant mixture of chitosan and alum [12]. This may be due to the different type of shrimp used to extract chitosan and different chitosan extraction method was used where heating was included during deproteinization and deacetylation process. The traditional method of chitosan extraction was used in this study where all the process done at room temperature 25-30^{O}C.

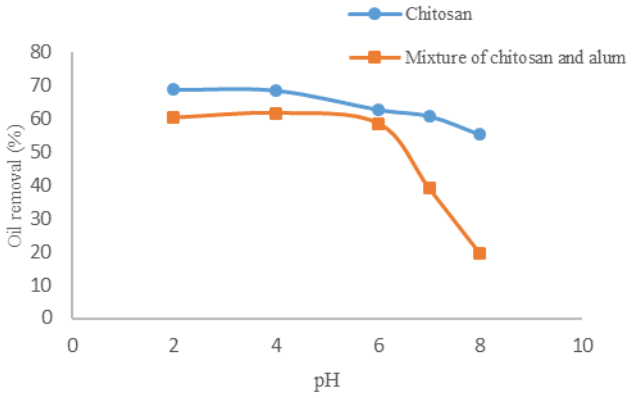

Fig. 3: Percentage of oil removal by using chitosan and mixture of chitosan and alum at different pH of OPW.

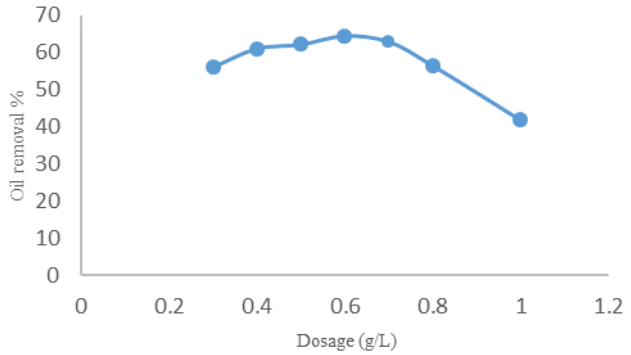

Fig. 4: Percentage of oil removal in OPW at the different dosage of chitosan.

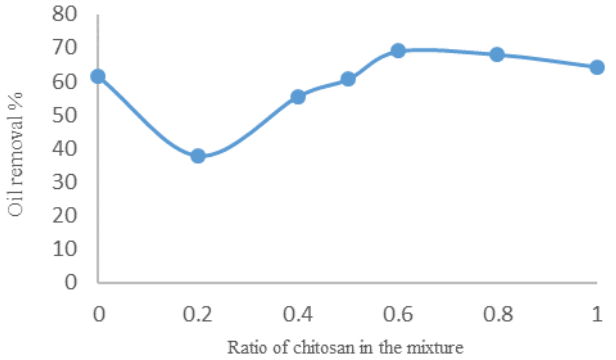

Fig. 5: Percentage of oil removal in OPW using the mixture of chitosan and alum at the different ratio.

IV. Conclusion

The results showed that the mixture of chitosan and alum had the ability to remove oil from OPW. The mixture of chitosan and alum work best in the acidic condition which was pH 2-4 and the optimum dosage of coagulant was 0.6 g/L which had oil removal percentage of 69% and 64% respectively. The best coagulant mixture was 6:4 of chitosan to alum. The highest oil removal percentage after applying all optimum condition was 69%. The OPW treatment was considerably affected by pH, coagulant dosage, and the ratio of coagulant mixture. The local red shrimp (Metapenaeus lysianassa) could be used to extract chitosan using the traditional method. Chitosan with DD of 63% was extracted and used in this study. However, adding heat during the deacetylation process may be recommended to get higher DD. Usage of chitosan in a medical application such as for tissue engineering can be studied for future prospect.

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