A comparative study of dynamic adsorption of anionic synthetic and nanocellulose-based surfactant in Malaysian reservoir

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Abstract This project is aimed at studying the applicability of nanocellulose-based surfactant as a sustainable surfactant for enhanced oil recovery process (EOR) in Malaysia. Abundant biomass waste from palm oil industry in Malaysia is hard to be disposed of. Therefore, potential application of biomass in chemical EOR is an attractive alternative to minimize these problems. For this study, nanocellulose is synthesized from oil palm empty fruit bunch (OPEFB) and undergoes chemical modification for it to act like a surfactant. All methods and techniques in synthesizing nanocellulose and preparing nanocellulose-based surfactant are made inhouse. While waiting for the material preparation, adsorption study is carried out by using anionic synthetic surfactant. Characterization result shows the nanocellulose undergoes chemical modification successfully. The IFT results for the nanocellulose-based surfactants are also in a good and acceptable range, but there are some limitations in using nanocellulose-synthesized surfactant. The average particle size of nanocellulose is 283.5 µm which is larger than size of the reservoir pore throat. Dynamic adsorption cannot be performed as the large particle size of nanocellulose might plug the porous domains. Therefore, it is recommended to further improve the method of synthesizing nanocellulose from OPEFB because the nanocellulose-based surfactant is expected to have potential of lower adsorption in porous media once it becomes nanosized and due to its advantages such as being of lower cost and environmental friendly compared to other commercial surfactants.

Keywords Nanocellulose · Surfactant · Dynamic adsorption · Chemical enhanced oil recovery

Introduction

Malaysia is well known among the largest producers and the exporters of Palm Oil in the world. Malaysia has more than 400 palm oil mills on roughly 5 million hectares of land (Board 2011; Bhat et al. 2018). In reality, palm oil production is only about 10%, while the rest 90% are biomass waste. Several examples of palm waste are empty fruit bunch (OPEFB), palm kernel (OPK), palm fronds (OPF), and palm fiber (OPMF). It has been discovered that OPEFB has contained the highest cellulose compared to other waste stated (Board 2011; Bhat et al. 2018; Wei et al. 2016). This abundant biomass can be easily obtained at low price in Malaysia (Board 2011). Large amount of oil palm waste in Malaysia is hard to be disposed of. Therefore, potential application of biomass in chemical enhanced oil recovery (CEOR) is an alternative to minimize the operational problems.

Combined with the recent advancements in nanotechnology, a new type of green surfactant and cellulose extracted from OPEFB can be converted into nanosize and modified to act like surfactant primarily to reduce the interfacial tension (IFT) for CEOR purposes (Bryan and Kantzas 2007; Morsy 2014; Mishra et al. 2014; Iwamoto et al. 2008; Mohajeri et al. 2015). The application of surfactant in CEOR is not new, and the surfactant injection for oil recovery was started in the 1920s. In the early age of surfactant development, the reaction chemistry and process was not well understood,
The use of surfactants for EOR was considered similar to “micellar/polymer” flooding (Chen et al. 2009; Beck-Candanedo et al. 2005). Later on, the term surfactant flooding was associated with ways to improve gas/steam flooding. Many surfactants are available in the market these days. The specific requirement of surfactants for CEOR purpose includes chemical and thermal compatibility at desired reservoir conditions, salinity tolerance, low adsorption, in porous media. Moreover, in some cases, surfactant did not manage to lower the interfacial tension to a level required and results in a higher adsorption in porous media (Azam et al. 2013; Cheraghian and Hendraningrat 2015; Dong et al. 1998).

One of the remarkable characteristics of nanocellulose-based surfactant is that it can easily pass through typical pore throats in reservoirs. Nanocellulose-based surfactant, which can be extracted from OPEFB, is also a biodegradable material (bio-nano) and low-cost alternative compared with current chemical surfactant (Han et al. 2009; Ghaedi et al. 2017; Karnanda et al. 2013). This is expensive and may contaminate the environment if left under reservoir. Despite the positivity, during surfactant flooding, physicochemical attraction among the surfactant and pore walls may still lead to significant adsorption and loss of surfactant in the reservoir, which is not economical (Neale et al. 1981; Liu et al. 2008; Hong et al. 2007).

In this study, for the purpose of evaluating the applicability of nanocellulose-based surfactant as a sustainable surfactant for EOR process in Malaysia, effluent–surfactant concentration was measured enabling the evaluation of nanocellulose-based surfactant adsorption by conducting dynamic adsorption test on Berea sandstone. This hopefully will help the oil producers in meeting high energy demand and reducing abundant waste from Palm Oil industry.

Materials and methods

Materials

The main materials for this research are oil palm empty fruit bunch, sodium dodecyl sulfate, synthetic anionic surfactant, and Berea sandstone core samples. Chemical composition of Berea sandstone is indicating in Table 1 obtained from XRF analysis.

Apparatus and procedure

The synthetic Berea sandstone samples were purchased from the market. Prior to the experiments, the cores are cleaned by using Soxhlet extractor with toluene and methanol. After this, the cores were dried at 50 °C in the oven for 2 days. After cleaning and drying, these core samples will undergo characterization to investigate their properties (Table 2).

1. Core Sample Characterization X-ray fluorescence spectroscopic (XRF) tests were conducted to investigate the composition of Berea core samples. Other than that, POROPERM is also conducted to obtain the properties of core samples. Other parameters such as sample length, diameter, and mass are also measured.

2. Brine Preparation Brine is prepared to represent the formation water inside reservoir. For this research, sodium chloride solution (brine) of 35,000 ppm is used to represent the reservoir condition of salinity.

3. Synthetic Surfactant Preparation In this research study, while preparing for nanocellulose and nanocellulose-based surfactant, some extra work is done in which several commercialize surfactants are prepared to study their adsorption. These synthetic surfactants are prepared 10,000 ppm in 35,000 ppm brine.

4. Nanocellulose Preparation Empty fruit bunch (EFB) is used as the source for nanocellulose. There are several methods successfully in preparing cellulose fibril from cellulose fiber such as method recommended by Chen et al. (2009), Dong et al. (1998) and Beck-Candanedo et al. (2005). For this study, a method suggested by Iwamoto et al. (2008) is used in preparing cellulose fiber and nanofiber. For cellulose fiber, the method is as such: (a) OPEFB is cut to small length (b) Extractives such as resins, oil, fats and waxes are removed by using Soxhlet extractor by using an ethanol for approximately 2 days (c) The extracted fibers then are soaked several times in sodium chlorite solution with pH of 4–5 at 70 °C for 1 h before washed with deionized water. This process takes place in order to remove lignin.

| Material                          | Density (g/cm³) |
|----------------------------------|-----------------|
| Mineral oil                      | 0.863           |
| Brine                            | 1.020           |
| Nanocellulose-based surfactant   | 1.0073          |
| Synthetic surfactant             | 1.0240          |

| Sample                                      | IFT (mN/m) |
|---------------------------------------------|------------|
| Mineral oil + brine                         | 21.13      |
| Mineral oil + synthetic surfactant          | 3.31       |
| Mineral oil + nanocellulose-based surfactant| 9.39       |
5. **Nanocellulose-based Surfactant Preparation**

The extracted nanocellulose from the above experiments is now used in formulating the nanocellulose-based surfactant. The procedure for this experiment is based on research by Sagir et al. (2015), but nanocellulose is used:

(a) Mixed octadecylamine, extracted nanocellulose, and sodium dodecyl benzene sulfonate (SDBS) surfactant.
(b) 10,000 ppm brine is added to this mixture and warmed at 65 °C and stirred for approximately 1 day. The blend is prepared at a level of 2% total active surfactant.

6. **Nanocellulose and Nanocellulose-based Surfactant Characterization**

X-ray powder diffraction is carried out on the product extracted from EFB for the identification of crystalline materials (e.g., minerals and inorganic compounds). The nanocellulose is subjected to a powder form before being analyzed with D8 Pro Advanced XRD machine manufacturer by Bruker instrument. Other than that, particle size test is also run. The main objective is to check whether the product extracted from EFB is successfully converted into nanosized or not. Scanning electron microscope (SEM) is used to obtain information about the surface topography and composition. SEM is run for both nanocellulose extracted and nanocellulose-based surfactant. Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas (Rodriguez et al. 2009; Sodeifian et al. 2015; Srivastava et al. 2009). The FTIR is run on both nanocellulose extracted and nanocellulose-based surfactant.

7. **Nanocellulose-based Surfactant and Synthetic Surfactant Interfacial Tension Test**

Interfacial tension for nanocellulose-based surfactant and synthetic surfactant is investigated by using pendant drop tensiometer. Interfacial tension of mineral oil versus 35,000 ppm NaCl with 1.0 wt% nanocellulose-based surfactant, 1.0 wt% synthetic surfactant. To run this test, density of material such as mineral oil, brine water, nanocellulose-based surfactant, and synthetic surfactant is measured by using density meter. The external phase for IFT test is mineral oil.

### Dynamic adsorption test

The method of dynamic study applied in this project would be the effluent–surfactant concentration method measured by UV–visible spectrophotometer (Zhou et al. 2005; Yu et al. 2012; Zhou and Liu 2005). Benchtop permeability system (BPS) is used to perform core flooding or to inject surfactant into core. First, all core samples are saturated with 35,000 ppm brine for approximately 24 h. The pump is switched on for 30 min and left for approximately 24 h inside the vacuum pump. The weight of core samples is recorded. After installing the core into the core holder, formation brine, 35,000 ppm brine, is injected into the core sample at 1.0 cc/min. Accuracy of pump rate is measured to ensure that it is working effectively. Brine is injected for 300 ml to ensure the core is 100% saturated with brine to achieve steady-state condition (pressure is constant) and also cleaned from any chemicals. Before injecting surfactant, brine solution come out or produce from the system must be a clear solution. Surfactant is injected after clear brine produce. Sample is collected for every 0.15PV until it reached 6PV. Then, 100 ml secondary brine is injected. The samples collected are centrifuged at 3,700 rpm for 30 min. The supernatant is filtered out from each sample by using a syringe filter. Then sample of 0.151, 1.5–2.25PV, and 2.25–6 are diluted 3, 4, and 5 times, respectively. The process is repeated for each surfactant involved in this dynamic study. Before the concentration for each sample can be determined, a calibration graph for each surfactant needs to be established. Calibration graph is established by measuring the absorbance of 100 ppm, 200 ppm, 300 ppm, 400 ppm, 500 ppm, 600 ppm, 700 ppm, 800 ppm, 900 ppm, and 10,000 ppm for each surfactant with reference to 35,000 ppm brine as base. The accuracy of calibration graph is very important. R-squares value must be close to 1. After calibration graph for respective surfactant is established, the
absorbance for each sample is measured, and then the concentration can be calculated from the trend of calibration graph. Adsorption of the surfactant is calculated by using the following equation:

\[
q_e = \frac{V(C_i - C_e)}{M}
\]

where \(q_e\) is adsorption of adsorbent (mg/g), \(C_i\) initial concentration (mg/L), \(C_e\) equilibrium concentration (mg/L), \(V\) volume of the solution (L), and \(M\) mass of the adsorbent used (g).

**Results and discussion**

**X-ray powder diffraction**

XRD result shows for nanocellulose a single high intensity at 23°, which suggests that the depolymerization of hemicellulose and delignification has been successfully achieved. The sharp peak also describes the crystalline nature of the sample similar to a result reported earlier by Iwamoto et al. (2008). The degree of the crystallinity for the nanocellulose samples was determined by using the following equation:

\[
\text{Crystallinity(\%)} = \left(1 - \frac{I_{AM}}{I_{002}}\right) \times 100\%
\]

\(I_{002}\) maximum intensity of the peak, \(I_{AM}\) second maximum intensity of the peak.

The XRD of the nanocellulose extracted from OPEFB were discussed according to the diffraction peaks from “Appendix”—XRD diffraction results. From the figure, we can notice that there are two sharp peaks at \(2\theta = 22^\circ\) and \(2\theta = 15^\circ\). Therefore, the nanocellulose extracted from OPEFB results in 58.33% crystallinity of cellulose, which shows an excellent extraction of cellulose.

**Particle size of nanocellulose**

The mean size for nanocellulose produced is 283.5 µm. It is expected for the product to be in nanosize which is in range of 20 nm or 0.02 µm. The method or technique used for nanocellulose preparation for this study did not manage to successfully convert cellulose into nanosized. More research and time are still needed to make the cellulose successful to reach nanosize, but it is possible (Isogai 2012). Figure 1 shows scanning electron microscope...
(SEM) result for nanocellulose and nanocellulose-based surfactant.

From SEM result, it is can be observed that the nanocellulose is to be coagulated, while for nanocellulose-based surfactant, it can be seen that the surface topography has changed. The preparation method for nanocellulose-based surfactant successfully changed coagulated nanocellulose to be more disperse.

**Fourier transform infrared spectroscopy (FTIR)**

The result infrared spectroscopy for nanocellulose and nanocellulose-based surfactant is shown in Fig. 2.

From the infrared spectroscopy, IR spectra of nanocellulose were obtained; visually, there is no difference between spectrum of nanocellulose and nanocellulose-based surfactant. The strong and broad bands at 3332 cm⁻¹ (nanocellulose) and 3335 cm⁻¹ (nanocellulose-based surfactant) indicate the characteristic of OH group or phenolic compound. The bands at 2996 cm⁻¹ (nanocellulose) and 2922 cm⁻¹ (nanocellulose-based surfactant) are due to the bending of vibration in phenolic OH group, while the bands at 1029 cm⁻¹ (nanocellulose) and 1032 cm⁻¹ (nanocellulose-based surfactant) are characteristic of primary alcohol. From the above result, it shows that the extracted nanocellulose contained hydroxyl (O–H) and carbonyl (C=O) functional group that can contribute to stable surfactant formulation.

**Interfacial tension**

Density of nanocellulose-based surfactant measured by density meter:

The result of IFT is as such with mineral oil as external phase:

From the IFT result, the nanocellulose-based surfactant indicates good reduction in interfacial tension.

**X-Ray Fluorescence Spectroscopic** Composition of core sample is given in Table 3 below:

The surface chemistry for the core sample depends on silica and aluminum since they have the highest fractions. Four core samples are used in the experiment. PORO-PERM results are given in Table 4, where $K_{\infty}$ represents permeability of the air and $k_{\infty}$ represents average permeability.

Before running the core flooding, the BPS pump is checked for accuracy. At setting rate of 1 cc/min, the pump gives out 4 ml for 4 min. This test is repeated three times, and the result is the same. This indicates the accuracy of the pump. After preflushing the core samples with brine, at some early time, the product that came out is not a clear solution; yellowish in color indicates that in the core there are other chemical substances. It is suspected for the yellowish solution is to be toluene. After some time, a constant clear solution came out which indicates brine water and means the core is fully saturated.

| Table 3 Component of Berea sandstone |
|-------------------------------------|
| Component | Amount (wt%) |
| SiO₂      | 60.8        |
| Al₂O₃     | 23.8        |
| Fe₂O₃     | 7.1         |
| K₂O       | 3.8         |
| P₂O₅      | 1.4         |
| MgO       | 1.2         |
| TiO₂      | 0.9         |
| CaO       | 0.6         |

| Table 4 Core parameter |
|------------------------|
| Parameter              | Sandstone #1 | Sandstone #2 | Sandstone #3 | Sandstone #4 |
| Core ID                | Z1           | Z2           | Z3           | Z5           |
| Length (cm)            | 6.50         | 7.37         | 6.24         | 7.23         |
| Diameter (cm)          | 3.81         | 3.76         | 3.77         | 3.74         |
| Mass (g)               | 164.974      | 182.242      | 151.567      | 177.392      |
| K (∞) (md)             | 29.54        | 51.06        | 44.91        | 22.70        |
| $K_{\infty}$ (md)      | 32.52        | 55.27        | 48.80        | 25.26        |
| Porosity (%)           | 22.32        | 19.14        | 20.43        | 20.03        |
| Pore volume (cm³)      | 16.92        | 15.67        | 14.23        | 15.91        |
with brine. Calibration graph of surfactant 1 is measured by using UV spectrometer. The peak of surfactant 1 is 240 nm (Figs. 3, 4).

In real situation of surfactant flooding, adsorption that occurs onto the reservoir rocks is dynamic. Thus, a dynamic adsorption method gives more practical and better description on the real situation and the result from it is more reliable.

Figure 5 shows the dynamic adsorption curve of surfactant 1 and also the pressure difference during surfactant flooding and pre-flushing. From the figure, it can be observed that the presence of surfactant is detected after 1PV. Before 1PV, it is purely brine. There are differences in pressure during surfactant flooding (grey line) and pressure during preflushing (orange line). That indicates that the surfactant controls the mobility factor. The surfactant reached equilibrium at 4PV. The adsorption results were determined by the decrease in surfactant concentration from the area integration during the stabilization process. The adsorption for the surfactant 1 is 4.81467 mg/g.

Conclusion

Dynamic adsorption of an anionic synthetic surfactant is successfully carried out, but the study of dynamic adsorption of nanocellulose-based surfactant cannot be proceeded due to some drawbacks in the particle size during synthesis of the nanocellulose. There were several bundles of fibril aggregates after the acid hydrolysis. The number of bundles of fibril aggregate can be decreased due to longer test duration for acid hydrolysis time. It is recommended that in order for the cellulose fibers to be obtained at nanosize, longer acid hydrolysis process is needed. Overall, the nanocellulose shows good result in lowering the IFT. Therefore, it is recommended to further study the potential of nanocellulose in chemical enhanced oil recovery with another method in converting the cellulose into nanosize. This is because the advantages of nanocellulose such as nanosized, lower cost and environmental friendly is a promising alternative for synthetic surfactant currently used in petroleum industry. It could overcome some limitation of the existing surfactant. Besides, we can contribute to producing a new green solution, potentially without impacting the environment.

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Appendix

See Fig. 6.
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Fig. 6 X-ray powder diffraction result for the nanocellulose
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