

# Utilizing Lignosulfonate from Coconut Husk as Sacrificial Agent to Reduce Surfactant Adsorption

N M A N Daud<sup>1,2\*</sup>, W M K W Jaafar<sup>2</sup>, N Ismail, R Junin<sup>2</sup>, M A. Manan<sup>2</sup> and A K Idris<sup>2</sup>

<sup>1</sup> Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis, Malaysia

<sup>2</sup> School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, Malaysia

E-mail: [nikazhar@unimap.edu.my](mailto:nikazhar@unimap.edu.my)

**Abstract.** The adsorption of surfactants from aqueous solutions in porous media is essential in enhanced oil recovery (EOR) from oil reservoirs. Surfactant loss that is due to adsorption by the reservoir rocks weakens the efficiency of the chemical slurry that is injected and decreases the oil-water interfacial tension (IFT). One of the ways to reduce the reduction is by using a sacrificial agent. This project will focus on utilizing the lignosulfonate (LS) from coconut husk as a sacrificial agent to reduce the surfactant adsorption. Lignin was extracted from coconut husk before sulfonated using sodium sulphite,  $\text{Na}_2\text{SO}_3$  to form lignosulfonate. Fourier transform infrared (FTIR) spectroscopy was used to characterize the lignin and lignosulfonate and compare them with the commercial product. The batch experiment then conducted using a clay mineral of illite as the adsorbent. Two types of surfactants were studied; anionic (Sodium Dodecyl Sulfate-SDS) and non-ionic (4-octylphenol polyethoxylate-TX100). The amount of adsorbed surfactant was determined by measuring the surfactant critical micelle concentration (CMC) before and after the adsorption tests. The result in the batch experiment shows that LS reduced the surfactant adsorption on illite by about 54.2% for SDS and 42.6% for TX100. This showed that lignosulfonate has the potential as a sacrificial agent to minimize the surfactant adsorption, and agriculture waste like coconut husk can be utilized for this purpose.

## 1. Introduction

Crude oil is extracted by three main processes: primary, secondary and enhanced oil recovery [1]. In the primary recovery, crude oil is spurred out of the oil reservoir by natural pressure from the trapped fuel. As the process goes, the pressure in the reservoir will drop to a certain value and the oil will stop moving to the producing well. In order to raise and sustain the current pressure in the reservoir, water or gas is then injected, which is generally known as the secondary oil recovery process. Depending on the characteristics of the oil and reservoir, the potential amount of oil extracted in both primary and secondary processes usually corresponds to about 20-50% of the deposit.

Tertiary oil recovery, also known as enhanced oil recovery (EOR) then applied to the reservoir to maximize the output of the production well [2]. One of the techniques in EOR is chemical flooding. Chemical methods utilize a chemical formulation dissolved in freshwater or brine as the displacing fluid, which promotes a decrease in mobility ratio and/ or an increase in the capillary number. The mobility



ratio is defined as the mobility of displacing fluid (gas) divided by the mobility of displaced fluid, while the capillary number is the ratio of viscous forces to surface or interfacial tension forces. Surfactant is one of the chemicals that can be used to achieve this. However, certain limitations have been observed, particularly the absorbance of this surfactant into the rock minerals [3]. The charge interaction between the surface of the minerals and the surfactant-assisted by surrounding parameters like pH and salinity, makes the surfactant adsorption increase and reduce the efficiency of the method [4].

Sacrificial agents may be used to reduce the adsorption of surfactants. The sacrificial agent is a substance that is injected in a manner that greatly prevents or conceals all probable rock adsorption sites within the hydrocarbon formation [5]. The sacrificial agent acts to modify the surface formation or be kept in the formation to reduce or eliminate the adsorption of the surfactant. The sacrificial agent can either be injected as a preflush or together with the surfactant. It should be cheap and abundantly available to make it suitable as a sacrificial agent. Chemicals such as alkali, henna and lignosulfonate can be used as sacrificial agents [6, 7].

Every year, Malaysia produces more than 160 million tonnes of biomass. Biomass usually contains 10- 25% of lignin, depending on the type of biomass [8]. The enormous biomass produced in Malaysia, making it abundant and cheap. There are several sources of biomass in Malaysia including oil palm frond (OPF), oil palm trunk (OPT), empty fruit bunches (EFB), palm kernel shell (PKS), rice husk (RH), rice straw (RS) and coconut. Coconut is the fourth largest agricultural product in Malaysia, amounting around 382000 metric tons in 2007 [9]. At present, coconut husks are used as fuel for coconut processing, as a domestic fuel and as a source of fibre for rope and mats [10]. To make better use of this cheap and abundant agricultural waste, it is proposed to extract the lignin from the coconut husk and use it to reduce the surfactant adsorption. The past study indicated that lignin content in coconut husk is around 31.9–53% [11]. In this paper, lignosulfonate will be synthesized from lignin extracted from coconut husk and used in the adsorption experiment as a sacrificial agent to reduce the adsorption of an anionic and non-ionic surfactant.

## 2. Methodology

### 2.1. Mineral Samples

Illite was collected from Jamaluang, Johor. The sample's mineralogical composition was determined by X-Ray Diffraction (XRD) measurements and shown in Table 2.1. The surface area was determined using BET analysis.

Table 2.1: Minerals composition in Illite sample

Sample	Mineral composition				Total
	Quartz	Kaolinite	Illite	Other	
<b>Illite</b>	~35	~25	~45	~5	~100

### 2.2. Surfactants

One anionic surfactant (sodium dodecyl sulfate, SDS) and one non-ionic (Triton X-100, TX-100) surfactant were used. TX-100 was purchased from Scharlau, Spain, and SDS was supplied by Molekula, India, with a high grade of purity (99%). All chemicals were used as received without further purification.

### 2.3. Extraction of lignin

The coconut husk raw material used in this study was obtained from the local plantation (Johor). For the chemicals, the lignin used as a standard was purchase from Aldrich while sodium hydroxide (pellets,

99% purity) was purchased from Qrec, Sulfuric acid (95 – 97% purity) was supplied by Qrec and sodium chloride (99.5% purity) was supplied by Merck. The extraction method is following the literature [12]. The lignin obtained was analyzed using Fourier Transform Infrared (FTIR) spectroscopy and compared with the commercial lignin.

#### 2.4. *Sulfonation of lignin*

The sodium sulphite was supplied by Sigma-Aldrich at 98 % purity. Approximately 15g of lignin powder was diluted in distilled water and 50 mL of 1N NaOH was added. 15 g of sodium sulfite was added and the mixture was cooked for 3 hours at 95 °C. After three hours, the mixture was dried in the oven at 60 °C for 2 days. The black brownish powder left was the lignosulfonate (LS). The LS was then crushed into powder. LS then characterized using Fourier Transform Infra-Red Spectroscopy (FTIR) and compared it with commercial LS.

#### 2.5. *Adsorption test*

Adsorption to minerals was determined by batch equilibrium adsorption procedure. Ten grams of illite samples were added to 60 mL surfactant (1:6 w/v ratio) in a 100 mL Schott bottle and allowed to equilibrate at 25±1 °C. The bottle was shaken on a gyratory shaker at 100 rpm (wrist orbital shaker) for 3 hours and allowed to rest for 16 h. Preliminary experiments indicated that within 3 hours of shaking, almost all adsorption to take place. Sixteen hours of contact time at rest is enough for equilibrium and complete separation to be obtained.

#### 2.6. *Pre-flush test*

10 g of illite with 60 mL of 1% LS solution was added into Scott bottle. The bottle was shaken on a gyratory shaker at 100 rpm (wrist orbital shaker) for 3 hours. The mixture was then transferred into a centrifuge tube and centrifuge at 4000 rpm for 15 minutes. The liquid phase was then discarded, and the minerals phase then put back into the glass vial. 60 mL surfactant was then added into the Scott bottle and allowed to equilibrate at 25±1 °C. The vials were shaken on a gyratory shaker at 100 rpm (wrist orbital shaker) for 3 hours and allowed to rest for 16 hours. The surfactant then collected and analyzed using the surface tension method

#### 2.7. *Surface tension measurement*

Surface tension is important to know the critical micelles concentration (CMC) of the surfactant. The CMC is the concentration of a surfactant in a bulk phase, above which aggregates of surfactant molecules, so-called micelles, start to form [13]. The difference of CMC before and after the adsorption test is related to the adsorption of surfactant on minerals. The surface tension measurement was carried out with a Kruss tensiometer using a platinum-iridium ring at a constant temperature. The tensiometer will be calibrated using the method described in ASTM D 1331- 89. Surface tension measurement will be analyzed according to the method described in ASTM D 1331- 89.

The Kruss tensiometer works on the concept of Du Nouy, in which the platinum-iridium ring is suspended from a torsion balance and the force (mN/m) necessary to pull the ring free from the surface film is measured. When a stable reading was obtained for a given surfactant concentration, the surface tension value was taken, as shown by at least three consecutive readings having almost the same value. To account for the tensiometer configuration, the average of a series of consistent readings for each sample was then corrected, providing a corrected surface tension value (Zuidema and Waters, 1941). A correction factor, F is multiplied by the average dial reading (pull on the ring in dynes) to obtain the corrected value for surface tension. The following empirical correlation in Equation 1 was proposed to calculate the correction factor [14, 15]:

$$F = 0.725 + \sqrt{\left[ \frac{9.075 \times 10^{-4} (ST_{orIFT})}{\pi^3 \Delta \rho g R^3} - \frac{1.679r}{R} + 0.04534 \right]} \quad (1)$$

where:

- F = the correction factor  
 R = the radius of the ring, cm  
 r = the radius of the wire of the ring, cm  
 ST/IFT = the apparent value or dial reading, dyne/cm (mN/m)  
 $\Delta\rho$  = the density difference between the lower and upper phase, g/cc.  
 g = acceleration due to gravity, 980 cm/sec<sup>2</sup>

This equation is applicable only when  $0.045 \leq \Delta\rho g R^3 / ST \leq 7.5$

### 3. Results and Discussion

#### 3.1. Lignin and lignosulfonate characterization

The extraction of lignin from the coconut husk shows a 24.52% extraction yield. The yield is a little bit lower than the literature [16], due to the different method used. In the infrared spectroscopy, IR spectra of lignin are shown in Figure 3.1. Visually there is no difference between the spectrum of standard lignin and extracted coconut lignin. The strong and broad band at 3412 cm<sup>-1</sup> (standard lignin) and 3435 cm<sup>-1</sup> (extracted lignin) indicate the characteristic of the -OH group or phenolic compound. The band at 1330 cm<sup>-1</sup> (standard lignin) and 1345 cm<sup>-1</sup> (extracted lignin) are due to the bending of vibration in the phenolic OH group, while the band at 1042 cm<sup>-1</sup> (standard lignin) and 1042 cm<sup>-1</sup> (extracted lignin) are characteristic of primary alcohol.

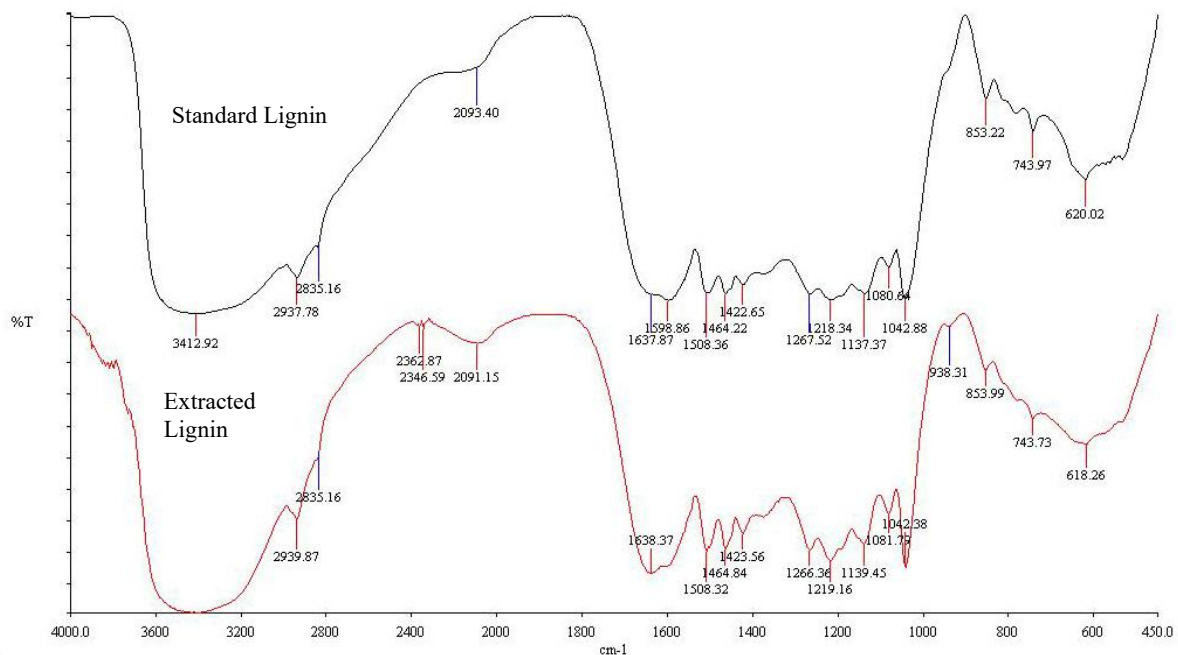


Figure 3.1: FTIR Spectra for commercial lignin and extracted lignin

The clear shoulder at 2937-2835 cm<sup>-1</sup> for the standard lignin is attributed to the vibration of a C-H stretch in the methyl and methylene group while slightly different values were observed for extracted

lignin ( $2939\text{--}2835\text{ cm}^{-1}$ ). The band at  $1464\text{ cm}^{-1}$  for both lignins is assigned to C-H deformations, asymmetry in  $-\text{CH}_3$  and  $-\text{CH}_2-$  and the broad medium band at  $1637\text{ cm}^{-1}$  (standard lignin) and  $1638\text{ cm}^{-1}$  (extracted lignin) is due to conjugated carbonyl stretching. The three bands at  $1598\text{ cm}^{-1}$ ,  $1508\text{ cm}^{-1}$  and  $1422\text{ cm}^{-1}$  (standard lignin) and  $1599\text{ cm}^{-1}$ ,  $1508\text{ cm}^{-1}$  and  $1423\text{ cm}^{-1}$  (extracted lignin) are characteristic of aromatic rings due to aromatic skeleton vibrations, and the band at  $853\text{ cm}^{-1}$  for both lignins indicates C-H deformation and ring vibration. The band at  $1267\text{ cm}^{-1}$  for standard lignin and at  $1266\text{ cm}^{-1}$  for extracted lignin was due to the vibration of a phenolic OH group or the vibration of a Caryl-O in syringyl derivatives. The bands at  $1266\text{--}1267\text{ cm}^{-1}$  and  $1218\text{--}1219\text{ cm}^{-1}$  for both lignins correspond to a syringyl unit and the small bands at  $1042\text{ cm}^{-1}$  for both lignins are assigned to guaiacyl unit of lignin molecules.

IR spectra of synthesized and commercial LS are shown in Figure 3.2. Visually there is no significant difference between the spectrum of commercialized LS and synthesized LS. The strong and broad band at  $3434\text{ cm}^{-1}$  (commercialized LS) and  $3436\text{ cm}^{-1}$  (synthesized LS) indicate the characteristic of OH group or phenolic compound. The band at  $1042\text{ cm}^{-1}$  for both commercialized LS and synthesized LS indicated the characteristic of C-O stretching band. The clear shoulders at  $2942\text{ cm}^{-1}$  and  $2946\text{ cm}^{-1}$  for the commercialized LS and synthesized LS are attributed to the vibration of a C-H stretch in methyl and methylene group while other shoulders at  $2840\text{ cm}^{-1}$  and  $2845\text{ cm}^{-1}$  are resulted from the methoxyl group. The bands at  $1459\text{ cm}^{-1}$  and  $1458\text{ cm}^{-1}$  for both LS is assigned to C-H deformations, asymmetry in  $-\text{CH}_3$  and  $-\text{CH}_2-$  and the broad medium band at  $1636\text{ cm}^{-1}$  (standard LS) and at  $1625\text{ cm}^{-1}$  (synthesized LS) is due to conjugated carbonyl stretching.

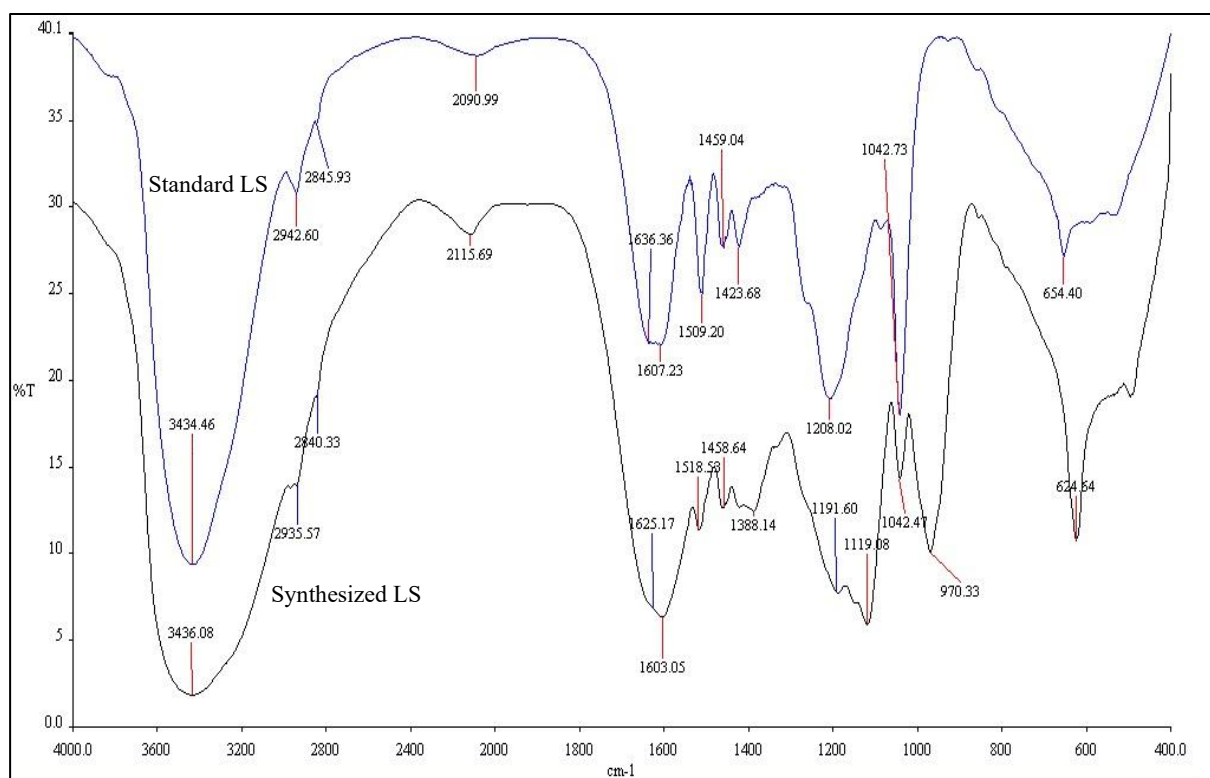


Figure 3.2: FTIR Spectra for standard liginosulfonate and synthesized liginosulfonate

The most important S=O band which confirms the sulfonate group is existing in the compound were the strong band at  $1208\text{ cm}^{-1}$  for LS and at  $1191\text{ cm}^{-1}$  for synthesized LS. These bands correspond to the symmetric stretch in sulfonate group. A strong, broad band at  $654\text{ cm}^{-1}$  and  $624\text{ cm}^{-1}$  for both commercialized LS and synthesized LS corresponded to  $=\text{C-H}$  bend in alkenes. A wide peak at  $2090$

$\text{cm}^{-1}$  and  $2115 \text{ cm}^{-1}$  indicated the  $-\text{C}\equiv\text{C}-$  stretch in alkynes. Other banding that existed in the LS may be caused by the impurities that existed in the synthesized LS sample.

### 3.2. Adsorption test

The pre-flush test was conducted using the LS synthesized from coconut husk. The mineral used for this experiment was illite and the brine used was 2% NaCl. The reason for using illite as the testing mineral was due to the behavior of illite that adsorbs the surfactants strongly. Moreover, illite was one of the common minerals in reservoirs. The adsorption test with preflush was then compared with the adsorption test without preflush to determine the adsorption reduction.

The surface tension data is plotted against the concentration of surfactant. The intercept between the decreasing trends of surface tension with the constant reading of surface tension was determined as a critical micelle concentration (CMC). The difference of CMC before and after the adsorption test corresponds to the amount of surfactant adsorbed. The amount of surfactant adsorbed was calculated using Equation 2.

$$A = \frac{\Delta \text{CMC}}{m} \times V \quad (2)$$

where:

- A = amount of adsorbed surfactant/ normalized value (g/kg )  
 $\Delta \text{CMC}$  = difference between the CMC before and after the adsorption test (g/kg) ,  
 m = amount of mineral used (kg)  
 V = amount of surfactant used (kg).

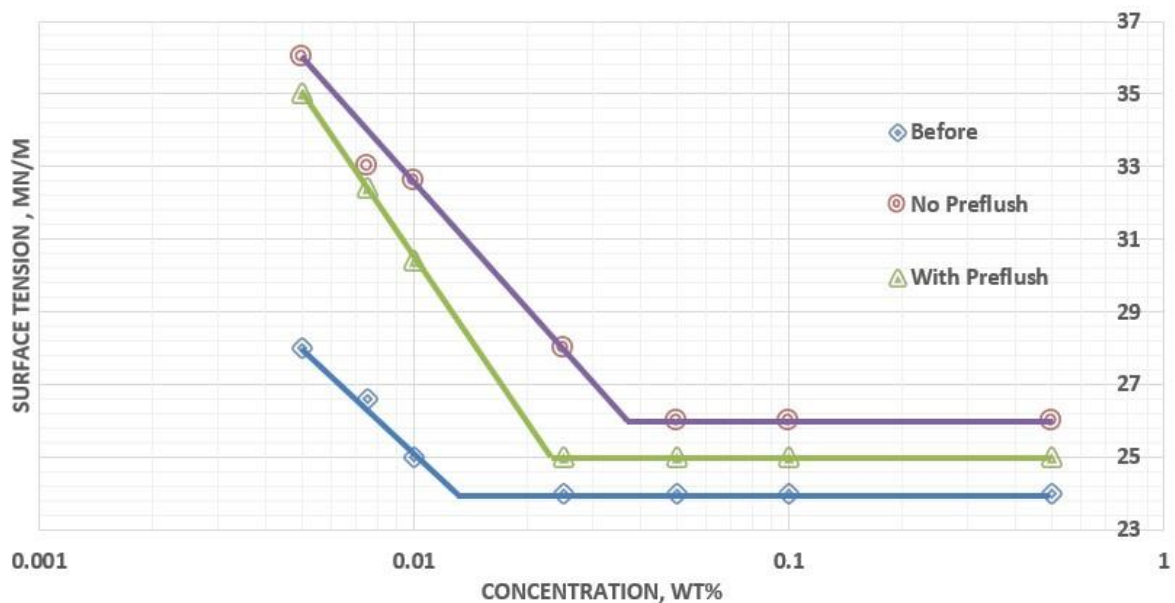


Figure 3.3: Adsorption of SDS on Illite

As shown in Figure 3.3, the adsorption for SDS was lower significantly. The CMC for the batch experiment without pre-flush was approximately 0.038 wt% and with pre-flush was approximately 0.025 % wt. The adsorption amount was 1.44 g/kg for without pre-flush experiment and 0.66 g/kg for the pre-flush experiment. The adsorption was decreased by about 54.2%. The decrease of the adsorption amount was due to the behaviour of LS which adsorb onto the adsorption site on illite [17]. The

adsorption occurred by the electrostatic charge and ion exchange. LS have a highly negative head will eventually being attracted by the positive charge adsorption site on illite. LS molecules that adsorb on the adsorption site will block the SDS molecules from adsorbing to it, hence lowering the adsorption.

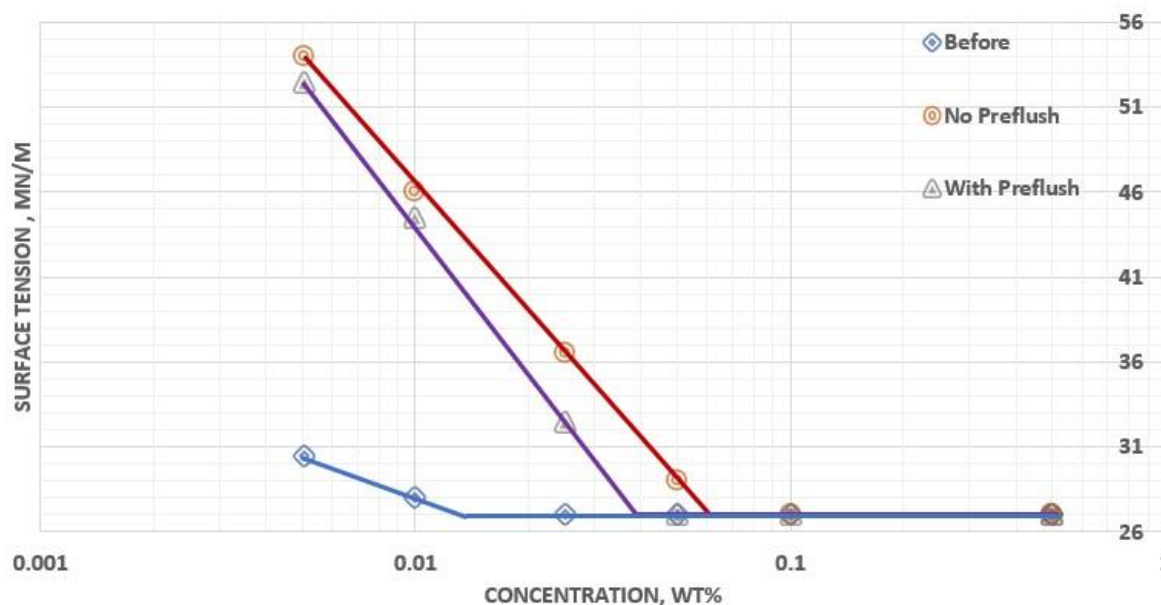


Figure 3.4: Adsorption of TX-100 on Illite

As shown in Figure 3.4, the CMC of TX100 lowered from around 0.06 wt% without pre-flush to around 0.04 wt% with pre-flush correspond to adsorption amount of 2.82 g/kg without pre-flush and 1.62 g/kg with pre-flush. The adsorption amount was decreased by about 1.2 g/kg after the pre-flush. The decrease is about 42.6% which shows that LS adsorb first at the surface of illite, preventing the TX100 from adsorbing onto it. As mentioned above, LS adsorb by electrostatic charge and ion exchange with illite [17]. These results have confirmed that LS can be used in lowering the adsorption in surfactant flooding.

#### 4. Conclusion

Around 24% of lignin can be recovered from the coconut husk showing a reasonable amount of lignin in the coconut waste. The FTIR from both extracted lignin and standard lignin is very similar. This similarity shows the extracted compound has good quality as the standard one. The synthesized LS also has the same similarity as the standard LS. This similarity shows the effectiveness of the synthesis method to functionalized lignin into LS. The batch adsorption shows that anion surfactant (SDS) has a higher adsorption rate compared to non-ionic surfactant (TX-100). The use of LS in preflush can reduce the adsorption of both surfactants onto the illite showing the potential usage of it in the surfactant flooding. The result also suggests the possibility of coconuts waste to be converted to a useful chemical for industrial use.

#### References

- [1] Abbas A H, Sulaiman W R W, Jaafar M Z, Olayink A A, Ebrahimi S S and Elrufai A 2018 *J. King Saud Univ. Sci.* **31** pp 91-99
- [2] Kamal M S, Hussein I A and Sultan I S 2017 *Energy Fuels* **31** pp 7701-7720
- [3] Park S, Lee E S and Sulaiman W R W 2015 *J. Ind. Eng. Chem* **21** pp 1239-1245
- [4] Belhaj A F, Elraies K A, Mahmood S A, Zulkifli N N, Akbari S and Hussien O S 2020 *J*



- Petrol Explor Prod Technol* **10** pp 125–137
- [5] Musa M S M, Sulaiman W R W, Majid Z A, Majid Z A, Idris A K and Rajaeia K 2019 *J. King Saud Univ. Sci.* **32** pp 1-5
- [6] Jazeyi H S, Hirasaki G J and Verduzco R 2013 *SPE Int. Symp. on Oilfield Chemistry (Texas)* (Society of Petroleum Engineers: Texas) pp 1-16
- [7] Daud N M A N, Junin R, Manan M A, Idris A K, Jaafar W K W and Ismail N 2009 *Proc. of 4th Int. Conf. on Recent Advances In Materials, Minerals & Environment and 2nd Asian Symp. on Materials and Processing (Penang)* (Universiti Sains Malaysia : Penang) pp 1-8
- [8] Sohni S, Norulaini N A, Hashim R, Khan S B, Fadhullah W and Omar A K M 2018 *Ind. Crops & Prod.* **111** pp 642–650
- [9] Sivapragasam A 2008 *Second International Plantation Industry Conference and Exhibition* (Shah Alam)
- [10] Tan I A W, Ahmad A L and Hameed B H 2008 *J. Hazard. Mater.* **154** pp 337–346
- [11] Muensri P, Kunanopparat T, Menut P and Siriwattanayotin S 2011 *Compos. Part A* **42** pp 173–179.
- [12] Jaafar W K W, Manan M A, Idris A K and Junin R 2010 *J. Mater. Sci. Eng.* **4** pp 55-61
- [13] Deodhar S, Rohilla P, Manivannan M, Thampi S P and Basavaraj M G 2020 *Langmuir* **36**, pp 8100–8110
- [14] Zuidema H H and Waters G W 1941 *Ind. Eng. Chem. Anal.* **13** p 312.
- [15] Muherei M A and Junin R. 2007 *J. Appl. Sci.* **7** pp 1362–1371.
- [16] Khalil H P S A, Alwani M S and Omar A K M 2006 *BioRes.* **1**(2) 220-232.
- [17] Lee J F, Hsu M H, Lee C K, Chao H P and Chen B H 2005 *J. Chin. Inst. Eng.* **28** pp 375-379.

### Acknowledgement

The authors are grateful to express their appreciation to Universiti Teknologi Malaysia and Malaysian Ministry of Science, Technology and Innovation for their financial support for this research.