Faculty of Science and Engineering

A mud design to improve water-based drilling in clay rich formation

Nikoo Fakhari

0000-0001-7747-9062

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Declaration

I, Nikoo Fakhari, declare that this dissertation entitled ″ A mud design to improve water-based drilling in clay rich formation″, and corresponding work are completely belonging to my own original research. This research work has been conducted at the department of chemical Engineering, Curtin University Malaysia and supervised by Associate Professor Chua Han Bing. This report has not been published or submitted for the award of a degree, diploma, or relevant academic qualification at this or any other universities. All the materials contained in this thesis has been appropriately cited and acknowledged.

Abstract

Environmentally friendly water-based mud (WBM) is the conventional drilling fluid used for drilling in various geological conditions as it is relatively cheap compared to oil and synthetic-based fluids. However, WBM still have major issues when it comes to drilling in deep intervals or shaly formations where conventional additives lose their functionality. Various additives have been proposed to improve the performance of water-based muds in these circumstances, but they are either expensive or unsuccessful in practise. Therefore, the search is still on for an additive that stabilises the well by providing good rheology, filtration control and shale inhibition. It seems that green surfactants extracted from plants and leaves can be a solution to this problem, but the selection, extraction, characterisation and efficiency of such a surfactant is challenging. The aim of this study is to develop a WBM using green surfactant that not only provides good rheology and filtration control under normal drilling conditions, but also prevents shale swelling in complex geological formations. For this purpose, two green surfactants were extracted, and several laboratory measurements were carried out to evaluate the performance of the developed WBM. The results obtained show that the method used to extract the surfactants gave a good yield of flaxseed mucilage (FM) and flaxseed protein (FP). The zeta potential measurements showed that the flaxseed mucilage is a very weak anionic surfactant with an average zeta potential of -8mV. The flaxseed protein, on the other hand, is a cationic surfactant with an average zeta potential of 44mV. It was also found that the critical micelle concentration (CMC) of the flaxseed mucilage is 4, while that of the flaxseed protein is 3. The conductivity measurements showed that both surfactants perform well under temperature fluctuations and can survive in the subsurface geological environment. The same observations were made when the salt stability tests were carried out under different temperature conditions. Based on the pH measurement, both surfactants appeared to create a weakly acidic environment. From a series of thermogravimetric analyses (TGA) performed, both surfactants also exhibited high thermal stability compared to CTAB, which is widely known as a commercial high-performance surfactant. The surface tension caused by these two surfactants was also measured. It was found that increasing the concentration of the surfactants reduced the surface tension from 72° to 23.28° for FM and from 72 ° to 35.75° for FP before reaching the CMC point.

Rheological measurements of the WBMs showed that increasing the concentration of FM in the drilling fluid increased the yield point and plastic viscosity. On the other hand, adding FP increased the plastic viscosity of the mud, but the yield point remained almost the same. Similar results were found when nano-glass flakes (NGFs) and nano-silica (NS) were modified by adding FP and FM. This indicates that FM and FP act as deflocculants and prevent flocculation of particles in the drilling fluid system. Filtration loss tests showed that the addition of FM and FP to the drilling fluid reduced the filtrate volume, but the surfactants did not have a significant effect on the mud cakes, which is often observed in the WBM samples with surfactants. Bentonite and shale dispersion tests also confirmed that FP and FM have good ability to modify the surface charge of clays and reduce clay swelling over time. The results of the wettability measurements showed that the surfactants can make the shale surface less hydrophilic by increasing the contact angle for the base mud from 38.4° to 69.9° for FM and from 38.4° to 51.6° for FP. It seems that the combination of surfactants and nanomaterials may also reduce clay hydration and improve well stability.

It can be concluded that natural surfactants, if characterised and used widely, can improve the performance of WBMs under various geological conditions, especially in shale formations where clay hydration can cause significant operational difficulties. Although the results obtained in this study could be validated using various measurements, further studies are needed to ensure that the natural surfactants extracted in this study (FP and FM) can be used at field scale.

Keywords: Water based mud, natural surfactants, shale, clay swelling, nano particles

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Chapter One: Introduction

1.1. Introduction

With the depletion of conventional reservoirs in recent years, major oil companies have considered the possibility of drilling for deep reservoirs under various temperature conditions. Water-based muds (WBMs) are often used in many wells due to their efficiency, low cost and environmentally friendly properties. However, WBMs cause wellbore instability in shaly intervals and lose their functionality when temperature rises due to the disintegration of additives used to control viscosity and fluid loss (Ali Khan et al, 2018). Although thermal extenders have been proposed and used to improve the stability of the colloidal solution, the poor functionality of WBMs has not been fully resolved. Several other approaches have been presented so far to improve the functionality of water-based mud where modification of bentonite clay, employing polymers (Saboori et al., 2018), adding nanomaterials (Ali Khan et al, 2018; Elochukwu et al. 2017) and using complex shale inhibitors (Jingyuan et al., 2022) are being suggested but little success has been reported to the application of these approaches given their cost or limited functionalities under various geological settings. Thus, a relatively cheap, effective, and less complex WBM is still in demand for a better, faster, and safer drilling for deep reservoirs.

1.2. Background

1.2.1. Nano Fluids

Nanoparticles have found their applications in the oil and gas industry particularly in the enhanced oil recovery (Marwan et al., 2019), reservoir deliverability (Prithvi., 2019) and drilling fluid design. They have been the subject of interest due to their active surfaces and stability under different temperature and pressure conditions. They could also fit into the nano pore structure of clays and reduce the shale swelling under different circumstances. Therefore, many attempts were made to use nanoparticles in the formulation of WBMs (Dehghani et al, 2019; Saboori et al., 2018).

For instance, Salih and Bilgesu (2016) studied the effect of nanosilica and highlighted the negative impacts of nanosilica on the rheological properties such as yield point and gel strength. Elochukwu et al. (2017) conducted a series of experiment to improve the cutting carrying capacity of WBMs by adding nanosilica. They emphasised that by adding nanosilica, the rheological properties of WBMs such as yield point decreases, which reduces the cutting carrying capacity of the fluid. They used surface modification method and indicated that filtration loss can be reduced, and a thinner mud cake can be produced once the surface of nanosilica is modified. Zamani et al., (2018) argued that the interactions between nano materials and WBMs have not been deeply understood. They used nano-bentonite to improve the rheology and filtration control of WBMs. Although they have shown the application of nano-bentonite in improving the rheology and the filtration control of the WBMs, they were unable to overcome on the issue of reduction in the mud density once nanomaterials were added. They also did not report the performance of their mud design under the reservoir condition. Ghasemi et al. (2018) performed a series of rheological analyses on a drilling fluid formulated with TiO_2 nanoparticles. They found that the yield point, plastic viscosity and filtration loss decrease, and gel strength increases as nanoparticles are added to the mud. They also emphasised on the complexity of nanoparticle dispersion. Husin et al. (2018) evaluated the performance of drilling fluids with silver nanoparticles and graphene nanoplatelets. They concluded that both nanoparticles can improve plastic viscosity and reduce filtration loss but will decrease the yield point. Prakash et al., (2021) used nanosilica to improve the rheological properties of water-based mud under various pressure and temperature conditions. They indicated that nanosilica can reduce the filtration loss and improve the viscosity and gel strength, but the changes were sometimes unnecessarily high. In view of these experiences, it seems that nano particles can reduce the cutting carrying capacity of the mud and cause significant drilling issues. This is mainly due to the presence of bentonite with its negative surface charge that induce a repulsive force once nano particles are added to the mud. This repulsion may cause deflocculation, increase the viscosity, and reduce the yield point.

1.2.2. Surfactant

Later, it was found that surfactants can be used as surface-active agents to change the surface charge of nanoparticles in WBM and prevent the negative interactions between bentonite clay and nanoparticles (Guan et al., 2020). Surfactants can also alter the interfacial tension between fluids in a two- or three-phase fluid system and change the surface wettability between rocks and fluids (Peng et al., 2020). These two phenomena can reduce mud invasion (fluid loss) in permeable formations and reduce the affinity of clay to interact with water (Abu-Jdayil et al., 2021). In fact, if the wettability and interfacial tension can be properly modified, the threshold capillary pressure, which acts as a barrier to fluid flow, can be increased, leading to a reduction in fluid loss during drilling (Kassa et al., 2020). However, the mechanisms behind the change in wettability and reduction in IFT due to surfactants are not yet fully understood, especially when it comes to drilling with WBMs. According to studies conducted in recent years (e.g., Kinai et al., 2018; Zuoli et al., 2020), surfactant, low salinity water and nanofluid can alter surface wettability. However, their performance in the presence of bentonite clay have not been fully evaluated.

In addition, the use of surfactants has been significantly limited due to their toxicity and low survival rate in various geological formations. Another disadvantage of surfactants is their adsorption on rock, which can increase operating costs and reduce drilling fluid performance (Olakunle et al., 2019; Haghighi and Firozjaii, 2019, Hosseini et al., 2019; Peng and Nguyen, 2020). Therefore, a good surfactant that can act as a non-toxic, cheap and environmentally friendly additive for WBM is still in demand. Such a surfactant can be used independently or in combination with nano materials to improve the mud rheology and reduce the affinity of clay to interact with water.

1.2.3. Mud Compatibility

Swelling of clay and fine migration during drilling with WBMs is one of the biggest challenges in drilling operations. Salts (e.g., KCL) are commonly used to prevent these problems in the caprock and reservoir intervals, but they can cause compatibility problems with surfactants once they are added to the WBMs (George et al., 2009). The presence of salts in WBMs can also affect the size, specific surface area and charge of nanoparticles. Consequently, the physical properties and surface characteristics of nanoparticles can change when salts are added to the solutions. In fact, salts often reduce the surface charge of nanoparticles and increase the likelihood of agglomeration (Parizad et al., 2018). The addition of salts to a surfactant solution can also alter the intramicellar and intermicellar interactions of the surfactants (Keshavarzi et al., 2020). Accordingly, a fundamental understanding of how salt affect the behaviour of nanoparticles and surfactant solutions can lead to more effective use of this additive in various applications.

1.3. Problem Statement

There have been several attempts to improve the functionality and application of WBMs in deep intervals, especially in shale formations. However, none of these methods have been completely successful once tested under field conditions. This is due to the complex interactions between additives or between additives and rocks under subsurface conditions. Nanomaterials could be a good option in these circumstances due to their large active surface area, but their interactions with bentonite can reduce the performance of the slurry. Surfactants can solve this problem by changing the surface charge of the nanomaterials, but they are expensive, toxic and easily adsorbed by the formations. Surfactants can also alter the IFT and surface wettability of rocks and reduce the affinity of clay to interact with water. However, they can cause compatibility problems with other additives such as salts when drilling in formations with clays. Therefore, if an environmentally friendly, non-toxic, compatible, relatively inexpensive and high-performance surfactant can be developed that improves mud rheology, reduces fluid loss and inhibits clay swelling at the same time, a good step is taken towards safer and more cost-effective drilling operations.

1.4. Research Significance

As mentioned earlier, surfactants seem to be a good way to improve the functionality of nanoparticles, change the surface wettability of rocks such as shale and reduce their affinity to interact with water. However, surfactants have their own drawbacks and many of the commercial surfactants are either expensive or unable to perform the desired functions. Green surfactants extracted from plants and leaves may be a good choice in these circumstances as they are relatively cheap and have even shown good performance as clay inhibitors in the literature (Jiang et al., 2019; Quainoo et al., 2021). However, the challenge is to select and extract a green surfactant that is compatible with salt, bentonite and nanoparticles while modifying surface wettability and inhibiting water-clay interactions.

1.5. Research Objectives

The main objective of this research is to develop and evaluate the application of green surfactants as surface-active agents that can improve the performance of WBMs during drilling, particularly in shaly formations. The following objectives were also aimed at:

i. Selection, extraction, and characterization of green surfactants that can be used to for drilling operation
ii. Evaluating changes in rheological and fluid loss of WBMs once the green surfactants and nano materials are added.
iii. Evaluating the performance of the new formulated WBMs in shaly rocks.
iv. Developing a methodological procedure to formulate an efficient WBMs for shaly intervals.

1.6. Research Questions

Given the objectives, the following questions should be answered:

1. What is the best method of extracting biodegradable surfactants? Can they perform as good as a commercial surfactant?
2. How nano particles can be used in a WBM without having negative impacts on the mud properties?
3. How can the interaction of WBMs with shaly formations be mitigated using green surfactants?
4. What is the best methodology to prepare WBMs for drilling into shaly formations?

1.7. Thesis Structure

Following this chapter, **Chapter 2** provides a detailed literature review of the recent challenges of WBMs in different geological settings and the methods developed to address these challenges. The advantages and disadvantages of the different proposed methods are presented, and the remaining challenges are highlighted. **Chapter 3** presents a method for the extraction of two green/biodegradable surfactants from flaxseed while **Chapter 4** describes different experimental approaches to characterise the extracted surfactants. **Chapter 5** then looks at the applications of nanomaterials and the new surfactants to improve rheology, filtration control and shale stability. Finally, **Chapter 6** draws the conclusions and provides some recommendations for future studies.

Chapter Two: Literature Review

2.1. Introduction

Drilling fluid is a combination of solids and liquids used to safely drill a borehole. In a drilling operation, drilling fluid performs several functions, including lubricating and cooling the drill bits, stabilising the borehole, sealing the permeable formation, maintaining hydrostatic pressure, cutting transport, and controlling erosion of the drill pipe/casing. It is therefore important to select a good drilling mud that will maximise performance and minimise costs during operation.

Drilling muds are divided into three categories: Water-based muds (WBM), Oil-based muds (OBM) and Synthetic-based muds (SBM), all of which have different applications in different circumstances (Ahmed, 2019). Among these three, WBM is used in more than 90% of cases and is the main subject of this study.

2.2. Water-Based Mud

WBM is a mixture of bentonite and a base fluid (fresh water or brine), which is divided into three groups: inhibiting, non-inhibiting and polymeric fluids. Inhibitive fluids minimise reactions between the drilling fluid (i.e., saltwater drilling fluid) and the formations by preventing the clay from swelling. Non-inhibitive fluids are those without sodium, calcium, and potassium ions. These fluids maintain the stability of the shale by preventing the hydration of clays. Polymeric fluids are organic or synthetic polymers that act as viscosity mediators, fluid loss control agents and shale stabilisers (Ahmed, W., 2019). Two main problems when drilling with one of these WBMs are fluid loss in permeable formations and the interaction of the fluid rock with clays in shaly intervals. Wellbore instability caused by the shale is perhaps a greater challenge than fluid loss. These problems become even greater when the temperature rises in deeper sections, as many additives commonly used to control fluid loss or prevent clay swelling dissolve (Anietie, N., 2020).

2.3. Filtration Loss

Filtration loss refers to the penetration of drilling fluid into permeable formations (Anientie, 2020). The difference in pressure between the drilling fluid and the formation pressure causes the fluid to flow into formations with lower pressure gradients. This leads to the formation of a layer of solid material that is deposited on the walls of the boreholes and is called filter cake or mud cake (Asif et al, 2017). Filtration loss needs to be controlled during drilling as serious problems such as formation damage and wellbore instability can occur, which have a significant impact on well production (Tianbo et al., 2017). In addition, filtration losses increase the cost of the drilling operation. Therefore, controlling filtration losses is important, especially when drilling through highly permeable zones and formations with faults (Feng and Grey, 2016). Another issue with filtration losses is the extension of non-production time (NPT), which adds additional costs to the drilling operation. Therefore, an assessment of filtration loss should be made, and the best method selected to minimise the risk during drilling.

The amount of mud flow into the formation determines the severity of filtration loss. This is an important factor to consider because if the causes are identified, various remedial measures can be taken. Appropriate measures must be taken to control filtration loss to avoid excessive operating costs and serious problems. The hydrostatic pressure of the mud decreases as it flows into the formation. This can cause fluids to flow back from the formation into the wellbore, resulting in a kick or well collapse (Lavrov, 2016). The severity of filtration loss is often classified into four different categories, including seepage loss, partial mud loss, severe mud loss and complete mud loss, as given in Table 2.1. It is crucial to find the best way to control filtration, as this increases the cost and time of drilling certain intervals (Lavrov, 2016).

Table 2.1: Severity of Filtration Loss (Cook et al., 2012)

Severity	Rate of Loss	Type of Formation
Seepage	Less than 10 bbl/hr	Porous and permeable sands
Partial	In between 10 to 100 bbl/hr	Coarse sands and gravels
Severe	More than 100bbl/hr	Faults, fractures, vugs,
Total	No fluid returned to surface	Faults, fractures, vugs,

2.3.1. Filtration Control additives

Filtration loss is one of the problems that requires careful assessment and consideration. Technically, there are two remedies that well engineers use to reduce filtration loss and seal the pores or fractures: Wellbore Strengthening Materials (WSM) and conventional Lost Circulation Materials (LCM) (Zamani, A., 2018). However, once added to the WBM, these additives may cause favourable or unfavourable changes in the rheological properties. Therefore, selecting a suitable additive to reduce filtration losses is not a simple and straightforward task. A suitable additive can also reduce environmental impact and operating costs (Saboori, R., 2018). In the next sections, different additives are presented with their advantages and disadvantages to determine the best additives for different geological conditions.

2.3.1.1. Local Additives

Natural resources such as sugarcane stalks and rice husks are organic polymers that can be used as local additives to control filtration loss. Rice husks, for example, are 50% cellulose, 25-30% lignin and 15-20% silica (Agwu. O.A et al., 2019), making them a good choice to quickly close the pore space of formations and reduce the filtration loss of WBMs. Muthuraja et al. (2020) showed that rice husks have good resistance to temperature, water ingress and fungal decomposition due to polymer formation of lignin and silica with phenylpropanoid structure. Control of filtration loss of rice husks was also studied by Okon et al. (2020), comparing filtrate volume and mud cake thickness between rice husks, carboxymethyl cellulose (CMC) and polyanionic cellulose (PAC). They compared all these additives at constant temperature with the results given in Table 2.2.

Table 2.2: Filtration characteristics of different additives reported by Okon et al., (2020)

Additives	Mass of Additive: 5.0g		Mass of Additive: 10.0g	
	Filtrate volume (mL)	Mud cake thickness (mm)	Filtrate volume (mL)	Mud cake thickness (mm)
Rice Husk	42.5	1.0	35.0	1.5
CMC	29.5	1.8	17.5	3.3
PAC	31.0	1.8	19.0	3.5

As can be seen in Table 2.2, although rice husk seems to be a good additive to reduce the thickness of the mud cake, its efficiency in controlling the filtrate volume is not as good as that of CMC and PAC. However, rice husk is extremely cheaper than CMC and PAC, which may justify its lower performance compared to the other two.

2.3.1.2. Carboxymethyl Cellulose

One of the common additives used by the industry for filtration control is a water-soluble anionic cellulose, also known as CMC. According to Kuma et al. (2019), CMC can also act as a good shale stabiliser because its negative surface charges generate electrostatic forces and interact with the cationic charges at the edge of the clay particles. As a result, the addition of CMC to the drilling fluid can create a rigid and connected structural network that can significantly reduce filtration loss. In addition, the addition of CMC to the drilling fluid can result in higher viscosity and optimisation of flow properties at different temperature conditions.

2.3.1.3 Polyanionic Cellulose

One of the best substitutes for CMC is polyanionic cellulose (PAC), which can control fluid loss by forming an electrolyte solution in the presence of clays (Tianbo et al., 2017). The difference between PAC and other additives is perhaps its renewability, which has been reported in many studies (Busch et al., 2018). When PAC is added to the drilling fluid, it can reduce filtration loss due to its high degree of polymerisation, which creates a rigid and cross-linked network in the philtre cake. In addition, PAC can act as a viscosity regulator and increase the viscosity of the drilling mud. However, adding PAC to the WBM creates a thicker mud cake, which increases the likelihood of differential sticking. Therefore, attempts have been made to replace PAC with other drilling mud additives such as xanthan gum.

2.3.1.4. Xanthan Gum

Xanthan gum is known to be an anionic heteropolysaccharide due to the presence of glucuronic and pyruvic acids in its side chain. The pseudoplastic property of xanthan gum such as its shear thinning behaviour and salt stability have increased the popularity of this additive in the industry (da Luz et al., 2017). Xanthan gum has also been shown to improve the stability of rheological and filtration properties even at high temperatures (more than 80°C) (Jha et al., 2016). When xanthan gum is added to drilling fluids, it combines with other particles and creates a synergistic effect. This phenomenon reduces the permeability of the mud cake and reduces filtration loss (Emmanuel et al., 2020). However, this gum starts to degrade in the presence of acids and oxidants, which limits its application. As a result, many studies have been conducted to find other mud additives that do not have the limitations that xanthan gum has.

2.3.1.5. Nanoparticles

Nowadays, nanoparticles are of interest in different fields of industry due to their functionalities and performance on different occasions. Nanoparticles can have a great impact on filtration loss in permeable formations (Mikhienkova et al., 2018). According to the concept of particle bridging, the width of the particles should be at least three times smaller than the pore throat of the rock to ensure effective sealing. The average size of the pore space in rocks is usually between 10nm and 30nm, while nanoparticles have a size of 1nm to 100 nm (Al Ruqeishi et al, 2018). This means that nanoparticles may be able to seal the pore throat and reduce filtration loss (Yuxiang, C., 2020). Furthermore, nanoparticles can form a thin and compact philtre cake, which would further reduce filtration loss.

Nanoparticles also have good resistance to temperature fluctuations and could be a good option for drilling in reservoirs (Aftab et al., 2017). However, they may have negative effects on rheological parameters, which need to be addressed. Their proper dispersion is another problem that needs to be studied extensively. The dispersion issue could be resolved through surface modification by surfactants which will be explained in the following section. Some of the most effective nanoparticles used so far to improve the filtration control of WBMs are described below.

i. Nanosilica

Nanosilica has great properties such as good compatibility with ions and high thermal stability (Amanullah et al., 2017). Salih and Bilgesu (2016) suggested that nanosilica has a significant negative effect on the rheology of WBMs but can improve the filtration control by closing the pore closures of rocks. Salih et al. (2016) claimed that the rheology of WBMs increases with the addition of nanosilica, but filtration control improves while the thickness of the mud cake decreases. Elochukwu et al (2017) conducted a series of tests with nanosilica modified with a cationic surfactant called alkylbenzyldimethylammonium chloride (ABDACl). They concluded that nanosilica modified with the surfactant can improve the rheology and reduce filtration loss.

ii. Nano Glassflake

Nano Glass Flake (NGF) has become a well-known nanomaterial due to its unique chemical, mechanical and physical properties (Zuo et al., 2017). These particles have a density of 2.60 g/cm^3 and high softening and melting points of 688°C and 950°C, respectively. They also have tremendous mechanical strength. Another impressive property of these nanoparticles is their high resistance to chemical corrosion, which makes them a perfect erosion barrier (Amanullah et al., 2017). Being relatively cheap and having ideal properties, NGFs are a great additive to control the filtration loss of WBMs fluid. Guan et al. (2020) indicated that the addition of modified NGFs with CTAB can improve filtration control under different temperature conditions. According to their study, the ionic interaction of the modified NGFs leads to the formation of a strong and dense network that reduces the thickness and permeability of the mud cake. They also pointed out that the conductivity of the drilling mud can be improved by the addition of NGFs, which can ultimately increase the efficiency of WBMs.

iii. Silver nanoparticles

Husin et al. (2018) conducted a study on the application of nanosilver and graphene nanoplatelets on the rheology and filtration control of water-based mud. They performed a series of laboratory measurements under different reservoir conditions and investigated different approaches to prepare NPs mixtures. They followed certain available standards and concluded that the nanosilver and graphene nanoplatelets can improve plastic viscosity by 64% and 89%, respectively. They can also reduce filtration to a great extent, but they had a negative impact on the yield point. In fact, the yield point was reduced by both nanoparticles and the cutting carrying capacity of the slurry was decreased.

iv. Multi Walled Carbon Nano Tubes

Carbon nanotubes are cylindrical molecules consisting of coiled sheets of single pr multi layered carbon atoms (graphene). Carbon nanotubes are often used to reinforce different materials and polymers given their strength which is 100 times greater than steel. Carbon nanotubes are divided into single-walled (SWCNTs) and multi-walled (MWCNTs) carbon nanotubes. Multi-walled carbon nanotubes are non-conductive in width but have a very good thermal conductivity in length. Ruqeishi et al. (2018) used carbon nanoparticles together with WBM to formulate a high-performance drilling fluid. They evaluated rheology and filtration control of the mud were based on available conventional standards and indicated that carbon nanoparticles have a retarding effect and can maintain the homogeneity of the drilling fluid for a longer period. Table 2.3 summarises the performance of different nanoparticles used to formulate water-based mud.

Table 2.3: Summary of the performance of different nano particles used to formulate water-based drilling mud

Author (s)	**Type of nanoparticles**	**Fluid loss volume (mL)**	**Initial Gel strength (Pa)**	**10 min Gel strength (Pa)**
Husin (2018)	Silver	2	-	-
Jain (2016)	MWCNT	9	4.5	7
Ismail (2016)	Nanosilica	7	-	6
Kumar (2014)	MWCNT	5	-	7
Mao (2015)	Silica	4.8	-	-
Jain (2015)	Silica	7.2	-	-
Cheraghian (2019)	Silica	10	13	32
Gbadamosi (2019)	Silica	5.1	7	8
Guan (2020)	NGFs	5	-	-

2.3.1.5.1. Surfactants and Nanomodification

Surfactants are conventional additives used as surface-active agents to change the behaviour of the interface between two different liquids. These surfactants are composed of polymeric molecules and can adsorb on the substrate surface (Negin et al., 2017; Sarmah et al., 2020). As shown in Figure 2.1, surfactants have a hydrophilic head and a hydrophobic tail in their molecular structure. They are divided into three main groups: cationic, non-ionic and anionic surfactants.

Figure 2.1: Structure of a surfactant molecule (Charles et al., 2019 is unable to be reproduced here due to copyright restrictions. The content can instead be accessed via https://www.pirika.com/NewHP/PirikaE2/Surfactant.html)

Non-ionic surfactants are a group of non-toxic substances that carry no charge and do not release ions into water (Kania et al., 2021). Therefore, they have a high stability in brine solutions or hard water. Anionic surfactants, on the other hand, have a negative charge in the head and are biodegradable and resistant to high temperatures and salt (Wang et al., 2016). In contrast, cationic surfactants have a positive surface charge, good pH resistance and great solubility in water (Wang et al., 2016). When surfactants are adsorbed on the surface of a charged particle, significant charge distribution, instability and disintegration may occur (Basim, A., 2016). Therefore, care must be taken when selecting a suitable surfactant for surface modification under various conditions.

2.3.1.5.2. Surface Modification

Apart from the properties mentioned for surfactants, they can also be used to improve the stability of nanoparticles in solutions. It should be remembered that the surface structure and surface interaction of nanoparticles differ significantly from other particles suspended in solution. In general, these particles have a higher tendency to aggregate, which has a great impact on the functionality of the fluids (Hidehiro et al., 2010). This tendency to aggregate can be described by Brownian motion (Hidehiro et al., 2010), which is described below:

$$\Delta x = \sqrt{6 D_B \Delta t} \tag{2.1}$$

$$D_B = \frac{k\ T}{3\pi\mu d_p} \tag{2.2}$$

In the above equation, Δx (µm) is the three-dimensional mean displacement, DB (m^2/s) is the Einstein's Brownian diffusion coefficient and Δt (s) is the diffusion time. In Eq. (2.2), k is the Boltzmann constant, T (K) is the temperature, µ (cp) is the medium viscosity and d_p (μm) is the size of the particles. According to these two equations, the displacement due to Brownian motion increases when the size of the particles decreases. As a result, the nanoparticles move towards each other and agglomerate due to the van der Waals force. To solve this problem, the surface of nanomaterials can be modified with surfactants. According to Elfeky et al. (2017), cationic nanoparticles such as CTAB are able to interact with nanoparticles, grafted onto their surface, changing their surface charge and creating repulsive forces that prevent agglomeration (see Figure 2.2). In addition, the surfactants grafted onto the surface of the nanoparticles increase the distance between the nanoparticles and improve dispersion. However, the size of the nanoparticles and the pH of the solution are important to achieve the best performance once surfactants are added to the solutions. For example, to modify nanosilica, a pH of 8-9 is best, as the hydroxyl group is then available. Furthermore, with a size of 15-20 nm, nanosilica has a large surface area for interaction with cationic surfactants (Elochukwu et al., 2017).

Figure 2.2. Process of modifying the surface of nano silica using CTAB (Xiao et al. (2010) is unable to be reproduced here due to copyright restrictions. The content can instead be accessed via https://doi.org/10.1016/j.colsurfa.2010.01.051)

2.4. Shale

Shale is a sedimentary rock commonly found in various geological formations (Britannica, 2018). It is often composed of fine-grained sediments and clay minerals (Yang et al., 2017). Clays are a group of hydrous aluminosilicates with a size of less than 2 micrometres and a negative surface charge. Kaolinite, chlorite, montmorillonite and illite are the most common clays observed in different geological settings.

Depending on the type of clays, shale is classified into ductile and brittle groups. The problem of fracturing of boreholes is caused by the brittle shale, which can lead to well bridging or pack-off. Hydratable shales, on the other hand, have a greater tendency to deform plastically and swell in the presence of water. As a result, they can lead to stuck pipe, borehole plugging, differential sticking, borehole wall failure and even stuck drill string.

Swelling is observed in the shaly formations dominated by montmorillonite, smectite and double layer illite clays. These clays have a lattice structure that can absorb water and expand. When the hydration force is extremely high, the distance between the layers increases and the lattice expands, resulting in swelling (Han et al., 2019).

Many approaches have been developed to mitigate the swelling of the shale during drilling in different geological environments. KCl with a concentration of 3-20 wt% is often used as one of the means to reduce drilling problems in shaly sections. However, WBMS with a salt concentration of more than 1 wt% is not approved for offshore drilling. Oil-based muds can also be used to prevent shale, but they have a huge impact on the environment and are often banned by governments. Considering that shale is recognised as a capillary closure, creating a hydrophobic surface (changing the surface wettability) for clays can be a good option to reduce interaction with WBMs (Huang et al., 2017). This approach is one of the main focuses of this study and is discussed in the following sections.

2.4.1. Clay types

Shales can contain different types of clays with different structures that can cause problems with wellbore instability and cuttings disintegration due to their nature and surface charge. This section introduces these clays and discusses their sensitivity to WBMs.

2.4.1.1. Smectite (montmorillonite, bentonite)

Montmorillonite is the main member of the smectite family that is often recognized by its high CEC value significant hydration tendency. They are made of three basic units including a silica tetrahedron, an alumina octahedron and a silica tetrahedron. Due to the large distance between these three units and their weak bonding, montmorillonite has a significant swelling tendency. This tendency can be decreased by adding counter ions such as Na^+ and Ca^{++} into the shale but the success rate depends on the pH and the presence of other ions in the aqueous phase. KCl (K^+ ion) can also be used to reduce under these circumstances given a unique hydrated size that fits precisely into the tetrahedral layer of the clay. Potassium ion is exchanged into the clay lattice and cannot be easily removed, thereby fixing the distance between the unit. It should be recalled that montmorillonite and its family members are often observed in shallow intervals and transformed into illite as depth increases. However, illite produced from this transformation may still have a swelling tendency (Huang et al., 2020).

2.4.1.2. Illite

illite is less prone to hydration in fresh water, although it has the same two tetrahedral silica layers as montmorillonite. This is mainly because of the lack of an expanding lattice in illite and as such water cannot enter between the layers. The strong bond between the layers can be linked to the presence of surface charge in the tetrahedral layer. Ion exchange can still occur at the outer surfaces of the individual illite layers, but the increase in volume is much less than in the hydration of montmorillonite. Illite is formed by the transformation of muscovite and feldspar in weathering and hydrothermal environments. As a result, the space between individual clay crystals is occupied by poorly hydrated potassium cations, which prevents illite from exhibiting a tendency to swell (Chen et al., 2020). However, there is another type of illite that is formed by the transformation of smectite in deep sections where conditions of high pressure and temperature prevail. These mixed layer illite may be more prone to swelling than their original version.

2.4.1.3. Chlorite and kaolinite

Chlorite and kaolinite, like the other members of the clay family, have no appreciable hydration capacity, although kaolinite can disperse. It is a phyllosilicate mineral with a tetrahedral layer of silica associated with octahedral layers of alumina. Kaolinite has a low swelling tendency and a low cation exchange capacity (1-15 meq/100 g). It is a soft and white mineral formed by the chemical weathering of aluminium silicates such as feldspar. Shales with a high proportion of kaolinite often exhibit brittle behaviour and are the subject of interest in wellbore mechanical stability issues (Zhang et al., 2020). Chlorites, on the other hand, are a group of phyllosilicate minerals that are classified into four groups of clinochlorite, chamosite, nimite and pennantite. The wide range of composition in chlorite has resulted in significant differences in their physical and chemical properties. This has also allowed them to exist in a wide range of temperature and pressure conditions.

2.4.2. Shale inhibition Mechanisms

2.4.2.1. Ion inhibition

Ion inhibition is an effective approach to reduce the dispersion of clays in WBMs by exchanging the cations originally present with cations that contribute to the stabilisation of the shale. The degree of success depends on the type and concentration of inhibitors, but the effect of hydration may not be completely eliminated (Qu et al, 2022). The surface of clay has strong negative surface charges. As a result, the cations contained in the mud are adsorbed on these surfaces due to the attraction created. Potassium and ammonium are the most inhibitory ions used in drilling through shale (Qu et el, 2022). This is mainly due to their diameters, which are very close to the distances between the layers of montmorillonites and illite, their low hydration energies and small hydrated diameters. Potassium cations often perform very well in shales with a large amount of illite, as they are able to convert illite to its pure form, which is a non-swellable clay. There are other ion inhibitors including ammonium potassium formate, saccharide derivatives, sulphonated asphalt, grafted copolymers, polyoxyalkylene amines and anionic polymers. Given the diversity of clays and their complex behaviour, the response of a particular shale is almost unpredictable.

2.4.2.2. Encapsulation

Drill cuttings from reactive shale formations must be protected on their way to the surface. During circulation, they are subjected to considerable forces and grinding processes in the annulus. This protection must be applied quickly to prevent further deterioration of the cuttings exposed to the water-based mud. A common strategy is to use long-chain polymers such as partially hydrolysed polyacrylamide (PHPA), which adhere to the surface of the cuttings, slowing water penetration and allowing them to retain their size. If the encapsulation polymer is successful, the cuttings that come over the shakers are firm and not sticky (Guecioue r et al., 2017). However, the application is limited to those shales that produce medium to hard cuttings when drilled. It should be noted that a sufficient amount of encapsulation polymer must be present in the drilling fluid at all times to be effective. The concentration must also be measured and replenished as the amount of polymer in the mud decreases over time. This is mainly because soft shale tends to break down mechanically and small particles can absorb the polymers quickly (Mukarram et al., 2018).

2.4.2.3. Physical plugging

The increase in pore pressure near the borehole wall is one of the main mechanisms leading to the failure of the shale. The differential pressure between the drilling fluid and the pore fluid creates a filter cake on the borehole wall in permeable formations. However, shale is almost impermeable formations with a permeability of 10^{-6} to 10^{-12} Darcy. In this case, no filter cake can be created with the mud pressure applied directly to the formation, resulting in slow penetration and infiltration of the mud into the shale. This slow increase in pore pressure reduces mud support and increases rock stress around the wellbore, ultimately leading to excessive rock failure. Under these circumstances, ionic inhibition and encapsulation may not fully work and physical plugging of the pore necks may be the best option (Akhtarmanesh et al., 2013). Thermally activated polyglycols may be the best option given the fact that their molecules are normally stable in a drilling fluid under surface conditions. Once the temperature exceeds a critical point, the polyglycol generates hydrophilic and hydrophobic phases. This transition in temperature is called the cloud point, which can be regulated with certain types of polyglycol and adjusting the salinity of the drilling fluid. The resulting microgels are large enough to block the pores of the shale and prevent pressure transfer. However, there are many additives that can affect this transition to the cloud point. The correct cloud point must be carefully developed in the laboratory and the drilling fluid must contain a sufficient concentration of glycol. The glycol concentration must also be monitored in the field, as the glycol is consumed over time. Asphaltenes and gilsonite are other options to block the pores of shale rock and its microfractures. However, they need to be combined with suitable loss circulation materials (LCM) (Gholami et al., 2018).

2.4.3. Classification of Shale Inhibitors

2.4.3.1. Low molecular amine-based inhibitors

Small molecule amine-based inhibitors such as ammonium lauric acid salts and ammonium malic acid salts are a good choice to inhibit clay hydration. They work based on the Ion exchanging concept described earlier and do not contain toxic substances (Rana et al., 2019). In these inhibitors, ammonium cations are exchanged with hydrated cations in the bentonite and adsorbed on the clay surface through electrostatic and hydrogen bonding, which prevents further water penetration into the clay layer. The inhibition mechanisms of piperazine-based quaternary ammonium salts in the presence of montmorillonite (MMT) are shown in Figure 2.3. As can be seen in the figure, QAs molecules are adsorbed on the surface of MMT and form a hydrophobic film that prevents water molecules from entering the clay structure. Technically, the longer the hydrophobic tail of the QAs, the better the inhibition effect.

Figure 2.3. Inhibition mechanism of piperazine-based quaternary ammonium (Zhou et al., (2020) is unable to be reproduced here due to copyright restrictions. The content can instead be accessed via https://doi.org/10.1016/j.cej.2019.123190)

However, the larger the molecule, the more irregular the arrangement and the larger the holes in the structure through which water molecules can penetrate the clay structure. A solution to this circumstance may be the amine DTHDB, which has a hydrophobic nature, quaternary amine and alcohol functions (Du et al., 2018). DTHDB can not only adsorb on the surface/intermediate layers of clay and compress the electrical double layer, but also convert the hydrophilic clay surface into a hydrophobic surface, which reduces the affinity of clay to interact with water. Later, Du et al. (2020) synthesised a new inhibitor, polyhydroxy organic shale hydration inhibitor (THEED), which can compress the diffusion double layer of clay due to the presence of hydroxyl and amine functional groups. However, most organic amines tend to release NH_3 (harmful gas) and produce toxic WBM solutions.

Polyamine has a high inhibitory capacity and is a non-toxic and non-hazardous material. Zhang et al (2018) prepared a series of polyammonium shale inhibitors and pointed out that at a concentration of 0.8%, the anti-swelling rate can reach 97.8%. They emphasised that the combination of two inhibitors can achieve the best inhibition performance. Xie et al (2020) synthesised two low molecular weight polyamines, namely BEN -5NH_2 and NETS. They concluded that the larger the number of primary amino groups in the inhibitors, the better the inhibitory performance in the long run. They argued that low molecular weight polyamines can penetrate the clay layers and replace the cations in the intermediate layers due to their strong electrostatic effect.

However, amine inhibitors are randomly coiled in WBMs and often exhibit weak interactions with shale. Moreover, the inhibitory part of the amine groups is located only at the ends of the molecular chain, resulting in very few chemical positions, which are insufficient for effective inhibition (Wang and Pu, 2019).

2.4.3.2. Dendrimer inhibitors

Dendrimer is a type of functional polymer with large number of end groups, good water solubility and small hydrodynamic radius. It can be uniformly adsorbed on the surface clay and do not pose significant interactions with other polymer additives in drilling fluid due to Its hydrodynamic radius. Amine-terminated polyamidoamine dendrimers (PAMAM) and hydroxyl-terminated polyamidoamines (PAMAM-OH) are two potential shale inhibitors proposed by Zhong et al. (2015). Bai et al., (2017) developed an amine-terminated hyperbranched polymer (HBP-NH_2) and stated that HBP-NH_2 had a strong hydration inhibition and encapsulation characteristics. Figure 2.4. shows the interactions of HBO-NH_2 with bentonite in WBMs. As can be seen in Figure 2.4, HBO-NH_2 is adsorbed by the hydrogen bonds between the clay layers, displacing water molecules and reducing the distance between the layers.

Later, Yang et al., (2020) proposed the use of a supramolecular composite polymer solution in combination with dendritic poly (amidoamine) (h-PAMAM) guanidine. They argued that the supramolecular complex system can increase the inhibition performance to 87.6% and does not get affected by the changes in the salinity and temperature condition.

Figure 2.4: Intercalation of HBO-NH_2 with bentonite in WBMs (Wang and Pu, (2019) is unable to be reproduced here due to copyright restrictions. The content can instead be accessed via https://doi.org/10.1115/1.4042528)

Feng et al (2020) developed the hyperbranched cationic clay stabiliser (HBP-QAT) as a high-performance and long-term inhibitor. The low molecular weight of HBP-QAT could reduce the excessive flocculation of the clay and prevent the closure of the pore space in the formations. Ibrahim and Saleh (2021) used dendrimers to modify activated carbon and developed a composite of polyvinylpyrrolidone (PVP). PVP has amphiphilic biocompatibility and can provide good functionality even in an alkaline environment. They argued that their composite can form a film on the surface of the clay and reduce the hydration tendency. The electrostatic interaction and hydrogen bonding between the dendrimer groups and the clay could promote the adsorption of the polymer film on the clay surface and improve the performance of the inhibitor in WBMs (Ibrahim and Saleh, 2021).

2.4.3.3. Nanomaterial inhibitors

Nanomaterials could be suitable shale inhibitors as they can block pore throats of formations and reduce water entry into shale (Taraghikhah et al., 2015; Saleh and Ibrahim, 2019). However, there are two important factors that can influence pore plugging: i) the particle size of the nanomaterials and ii) the type of nanomaterial (Gao et al., 2016). Nano-silica, nano-alumina, nano-magnesia, carbon nanotubes and nano-polymers have been investigated for their ability to stabilise shale formations (El Sherbeny et al, 2014), with reported reductions in shale permeability, high temperature resistance, reduction in water activity, good lubrication (Yang et al, 2017) and resistance to cyclic friction (Xu et al, 2018).

Liu et al. (2017) reported the use of laponite as an effective nanopore plugging additive. They argued that even at a low concentration, laponite not only reduces clay swelling but also maintains the shear-thinning behaviour of WBMs. Later, Huang et al. (2018) found that laponite can also reduce the interlayer spacing between units in the clay lattice through electrostatic interaction. They observed a nanofilm around the clay particles, which could be an important mechanism to reduce clay hydration. Xu et al. (2018) developed a nano-polymer emulsion (SDPE) to inhibit shale. They proposed that SDPE can reduce the capillary effect, reduce the surface tension of fluids and change the surface wettability of shale to oil.

It was later reported that nanomaterials need to be chemically treated (modified) for proper dispersion in WBMs, otherwise their use as inhibitors is only effective in the short term (Pramanik et al., 2017). Rana et al. (2020) modified carbon nanotubes with polyvinylpyrrolidone and observed improvement in inhibiting shale and controlling fluid loss. They argued that carbon nanotubes can improve mechanical strength and hydrophobicity required by inhibitors, while PVP improves dispersion. Oseh et al (2020) suggested using triethoxysilane to modify polymer-silica nanoparticles to improve dispersion. They pointed out that their nanocomposite has small size and high surface energy, which can improve the wellbore stability. The presence of amino cations also provides a powerful combination that inhibits the hydration of clay.

In view of these experiences, it seems that nanomaterials are effective inhibitors that can reduce clay hydration through physical and chemical mechanism. Agglomeration of nanoparticles, however, is a challenge that may limit their application as an effective shale inhibitor. Surface modification is an effective approach to improve the dispersion of nano materials, but the toxicity of surface modifier may cause environmental concerns though.

2.4.3.4. Surfactant inhibitors

2.4.3.4.1. Surface Wettability

The capability of a fluid to attach on the solid surface in a multiphase flow system is called wettability. This system comprises of a rock (solid surface) and two fluids (oil, water or air). There are many approaches proposed to determine the surface wettability, among which the contact angle measurement is perhaps the most accurate method. In this method, the contact angle between the fluid and the rock surface is measured and linked to the surface wettability. It is crucial to evaluate various factors such as rock minerology and fluid characteristic during the contact angle measurements given their significant impact on the fluid and rock interactions (Dandekar, 2013). Figure 2.5 defines the surface wettability based on the contact angle where a surface can be water-wet, oil-wet, or mixed (weakly water/oil) wet (Mousavi Moghadam, 2019).

Figure 2.5: Changes of the surface wettability based on the contact angle (Bhairavi. D et al., (2018) is unable to be reproduced here due to copyright restrictions. The content can instead be accessed via https://doi.org/10.1016/j.watres.2018.02.034)

Hou et al. (2015) used three different surfactants, including TX -100 (non-ionic), CTAB (cationic) and POE (anionic), to alter the surface wettability of quartz. They found that these surfactants can reduce the contact angle and alter the surface wettability to a great extent. The effects of the surfactants SDS (anionic) and CTAB (cationic) on the surface wettability of carbonate rock was investigated by Hajibagheri et al. (2016). They found that the contact angle increases with increasing concentration of surfactants, which is not a good sign. In a similar study, Kumar and Mandal (2016) showed that SDS and CTAB in an alkali solution (NaCl) can decrease the interfacial tension and reduce the contact angle of the oil-quartz system. Totland and Lewis (2016) used alkyl polyglucoside (non-ionic) surfactant on a hydrophobic calcite surface to change its wettability. The result showed that alkyl polyglucoside can absorb on the surface of calcite by replacing stearic acid on the positively charged sites (Ca^+) of the surface. Thus, due to the larger surface area of alkyl polyglucoside compared to stearic acid, a strong surface interaction was induced. According to Huang et al. (2017), swelling can be prevented by surface modification of shale with cationic surfactants. According to their study, modifying the shale surface with surfactants such as twelve-alkyl-two-hydroxyethylamine oxide and polyamine can reduce the affinity of the shale surface for water. In another study by Kiani et al. (2018), the surface wettability of a carbonate rock was changed from oil-wetted to water-wetted by using a water-based glycol drilling fluid containing 7 wt% non-ionic surfactant polyethylene glycols (PEG) in combination with acrylamide hydrolysis (PHPA). Later, Ghasemi et al. (2019) showed that treating the shale with a surfactant can change the surface wettability of the shale towards a less water-wet state, which reduces the risk of swelling during drilling. Jalali et al. (2019) used a new surfactant extracted from the leaf of Cordia myxa to improve oil recovery at laboratory scale. They evaluated the effect of their natural surfactant on IFT and wettability of carbonate core samples. The results showed that the IFT could be reduced from 33.28 mN/M to 16 mN/M after adding 6 wt% surfactant to the EOR fluid. They also found that the contact angle decreased from 137.05° to 130.65° when 5.5 wt% surfactant was used. Lim et al. (2020) used two types of anionic surfactants, sodium lignosulfonate (SLS) and calcium lignosulfonate (CLS), to modify the wettability of rocks. The results show that after adding these surfactants, the surface of the rock was more wetted with water, which could improve oil recovery.

2.4.3.4.2. Inhibitors

Given the biodegradability and toxicity of commercial (chemical) surfactants, environmentally friendly surfactants have always been in demand. Green surfactants extracted from natural materials (seeds, plants, leaf, etc.) have the advantages of non-toxicity, biodegradability, and ecological safety (Ahmed et al., 2019). The molecular structure of the surfactant is amphiphilic, with a hydrophilic group on one end and a hydrophobic group on the other end. Generally, surfactants as shale inhibitors can inhibit surface hydration by changing the wettability of the shale surface. They can enter between the clay layers, reduce the Zeta potential, and reduce the swelling capacity of clays by reducing the layer spacing. They can also be adsorbed on the surface of the clay, and encapsulate the clay particles, thereby reducing the dispersion and hydration of the clay. Shadizadeh et al. (2015) reported the application of the nonionic surfactant-Zizyphus Spina-Christi extract (ZSCE) as an effective shale inhibitor. They argued that the hydrogen bond between the hydrophilic tail of the ZSCE and the available oxygen atoms on the silica surface of the clay can form a hydrophobic film on the clay surface which reduce shale hydration. Moslemizadeh et al. (2017) used saponins as non-ionic biosurfactants and pointed out their good inhibitory properties due to the presence of a hydrophilic group that can help form a hydrophobic shell around the clays. Zhang et al. (2019a) argued that the inhibition mechanism of saponins is also due to the hydrogen bonds formed between the hydrophilic part of the saponin molecule and the available oxygen atoms on the siloxane surface of the clay. Liu et al. (2019) found that combining sorbitol sorbate with polyoxyethylene sorbitan monostearate can form a hydrophobic film on the surface of the shale which inhibit the hydration swelling of shale.

Jiang et al (2019) studied that gelatine is an amphoteric polymer containing large amounts of amino, carboxyl and hydroxyl groups. They indicated that it can be adsorbed on the surface of bentonite and form a hydrophobic film and hydrogen bond that can prevent water penetration. They also recommended a combination of gelatine with ammonium salt (GT) which could improve the inhibition performance due to effective encapsulation of clay particles. Ghasemi et al, (2019a) studied the performance of henna extract in reducing water hydration. They indicated that the extract can establish hydrogen bonding between hydroxyl groups and available oxygen atoms in clays and increase the hydrophobicity of the clay surface. It was also observed that henna extract can block the pore throat of shales and completely prevent the transfer of pore pressure. Zhang et al. (2020b) compared grapefruit peel powder and KCl in reducing clay swelling. They concluded that although the powder is not as effective as KCl, it has greater advantages in terms of cost and environmental protection. Quainoo et al. (2021) argued that natural amino acids (alanine, arginine and proline) can be a good clay stabiliser due to the strong hydrogen bonding between amino acids and water, which can act as a hydrophobic shield around the clay, reducing its hydrophilicity and reducing hydration.

It appears that green surfactants can reduce the hydration tendency of shale by altering the surface wettability of clays and lowering the surface tension of the liquid. They are also biodegradable and have environmentally friendly properties. However, their compatibility with other additives such as salt in WBMs, temperature resistance and adsorption need further research (Li et al. 2020a, 2020b).

2.5. Conclusion

Controlling mud loss in deep geological formations has always been a challenge. Various additives have been proposed to improve the rheological properties and filtration control of water-based muds (WBMs), but few successes have been achieved once tested under real conditions in a reservoir. It seems that nanomaterials may be able to solve this problem and reduce the loss of mud in permeable formations.

However, the proper dispersion, functionality and cost of these nanomaterials remain unknown and have been the subject of numerous studies.

Surfactants are one of the additives that can be used to improve the stability and dispersion of nanomaterials in WBMs. They can change the surface charge of nanoparticles and reduce particle agglomeration. They can also alter the surface wettability of rocks and impede the movement of water as it enters formations, reducing clay swelling and associated problems. However, the ecological footprint and functionality of surfactants under real reservoir conditions are still questionable.

Chapter 3: Surfactants Extraction

3.1. Introduction

Surfactants are used in various operations in the petroleum industry. They are commonly used for cement slurry design, fracturing, acidification, demulsification, corrosion protection, transportation, purification, water flooding and foam flooding. However, as mentioned in chapter two, surfactants are often toxic and can be absorbed at the surface of formations during drilling or production. Therefore, green surfactants, which can be derived from natural plants, have good potential to replace industrial/commercial surfactants due to their lower cost, biodegradability and low toxicity.

3.2. Flaxseed Mucilage (First Surfactant)

Flaxseed is a yellow to brown seed that contains phytoestrogens and soluble fibres. They usually contain polyunsaturated fatty acids, proteins, polysaccharides and lignans. Their oil is commonly used in industrial materials such as paints, varnishes, linoleum, wax cloths, printing inks and soaps. Flaxseeds have an average oil content of 30%, consisting mainly of polyunsaturated fatty acids (Aleksander, 2019), such as α-linolenic acid (ALA), linoleic acid (LA), oleic acid and palmitic acid, as shown in Figure 3.1.

Figure 3.1: Structure of palmitic acid, oleic acid, linoleic acid (LA) and α-linolenic acid (ALA) (Aleksander, (2019) is unable to be reproduced here due to copyright restrictions. The content can instead be accessed via doi:10.1093/advances/nmz004)

Two main methods for preserving flaxseed oil are cold pressing and extraction from crushed seeds (Mizera, C., 2018). However, to further improve the quality of flaxseed oil obtained by the above methods, it would be best to extract the polysaccharides from the flaxseeds before oil extraction. These polysaccharides usually make up 28%

of the total weight of the flaxseed and are divided into two groups of soluble and insoluble components. Among these, the amounts of soluble polysaccharides are usually greater than that of insoluble ones (Hong et al, 2018). Cellulose and lignin are the main components of the insoluble polysaccharides, while mucilage is the main component of the soluble polysaccharides. The mucilage in flaxseeds typically accounts for 6.5% to 10.2% of the total weight and can be used for a variety of different applications where a thickening and gelling agent is required (Hu et al., 2020). Figure 3.2 shows the microphotographs of flaxseed. Given the solubility and gelling properties of mucilage, this study sought to extract it as a potential surfactant.

Figure 3.2: Micrographs of flaxseed showing its structure (Shim, (2014) is unable to be reproduced here due to copyright restrictions. The content can instead be accessed via https://doi.org/10.1016/j.tifs.2014.03.011)

During mucilage extraction, the combination of carboxylic acids and glycerol in the mucilage produces hydrolysed fatty acids (acyl group) through the esterification of the fatty acid in the shell of the flaxseed at a very low concentration (Douglas et al., 2019). It should be recalled that the glycerol in flaxseed mucilage is a sugar alcohol with three hydrophilic hydroxyl groups in its structure, which improve the water solubility of the mucilage. During the mucilage extraction process, these three hydroxyl groups of glycerol can form a bond with fatty acids and initiate esterification of the acyl groups (Kamal et al., 2017). This esterification is the main reaction that occurs during the extraction of mucilage and produces certain esters that are required for a fully functional surfactant. Figure 3.3 shows the synthesis and esterification of monoglycerides (esters) from fatty acid and glycerol in the structure of mucilage.

Figure 3.3: Synthesis and esterification of monoglycerides (esters) from fatty acid and glycerol in the structure of mucilage (Nilesh et al., (2017) is unable to be reproduced here due to copyright restrictions. The content can instead be accessed via http://dx.doi.org/10.4172/2472-0542.1000128)

Considering the above components, flaxseed mucilage and protein are used to evaluate their performance as a potential shale inhibitor. This is done through a series of extraction, characterisation and performance evaluation steps summarised in the flow chart in Figure 3.4.

3.2.1. Extraction Process

Extraction is one of the most important steps that must be carefully carried out to obtain the selected substance from the raw materials. In general, mucilage extraction involves two main steps: preparation of the raw material and extraction. The preparation phase includes sieving and removal of impurities. In the extraction phase, there are three main methods for mucilage extraction: 1) separation of the shell, 2) crushing of the seeds and 3) crushing the whole seeds. In this study, the last method was chosen because the separation of the hull could cause technical problems and the crushing can lead to the extraction of other substances that reduce the quality of the mucilage extract. Therefore, the extraction of flaxseed mucilage was performed using the whole seed (Ziolkovaska et al., 2012). Since the flaxseed mucilage can be completely dissolved in water, water was used as an effective extraction method, which is also an economically viable option. Therefore, the flaxseed mucilage was extracted with distilled water with a pH of 7 under ambient conditions using a magnetic stirrer.

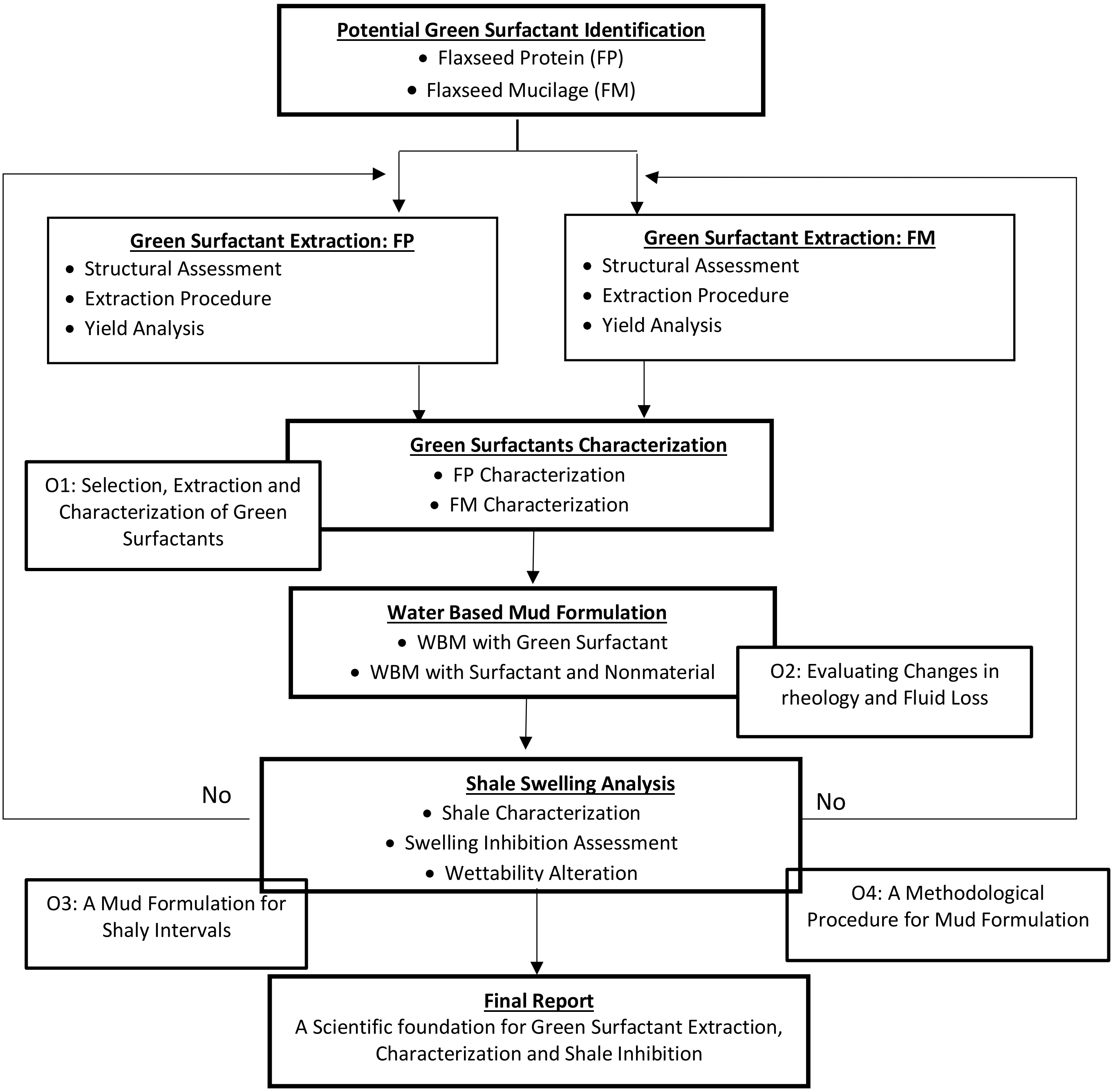


Figure 3.4. A Flow chart showing the steps taken in this study for completion

3.2.2. Materials and Methods

In this study, flax seeds were purchased as raw material for the extraction process from a market in Miri, Malaysia. The moisture content of the seeds was about 7.8% according to the supplier's information sheet. Ultrapure water with a resistivity of 5.4 MΩ.cm was obtained from the Elga water purification system for the surfactant extraction. A plastic mesh with a size of 1 mm × 1 mm was used to separate the mucilage from the seeds. Binder's drying oven was used to dry the extracted mucilage.

IKA@ C- MAG HS7 digital stirring hot plates were also used to heat the solution while the mixture was stirred with the magnetic stirrer. Table 3.1 summarises the materials used, their purity and the supplier.

Table 3.1: Summary of the materials used in this study, their purity and the supplier.

Product	Purity	Company
Deionized water	-	-
Flaxseed	100%	Local market
Hexane	95%	MERCK
Tris buffer	99.9%	MERCK
HCl	10%	MERCK
NaOH	99%	MERCK

3.2.3. Extraction Methodology

As can be seen in Figure 3.5, the extraction process of flaxseed mucilage involves three stages. In general, various factors such as temperature, dilution, pH, time, heating and stirring method should be considered in the aqueous extraction of vegetables. These parameters affect the amounts of water-soluble compounds released into the solution. During the extraction process, the application of high temperature would increase efficiency (Hu et al., 2020). However, this may lead to an increase in protein content in the mucus, which is not desirable. Therefore, we performed the extraction process at a mild temperature of 50 ^{o}C for 30 minutes. This duration was chosen to ensure that the proteins were not hydrated (Christian Kwesi et al. 2018, Fabre et al., 2015). Another important factor is dilution, which must be considered to avoid high viscosity. With this in mind, a standard concentration of 5% seeds to water (w/v) was chosen for the extraction process (In this work 200g of raw flaxseed with 1L deionized added together), as shown in Figure 3.6.

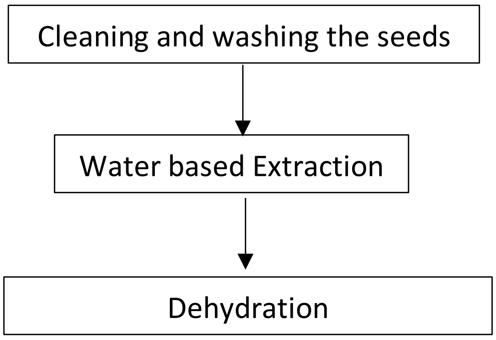


Figure 3.5. Schematic process flow diagram used to extract the mucilage (FM) from flaxseed

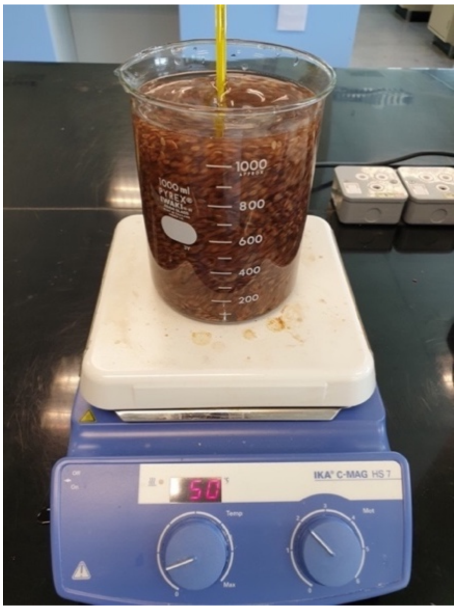


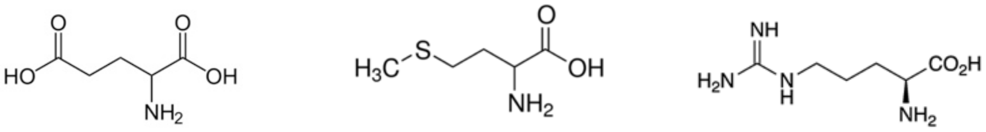
Figure 3.6: Mucilage extraction at 50°C with magnetic stirring for 30 minutes

It has also been found that increasing the acidity of the solution can increase the efficiency of extraction. However, this can lead to deterioration of the seeds and complete hydrolysis of the mucilage (Martínez-Flores et al., 2006). Therefore, a neutral pH (pH=7) was chosen for the extraction process. Finally, the extracted mucilage was removed from the seeds with cheesecloth and dried in an oven at 103 °C until the weight stabilised (see Figure 3.7).

Figure 3.7: Dried mucilage in oven

3.3. Flaxseed Protein (Second Surfactant)

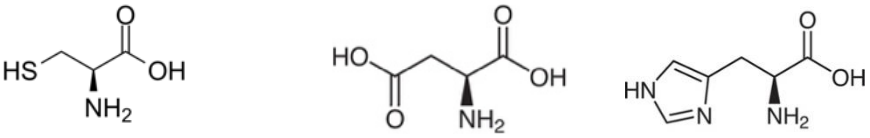
As mentioned earlier, flaxseeds are an excellent source of polyunsaturated and saturated fatty acids, but they also contain protein components that have been little studied. According to these studies, there are two protein fractions, including a predominantly salt-soluble component and a water-soluble basic component. It is important to note that the salt-soluble protein has a high molecular weight, while the water-soluble proteins have a low molecular weight. The latter were considered in this study. Some of the water-soluble proteins in flaxseed are glutamic acid, methionine, arginine, cysteine and aspartic acid (Figure 3.8) (Chung et al., 2005).



Glutamic acid

Methionine

Arginine



Cysteine

Aspartic acid

Histidine

Figure 3.8. Chemical structure of water-soluble protein of flaxseed

3.3.1. Extraction Process

In general, various techniques for protein extraction have been proposed by different researchers. For example, conventional isolation techniques such as alkaline/isoelectric precipitation, acidic pre-treatment with ultrafiltration and micellization technique (ammonium sulphate precipitation). However, to facilitate protein recovery from the raw materials, the mucilage must be extracted, the mucilage removed, and the flaxseed defatted and milled before using the above methods (Gutiérrez et al., 2010). The following sections explain the protein extraction methods used in this study.

3.3.1.1. Isoelectric Precipitation

One of the most common methods of protein extraction is isoelectric precipitation, which requires pH control of the solution to control protein precipitation. In this technique, defatted flaxseed is suspended in water (usually at a ratio of 1:10 or 20 w/v) and an alkaline extraction is performed at a high pH (around 9-10) (Christian et al., 2018). In the next step, the supernatant and residue are separated from the extracted protein slurry using a centrifuge. The pH of the supernatant is then adjusted to 4.5-5 at room temperature, resulting in precipitation of the flaxseed proteins. Finally, the extracted protein precipitate is collected with a centrifuge and suspended in distilled water.

3.3.1.2. Partial Enzyme Hydrolysis-Assisted Extraction

In this extraction method, after the flaxseeds have been demucilaged and defatted, they can be treated with proteases such as papain. In the first step of hydrolysis, the optimal pH for the enzyme is set and the mixture is incubated to cleave the proteases. After a few hours, the reaction inside the mixture is stopped and the protease is deactivated by applying heat and rapid cooling. The suspension (mixture) is then sonicated, centrifuged and freeze-dried to obtain the solubilised protein (Avramenko et al., 2016, Karama et al., 2016). This partial enzymatic hydrolysis has several advantages, such as improving the functional properties of proteins (e.g., emulsification, foaming, water-holding capacity and fat-absorbing capacity) (Avramenko et al., 2016). However, this extraction method is expensive and was not considered in this study.

3. 3.1.3. Micellization

Similar to the isolation technique, micellization is able to preserve the native state of the protein and remove non-protein components (Hadnadjev et al., 2017). In this method, the protein is precipitated with different salt concentrations, usually using ammonium sulphate. The main reason for using this salt for protein precipitation is its high solubility, low cost and buffering capacity compared to many other salts (Christian et al., 2018). Protein extraction using micellization requires a salt solution in an ice bucket followed by a centrifuge to remove insoluble materials (Hadnadjev et al., 2017). Proteins extracted using the micellization technique have low levels of phytic acid and pentosans, high enthalpies (high structural order) and bright colours (Hadnadjev et al., 2017). However, this method suffers from the precipitation of ammonium sulphate (Christian et al., 2018).

3.3.1.4. Acid Pre-Treatment with Ultrafiltration

In this method, flaxseeds are pre-treated with acid that flows through ultrafiltration (Marambe et al., 2017). In this method, defatted flaxseeds are suspended in water with a pH of 4.5 for a few hours at room temperature. The acidic solution is then separated from the residue in the protein extraction phase using a centrifuge. To increase the amount of protein, this procedure is repeated a few times. Then the protein extract is combined and filtered to obtain retentate and permeate. Finally, the retentate is spray-dried to obtain the protein. This method of ultrafiltration has some advantages such as improving the functional and nutritional quality of the protein extract (Christian et al., 2018). However, the protein yield of this method is very low.

3.3.2. Materials and Method

The brown flax seeds used in this study were purchased from a local market in Miri. All chemicals like NaOH, hexane, HCl and Tris buffer were obtained from commercial sources and used without any further treatment. Ultra-pure water with a resistivity of 5.4 MΩ.cm was supplied by Elga water purification system for surfactant extraction. For grinding the flaxseed meal, the model PSN-MXAC400 mill was used along with a double-layered cheesecloth to separate large residues. Mesh sieves with a size of 0.15 mm from Merck KGaA were used to separate the flaxseed meal from the hull. The drying oven of the company Binder was used for drying the demucilaged seeds. IKA@ C- MAG HS7 digital stirring hot plates were used to heat the solution and stir the mixture. Centrifuge 320R was used for separation while freeze dryer was considered for evaporation of water from protein solution.

3.3.2.1. Preparation of FP

The procedure used for the flaxseed protein extraction is shown in Figure 3.9.

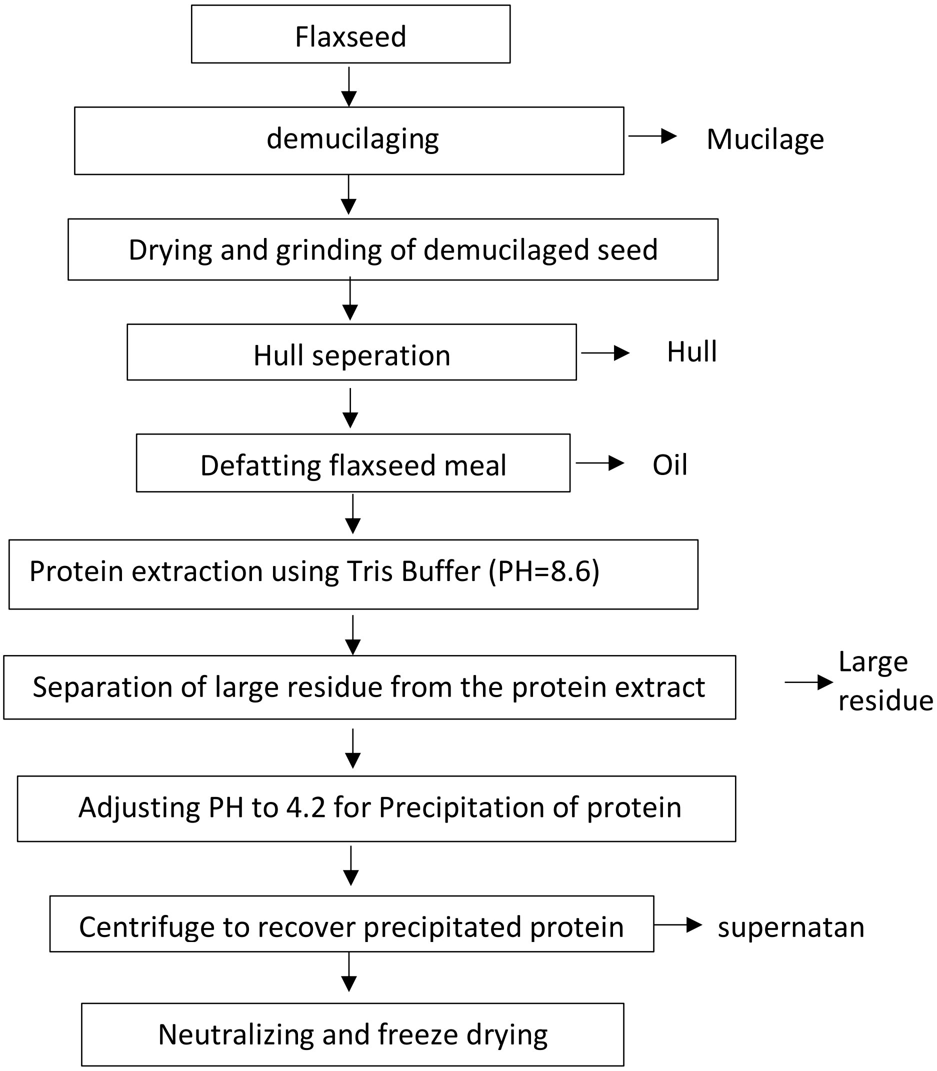


Figure 3.9. Flow diagram used to extract the protein isolate (FPI) from the flaxseed

As shown in Figure 3.10, the flaxseeds were soaked in the ultra-pure water at 50°C for 3 hours at a ratio of 1:20 to be demucilaged (50g of raw flaxseed with 1L deionized water). This process was repeated three times to ensure that the mucilage was properly removed. It is important to note that demucilaging at a temperature of 50°C yielded flaxseed proteins with a purity of more than 90%. As mentioned earlier, this temperature was chosen because a high temperature during the demucilaging process reduces the functional properties of the flaxseeds (Christian et al., 2018).

Figure 3.10: Demucilaged flaxseed obtained based on the procedure used

After demucilaging, the meal was dried in a hot air oven at 50 °C for 24 hours and grounded by a coffee grinder. To reduce interference from the mucilage during protein extraction, the hull was separated from the meal using a 0.15 mm sieve (see Figure 3.11). The grounded flaxseed meal was then defatted with hexane at a ratio of 1:16 (25g of flaxseed meal with 400ml of hexane). This would help to remove the fatty acid for the protein.

Figure 3.11: Sieving and defatting of the flaxseed meal

After the defatting phase, the flaxseed meal was soaked for 24 hours in 0.1 M tris buffer (pH 8.6) at a ratio of 1:16 (25g of flaxseed meal with 400ml of tris buffer). The large residues were then separated from the protein extract using a double-layered cheesecloth. The solution was then centrifuged for 20 minutes to collect the supernatant liquids, which were the solution of the surfactant of interest. This could help to remove the precipitated impurities at the bottom of the tube. The pH of the supernatant was then adjusted to 4.2 with 0.1 M HCl to precipitate the flaxseed protein. The acid was added dropwise and stirred to mitigate the effect of the acid on the disintegration of the protein (see Figure 3.12).

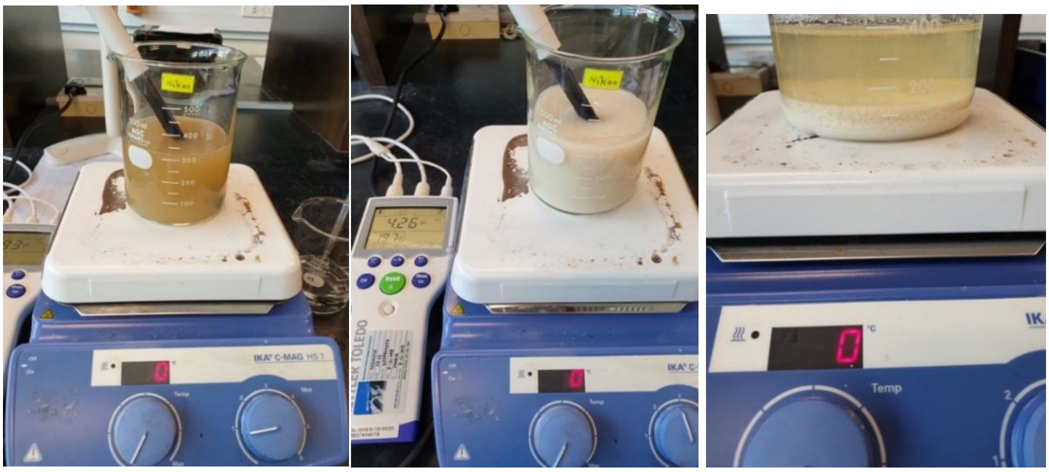


Figure 3.12: Precipitation of flaxseed protein by decreasing PH to 4.2

To achieve complete precipitation of the protein, the solution was stored in the refrigerator at 4°C for 16 hours. In the next step, each solution was transferred to 50 ml centrifuge tubes and centrifuged for 30 minutes at 4°C in the Hettich Universal 320R Benchtop Centrifuge (see Figure 3.13).

Figure 3.13: Protein precipitation obtained from centrifuge

The precipitate, which was the pure protein, was collected and transferred to a beaker. This precipitate was then dispersed in ultrapure water and treated with 0.1 M NaOH as shown in Figure 3.14.

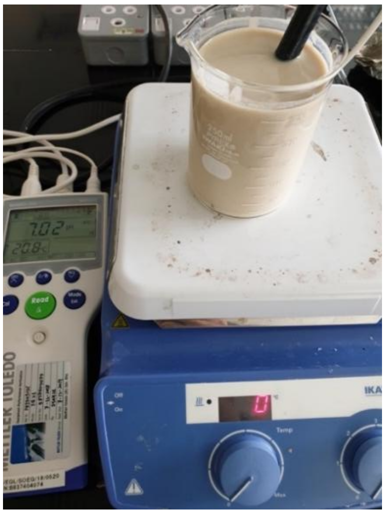


Figure 3.14: Neutralization of protein solution

Finally, freeze-drying was used to dehydrate the flaxseed protein, as shown in Figure 3.15. In this method, water is extracted at low temperature by reducing the pressure and applying heat. However, before starting the freeze dryer, the samples need to be transferred into a small plastic bottle with a wide opening. This increases the surface area of the sample so that the freezing time and dehydration of the water takes less time. In the next step, the samples were placed in the ultra-low freezer at -80^{o}C for 48 hours. Then all samples were placed in the freeze dryer at a temperature of -45°C to start the freeze-drying process. After water drying, the remaining white powder was a pure flaxseed protein, which was transferred to a glass container, sealed and stored at 4°C for further use.

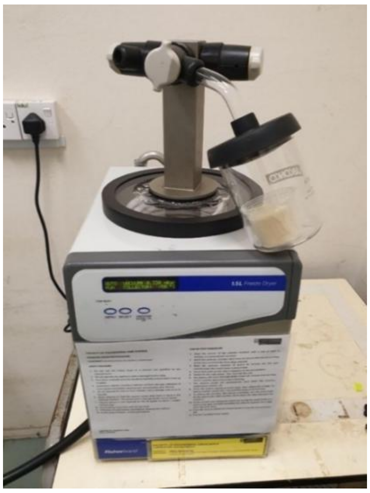


Figure 3.15: Flaxseed protein obtained from the freeze-drying process

3.4. Extraction yield

At the end of the extraction process, the flaxseed mucilage and flaxseed protein powders were obtained with a golden brown and white colour, respectively. The weight of each powder was then weighed and equation (3.1) was used to determine the yield of the extraction method. The results obtained are reported in Table 3.1.

$$Yield(wt\%) = \frac{Weight\ of\ Extracted\ (g)}{Weight\ of\ Feedstock\ (g)} \times 100\% \tag{3.1}$$

The most important factors in yield calculation are the cost of extraction, the complexity of the extraction process, production safety and environmental impact. Table 3.1 shows that the yield of flaxseed mucilage and flaxseed protein were 37 and 25 wt%, respectively. Given the complexity of the process for flaxseed protein and the lower extraction yield, it appears that flaxseed mucilage with a yield of 37% is a very cheap and simple extraction technique.

Table 3.2: Summary of the Yield percentage determined for the extracted surfactants

Surfactant	**Solvent**	**Solid/Liquid Ratio (g/ml)**	**Yield (wt%)**
Flaxseed Mucilage	Ultra-pure water	1:20	37
Flaxseed Protein	Ultra-pure water	1:20	25

3.5. Conclusions

In this study, two different extraction procedures were used to extract surfactants from different parts of flaxseed. To ensure the accuracy of the extraction process and the quality of the extracted surfactants, a specific procedure adopted from the literature was used. The yield calculated at the end seems to be high and the approaches followed were able to provide the required quality. In the next section, the extracted surfactants are fully characterised in order to evaluate their functionalities and applications.

Chapter 4: Surfactants Characterization

4.1 Introduction

In this chapter, various tests were conducted to determine different components and properties of the extracted surfactants. These tests include zeta potential, conductivity, interfacial tension (IFT), surface wettability, Fourier transform infrared spectroscopy (FTIR) and gas chromatographic (GC) measurements. Conductivity tests at different temperatures were also carried out to evaluate the efficacy/survivability of the surfactants at high temperatures. Thermogravimetric analysis (TGA) was also performed to evaluate the thermal stability and weight loss of the surfactants during combustion.

4.2. Material and Methods

4.2.1. Surfactant Solutions Preparation

To prepare the surfactant solutions, the extracted surfactants (flaxseed mucilage and flaxseed protein) were dissolved in ultrapure water in the ratios given in Tables 4.1 and 4.2. To prevent agglomeration or clustering of the surfactant molecules, all samples were prepared immediately before the measurements. To produce a homogenised, stable and uniform solution, magnetic stirring was performed for 30 minutes at room temperature.

Table 4.1: Flaxseed mucilage solutions with different ratios

Total weight (wt%)	Flaxseed mucilage (g)	Ultra-pure water (ml)
0.5	0.5	100
1	1	100
1.5	1.5	100
2	2	100
2.5	2.5	100
3	3	100
3.5	3.5	100
4	4	100
4.5	4.5	100
5	5	100
5.5	5.5	100

Table 4.2: Flaxseed protein solutions with different ratios

Total weight (wt%)	Flaxseed protein (g)	Ultra-pure water (ml)
0.5	0.5	100
1	1	100
2	2	100
3	3	100
4	4	100
5	5	100
6	6	100
7	7	100
8	8	100
9	9	100

4.2.2. Methods Used

The Zetasizer Nano ZS from Malvern Panalytical was used to measure the zeta potential. To determine the CMC of the surfactants, the electrical conductivity was analysed using an electrical conductivity metre. The water treatment system was considered as ultrapure water with a resistivity of 5.4 MΩ.cm, which was required for the preparation of the surfactant solutions. IKA@ C- MAG HS7 digital stirring hot plates were used to stir the mixture. A laboratory thermometer was used to measure the temperature of the surfactant solutions. Kruss Drop Shape Analyzer model DSA 100B was used for the measurements of IFT and surface wettability. Fourier transform infrared spectroscopy (FTIR) together with gas chromatography was used to determine the organic functional groups in the extracted surfactants. A Mettler Toledo thermogravimetric analyser (TGA) was also used to investigate the thermal stability of the surfactants.

4.3. Zeta Potential

The zeta potential (ζ) is the electrostatic force between two different particles dispersed in a solution (Claure et el, 2020). This zeta potential also indicates the stability of the solutions with different particles. The higher the zeta potential, the greater the electrostatic stability. The zeta potential of different surfaces can be positive, negative or neutral, which for surfactants can indicate whether they are cationic, anionic, non-ionic or amphoteric. In this study, 0.5 grammes of flaxseed mucilage and 0.5 grammes of flaxseed protein were mixed with 100 ml of ultrapure water to measure their zeta potential using the Zetasizer Nano ZS (see Figure 4.1). Magnetic stirring was performed for 30 minutes to obtain a homogenised mixture. After preparing the samples, the zeta potential test was performed immediately to avoid contamination and self-agglomeration of the surfactants. Figure 4.2 shows the results of the zeta potential measurements.

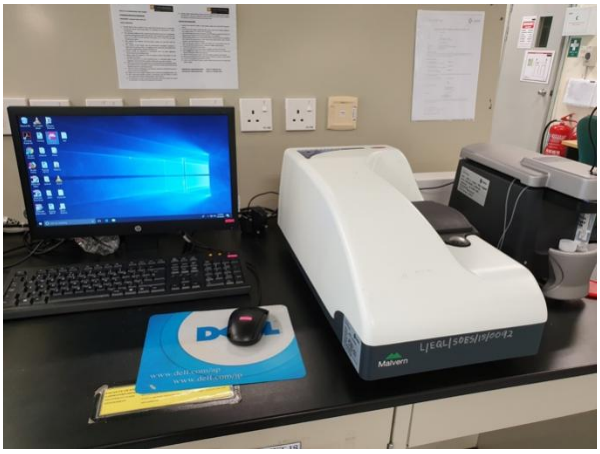


Figure 4.1: Zetasizer Nano ZS produced by Malvern Panalytical

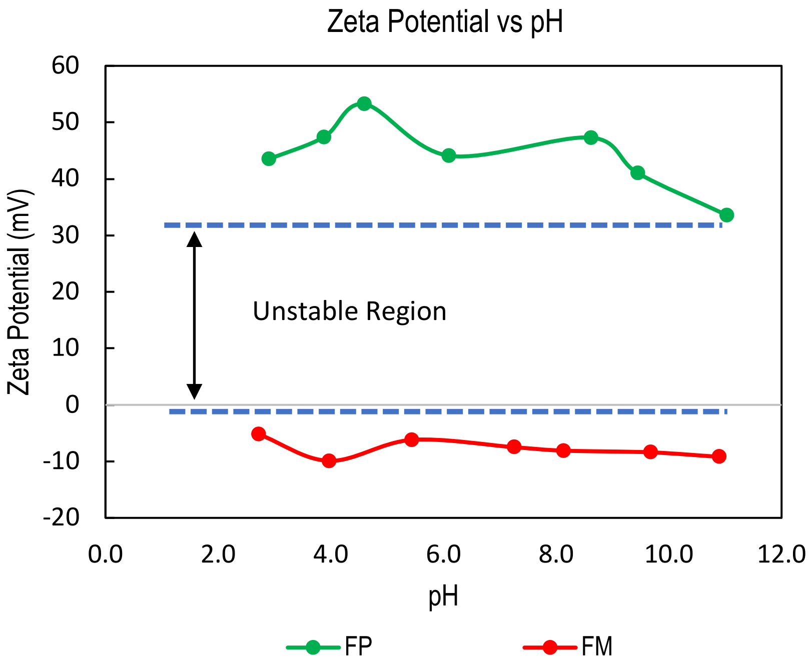


Figure 4.2: Zeta potential of the FP and FM

The results of the zeta potential (ZP) measurements show that FP releases positive ions into solution and is a cationic surfactant with an average zeta potential of 44 mV at pH 6. FM, on the other hand, appears to be a surfactant with a surface charge of -8 mV.

4.4. Conductivity

Conductivity is defined as the ability of a solid/liquid to transmit electric current. In liquids containing ions (electrolyte solution), the electric current is transmitted by ionic movements and changes in the net electric charge. Indeed, ion type and concentration play an important role in the electrical conductivity of solutions. Surfactants, once dissolved in water, release certain ions with surface charges in the solution that can increase electrical conductivity. Thus, one of the ways to evaluate the performance of a surfactant is to measure the changes in the electrical conductivity of the solutions once they are dissolved in it.

To measure the electrical conductivity of the surfactant solutions, the Mettler Toledo Seven MultiTM multirange metre was used. Before the measurements, the probe was calibrated to ensure the accuracy of the result. The measurements were repeated three times at room temperature. A total of 20 samples (10 FM and 10 FP solutions) were prepared with concentrations ranging from 0.5 to 9 wt%. Figure 4.3 shows the results of the conductivity measurements.

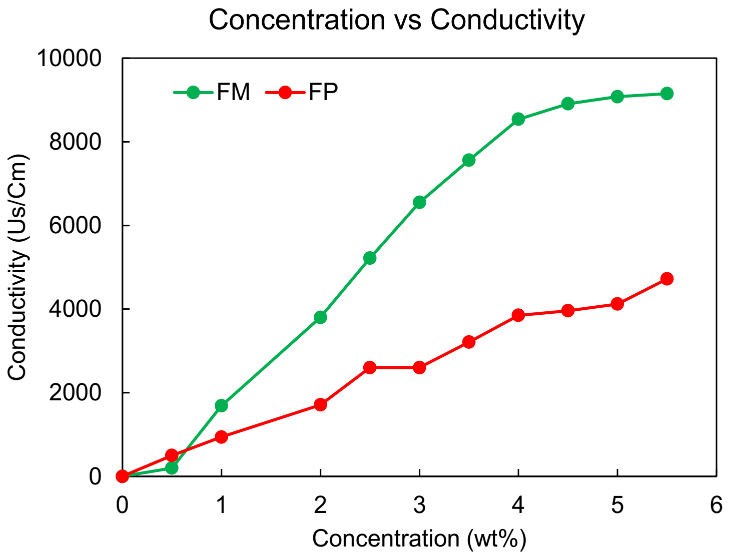


Figure 4.3: Conductivity of the FM and FP solutions in different concentrations

A look at Figure 4.3 shows that the conductivity improves with increasing concentration of the two surfactants due to their good solubility. As already mentioned, the surfactants with good solubility release ions with surface charges in the solutions, which can increase the conductivity.

4.5. Critical Micellar Concentration (CMC)

As soon as a surfactant is added to a solution, the surface or interfacial tension of the solution decreases. However, when the concentration of the surfactant at the interface of two liquids increases and reaches a threshold value, the surfactant molecules begin to aggregate and form "micelles" due to saturation, which reduces the functionality of the surfactants. The concentration at which the micelles begin to form is called the Critical Micelle Concentration (CMC) (Ramesh et al., 2021).

In this study, the CMC was determined using conductivity measurements at different concentrations of the surfactants FM and FP. In this measurement, any sudden change in conductivity at a given concentration of surfactant is associated with the formation of micelles and interpreted as a CMC point (Nowrouzi et al., 2020). Figures 4.4 and 4.5 show the results of the conductivity measurements used to determine the CMC points for both surfactants.

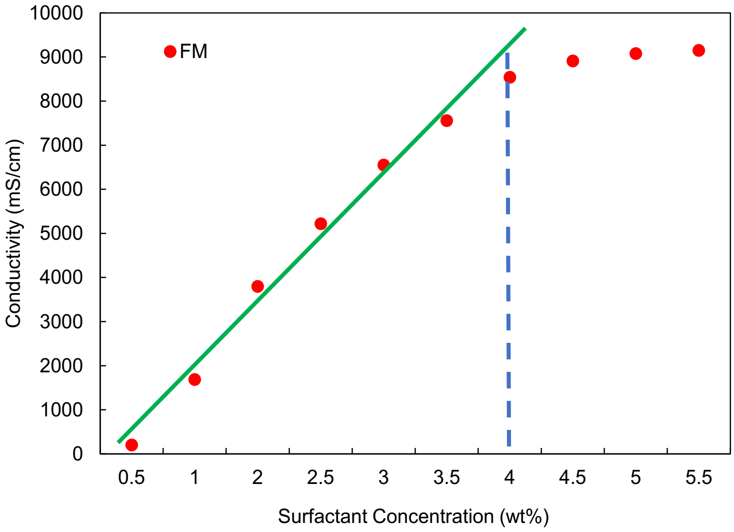


Figure 4.4: CMC point of the FM surfactant

As can be seen in Figure 4.4 and 4.5, the slope of the lines, the CMC point of FM is about 4 wt%, while that of FP reaches 3 wt%. Beyond these points, the molecules begin to agglomerate and form micelles, which reduces the electrical conductivity. Once micelles have formed, hydrophilic head groups with similar charges repel each other and begin to interact with hydrophobic tail groups, which weaken the binding site and neutralise the charges in the solutions (Perinelli et al, 2020).

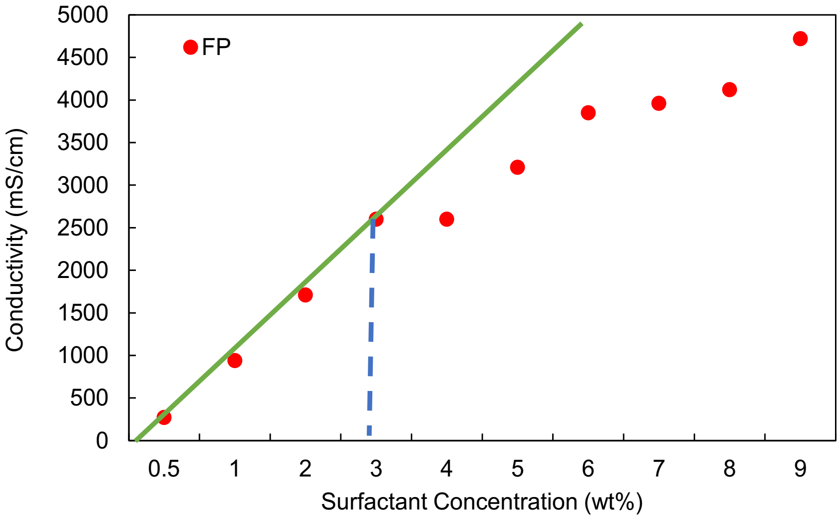


Figure 4.5: CMC point of the FP surfactant

4.6. Temperature

The survivability of surfactants under high temperature conditions is one of the evaluation steps that should be taken to ensure their thermal stability. For this purpose, surfactant solutions were prepared with different concentrations of FP and FM and their conductivity was measured under different temperature conditions. As shown earlier, the surfactants could increase the conductivity at room temperature. Therefore, the changes in conductivity at high temperatures could give an indication of the degree of survivability of each surfactant. For the tests, a total of 10 samples were prepared for each surfactant and the electrical conductivities were measured at different temperatures (298^{o}K, 313^{o}K, 323^{o}K, 333^{o}K and 348^{o}K). The results obtained are shown in figures 4.6 and 4.7.

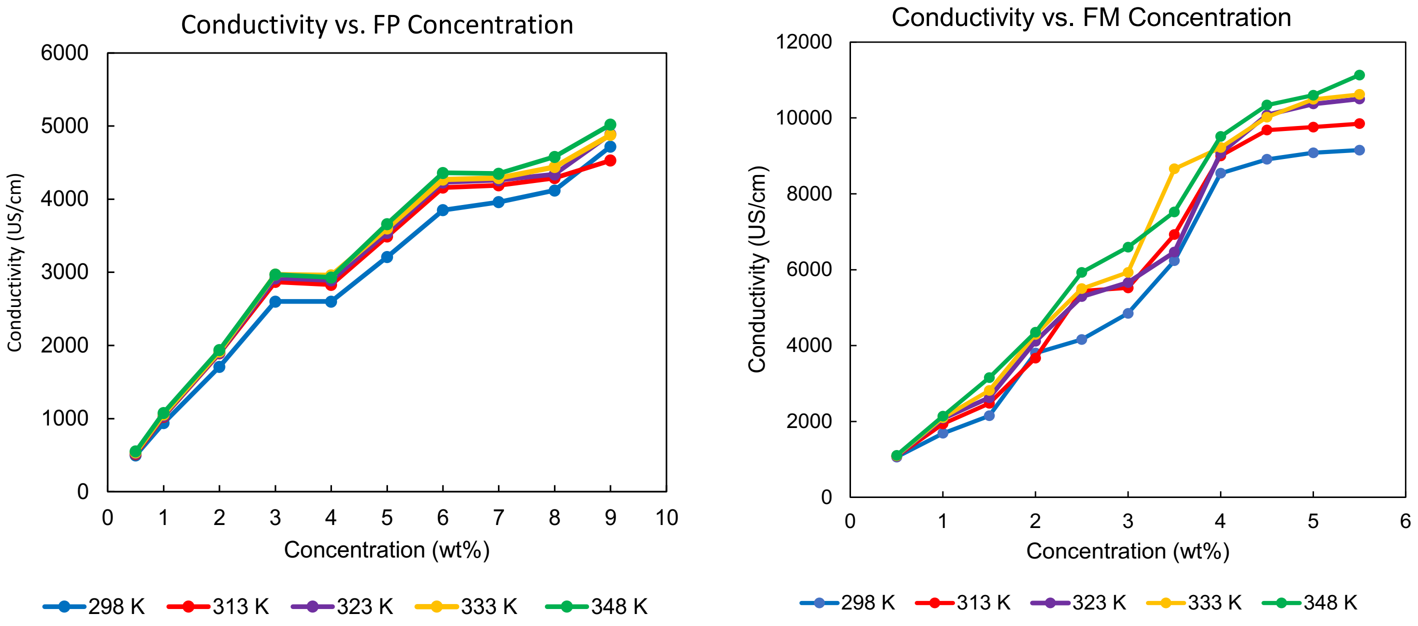


Figure 4.6. Electrical conductivity versus surfactant concentration under different temperatures for the FP (left) and FM (right)

As can be seen in Figures 4.6 and 4.7, the conductivity of both surfactants increases even at high temperatures, indicating their survivability and functionality under harsh subsurface conditions. It should be noted that changes in the trend of the curves are related to reaching the CMC points where micelles form and the surfactant's performance decreases.

4.7. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is an analytical approach that measures the absorption of infrared radiation and identifies the functional groups of organic and inorganic compounds (Mester, 2020). In this technique, infrared radiation is absorbed by molecules after they are excited and used to determine the structure of materials. The result is an interferogram of the sample signals and an infrared spectrum that can provide useful information about the functional groups of organic and inorganic compounds (Francesco, 2016). Figure 4.7 shows the FTIR instrument used in this study. In this study, only a small amount of the surfactants FP and FM were used for the analysis and functional group assessment.

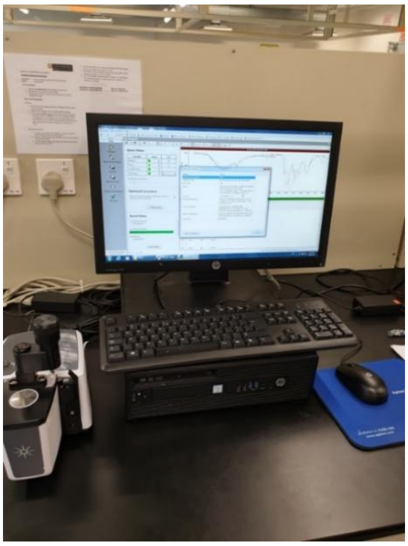


Figure 4.7. Fourier Transform Infrared Spectroscopy (FTIR) apparatus used in this study

4.7.1 FTIR of Flaxseed Mucilage (FM)

The organic functional groups of FM, which emerge from the FTIR analysis, are shown in Figure 4.9. These functional groups provide a large number of adsorption sites that can lead to the coagulation-promoting bridging effect between the particles. The peaks at 950-1200 cm^{-1} are due to the stretching vibration of C-O in the COH bonds. The peak at 1415 cm^{-1} is due to the presence of C- OH in the structure. The bond at 1600 cm^{-1} is associated with the C=O stretching vibration. The peaks observed at 2929 cm^{-1} can be attributed to the C-H group. The peaks between 3000 and 3500 cm^{-1} are associated with the O-H groups stretching in the structure of the carboxylic acid (Asep. B et al ., 2019). The broad peak can also be associated with the hydrogen bonds of the O-H groups in the structure. Considering the functional groups observed in Figure 4.8 and the list of components in the FTIR library, it appears that two major components shown in Figure 4.9 are present in the structure of FM. These components are esters known as hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl) ethyl ester and 9-octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester. These esters are also known as monoglycerol and are formed from the esterification of glycerol and a small percentage of fatty acids (palmitic acid and oleic acid) found in the hull of flaxseed (Sari et al., 2017). These esters are surfactants with a hydroxyl group at the head and an alkane chain at the end.

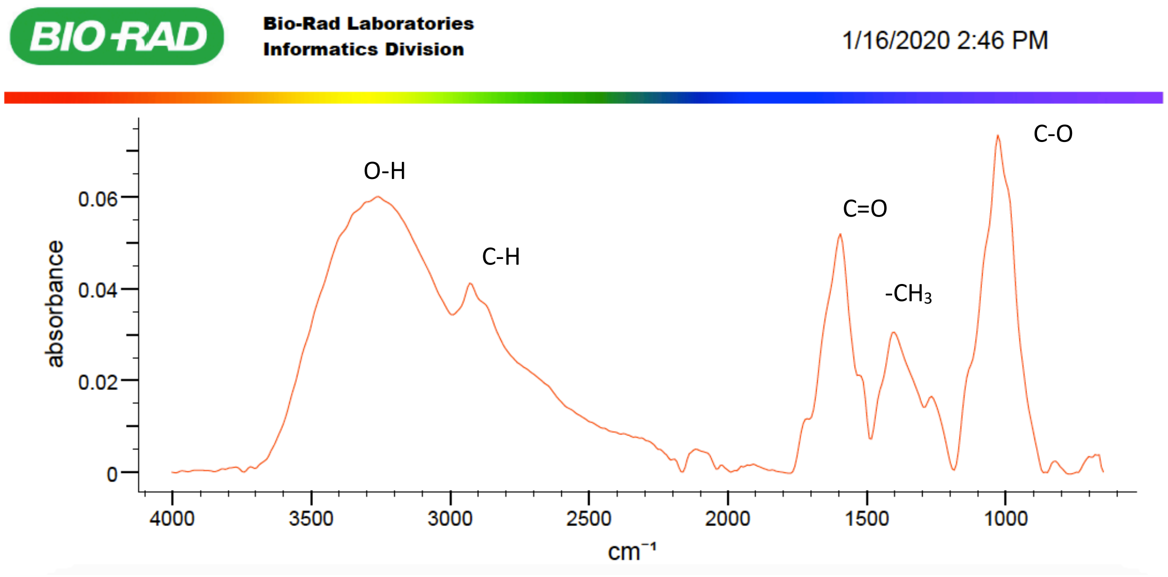
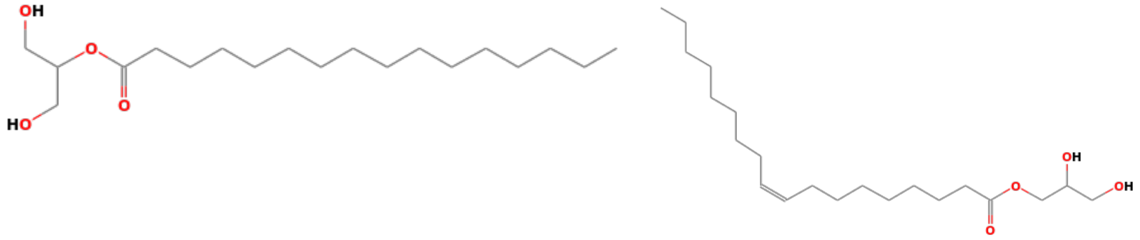


Figure 4.8. FTIR curves of the flaxseed mucilage (FM) surfactant



Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl)ethyl ester

9-Octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester

Figure 4.9. Two major organic components observed in structure of the FM

4.7.2. FTIR of Flaxseed Protein (FP)

Figure 4.10 shows the functional groups in the structure of FP, as detected by FTIR analysis. The peaks at 950-1200 cm^{-1} are associated with the stretching vibration of the bond of C-O in the COH bonds of the carbohydrates. The first peak at 700 cm^{-1} represents the C-S b0nd in the structure of the extracted protein. There is a small peak at 1268 cm^{-1} indicating binding for CN. The second small peak at 1380 illustrates the C-H group and another peak at 1550 indicates the Primary amine, NH bend (Asep et al ., 2019). The peaks at 2900 cm^{-1} can be assigned to the CH_2 group, while the broad peak observed at 3250 cm^{-1} is related to the COOH group, as hydroxyl group has a broad peak in 3200-3570 (Asep et al., 2019). Considering these functional groups and comparing the proposed components listed in the library of the FTIR tool, it was concluded that the two organic components shown in Figure 4.11 are included in the constriction of the FP. These two water-soluble components are cysteine and methionine, which are sulphurs containing amino acids. Cysteine contains an α-amino group (in the protonated $-NH_3^+$ form), a carboxyl group (in the deprotonated - COO^- form) and a SH group, while methionine has a SCH_3 group.

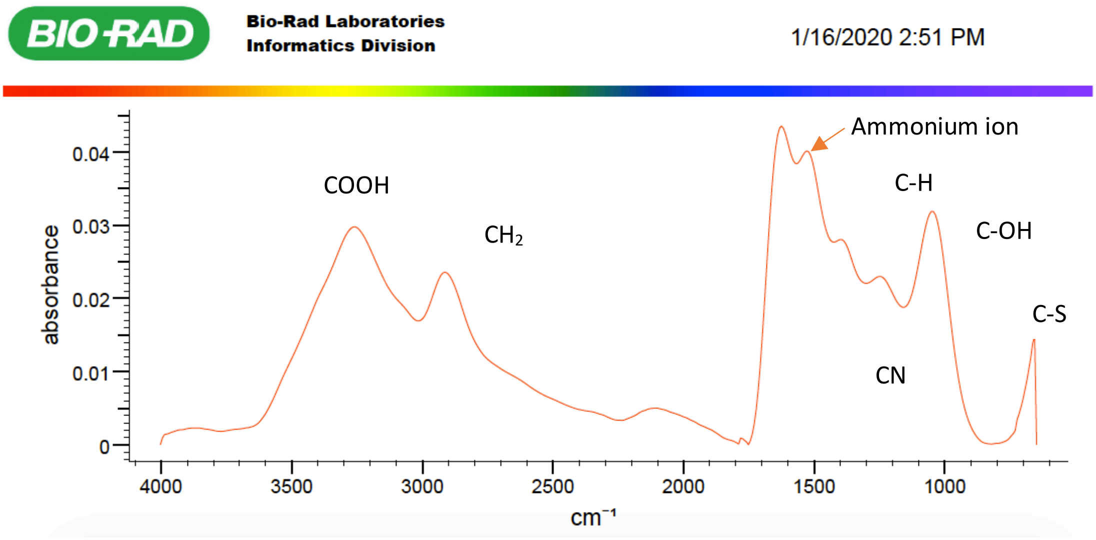
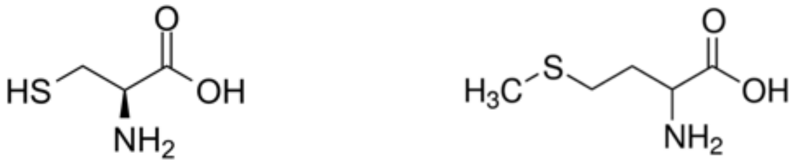


Figure 4.10. FTIR curve of the flaxseed protein (FP) surfactant



Cysteine

Methionine

Figure 4.11. The component structures of extracted flaxseed proteins

4.8. GC-MS of Flaxseed Mucilage (FM)

GC-MS is a combination of gas chromatography (GC) and mass spectrometry (MS). Generally, the GC technique uses a capillary column that separates the components of the samples using a mobile phase. During this process, the components in the samples start to elute at different times, which is called retention time. This retention time can be measured with a mass spectrometer. The method MS, on the other hand, shows the main components of a sample as a function of the ratio of mass to charge.

The combination of these two methods can thus lead to a better detection of the components.

In this study, a sample with a concentration of 0.5% was prepared for the GC-MS measurements using the apparatus shown in Figure 4.12 by dissolving 5g of flaxseed mucilage powder in 100 ml of water. This sample was further filtered to prevent clogging of the GC column. Finally, only a small amount of the sample was injected into the GC column using the syringe and the test was run in the temperature range of 100°C to 325°C for 45 minutes using the inert carrier gas nitrogen. The result obtained is shown in Figure 4.13.

The results obtained show that the fatty acid methyl esters extracted from the flaxseed mucilage can be identified by the method GC-MS. According to Figure 4.14, the fatty acid methyl ester is a mixture of unsaturated and saturated components (octadecanoic acid and hexadecenoic acid). The composition of the fatty acid methyl ester was also compared with the molecular formula listed in the instrument's library for various derivatives that form the components of the fatty acid. Among the identified esters, hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl) ethyl ester was found to be the major constituent of flaxseed mucilage with a retention time of 26.45 minutes. It was also found that 9-octadecenoic acid (Z)-, 2,3-dihydroxypropyl ester with a retention time of 28.02 minutes is the second major component in the structure of the extracted mucilage (Solomon et al., 2014), as already shown in Figure 4.9.

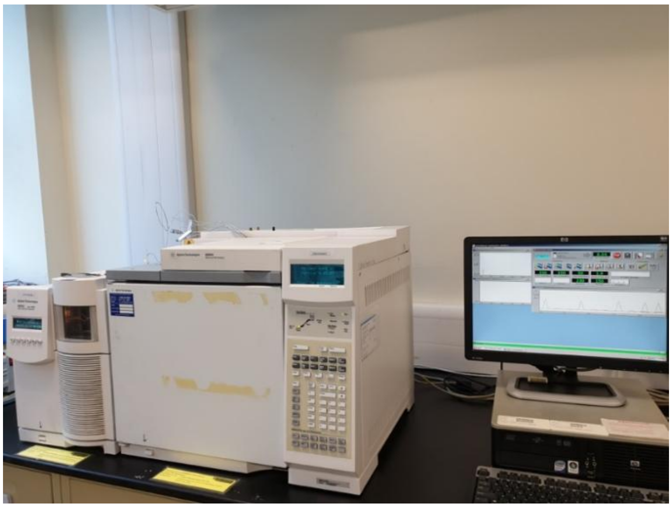


Figure 4.12. Gas Chromatography-Mas Spectroscopy apparatus used in this study

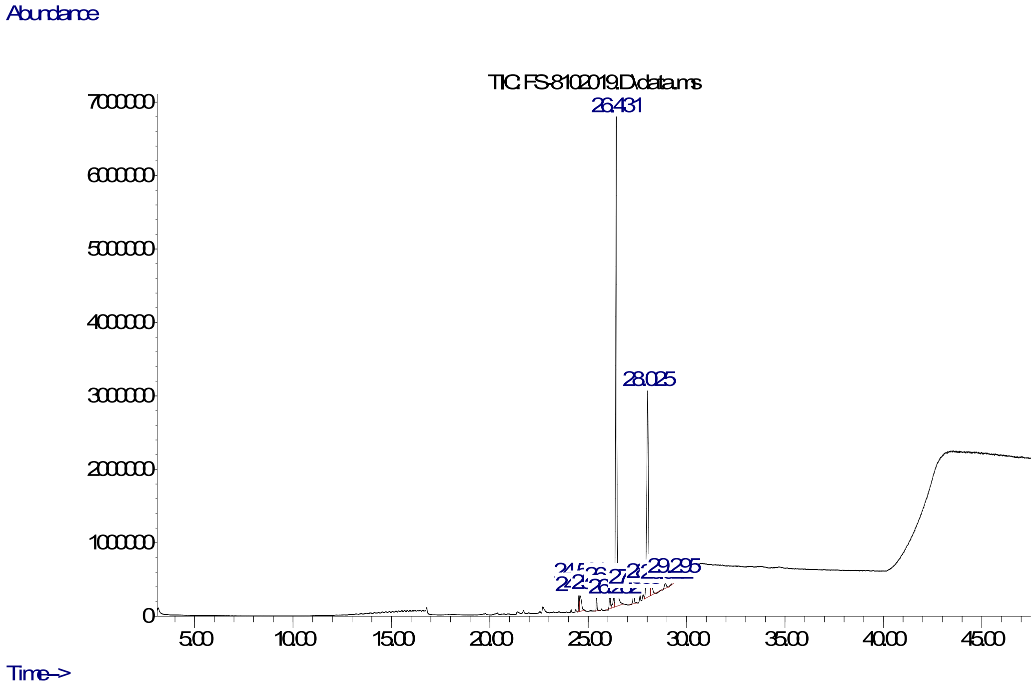


Figure. 4.13. Gas chromatogram of different components observed in the Flaxseed mucilage (FM)

4.9. Thermal Gravimetric Analysis

Thermogravimetric analysis (TGA) is a technique for determining the change in weight of materials as a function of temperature (or time) under controlled conditions. The main application of TGA is to measure the thermal stability of fillers in polymers, moisture and solvents and their proportion in the materials. In this method, the temperature in a chamber is slowly increased, combustion is induced and the change in weight of the materials over time is studied. At the end, a diagram can be produced showing the thermal transition and decomposition of the various components in the structure of the materials studied.

The thermal stability of the flaxseed surfactants was investigated using the (TGA) apparatus shown in Figure 4.14. In the test, a small amount (5 g) of FS and FP was heated from 30°C to 700°C in the presence of nitrogen at a rate of 10°C /min. The percentage weight losses were then plotted against temperature as shown in Figure 4.15 and Figure 4.16.

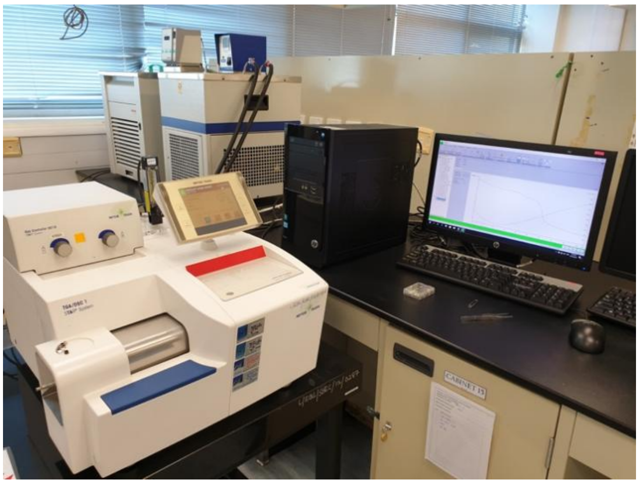


Figure 4.14. Thermal Gravimetric Analysis equipment used in this study

CTAB, a commercially available cationic surfactant, was also used for comparison purposes. The results show that the initial thermal loss for both FP and CTAB starts at 210°C and continues to 280°C for CTAB and 500°C for FP. While CTAB loses all its weight, FP loses almost 70% of its weight (3.5 mg). The initial decomposition of FP, observed at low temperature (50°C), could be related to the removal of moisture from the surfactant. Above 500°C, no further weight loss was observed, indicating the thermal stability of the surfactant FP at higher temperatures. This clearly shows that the surfactant synthesised from flaxseed can be used for applications where high temperature stability is required.

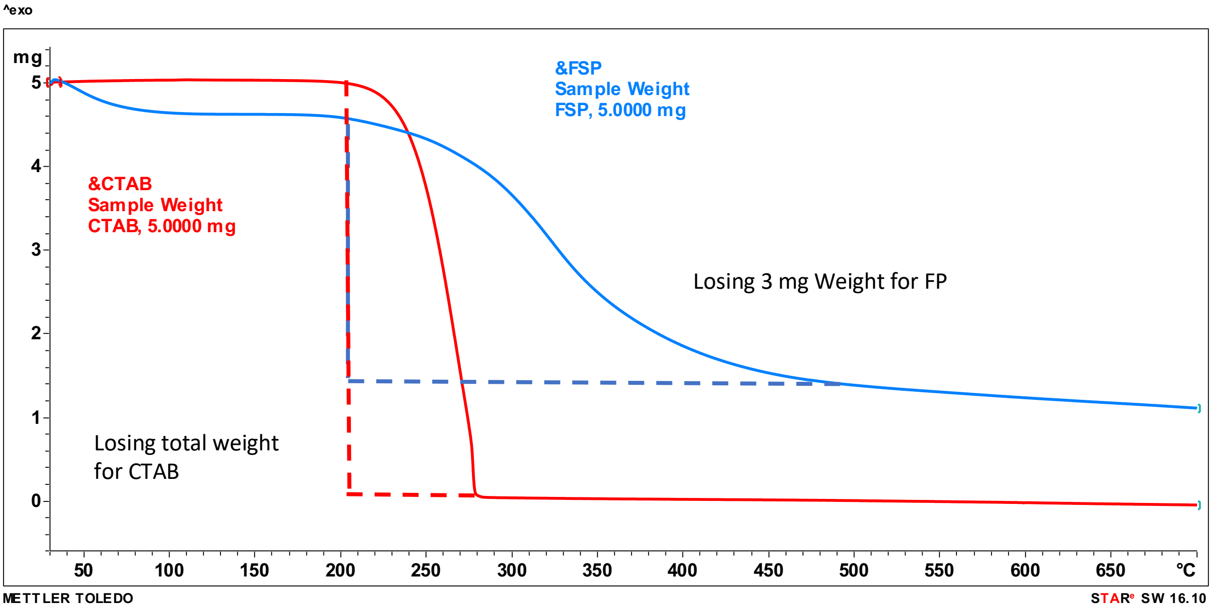


Figure 4.15. Thermal stability curve of the FP surfactant and CTAB

Similarly, the TGA plot of FM in Figure 4.17 shows an initial moisture removal at low temperatures (10-20°C). This was followed by a thermal loss for the flaxseed mucilage (FM) that started at 230°C. As can be seen in this figure, this decomposition continues up to 500°C, with 3 mg of flaxseed mucilage lost. The second weight loss begins at 710°C and continues to 870°C with a total weight loss of 1 mg. After 870°C there is no further weight loss and at the end of the test there was still 1 mg FM. The TGA results show that both surfactants have relatively high thermal stability and can be used at high temperatures.

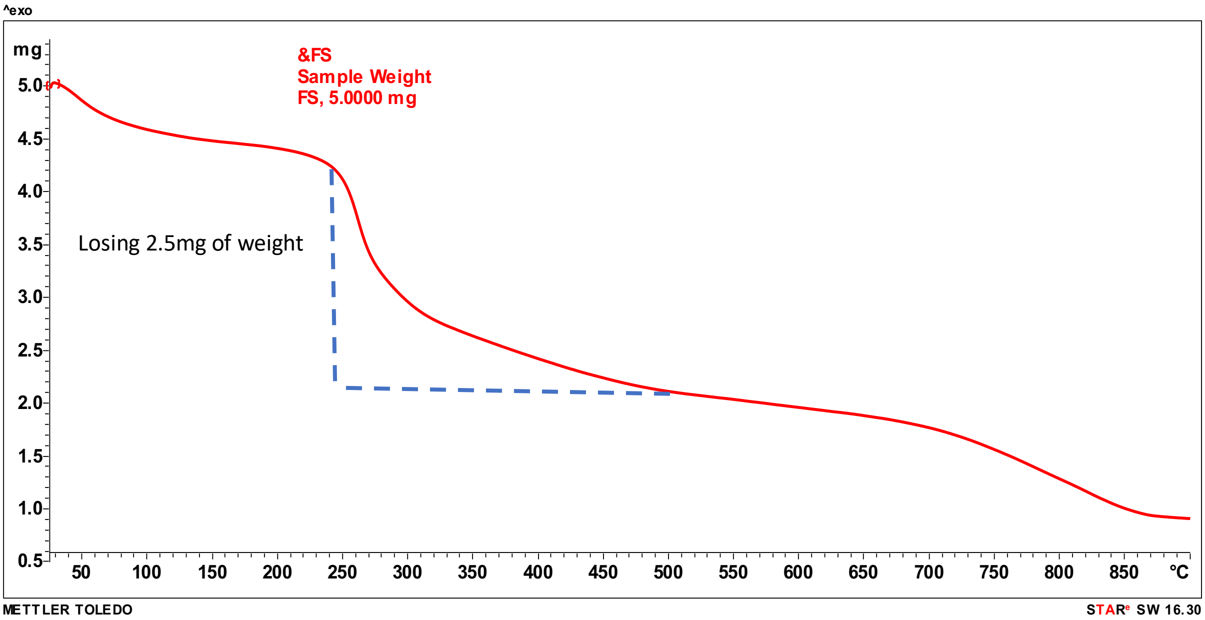


Figure 4.16. Thermal stability curve of the FS surfactant

4.10. Salt Stability

To evaluate the performance of surfactants in the presence of salt, a salt stability analysis was performed. First, the conductivity probe was calibrated with a deionised water solution. Then two sets of samples were prepared with pure surfactants and surfactants with 1 to 4 wt% KCl. For this purpose, the desired amount of salt was added to each solution and mixed for 15 minutes with a magnetic stirrer. Finally, the stable values indicated by the conductivity metre were recorded for each solution. All measurements were taken at least three times to ensure accuracy and repeatability of the results. The conductivity values before and after the addition of salt are shown in Figure 4.17. It can be seen from the figure that the salt content would lower the CMC point of the surfactants. This is mainly because the salts can decrease the electrostatic repulsions between the head groups of the surfactants and lead to higher hydrophobicity. The increase in hydrophobic interaction between the surfactant molecules can then lead to aggregation at a lower CMC. In fact, the addition of salt increases the formation of micelles (Fatih. 2019). Although the formation of micelles may increase the adsorption of surfactants on the rock surface, it seems that it would have a significant impact on the CMC once a high concentration of surfactants is used.

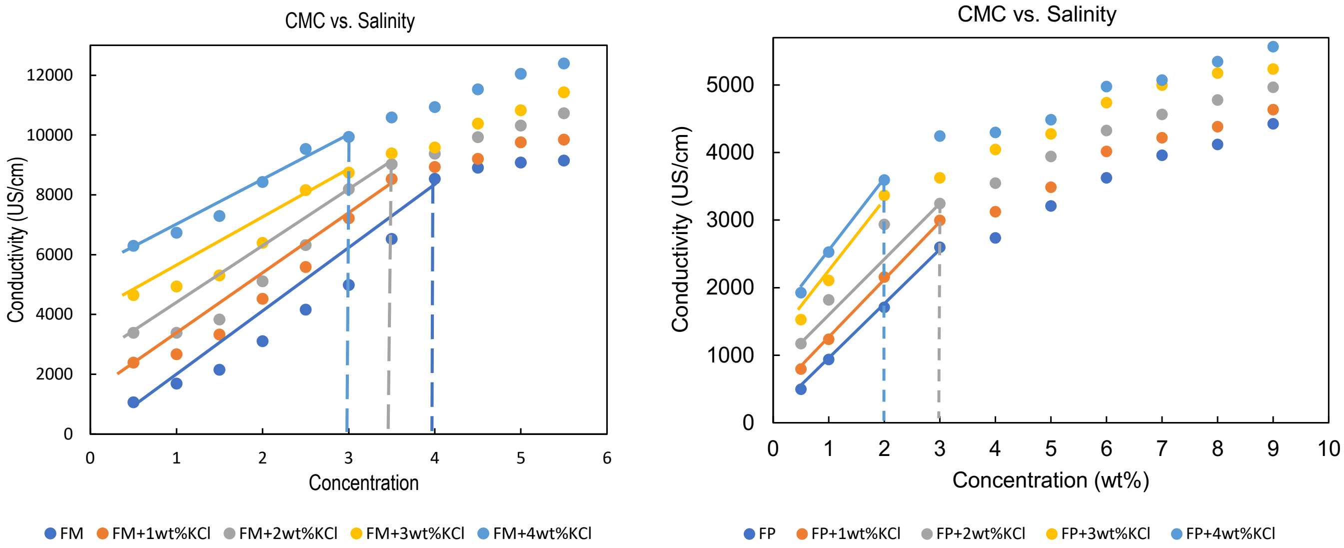


Figure 4.17: Variation of conductivity in different surfactant solutions in the presence of KCl

4.10. Surface Tension Measurements

Surface tension or interfacial tension is the energy between the surface of immiscible phases that restricts their movement. When a molecule near the interface has a different interaction than a corresponding molecule in the main fluid, the interfacial tension is established. For example, in water there are two groups of molecules called exterior and interior molecules. The interior molecules are surrounded by other molecules, while the exterior molecules are connected to other molecules on one side (see Figure 4.18). This arrangement results in the interior molecules having less energy than the exterior molecules. In this case, the exterior molecules would form a large surface area with other molecules from a different phase and interfacial tension is induced. Surfactants added to water move to the interface, reduce the surface area between two phases (e.g., water and oil) and reduce the interfacial tension.

Figure 4.18. Surface tension of interior and exterior molecules in water is unable to be reproduced here due to copyright restrictions. The content can instead be accessed via https://saylordotorg.github.io/text_general-chemistry-principles-patterns-and-applications-v1.0/s15-03-unique-properties-of-liquids.html.

The drop shape analyser was used to measure the surface tension, as shown in Figure 4.19. In general, the surface tension decreases with increasing concentration of surfactants in the solution until it becomes relatively constant due to surface saturation. This decrease has a similar trend to the conductivity measurement where the CMC is determined. In fact, the measurement of surface tension can also be used to determine the CMC of the surfactants.

Figure 4.19. Drop shape analyser used for the purpose of this study

The surface tension of the extracted surfactants was measured at different concentrations and repeated three times to ensure consistency of the results. Figures 4.20 to 4.23 show the results of the surface tension measurements of the two surfactants. It was found that increasing the concentration of the surfactant decreases the surface tension as the adsorption of the surfactant molecules at the interface between air and water increases. This trend continues until the CMC point is reached. In Figure 4.20 and 4.22 you can see that the CMC determined from the surface tension is 4 and 3 wt% respectively, which corresponds to what was previously observed in the conductivity measurements.

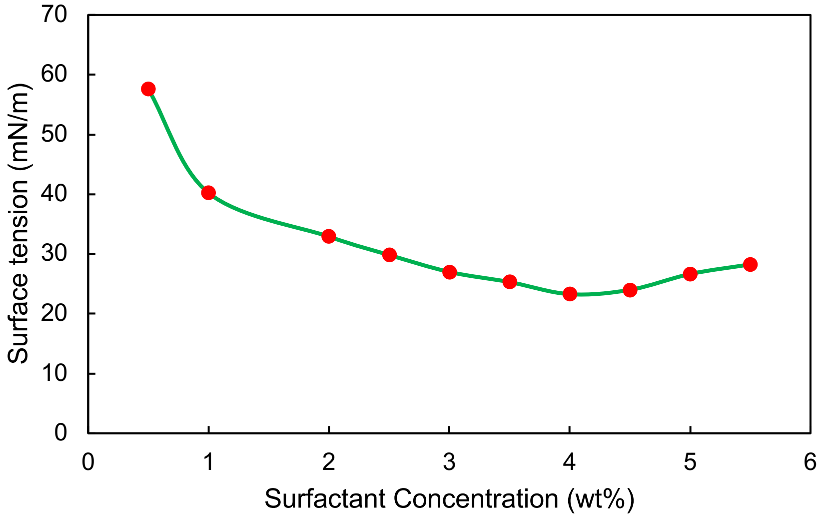
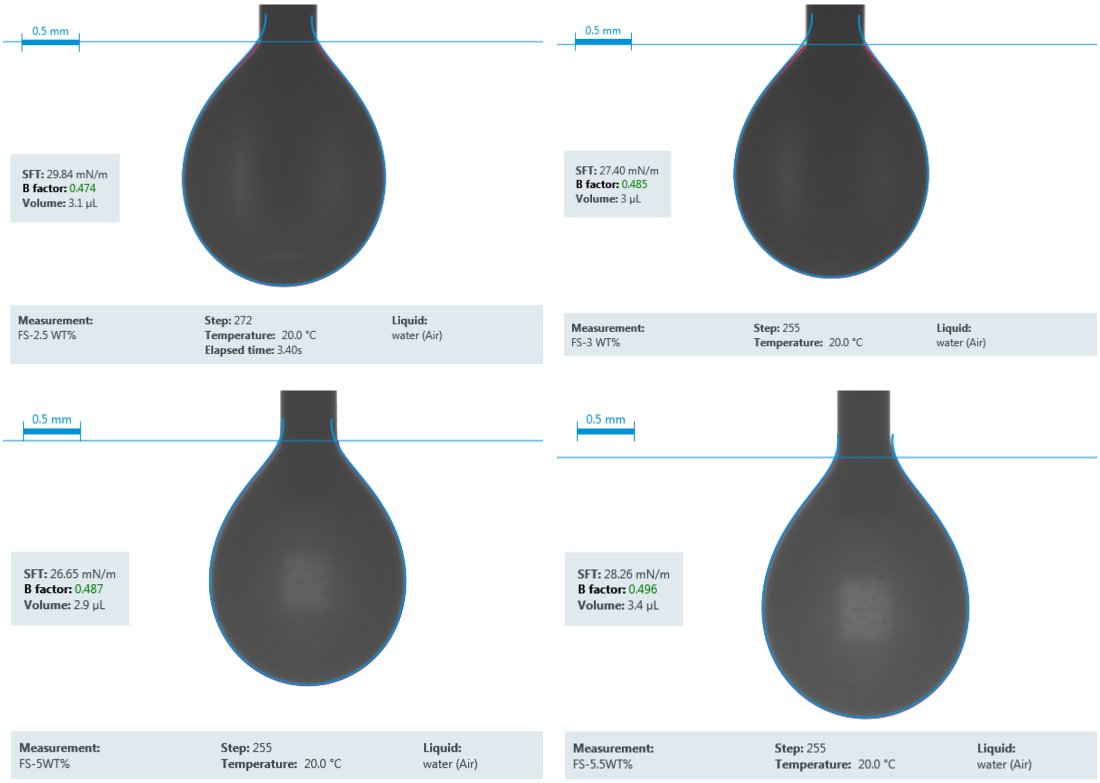


Figure 4.20: Variation of surface tension with the concentration of the synthesized flaxseed mucilage (FM)



SFT: 29.84 mN/m
B factor: 0.474
Volume: 3.1 µL

Measurement: FS-2.5 WT%
Step: 272
Temperature: 20.0 °C
Elapsed time: 3.40s
Liquid: water (Air)

SFT: 27.40 mN/m
B factor: 0.485
Volume: 3 µL

Measurement: FS-3 WT%
Step: 255
Temperature: 20.0 °C
Liquid: water (Air)

SFT: 26.65 mN/m
B factor: 0.487
Volume: 2.9 µL

Measurement: FS-5WT%
Step: 255
Temperature: 20.0 °C
Liquid: water (Air)

SFT: 28.26 mN/m
B factor: 0.496
Volume: 3.4 µL

Measurement: FS-5.5WT%
Step: 255
Temperature: 20.0 °C
Liquid: water (Air)

Figure 4.21: Measurement of the surface tension for the flaxseed mucilage (FM)

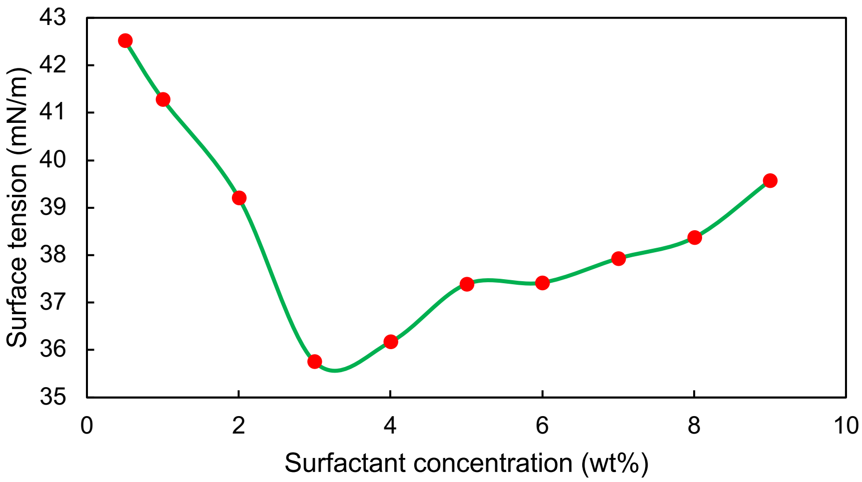
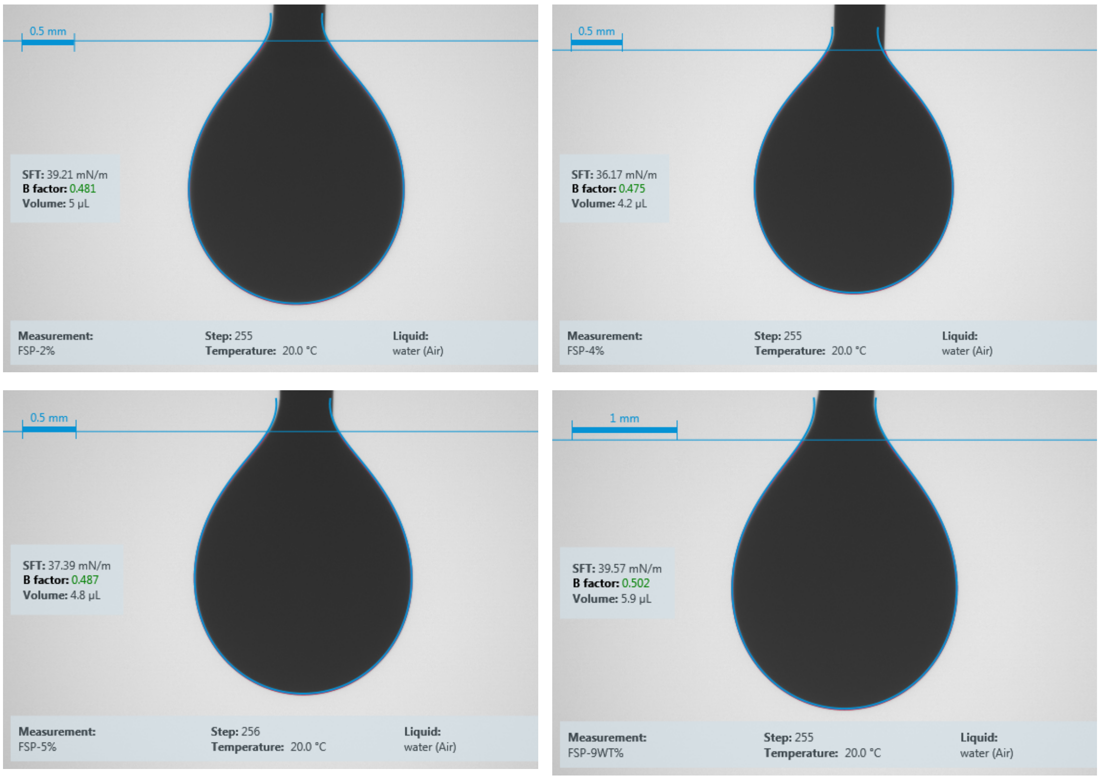


Figure 4.22: Variation of the surface tension with the concentration of the synthesized flaxseed protein (FP)



SFT: 39.21 mN/m
B factor: 0.481
Volume: 5 µL
Measurement: FSP-2%
Step: 255
Temperature: 20.0 °C
Liquid: water (Air)

SFT: 36.17 mN/m
B factor: 0.475
Volume: 4.2 µL
Measurement: FSP-4%
Step: 255
Temperature: 20.0 °C
Liquid: water (Air)

SFT: 37.39 mN/m
B factor: 0.487
Volume: 4.8 µL
Measurement: FSP-5%
Step: 256
Temperature: 20.0 °C
Liquid: water (Air)

SFT: 39.57 mN/m
B factor: 0.502
Volume: 5.9 µL
Measurement: FSP-9WT%
Step: 255
Temperature: 20.0 °C
Liquid: water (Air)

Figure 4.23: Measurement of surface tension for flaxseed protein (FP)

4.11. Conclusions

In this chapter, attempts were made to characterise FP and FM surfactants and to investigate their functionality under different temperature conditions. The results obtained can be summarised in the following points:

- Both surfactants exhibit good thermal stability, as shown by the conductivity measurements.
- FP is a cationic surfactant, while FM is an amphoteric surfactant, as shown by the surface charge measurements.
- The principal components obtained from FTIR and GC-MS indicate that the surfactants can provide the functionality required of a surfactant additive.
- The thermal stability of FP seems to be even higher than that of a commercial surfactant such as CTAB, as shown by the TGA results.
- It seems that both surfactants are able to change the interfacial tension and could be used for surface modification of nanoparticles and improving the filtration loss of WBMs.

Chapter 5: Water Based Mud Design

5.1. Introduction

As mentioned in the previous chapters, the aim of this work is to develop a water-based mud (WBM) that works better during drilling in shale and clay rich hydrocarbon reservoirs. Given the properties of the extracted surfactants (i.e., flaxseed mucilage (FM) and flaxseed protein (FP)), it appears that they can improve the properties of the mud. To assess this, a series of tests were conducted in this chapter on the mud samples modified by the surfactants to investigate their effects on the density, rheology, filtration loss and surface wettability of WBMs. The results obtained are discussed in the following sections.

5.2. Materials and Methods

5.2.1. Mud Samples

This section describes the standard procedure used to prepare the mud samples used in this study. The procedure for mixing the green surfactants with the WBMs has not been presented anywhere before and was presented here for the first time in this study (API RP 13B-1, 1997).

5.2.1.1. Water Base Mud

To prepare the base mud, 15 g of bentonite and 350 ml of deionised water were mixed using the FANN Multimixer 9B. To ensure that the slurry sample was evenly mixed and the bentonite did not coagulate, the mixture was mixed for 10 minutes at a constant rate of 11,500 RPM. The WBM was then subjected to density, rheology, filtration loss and surface wettability measurements.

5.2.1.2. WBMs with Surfactants

As mentioned earlier, there is no established method to mix the extracted surfactants with the WBMs mud at different concentrations. To mix the surfactants with the WBMs, in this study, different amounts of surfactants were weighed and mixed with 100 ml of deionised water using the magnetic stirrer for 30 minutes. The surfactant solutions were then added to the base slurry previously prepared with 15 g of bentonite and 250 ml of deionised water. The finished solutions were then mixed again for 10 minutes at a rate of 11,500 RPM. These samples were then subjected to the same tests as the base mud for comparison purposes.

5.2.1.3 WBM with nanoparticles

Nanoparticles, Nano Glass Flakes (NGF) and Nano Silica (NS) with a chemical structure dominated by SiO_2 were purchased from the US suppliers for the purpose of this study. Ns and NGFs were used to prepare the nano fluids. The average particle size of Ns was around 15 and 20 nm but NGFs had a bigger size in the range of 100 nm. In addition, the surface area of nanomaterials was approximately 170-2000 m^2/g and 50-700 m^2/g for NS and NGF respectively. A Silverson homogeniser with a constant rotation speed of 2,000 RPM for a period of 10 minutes was used to prepare the nanoparticle solutions. In the next step, the nanoparticles were sonicated with the LSP-500 Laboratory Scale Ultrasonic Liquid Processor for 15 minutes to obtain a nano solution with a high dispersion of particles. The ultrasonic liquid processor operated at a power of 500 W, a frequency of 20 kHz and an amplitude of 50%. The pulse mode was selected so that a pulse was transmitted every 20 seconds, followed by a 5 second pause. This is mainly to avoid overheating during sonication, as the water evaporates and the water content in the solution is reduced. It is worth noting that the nano solution was weighed before and after sonication to ensure that no overheating or water evaporation had occurred. This sonication method, after several trials, was the best approach to ensure that the nanomaterials were properly dispersed in the solution and particle agglomeration do not occur when observing the nanoparticle deposits at the bottom of the beaker. The nano solutions were then immediately mixed with the water-based mud and mixed for a further 10 minutes using the FANN 9B Multimixer at a speed of 11,500 RPM.

5.2.1.4. WBM with modified nanoparticles

For the preparation of modified water-based nanoparticle mud, the nanomaterials were first dispersed in water as described above. Then, another solution containing a surfactant was prepared. To prepare the surfactant solutions, different amounts of surfactant were weighed out and mixed with 100 ml of deionised water using the magnetic stirrer for 30 minutes. In the next step, the solution of dispersed nanoparticles was added to the surfactant solution and mixed with the magnetic stirrer for 15 minutes. Finally, the modified nanoparticles are added to the drilling mud and mixed with a multimixer for 15 minutes.

5.2.2. Shale Samples

The shale samples for this study were taken from one of the fields in Norway where clay swelling causes many problems for drillers. The mineral composition of the shale samples used in this study was determined by XRD analysis and is given in Table 5.1. As shown in Table 5.1, both samples had a variety of different clays, including smectite and double layer illite with swelling potential. In addition, the samples were found to have low TOC concentrations, which could complicate the interpretation of the results (Liu et al., 2018; Xue et al., 2021). To remove the TOC from the samples, both were oven dried at a temperature of 60°C for 48 hours. Figures 5.1 and 5.2 show the shale samples used in this study and their SEM images.

Table 5.1. Mineral Composition of the shale samples used in this study

Sample	Quartz (%)	Muscovite (%)	Smectite (%)	Kaolinite (%)	Chlorite (%)	Illite (%)
Shale 1	47.2	8.9	16.1	7.8	9.4	10.3
Shale 2	45.7	7.3	13.4	10.8	10.6	12.1
Shale 3	48.2	7.1	14.2	11.2	8.7	10.5
Shale 4	45.1	9.3	15.2	9.7	9.3	11.1
Shale 5	47.8	8.7	12.8	8.1	11.6	10.8
Shale 6	48.9	9.8	10.8	10.3	10.1	11.7
Shale 7	46.8	8.8	12.2	10.3	9.7	12.1
Shale 8	47.7	11.4	10.5	8.9	9.1	11.5

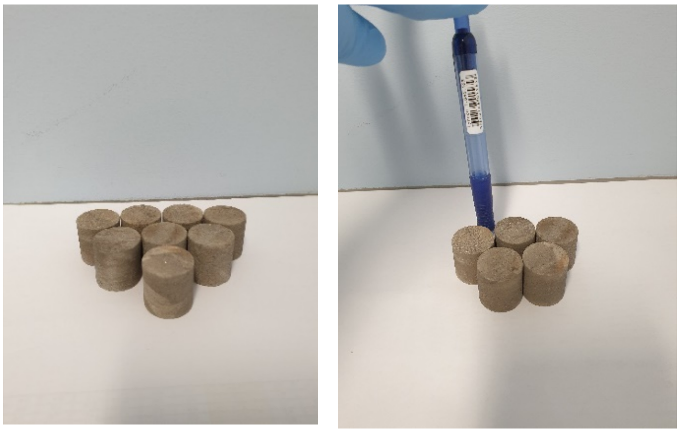


Figure 5.1: Shale samples used in this study

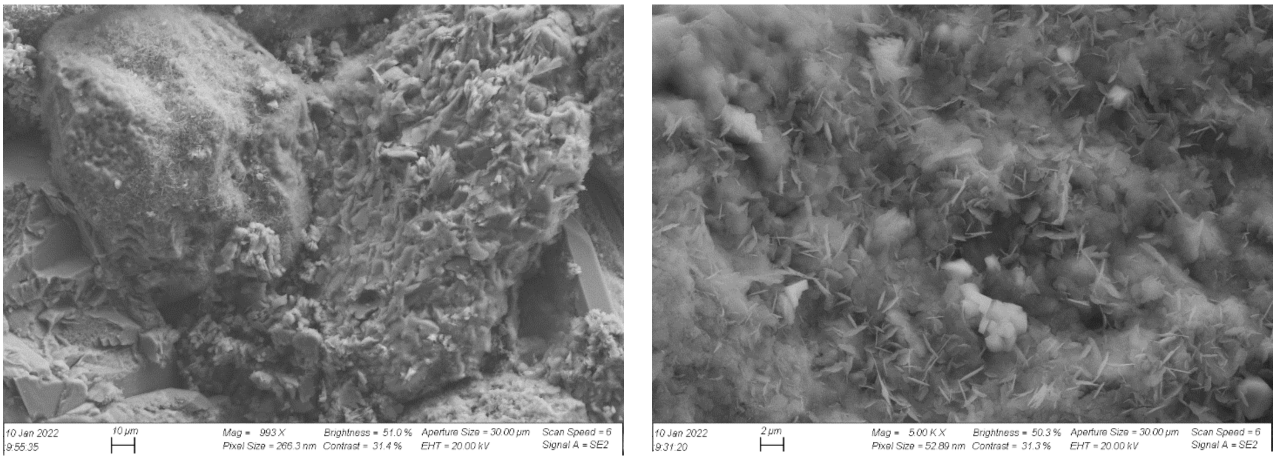


Figure 5.2: SEM images of the shale samples used for the purpose of this study

5.2.3. Measurements

Different devices were used to measure the density, rheology and filtration loss of the mud samples. The FANN Multimixer 9B was used to mix the bentonite with the rest of the water solution and to prepare the base mud samples. The FANN Viscosimeter 35SA was used to determine the rheological properties of the mud samples while FANN Filter Press Series 300 was used to calculate the filtration volume of the samples. The IKA@ C- MAG HS7 digital stirring hotplates were also used to stir the mixture and produce the final product. The Kruss drop shape analyser was used to evaluate the changes in surface wettability once the mud samples were modified by the surfactants.

5.4. Experimental Results

5.4.1. Density of Solutions

In order to evaluate the effect of surfactants and nanoparticles on the weight of the solutions, a series of measurements were carried out with the laboratory pycnometer. For the test, the empty pycnometer and the pycnometer filled with surfactants and nanoparticles were weighed and their difference recorded as the density of the additives. All measurements were carried out at room temperature (25^{o}C) and repeated three times. The density of ultra-pure water and water-based mud was used as a reference in the measurements. Tables 5.2-5.5 show the results of the measurements. These tables show that the surfactants (FP and FM) and nanoparticles (NGF and NS) do not significantly change the density of the solutions.

Table 5.2: Density of the flaxseed mucilage (FM) solution

Fluid	W(g)	volume V(cm^3)	Average Density ρ(g/cm^3)
Ultra-pure water	24.962	25	0.9985
1wt% FM	25.410	25	1.0164
2wt% FM	25.563	25	1.0225
3wt% FM	25.690	25	1.0276

Table 5.3: Density of the flaxseed protein (FP) solution

Fluid	W(g)	volume V(cm^3)	Average Density ρ(g/cm^3)
Ultra-pure water	24.962	25	0.9985
1wt% FP	25.682	25	1.0061
2wt% FP	25.750	25	1.0053
3wt% FP	25.943	25	1.0057

Table 5.4: Density of the nanoparticle solutions

Fluid	W(g)	volume V(cm^3)	Average Density ρ(g/cm^3)
Ultra-pure water	24.962	25	0.9985
0.05wt% NS	24.964	25	1.0045
0.5WT%NS	24.968	25	1.0049
0.75WT%NS	24.974	25	1.0056
1WT%NS	24.973	25	1.0074
0.05wt% NGF	24.663	25	1.0053
0.5WT%NGF	24.966	25	1.0064
0.75WT%NGF	24.971	25	1.0075
1WT%NGF	24.978	25	1.0089

Table 5.5: Density of the modified nanoparticle solutions

Fluid	W(g)	volume V(cm^3)	Average Density ρ(g/cm^3)
Ultra-pure water	24.962	25	0.9985
NS+FM	25.943	25	1.0084
NGF+FM	25.970	25	1.0073
NS+FP	25.937	25	1.0058
NGF+FP	25.944	25	1.0069

5.4.2 pH of Surfactant Solutions

To determine the pH of the solutions after addition of the surfactants, different concentrations of the FP and FM were prepared at room temperature. Before the measurements, the Mettler Toledo pH metre was calibrated with three standard solutions (4, 7, 14 buffer solutions) and all results were recorded after the pH was stabilised. The results obtained are shown in figure 5.3.

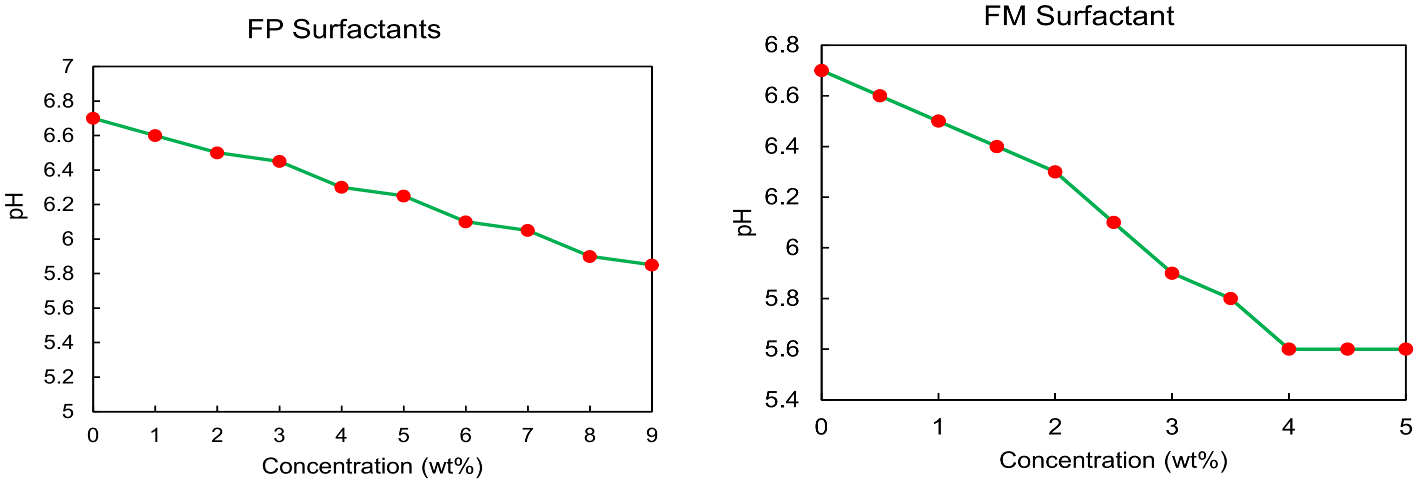


Figure 5.3: Changes in the pH with increasing the concentrations in the extracted surfactants

In Figure 5.3 you can see that as the concentration of surfactants increases, the pH decreases and the solutions become acidic. However, at the high concentrations of FP and FM there are significant changes in pH. Therefore, they can be considered as very weakly acidic surfactants (Hu et al., 2020). The process of pH measurement was also repeated by adding nanoparticles to the surfactant solutions, but no further changes in pH were observed.

5.4.3. Mud Rheology

Measuring rheological properties is critical to ensure that the WBM can provide the required efficiency during circulation, including transporting the cuttings accumulated at the bottom of the well and applying the required pressure to prevent well failure. In general, rheology is defined on the basis of flow resistance and is a function of temperature, pressure and the additives used in the mud. Bentonite clay is the additive commonly used to improve the viscosity of the mud samples as a hydrophilic material. It imparts thixotropic properties to the mud that create gels once the shear stress from the mud stops (Martin., 2015). The problem is some other additives such as surfactants that may interact with bentonite after addition to the mud and change the rheological properties of the mud unfavourably. According to Mohie (2017), different particles in the drilling mud need to reach equilibrium, otherwise unexpected rheological behaviours may occur during drilling. These unexpected behaviours can be complicated when the temperature and pressure in the borehole increase.

Bingham plastic and power-law models are two well-known mathematical models which can be used to describe the rheology of the mud. These two models are respectively expressed by Eq. (5.1) and Eq. (5.2).

$$\tau = \tau_y + \mu_p \dot{\gamma} \tag{5.1}$$

$$\tau = K\dot{\gamma}^n \tag{5.2}$$

Bingham plasticity (Eq. (5.1)) is defined by two parameters: plastic viscosity ((μ_p) and yield point (τ_y). Here, the plastic viscosity describes the viscosity of the mud samples and the yield point defines the ability of the mud to carry the cuttings to the surface. The power law model (Eq.5.2), on the other hand, is described by the flow consistency index (K) and the flow behaviour index (n). These two parameters are related to the plastic viscosity and yield point of the Bingham plastic. Table 5.6 shows the rheological properties of the slurry in this study. The calibrated FANN viscometer 35SA was used to measure the rheological properties. After filling the mud samples into the container, the intended gear was selected and after stabilising the value, the scale value was recorded.

As can be seen in Table 5.6, increasing the concentration of FM in the drilling fluid increases both the yield point and the plastic viscosity in the Bingham plastic model. The increase in yield point could be due to the highly gelling property of the flaxseed mucilage, which covers the negative sites of the bentonite and reduces the negative-negative repulsive force, leading to a reduction in flocculation. Technically, it appears that the addition of up to 1 wt% FM to the slurry does not cause significant changes in the rheological properties. On the other hand, the plastic viscosity of the mud increases with the addition of FP, but the yield point remains almost the same. This could be related to the fact that FP is a cationic surfactant that can interact with the negative sites of bentonite and reduce flocculation. It was also found that up to 2 wt% FP can be added to the slurry without causing rheological problems. Adding more FP may not be economically viable given the complexity of surfactant extraction.

A look at Table 5.6 shows that the plastic viscosity and yield point of the mud sample with nanosilica are higher than those of NGFs, which could be related to the size of the nanoparticles and their high surface area to volume ratio. Since nanosilica (20 nm) was smaller than NGFs (350 nm), it could increase the friction between the particles and absorb more water, leading to an increase in viscosity.

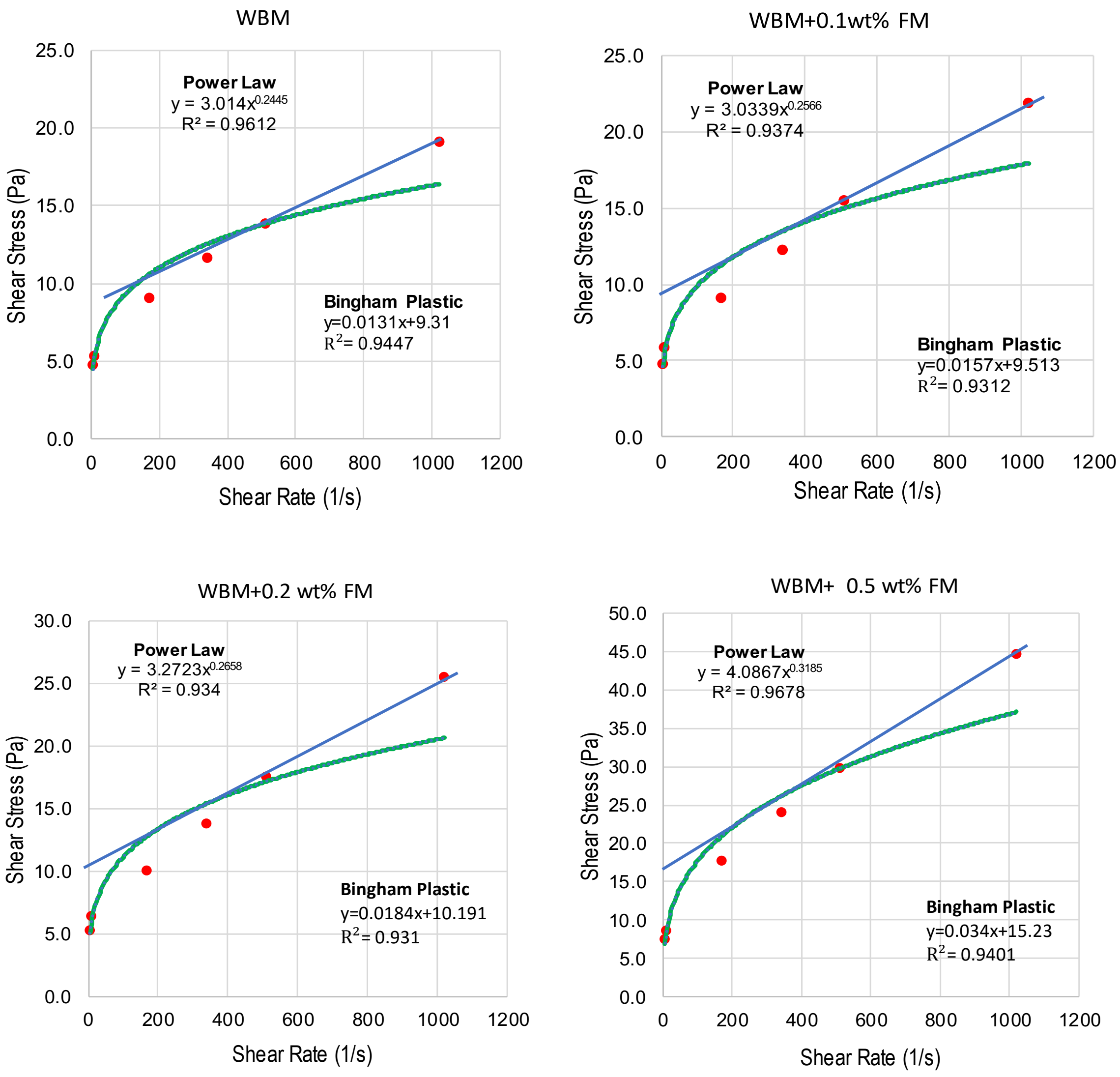
Table 5.6: Rheological properties of the mud samples with the best candidates highlighted

Samples	**Bingham Plastic**		**Power Law**		**Gel Strength (lb/100ft^2)**	
	τ_o (Pa)	**μ_p (cP)**	**K (Pa s^n)**	**n**	**10s**	**10min**
WBM	8.0	5.0	3.014	0.24	5	6
0.1wt%FM	8.5	6.0	3.0339	0.26	5	6
0.2wt%FM	**9.0**	**7.5**	**3.2723**	**0.27**	**5**	**6.5**
0.5wt%FM	14.0	14.0	4.0867	0.32	7.5	8.5
1wt%FM	17.0	32.0	4.3832	0.39	10	11
0.5wt% FP	6	5.5	2.4651	0.25	4.5	5.5
1wt% FP	6	5.5	1.9799	0.34	4	5
2wt% FP	**7**	**8**	**5.0938**	**0.21**	**4.5**	**6**
0.05wt% NS	8	6	4.6957	0.1897	6.5	8
0.5wt% NS	**11**	**8**	**5.1603**	**0.2037**	**7.5**	**8.5**
0.75wt% NS	12.5	9	6.0894	0.1815	8.5	10
1wt% NS	14	10	7.3722	0.1716	10	11
0.05wt% NGF	**8**	**5**	**3.6639**	**0.213**	**8**	**9**
0.5wt% NGF	8	6	3.1853	0.2339	10	12
0.75wt% NGF	7.5	6	3.0414	0.2323	10	13
1wt% NGF	7.5	7	3.0414	0.2323	12	15
1 wt% FM+ 0.5%NS	9	9	3.794	0.2221	8	8.5
1wt% FM+0.05% NGF	8.5	8	3.3589	0.234	8	10
2 wt% FP+0.5% NS	7.5	7	3.6365	0.2156	6	7
2 wt% FP+0.05% NGF	8	6	3.0811	0.2308	8	8

5.4.4. Rheological Models

WBM is a non-Newtonian fluid described by a complex relationship between the shear stress and the shear rate. As mentioned earlier, there are two generally acceptable models used to describe the rheological behaviour of WBMs, known as Bingham Plastic and Power Law. These two models along with their parameters were used to interpret the rheological behaviour of the slurry after the addition of the surfactants. Figure 5.4 shows the parameters obtained for the Bingham Plastic and Power Law models.

As can be seen in this figure, the flow behaviour index (n) determined for all the mud samples is less than one, indicating that the mud samples exhibit shear-thinning behaviour. The consistency index (K), on the other hand, indicates the ability of the mud to clean the borehole. In general, the higher the K parameter, the better the borehole cleaning capacity (Sadeghalvaad et al., 2015). Figures 5.5 show the relationship between the apparent viscosity and the shear rate of the mud samples.



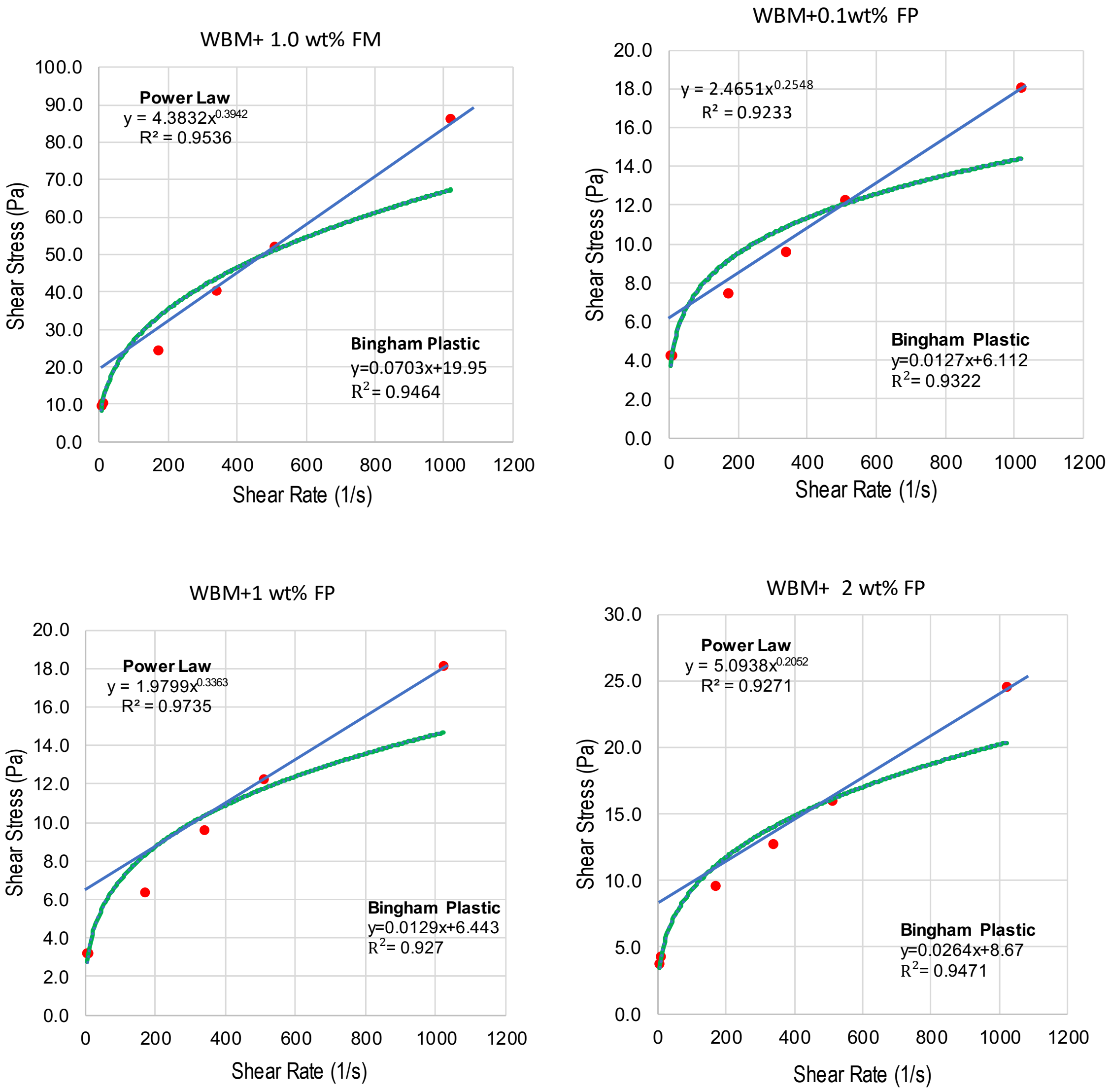


Figure 5.4: Rheological Models of different mud samples; a): WBM; b): 0.1wt% FM; c): 0.2wt%FM; d):0.5wt%FM; e): 1wt%FM; f): 0.1wt%FP; g): 1wt%FP; h): 2wt%FP

As can be seen in Figure 5.5, the viscosity decreases as the shear rate increases, further demonstrating the shear-thinning behaviour of the slurry samples modified with the surfactants, nanoparticles and modified nanoparticles. This is a very beneficial behaviour for drilling muds commonly used in industry. It appears that the mud samples act as deflocculants and prevent the particles from flocculating in the drilling fluid system. This would help the mud to perform better under subsurface conditions.

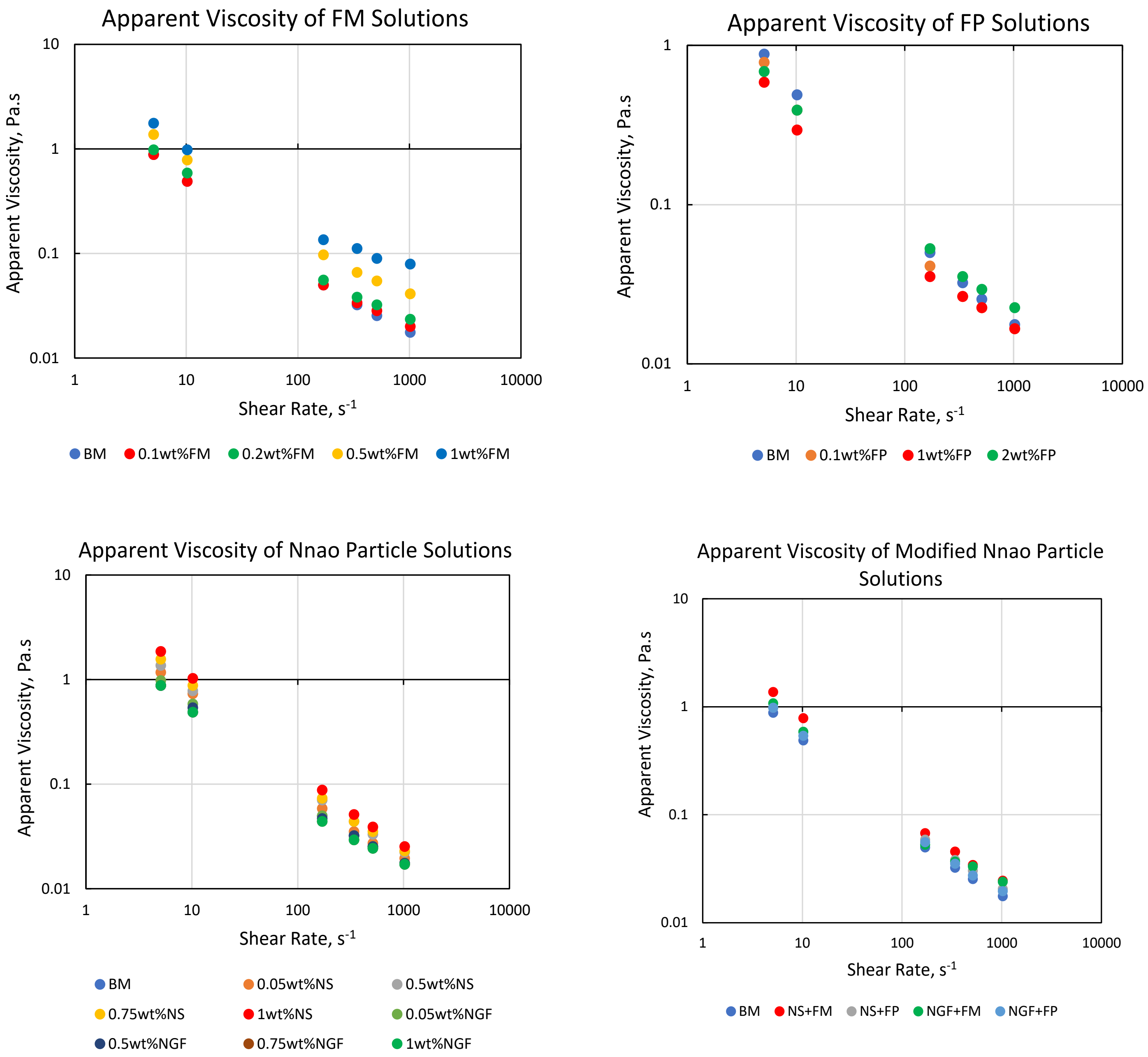


Figure 5.5: Viscosity Shear Rate Relationship of FM

5.4.5. Gel Strength

WBM often show thixotropic behaviour as soon as the shear stress exerted by the pump ceases. According to Vryzas and Kelessidis (2015), water-based drilling fluids tend to form a gelatine structure once they are subjected to shear stress. This gelatine structure enhances the ability of the mud to keep the rock material in suspension when the pump is off. This property is extremely important to ensure that the cuttings do not fall and accumulate at the bottom of the well when the pump is turned off. In addition, this gel must break with a very low shear stress once drilling resumes so that no additional pressure is applied to the pump to start circulation. Figure 5.6 shows the gel strength of the mud samples in this study formulated with different types and concentrations of surfactants and nanoparticles.

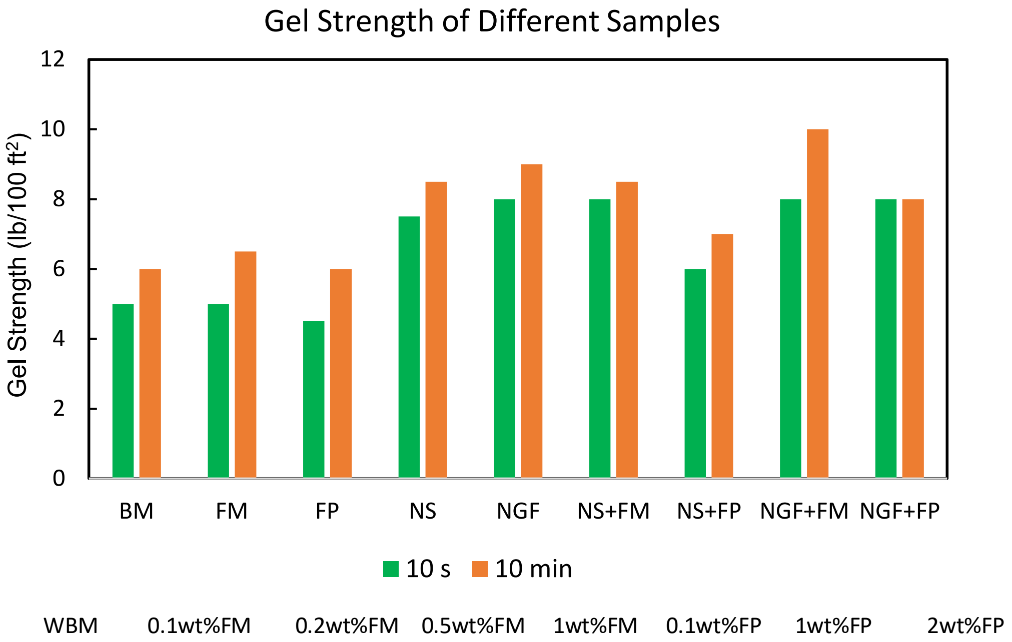


Figure 5.6: Gel Strength Profile of different samples formulated as part of this study

According to Ismail et al. (2016), the gel strength of WBMs with bentonite clay should be between 6 and 10 lb/100 ft^2, which agrees well with the gel strength of the base slurry used in this study. From Figure 5.6, it can be concluded that the gel strength of the slurry formulated with FM is higher than that of the base slurry. This indicates that the surfactants can improve the gel strength of the mud without having a significant effect on the recirculation problem. For the nanoparticles, it was found that NGF could have a greater impact on gel strength than nanosilica. This could be related to the parallel and wedge shape of NGFs, which can agglomerate faster when no shear stress occurs.

There is another term known as 'progressive gel'. It is defined as the difference between the 10s and 10min gel strength. This difference should not be very high, otherwise the WBMs may not be able to function normally during the stopping and starting of the circuit. As can be seen in Figure 5.6, there was not much difference between the gel strengths of the mud samples tested for 10s and 10 min. It seems that the gelling property of FM is the reason for the improvement in gel strength of the mud samples, as it can suspend bentonite in the drilling fluid and prevent the particles from flocculating. FP The positive charge of the clay, which can cover the negative sites of the bentonite and prevent the clay from flocculating, gives similar results.

5.4.6. Filtration Loss

The cumulative filtrate volume of the mud samples was measured using a 300 series FANN philtre press for 30 minutes and the amount of water loss was determined. The results obtained from the cumulative filtrate volume as a function of time are shown in Table 5.7and Figure 5.7. Figure 5.7 shows the mud cakes obtained at the end of the LPLT tests.

Table 5.7: Summary of the Filtration Test for the mud samples of this study

Sample	**Cumulative Filtrate Volume (ml)**	**Change in Filtrate Volume (%)**	**Mud Cake Thickness (1/32 in)**
WBM	19.4	-	2
0.1wt% FM	15.2	-21.64	2
0.2wt% FM	14	-27.83	2
0.5wt% FM	11.6	-40.20	2
1wt% FM	9.6	-50.51	3
0.5wt% FP	17.8	-8.24	2
1wt% FP	16	-17.52	2
2wt% FP	11.8	-39.17	2
0.05wt% NS	19.6	1.030	2
0.5wt% NS	20	3.092	2
0.75wt% NS	21.4	10.30	3
1wt% NS	23.4	20.61	3
0.05wt% NGF	19	-2.06	2
0.5wt% NGF	18.2	-6.18	2
0.75wt% NGF	17.4	-10.30	2
1wt% NGF	17.6	-9.27	2
FM+NS	14.8	-23.71	3
FM+NGF	14.2	-26.80	2
FP+NS	17.6	-9.27	2
FP+NGF	16.8	-13.40	2

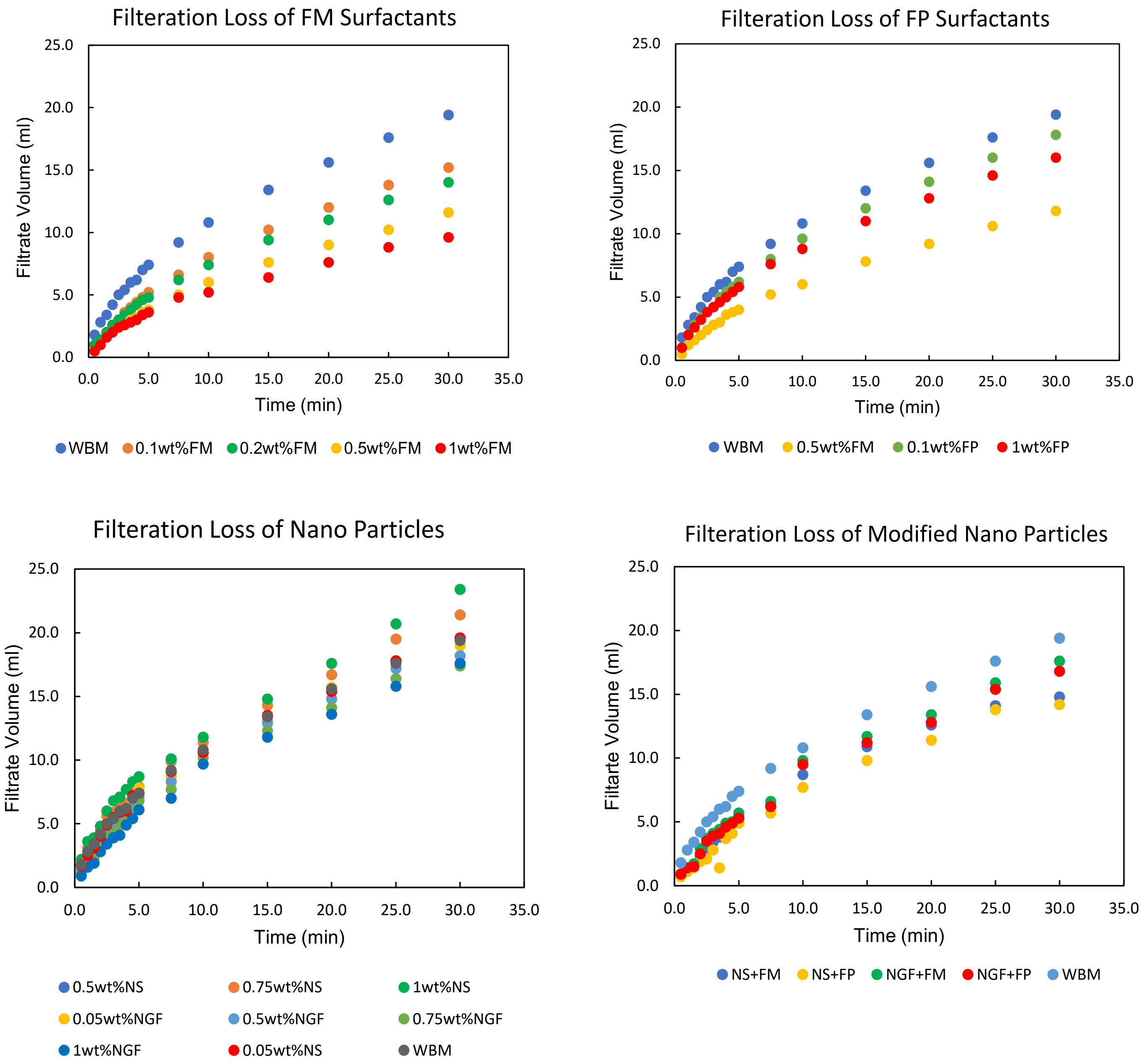


Figure 5.7: Filtrate Volume obtained from the filtration test on the mud samples with FM

A look at Table 5.7 and Figures 5.7 shows that the addition of both FM and FP reduces the filtrate volume. This significant reduction in filtrate volume could be due to the gelling properties of FM and the positively charged surface of FP, which neutralise the negative side of the bentonite. They seem to be able to prevent coagulation of particles while keeping the liquid in a well-dispersed system. The results also indicate that the surfactants do not have a significant effect on the mud cakes, which is very common in WBM samples with commercial surfactants.

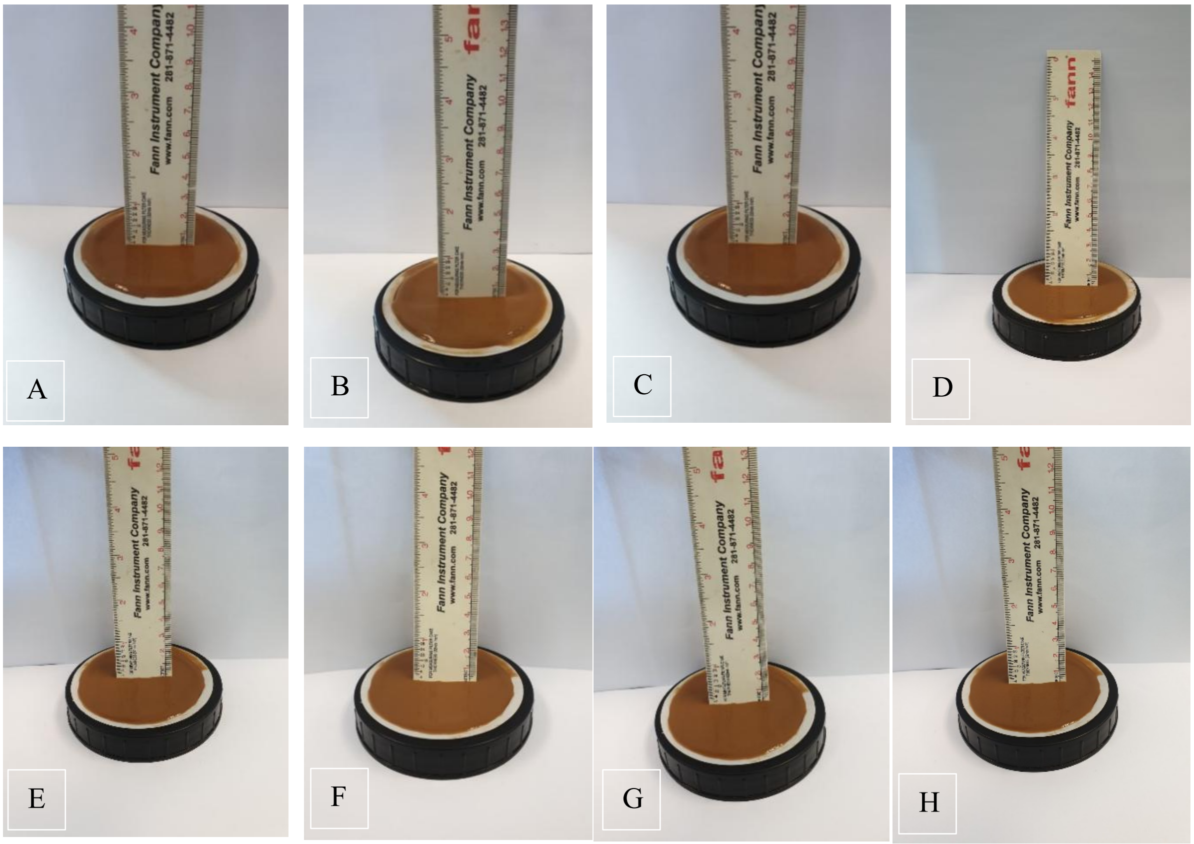


Figure 5.8: Mud cakes of different mud samples modified by the surfactants and nano particles: A) NS, B) NGF, C) FM, D) FP, E) FM+NS, F) FM+NGF, G) FP+NS, H) FP+NGF

In the case of nanoparticles, it was observed that the filtration loss increased significantly when nanosilica was added to the mud samples. This could be related to the negative surface charges and repulsive force of the nanosilica in the aqueous phase, which prevent the bentonite from forming the structure required to reduce the mud filtrate. This problem was not observed with the nano-glass flakes, perhaps due to their complex structure which can create a tortuous path within the mud cake against the movement of the filtrate.

However, the problem of high filtration loss due to the nanoparticles was solved by adding surfactants. It was found that FM can change the surface structure of the nanoparticles and reduce their interactions with the bentonite in solution. The combination of the gelling properties of FM and the closure of the pore spaces of the cake by the nanomaterials resulted in the filtration loss being significantly reduced. However, FP could not provide the same functions for the reasons mentioned above. NGFs also appear to be a better choice for controlling filtration loss than nanosilica.

5.4.7. Surfactant Adsorption

There are two main factors that influence the adsorption of surfactants on solid surfaces: the interaction of the surfactant with the surface and the hydrophobicity of the surfactant, also known as the hydrophobic effect. The latter driving force is closely related to the surfactant structure and the solubility of the surfactant in water but is often the dominant force in surfactant adsorbing systems. The interaction with the surface, on the other hand, plays a subordinate role in hydrophobic surfaces. This is because the surfactants adsorb with their hydrophobic tail towards the surface and their hydrophilic head towards the solution. This arrangement resembles a micelle configuration in the sense that the hydrophobic group is transferred from the aqueous environment during adsorption. However, on polar surfaces, such as the surface of clay/shale, the surfactants adsorb with their polar head groups towards the surface. This phenomenon is called hemimicelle and is only valid at low surfactant concentrations. At higher concentrations, two different structures are possible. If there is a strong attraction between the polar head groups and the surface, a monolayer is formed with the head groups facing the surface and the tails facing the solution. This creates a hydrophobic surface, which leads to further adsorption in the same way as described for hydrophobic surfaces. Therefore, at higher concentrations, a surfactant bilayer forms, which is called an admicelle. At intermediate attractive forces between the polar head groups and the surface, micelles or other surfactant aggregates form on the surface. This is because the attractive forces between the tail groups are stronger than the interaction of the head groups with the surface (Shilpa, 2019).

In order to evaluate the adsorption of the surfactants FM and FP on the shale surface, a series of measurements was carried out at different concentrations and temperatures. For this purpose, the conductivity of the surfactant solution was measured as a reference liquid. Then the shale samples were crushed into pieces, added to the solutions and mixed with a magnetic stirrer for 15 minutes. The conductivity of the solutions was then recorded as shown in figure 5.9.

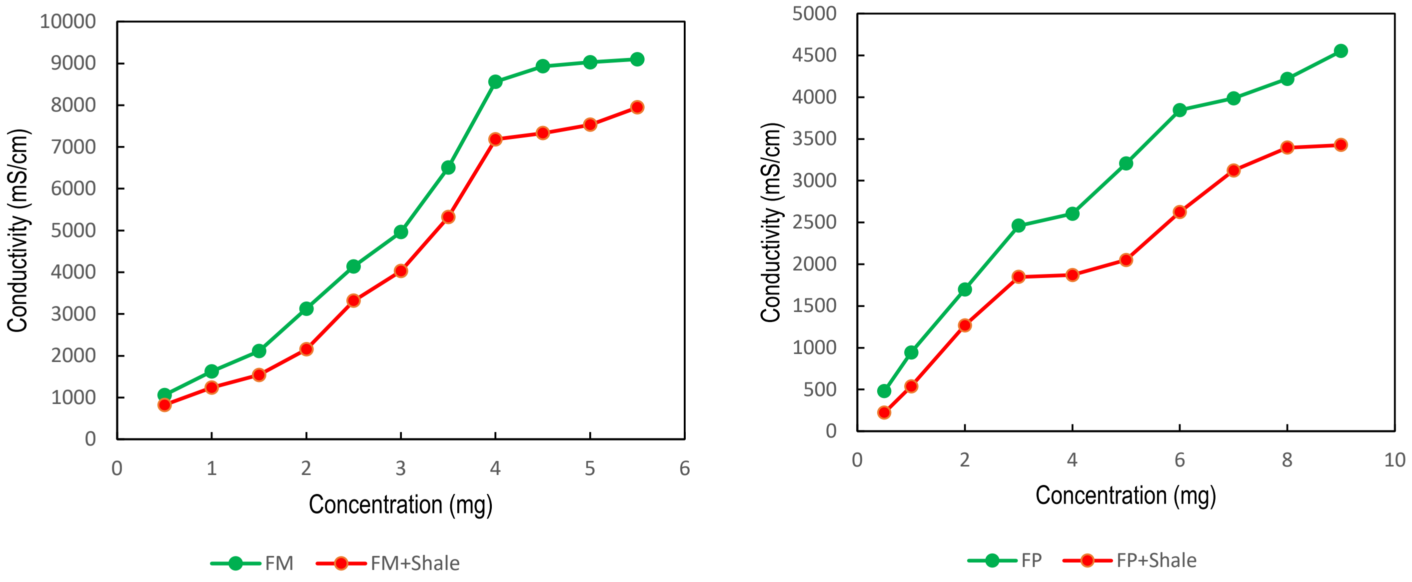


Figure 5.9: Variation of conductivity in different surfactant concentrations in the presence of the shale samples

The results obtained showed a decrease in conductivity before the CMC point. It was also observed that the adsorption of surfactants increases with increasing concentration after the CMC point due to the formation of micelles and availability of large clay surfaces for interaction.

The next step was to measure the conductivity of the surfactant solutions in the presence of shale at different temperatures. The measurement methods were the same as previously described, only the temperature was changed to evaluate its influence on the amount of surfactant adsorption and conductivity.

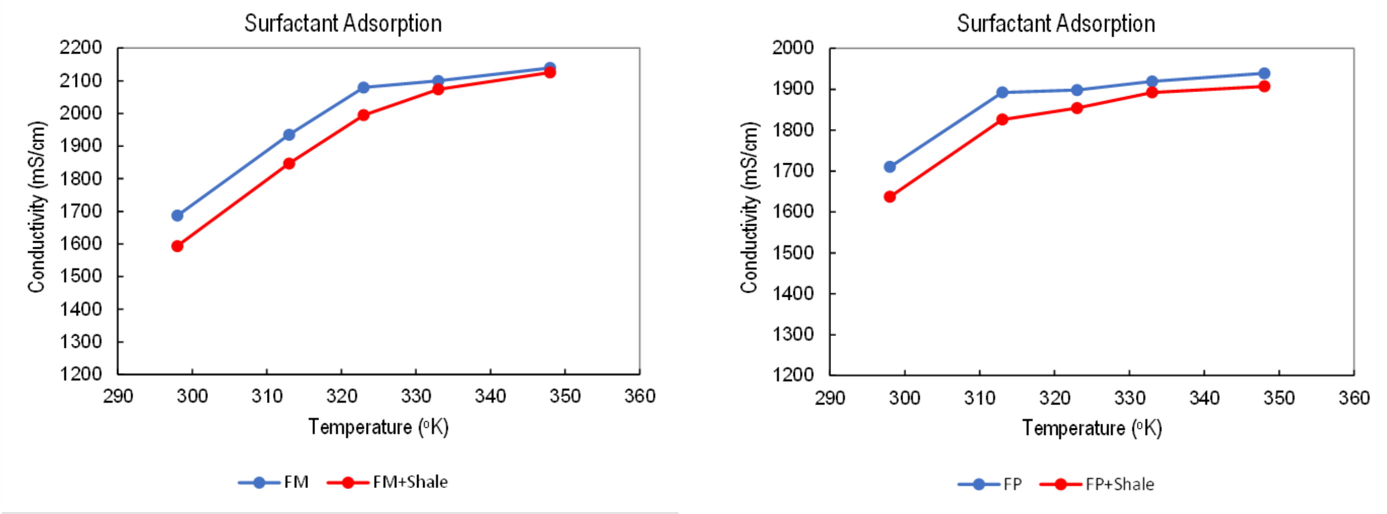


Figure 5.10: Variation of conductivity in different temperatures in the presence of shale

As can be seen from Figure 5.10, the difference in conductivity between the surfactant solutions in the presence and absence of the shale samples was not very large, indicating little adsorption of the surfactants on the shale surface. Furthermore, the adsorption of the surfactants would decrease at higher temperatures, which could be due to an increase in the kinetic energy of the ions in the solutions. It should also be noted that the presence of shale/clay in the solution increases the conductivity of the solutions. This suggests that the adsorption of the surfactants on the shale surface is much more significant than the conductivity measurements suggest. However, complete loss of adsorption was not observed, indicating the use of both FM and FP surfactants.

5.4.8. Shale Dispersion of Drilling Fluid

In general, shale formations are strongly associated with water molecules. Therefore, appropriate shale inhibitors have been introduced into water-based drilling fluids to prevent or minimise the interaction between drilling fluid and shale. This is done by reducing the permeability of the shale around the borehole by plugging the pore closures that can impede the flow of water from the borehole into the formation.

To evaluate the effectiveness of the surfactants and nanoparticles in reducing the interaction of shale with water, a dispersion test was conducted. Inhibition was evaluated based on hydration, dispersion and decomposition in the drilling fluid, using API's recommended standard procedure for water-based muds. The test involves exposing a measured amount of shale samples to the formulated drilling fluid containing surfactants and modified nanoparticles. The performance of KCl, a conventional shale inhibitor used as a reference, was also studied for comparison purposes. For the test, the shale samples were mixed with the prepared solutions under magnetic stirring at 70°C for 6 hours. At the end of the tests, the shale samples were removed from the solution using a sieve with a mesh size of 23 mm. They were then washed, weighed and dried at 80°C for 1 hour to assess the potential decay induced by the different solutions. The percentage difference was calculated based on the weight before and after the dispersion test. The results obtained are shown in Table 5.8.

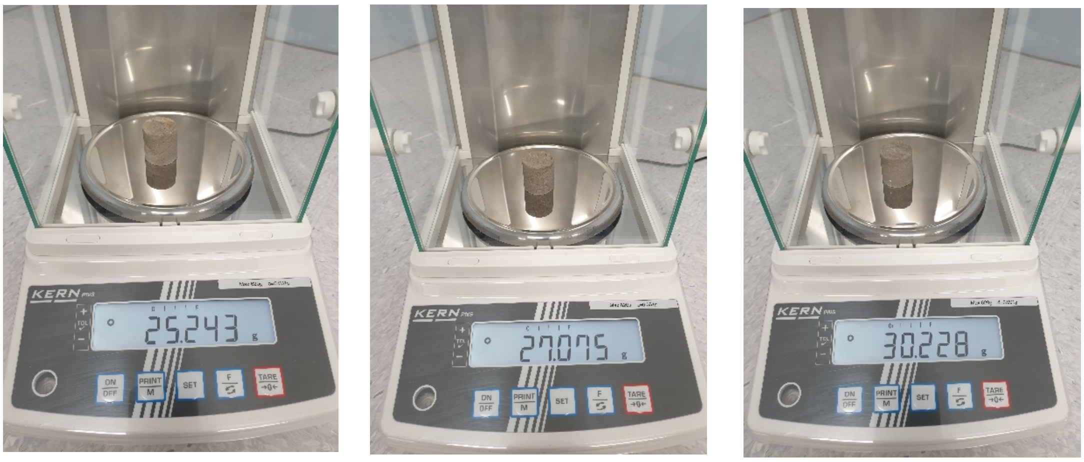


Figure 5.11: weighting of the shale samples

Table 5.8: Results obtained from shale dispersion test

Test fluid	Initial weight (g)	Shale recovered (g)		% Shale recovery	Mud filtrate Absorbed (g)	% Mud Filtrate absorbed
		Wet weight (g)	Dry weight (g)			
BM	27.07	18.65	11.26	44.62	7.39	39.62
KCL	25.24	19.82	16.21	64.22	3.61	18.21
FM	30.22	22.08	19.84	65.65	2.24	10.14
FP	26.67	19.49	15.29	57.33	4.20	21.54
NS	26.35	20.07	18.53	70.32	1.54	7.67
NGF	25.49	19.41	16.67	65.39	2.74	14.11
FM + NS	**30.01**	**25.07**	**23.68**	**78.90**	**1.39**	**5.54**
FP + NS	27.73	22.25	19.68	70.97	2.57	11.55
FM + NGF	**26.90**	**22.75**	**21.63**	**80.40**	**1.12**	**4.92**
FP + NGF	25.68	20.97	18.78	73.13	2.19	10.44

As can be seen in Table 5.8, the shale samples exposed to the base mud underwent severe hydration and ended with a low recovery of 44.62. On the other hand, relatively good recovery of the shale was observed in the mud sample with KCl, surfactants and nanoparticles. Surfactants were found to be able to adsorb on the surface of clays and reduce their affinity to interact with water. In this context, FM with its gelling properties forms a thin layer around the clay, while FP with its positive surface charge adsorbs on the clay surface. Both can therefore have a positive effect on the interaction of water with clay. Nanoparticles, on the other hand, once added to the base liquid, can clog the nanopores in the structure of shale/clay and reduce the penetration of water and subsequent hydrogen, thereby reducing the swelling and disintegration of clay in solution. Combining the action of surfactants and nanoparticles, as indicated in the table, can further reduce the interaction of clays with water, improving the integrity of the shale in the water-based slurry.

5.4.9. Bentonite Inhibition Test

Clays, especially smectite, montmorillonite and bilayer illite, are sensitive to water. So as soon as they come into contact with water, they begin to expand (swell), which causes many problems when drilling, including major problems with wellbore instability. This hydration (expansion) can be prevented by encapsulating the clays in a process known as stabilisation. Stabilisation can be achieved by exchanging ions on the surface of the clay, closing pore openings or manipulating the water affinity of the clay structure. This is where the shale/clay inhibitors come into play. In this study, we evaluate the performance of our surfactants and modified nanoparticles as shale inhibitors through a bentonite dispersion test.

The bentonite inhibition test evaluates the effectiveness of the additive used against the swelling of clay in an aqueous state. Bentonite contains a large amount of smectite and can represent sensitive clays/shales in subsurface layers. In the test, 5 grammes of bentonite was added incrementally to 500 ml of base drilling fluid and the changes in rheological parameters over time were assessed. During the test, the drilling fluid was gradually mixed with bentonite and aged at 60^{o}C and room pressure. The process of adding bentonite to the mud sample continued until the mud sample became too viscous.

The shale inhibitors used in this study focused on ion exchange and clay particle coating. The ion exchange technique used 2 grammes of potassium chloride (KCL) as one of the shale inhibitors. Due to the physical properties of the KCL molecules, the K^+ ions can perfectly insert between the clay lattice and the planar surface of the clay. This significantly reduces the attraction of the clay platelets to water molecules.

Surfactant-modified nanoparticles (nanosilica and nano-glass flakes) were considered for coating the clay particles. Although these nanomaterials are smaller than the K ions, they could seal the pores of clays and thus reduce the penetration of water. The results of the bentonite dispersion test are shown in Figure 5.12. and Table 5.9.

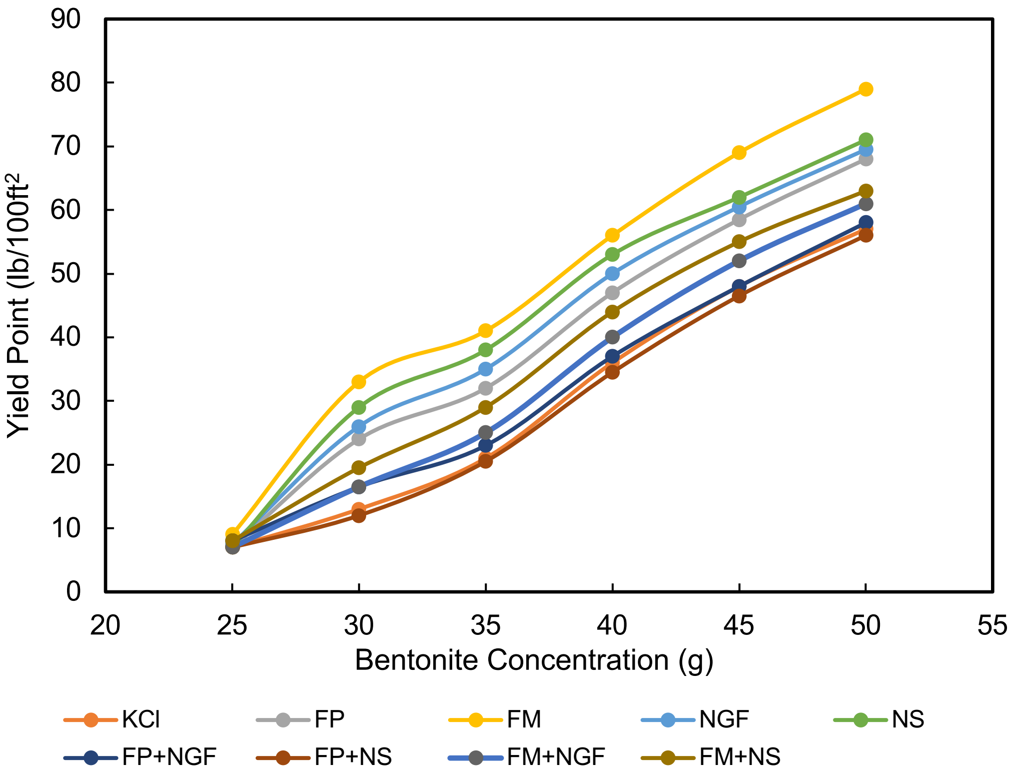


Figure 5.12: The yield point of different mud samples during the bentonite dispersion test

Table 5.9: The results of the bentonite dispersion test on different mud samples

Sample name	**YP (lb/100 ft^2)**					
	25g bentonite	30 g bentonite	35 g bentonite	40 g bentonite	45g bentonite	50g bentonite
BM	8	17	38	68	135	-
KCl	7	13	21	36	48	57
FM	7	24	32	47	58.5	68
FP	9	33	41	56	69	79
NGF	7.5	26	35	50	60.5	69.5
NS	7	29	38	53	62	71
FP+NGF	8	16.5	23	37	48	58
FP+NS	**7**	**12**	**20.5**	**34.5**	**46.5**	**56**
FM+NGF	7	16.5	25	40	52	61
FM+NS	8	19.5	29	44	55	63

The results obtained from the yield point value of the different samples showed an increase with gradual addition of bentonite. A total of 50 grammes of bentonite was added to the initial sample and any further addition of bentonite was delayed as the mud sample was too viscous. KCL was found to maintain yield point values and prevent the increase in rheology over time compared to the base mud. However, surfactants were not able to perform as well as KCL, but showed some potential to reduce the interaction of clays with water due to their gelling properties and surface charges. Nanoparticles also showed some potential in reducing clay hydration but could not match the performance of KCl. However, the combination of nanoparticles and surfactants (modified nanomaterials) appeared to be an effective method for reducing water-clay interaction during drilling. When the surfactant and nanoparticles enter the solution, they can cause both ion exchange and encapsulation so that the clays do not have access to the water for hydration.

5.4.7. Wettability Alteration

To investigate the change in wettability caused by the surfactants, the contact angle between the surfactant-modified mud samples was measured using the Kruss Drop Shape Analyser model DSA 100B. The mud samples were injected into the instrument using a syringe and a needle with an outer diameter of 0.5 mm. The sessile drop method was used for the contact angle measurements. The process of measurements was repeated 3 times to obtain a consistent and accurate result. Figure 5.13 and Table 5.10 shows the results of the contact angle measurement.

Table 5.10: Contact angle measurements for the base mud and the mud modified with the surfactants

Sample	Advancing Contact Angle	Receding Contact Angle
Base mud	38.8	42.7
Base mud	39.1	41.5
Base mud	40.3	42.1
Modified mud with FM	63.2	68.1
Modified mud with FM	64.1	69.9
Modified mud with FM	66.6	70.4
Modified mud with FP	57.2	61.7
Modified mud with FP	57.9	62.4
Modified mud with FP	59.2	64.8

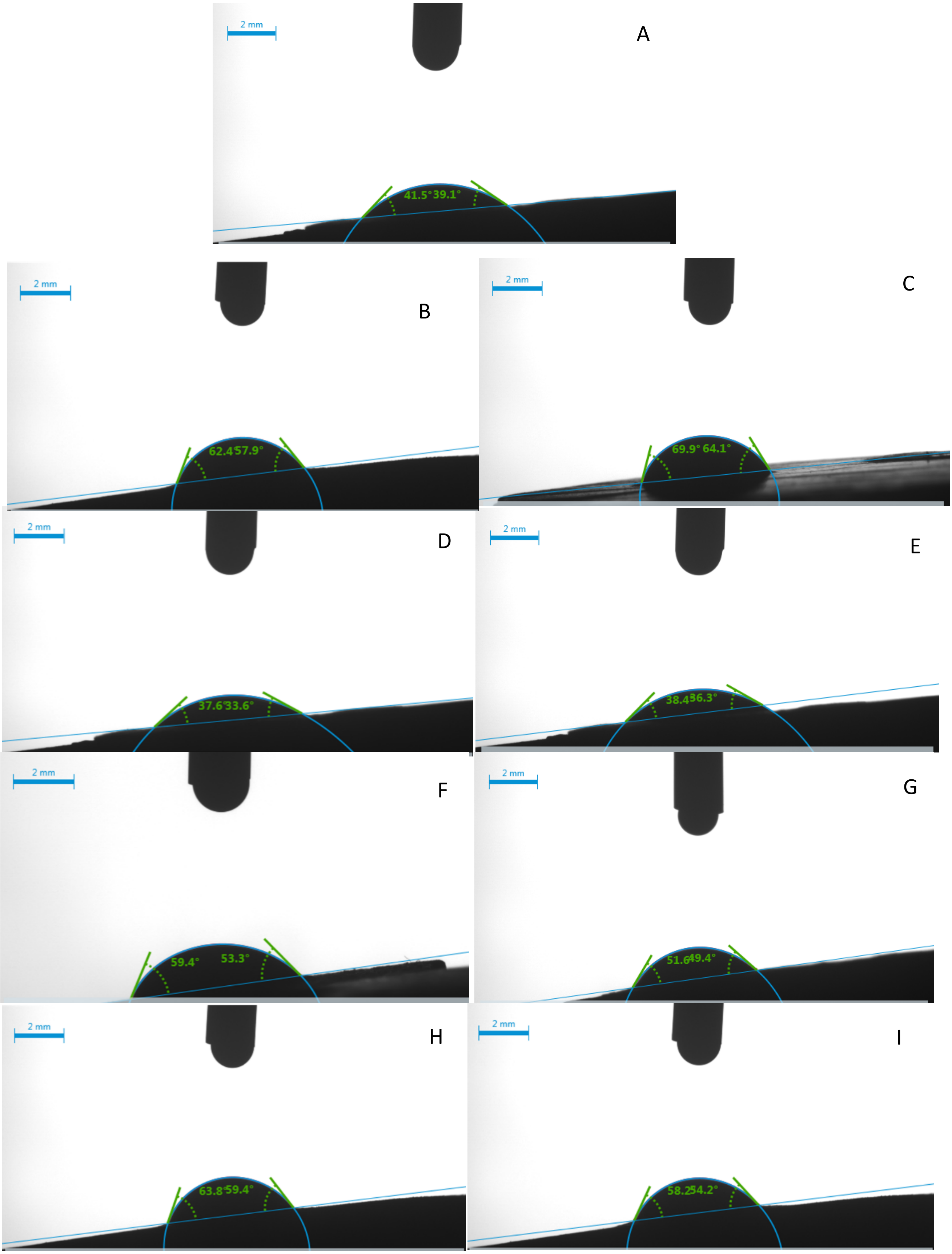


Figure 5.13: Contact angle measurements between shale and the base mud (A), mud sample with FP (B), FM (C), NS(D), NGF (E), FP+NGF (F), FP+NS (F), FM+NGF(H), FM+NS (I)

As can be seen in Figure 5.13 and Table 5.10, the advancing contact angle of the base slurry with shale is about 39°, which increases to 57.9° and 64° for FP and FM respectively. Addition of nanoparticles would decrease the contact angle to 33.6° and 36.3° for NS and NGF, respectively. After the addition of modified nanoparticles with FP, the contact angle increases to 53.3° and 49.4° for the modified NGF and NS. The contact angle for the modified nanoparticles with FM increases to 59.4° and 54.2° for NGF and NS, respectively. It seems that the surfactants and modified nanoparticles can create a hydrophobic surface. This can reduce the interaction of clays with water and improve the skin damage caused by the swelling of the shale.

5.5. Discussions on Potential Inhibition Mechanisms

5.5.1. Flaxseed Mucilage

Many mechanisms have been proposed to explain how surfactants can act as shale inhibitors and reduce surface hydration by altering surface wettability (e.g., Hajibagheri et al. 2016; Kiani et al. 2018; Ghasemi et al. 2019; Lim et al. 2020). Comparing the results obtained from this study with those in the literature, it appears that the FM can adsorb on the surface of clays and reduce hydration by encapsulation, as schematically shown in Figure 5. 14. This encapsulation occurs through the formation of a hydrogen bond between the hydrophilic tail of FM and the oxygen atoms on the silica surface of the clay which result in the formation of a hydrophobic film on the surface of the clay, preventing further interaction of the clay with water (See Figure 5.15).

Figure 5.14: A schematic diagram showing the encapsulation of clays by the formation a hydrophobic film around the clay surface (Liu et al., (2019) is unable to be reproduced here due to copyright restrictions. The content can instead be accessed via https://doi.org/10.1021/acs.energyfuels.9b00637)

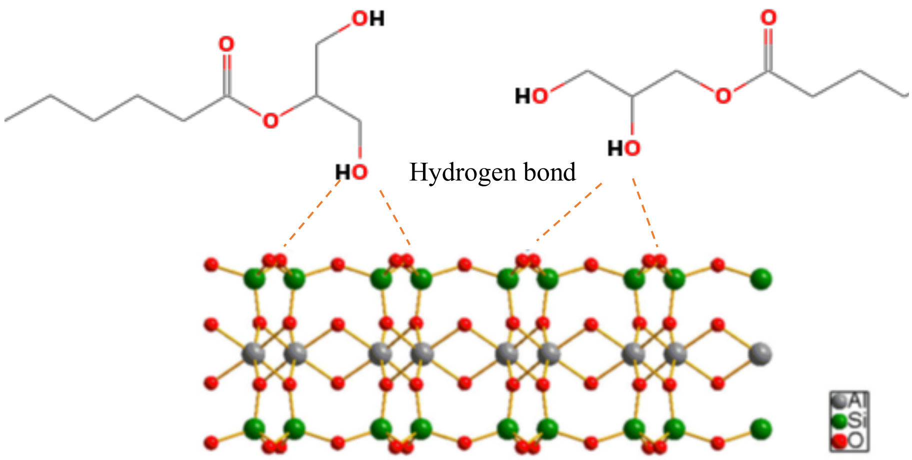


Figure 5.15: A schematic diagram showing how the hydrogen bond between FM and clay can be formed and prevent hydration and swelling

5.5.2. Flaxseed Protein

Cationic surfactants such as FP can act as low molecular weight amine-based inhibitors and reduce clay hydration by adsorbing on the surface of a negatively charged clay (montmorillonite, double layer illite, bentonite, etc.) (Chen et al., 2017., Zhang et al., 2019b). In fact, FP can exchange ammonium with bentonite and adsorb on the surface of clay due to electrostatic adsorption and hydrogen bonding, which can block the entry of water into the clay lattice (See Figure 5.16)

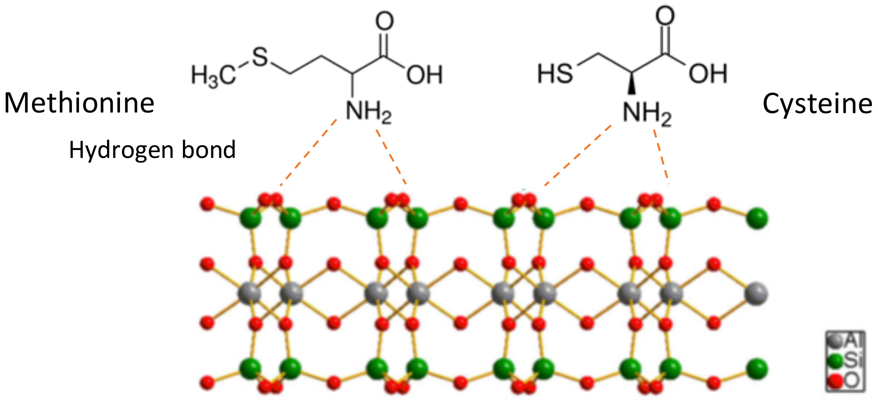


Figure 5.16: A schematic diagram showing how the hydrogen bond between FP and clay can be formed and prevent hydration and swelling

5.5.3. Modified Nanomaterials

Modified nano-silica and nano-glass flakes can be embedded in the pores and cracks of the shale under the pressure of the drilling fluid and inhibit fluid flow into the clay layers. Once modified with surfactants, they can also be absorbed into the clay surface through hydrogen bonds and further reduce clay hydration. Figure 5.17 shows how nanomaterials in combination with surfactants can reduce clay hydration.

Figure 5.17. A schematic diagram showing how nanomaterials can reduce hydration in combination with surfactants (Xu et al., (2018a) is unable to be reproduced here due to copyright restrictions. The content can instead be accessed via https://doi.org/10.1016/j.petrol.2018.01.007)

5.5. Conclusions

In this chapter, an attempt was made to evaluate the changes in the properties of Water Based Muds (WBMs) after they were modified by the surfactants and nanomaterials. A series of tests. The results obtained indicated that FM and FP can improve the rheology and filtration control of the mud samples and increase the functionality of the nanomaterials. The combination of surfactants and nanomaterials could also reduce clay hydration and improve well stability. It was also found that the surfactants can alter surface wettability and make the clay surface hydrophobic, which can reduce clay swelling. Further testing is recommended to validate the results of this study.

Chapter 6: Conclusions and Recommendations

6.1. Conclusions

In this work, two surfactants were extracted from the hull and flour of flaxseed. An efficient method was developed, which allows a cost-effective extraction. After the extraction process, various tests were conducted to characterise the surfactants and investigate their applications as an effective additive to improve the rheological properties, clay inhibition and filtration control of WBMs under different temperature conditions. The results obtained from the conductivity measurements at different temperatures showed that the surfactants have high survivability and functionality under the reservoir conditions. The zeta potential measurements revealed that FP is a cationic surfactant with an average zeta potential of 44 mV at pH 6, whereas FM has a surface charge of -8 mV. It was also revealed that the organic functional groups in the structure of flaxseed mucilage are mainly esters, while the organic functional groups of flaxseed protein were cysteine and methionine. Thermal gravimetric analysis (TGA) performed on both surfactants from 30°C to 700°C with a rate of 10°C/min showed that the surfactants have good thermal stability at higher temperatures. It was also observed that the pH of the solutions with surfactants can go down to 5.5, indicating a relatively weak acidic environment. The mud rheology was also improved, and the filtration loss significantly decreased by as much as 40% once the flaxseed surfactants were added to the mud samples. The results of the bentonite dispersion and shale inhibition tests also showed that the surfactants can be combined with nanoparticles to achieve an encapsulation in which the clay loses its tendency to interact with water. It appeared that surfactants could make the shale surface less hydrophilic. This can help to reduce clay swelling in the shales and reduce skin damage in the reservoir intervals.

6.2. Recommendations

Green surfactants seem to be a good choice to improve the stability of WBMs in shaly intervals under temperature conditions. Further studies are recommended to evaluate other potential green surfactants that can be used for similar purposes.

There are other surfactant extraction methods that were not tested in this study. Further studies are recommended to develop effective extraction methods that can improve the yield of the final surfactant. There are other effective but still unknown nanoparticles that may also be able to enhance the functionalities of WBM even better than NGFs and NS. More research is needed to show the potential applications of these nanoparticles.

Many other shale hydration tests, including linear swelling tests, can be done to confirm the application of the FP and FM surfactants. These tests could not be conducted in this study as the relevant equipment was not available. It is recommended that the performance of FP and FM as shale inhibition be further investigated.

The change in wettability was assessed in this study by measuring the contact angle, while there are other approaches such as USBM and Amott that can also assess the change in wettability. It is recommended to evaluate the efficiency of FP and FP in altering the surface wettability by these approaches.

Considering the use of flaxseed and the wide application of its oil in various industries, this study has attempted to utilise the part of the flaxseed that is often considered as waste. This will significantly reduce the cost of using flaxseed for surfactant extraction. However, an in-depth techno-economic analysis is recommended to evaluate the feasibility of extracting surfactants from flaxseed.

The results obtained from the filtration tests of different mud samples showed that the surfactants alone or in combination with nanoparticles can reduce mud loss. However, the tests were conducted under low pressure and temperature conditions. It is therefore recommended that a series of filtration tests be conducted under high pressure and temperature to confirm the results of this study.

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