Improvement of Nanoparticles Surfaces for Defining Water/Crude Oil Interface

By

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Supervised by

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CERTIFICATION OF APPROVAL

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Approved by,

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TRONOH, PERAK

May 2014

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(UMAR ISLAM BIN MUHAMMAD DIMYATI)

Acknowledgement

First and foremost I would like to express my thanks to Almighty God on successful completion of this project and report. This dissertation is a milestone in my academic career. I have been fortunate to learn theories, concepts and apply the engineering knowledge that I have learnt through this project. I hereby, express my sincere and profound gratitute to my Final Year Project supervisor, Professor Dr. Mariyamni binti Awang for her continuous assistance, support, guidance and understanding throughout the successful completion of my FYP. Her trust, patience, guidance and leadership had been a good inspiration and motivation for me and lead to a successful completion of my FYP.

Last but not least, I would like to express my gratefulness to my colleague, family for being very reassuring and giving me a plenty of guidance to compete this prestigious program successfully. Their presence is highly respected. The entire platform certainly brought us together to raise the value of friendship and family.

Abstract

Modification of Zinc Oxide surface was conducted using Oleic Acid coating and Silica Dioxide coating. After the completion of surface modification, the nanoparticles are evaluated using Zeta Potential measurement to verify the successfulness and the stability of surface-modified nanoparticles. The nanoparticle Zinc Oxide was chosen to be the base for the coating because it has been proven from previous experiment to aggregate best at the interface when is compared with other metal oxides nanoparticle, but may still needs improvement to improve its stability at the interface. The purpose of this experiment is to study the possibility of the surface-modified nanoparticles to aggregate at the water/crude oil interface using different type of crude oil. The crude oil use in this experiment is consists of Miri light crude oil, medium crude of Kikeh Crude and heavy crude oil Castilla Crude. Additionally, this research will help explore the possibility to assist the monitoring of the formation flood front. Using resistivity as one of the parameter would help in the monitoring of the nanoparticles to identify the absence and presence of the nanoparticles at the flood front. Unfortunately, the finding did not produce the expected result. There was little aggregation at the water/oil interface and the resistivity measured was not significant in comparison with previous experimentation. However, this study has help to see the relationship of zeta potential to the aggregation at the water/crude oil interface and the behaviour of surface-coated nanoparticles in different type of crude oil.

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Abbreviations and Nomenclature

EOR = Enhanced Oil Recovery

FESEM = Field Emission Scanning Electron Microscope

NdF3 = Neodymium Fluoride

NP = Nanoparticles

OA = Oleic Acid

SCIP = Sample Core IP Tester

SEM = Scanning electron microscope

SiO2 = Silica Dioxide

TEM = Transmission electron microscopy

ZP = Zeta Potential

ZnO = Zinc Oxide

Chapter 1: Introduction

1.1 Background

Nanoparticle is not an uncommon technology in this era, however it is relatively new to the oil and gas industry. In the oil and gas industry, nanoparticles are used in enhanced oil recovery (EOR) or drilling fluid additives. Due to the uniqueness of nanoparticles in term of size, optical, magnetic, mechanical, electrical and chemical properties it has become an essential material for the industries around the world In some applications of EOR it has proven to recover up to 50% of the residual oil.

Even with newer application of nanotechnology available, nanotechnology is still understudied and requires more research to unlock and enhanced its full potential in the oil and gas industry. This study is conducted to observe the interaction of different surface-modified nanoparticles at the water/crude oil interface and the ability of the surface-modified nanoparticle to sustain and stabilize at the interface.

Modification that is done towards nanoparticles surface usually results in a more increasing dispersibility of nanoparticles and reducing the agglomeration between the nanoparticles. This is not a preferable result that the author wishes to achieve. Based on Basa (2009) research, surface modification is attempting to add functionality or properties on top of a ready-functional nanoparticles base which will produced a hybrid structure and functionality of the particle. Based on previous experiment conducted, Zinc Oxide nanoparticles have been seen to be the best compared to other metal oxide to aggregate or stick at the water/crude oil interface but still several particles are still seen to disperse in the water media. With the known properties of Zinc Oxide that is incline to aggregate with the water/crude oil interface and with the surface improvement it is hope that it will further enhance and stabilize the aggregation. This research will be conducted on the basis to finding the surface improvement that will further improve the aggregation so it will stabilize at the interface.

1.2 Problem Statement

The amount of research and literature review available concerning the interaction of surface-modified nanoparticles at the water/crude oil interface is still very little and limited. Most of the research conducted on nanoparticles surface-modification is to control the dispersion and aggregation which is usually opposite the results that the author prefers which is to increase the aggregation and stabilization of nanoparticles at interface [Iijima et. al., 2009]. This study is aimed to help investigate the factors that contribute to the aggregation of nanoparticles at water/crude oil interface. Furthermore, there is also little or no experimentation on the effect of nanoparticles in different type of crude oil. In order to investigate further on the matter, these problems will be the basis of this study. Another difficulty that should be highlighted is the difficulties in monitoring the flood front, in which this study will help in the development of a tracer for the flood front. Studies in the effect of resistivity would also be conducted to investigate further the interaction with the surface-modified nanoparticles during the absence and the presence of the nanoparticles.

1.3 Hypothesis/Theory

The main hypothesis that has been establish for this study is that the modification of Zinc Oxide nanoparticle surface will help further improve the nanoparticles so that, it gives an improved aggregation at the water/crude oil interface. Additionally, the measure of resistivity changes in the absence and the presence of the surface-modified nanoparticles at the water/crude oil interface may assist in the possibility of tracking of the formation flood front.

1.4 Objectives and Scope of Study

This research has been attempted to study the possibility of the surface-modified nanoparticles to aggregate at the water/crude oil interface and to investigate the factors that contribute to the aggregation. Different surface modifiers have been used in the experiment to observe its interaction to the interface.

The objectives of this study are:

1. To observe the interaction of nanoparticles at the water/crude oil interface of surface-modified nanoparticles in different type of crude oil

2. To evaluate the synthesized surface-modified nanoparticle for analyzing the stability of the surface-modified nanoparticles.

3. To measure the resistivity at water/crude oil interface in the presence and the absence surfaced-modified nanoparticles for the development of a tracer for the flood front

1.4.1 Scope of study

The scope of the research covers in two parts which is first to study and observe the interaction of surface-modified nanoparticles at the water/crude oil interface in different type of crude oil and to measure the change of resistivity at the water/crude oil interface in the absence and presence of surface-modified nanoparticles. A single type nanoparticle is used in this experiment with two surface modifications.

Chapter 2: Literature Review

2.1 Waterflooding

Waterflooding is a method in which the use of water injection to displace the residual oil from the reservoir formation. The method is usually conducted after the completion of primary production. However, increasing production and injection rates may lead to a water breakthrough which will increase water cut and will result in reduction of oil recovery [Xu et. al., 2013].

Therefore, it is important to track the waterflood front to help identify the problem before it occurs. Nanoparticle has been seen to have a potential to act as a tracer to the waterflood front. The tracing of the magnetic contrast agents could have the potential in helping illuminate a waterflood and the tracking of the waterflood front [Rahmani et. al., 2014].

2.2 Surface Modification of Nanoparticles

A definition given by Basa (2009) on surface coating on nanoparticle, "When a core nanoparticle is coated with a polymeric layer or an inorganic layer like silica because the polymeric or inorganic layer would endow the hybrid structure with an additional function/property on top of the function/property of the core hence synergistically emerged functions can be envisioned". The realization on the potential of nanoparticle has given nanoparticle the highlights of nowadays research.

Nanoparticle that have large surface area-to-volume ratio tends to agglomerate to reduce their surface energy [Vayssières et. al., 1998]. For this particular reason magnetic nanoparticles need to be surface-coated by surfactants to increase the steric repulsion between each particle as the particles approach one another. Oleic acid is one of several type of surfactant used to modify the surface of magnetite particles. According to Wu et. al., (2003), supported by the research of Kataby et. al., (1998), the surfactant modifier oleic acid is often used on magnetic nanoparticles because the higher affinity to the surface of superfine magnetite compared to other surfactants. The hydrophobic tails of the Oleic Acid molecules will face outwards forming a nonpolar shell. The shell that is from by the hydrophobic tails will ensure that the nanoparticles will not move into the water zone and hopefully will aggregate and stabilize at water/crude oil interface.

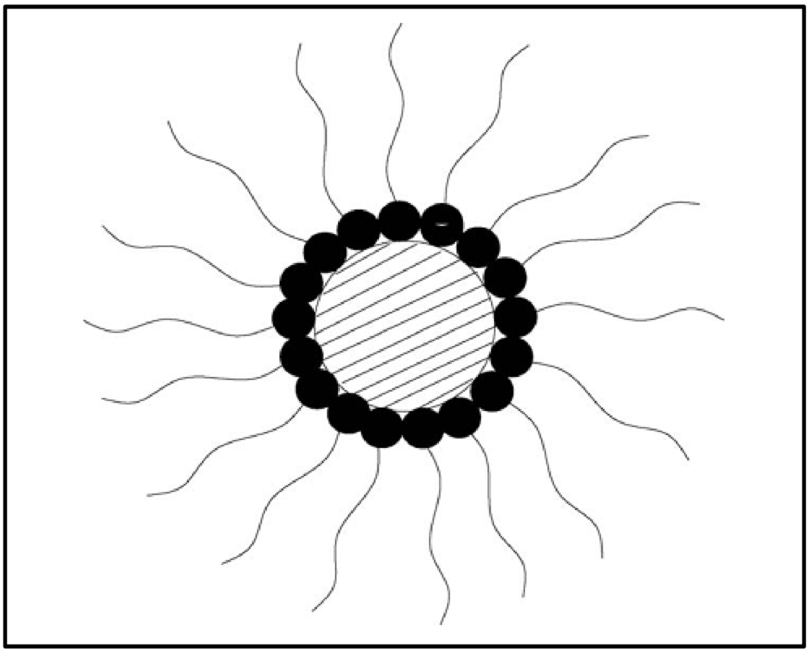

Figure 1: Structural model for oleic acid-coated Zinc Oxide Nanoparticles [Hong et. al., 2006]

The unique and different surface area of nanoparticles gives it an extremely high tendency to adhesive and aggregate to each other. Technique are develops to control the aggregation and dispersion to apply them into functional materials and product. Based on a research on the usage of polyethylene glycol surfactant as surface modifier on silica has shown a significantly decrease in the interfacial tension thus, stabilizing the dispersion [Metin et. al., 2012].

In an experiment using zinc oxide coated with silicon oxide was conducted [Hong et. al., 2006]. It found that the coating on the surface of zinc oxide has successfully improved the dispersibility and hence reduce the agglomeration of nanoparticles. However, according to an experiment on the synthesis of optically active silica-coated neodymium fluoride due to the silica-surface modification, the nanoparticles were found to aggregate to each other in ethanol solvent. Furthermore, the resulting silica surface modified NdF3 core–shell nanoparticles were not found to be well separated as observed by TEM [Ansari et. al, 2011]. The result of this modification has shown the possibility that it will help in the aggregation of the nanoparticles at the interface.

In the study of dissolution and aggregation of zinc oxide nanoparticles at circumneutral pH; A study of size effects in the presence and absence of citric acid, it shows in figure 2 on the fate of engineered nanoparticles once they are released to the environment [Rupasinghe, 2011]. The result that this study wishes to achieve is on the top right corner of the figure which shows a more stable dispersion and aggregation with less free nanoparticles. Moreover, in previous studies, zinc oxide has been seen aggregating to the water/crude oil interface better, in comparison with other metal oxides.

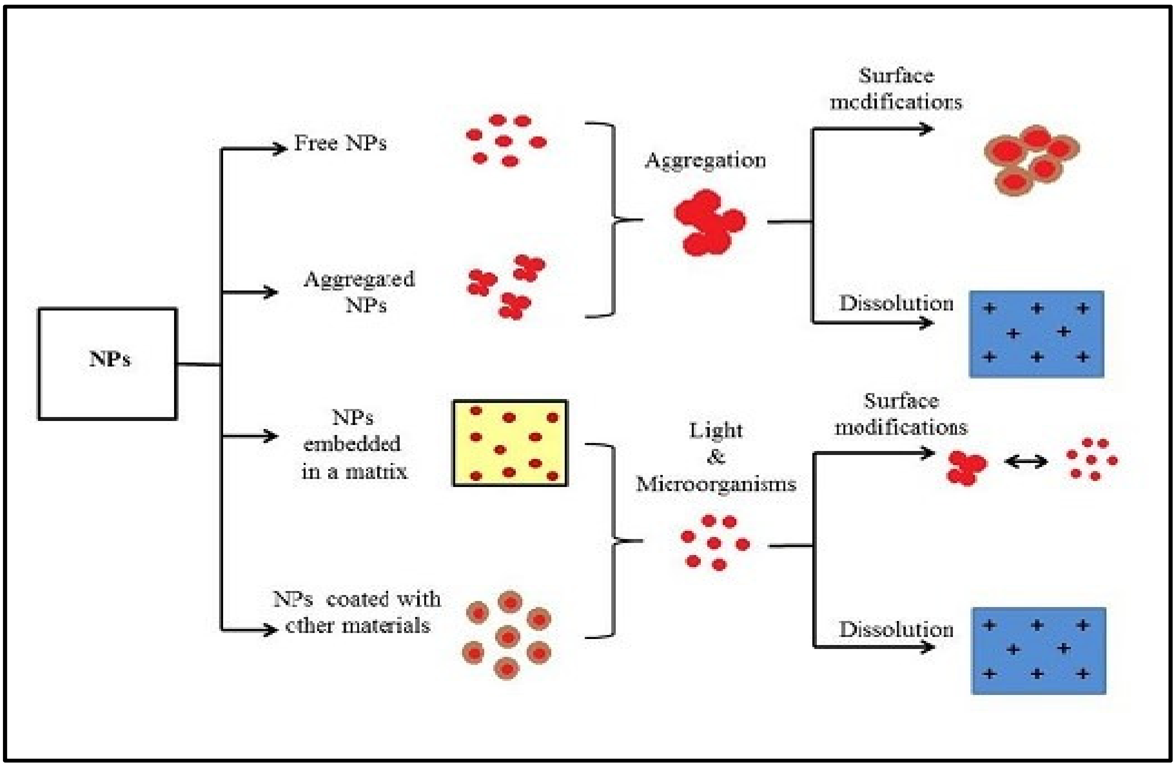

Figure 2: The fate of engineered nanoparticles once they are released to the environment [Basa, 2009]

The surface coating or modification of nanoparticle which enhance and stimulate the surface chemical and physical properties is the key for the understanding and successful applications of nanomaterials.

2.3 Concept of Resistivity

Resistivity is known in the oil and gas industry which comes in sets of tools in wireline-log method, in which to measure the absence and/or the presence of hydrocarbon. Since air or gas has lower conductivity, the readings in resistivity log will show a high reading. In oil there is also low conductivity which will show a higher reading than brine but lower than gas [Rider, 2002]. The illustration is shown in figure 3. This research will attempt to measure the resistivity at the water/crude oil interface in the absence and presence of surface-modified nanoparticle in which the interface will emulate the waterflood front during the secondary recovery in the application of the surface-modify nanoparticles.

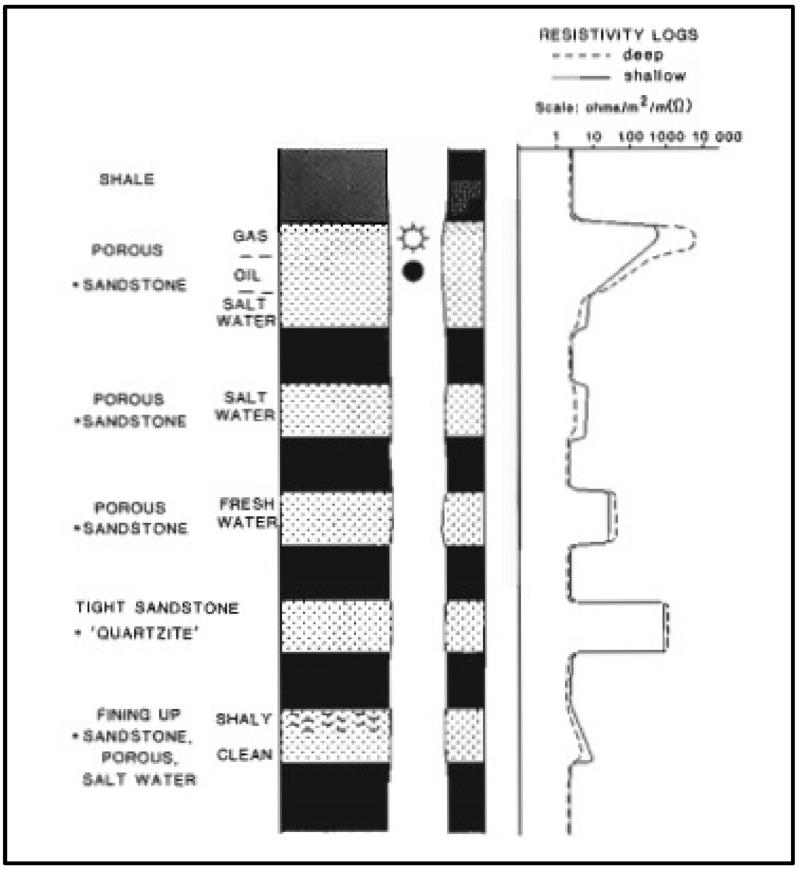

Figure 3: The illustration of resistivity log in a typical reservoir [Rider, 2002]

2.4 Zeta Potential

Zeta Potential is the measurement analysis in determining the surface charge of nanoparticles in solution or the proper term colloids. Nanoparticles have a surface charge that attracts a thin layer of ions of opposite charge to the nanoparticles surface. This double layer of ions travels with the nanoparticle as it diffuses throughout the solution shown in figure 4. The electric potential at the boundary of the double layer is known as the Zeta potential of the particles and has values that typically range from +100 mV to -100 mV [nanocomposix.com, 2012].

Due to the nature of this study which uses surface modification on nanoparticle. The need to measure its stability is with the new surface is a requirement. According to colloidal-dynamics.com (1999), a Zeta Potential more than +25mV or less than -25mV it said to have a high degree of stability and in surface modification it shows that the nanoparticles has been successfully modified.

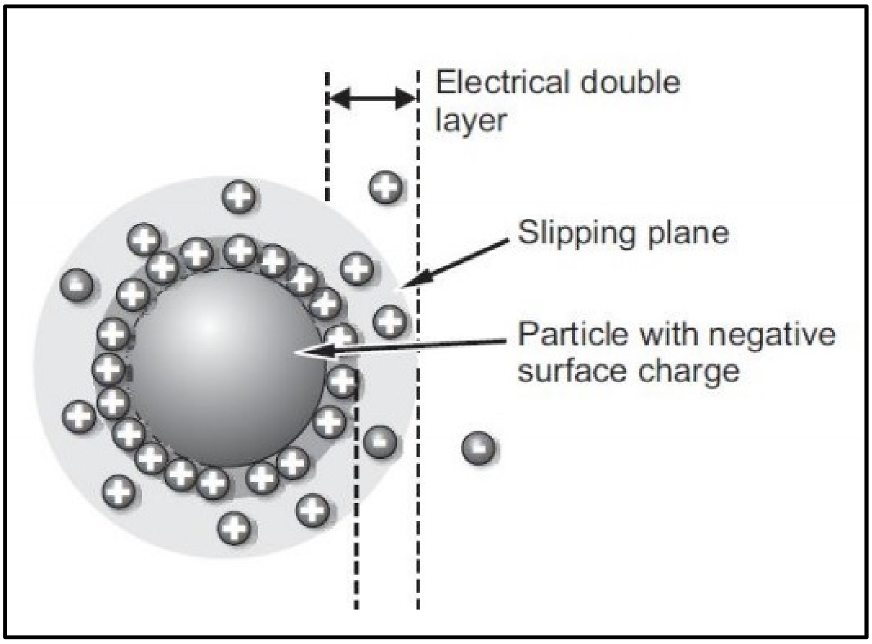

Figure 4: Electric double layer surrounding nanoparticle [nanocomposix.com, 2012]

2.5 Nanoparticles in Crude Oil

Studies of the affect nanoparticles in crude oils have been conducted usually to investigate how the nanoparticles would react in such fluid. A study by Shokrlu et. al. (2013) in their research in effect of nanoparticles in crude oil shows that the nanoparticles help in reducing the viscosity of the heavy crude oil. The study showed that at low temperatures, the metal nanoparticles reduces the heavy oil viscosity after it is mixed with the oil zone. The viscosity was reduced by the function of the concentration of the nanoparticles and there exists an optimum concentration of particles yielding maximum amount of viscosity reduction.

In another study by Pavia-Sanders et. al (2013), oleic acid-stabilized magnetic iron oxide nanoparticles is used to absorb crude oil. The nanoparticles were experimented as a purpose to be used for the removal of environmental pollutants if oil spilled would occur. From these two (2) papers, we may learn and may predict what might occur during the experimentation. Since, the factors that contribute to the aggregation are still unknown, it is best that we understand the relationship that helps in the aggregation of nanoparticles either by the fluid properties of the crude oil or the functionality of the nanoparticles itself.

2.6 Self-assembly of Nanoparticle at Water/Oil Interface

In a research conducted by Park et. al (2007) and Reincke et. al (2006), they suggested that certain metal oxide nanoparticles has the ability to destabilized which cause the nanoparticles to adsorb at the water/oil interface. The interactions of nanoparticle at the interface are dominated by three types of interactions, the types of interactions are as follows:-

i. The energy of the water/organic, water/particle and particle/organic interfaces in the system and the translational entropy of the particles at the interface

ii. Electrostatic repulsions between the colloids: the direct and screened Coulomb repulsions, and the dipole interactions between the incomplete double layer around the colloids

iii. The attractive Van Der Waals interactions between the colloidal particles adsorbed at the interface

Chapter 3: Methodology/Project Work

3.1 Research Methodology

Preliminary Research

Identify problem faced by industry, Basic understanding on fundametal concept and theories, Perform literature review.

↓

Planning

Critical planning on how to solve problem, conduct experiment and predict result.

↓

Preperation

Equipment and material avalibility for synthesising of sample and condcuting of experiment.

↓

Labaratory Work

Tracing aggregation of surface-modified nanoparticle at water/crude oil interface with suitable lab equipment.

↓

Analysis & Discussion

Analyze the observation and interaction. Discussion of results and findings of the lab experiment.

↓

Report Writing

Compilation of entire reseach, findings, literature review, experiment outcomes and result into finalize report.

3.2 Material and Equipment

The materials needed to conduct the research are as follows:

1. Oleic Acid Coated-Zinc Oxide Nanoparticles
2. Silica Oxide Coated-Zinc Oxide Nanoparticles
3. Crude oil
4. Brine water

Equipment use in the experiment:

Figures	Equipment
	Sample Core IP Tester • To help in measuring resistivity
	SurPASS Electrokinetic Analyzer for Solid Surface Analysis • To help in measuring Zeta Potential

Table 1: Equipment use in experiment

3.3 Methodology and Experiment

3.3.1 Modification of Nanoparticle Surface

Based on the paper Hong et. al., 2006, the following material, equipment are used to modify the surface of the nanoparticles. According to the paper, it has successfully achieved to modify the surface of Zinc Oxide using both Oleic Acid and Silica Dioxide coating.

I. Material

Oleic Acid Coating	Silica Dioxide Coating
1. Zinc Oxide Nanoparticles 2. Oleic Acid 3. Oxylene 4. Toluene	1. Zinc Oxide Nanoparticles 2. High Purity Water 3. Sodium Silicate 4. Dilute Sulphuric Acid 5. Deionized Water

Table 2: Material use in Nanoparticles Modification

II. Equipment

Oleic Acid Coating	Silica Dioxide Coating
1. Centrifuge 2. Heater 3. Retort Stand and Clamp 4. Stirrer 5. Oven (Vacuum) 6. Beaker 7. Flask 8. Measuring Cylinder 9. Weigher	1. Ultrasonicator 2. Heater 3. Stirrer 4. Thermometer 5. Retort Stand and Clamp 6. pH meter 7. Filter 8. Oven 9. Weigher 10. Beaker 11. Flask

Table 3: Equipment use in Nanoparticles Modification

III. Procedures

Oleic Acid Coating

1. Oleic acid was mix with O-xylene in flask to form the solution
2. Zinc Oxide was added to react for 1 hour at 50°C under stirring
3. The particles were collected by centrifugal separation
4. The collected particles were washed three (3) times with toluene
5. The particles were then dried (under vacuum) at 50°C

Silica Dioxide Coating

1. Zinc oxide was mix with high-purity water in a flask with vigorous agitation to form 20-30% (w/w) slurry
2. The slurry was stirred vigorously for 45 min
3. Then the slurry was agitated to achieve excellent dispersion of Zinc Oxide nanoparticles
4. Under the strong agitation, sodium silicate was added into the flask to set the pH value of slurry to 9.5
5. The slurry was heated and maintained at 85-90°C
6. Afterwards, sodium silicate solution was dropped again to make the ratio of silica to Zinc Oxide to be 2-3% (w/w)
7. Then the pH value was set to 8.5 using dilute sulphuric acid to make the silicic acid deposit on the surface of Zinc Oxide nanoparticles
8. The slurry was maintained at 85-90°C for 2 hours with vigorous agitation
9. The composite nanoparticles were collected by filtration and rinsed three (3) times with deionized water
10. The nanoparticles were dried at 100°C for 12 hours

3.3.2 Interaction at water/crude oil interface

In this part of the experimentation, surface-modified nanoparticle has been mixed with brine and crude oil in different containers to observe and monitor the interaction at the water crude oil interface. The methodology is a relatively simple experiment to observe the aggregation at the water/crude oil interface.

3.3.3 Resistivity Measurement

This method has been conducted using SCIP tester with the connection of two (2) copper rods using the equipment setup shown in the schematic in figure 5. The initial measurement of resistivity has been taken from the mixture of brine and crude oil with the absence of surface-modified nanoparticles and then preceded with the mixture of brine, crude oil with the addition surface-modified nanoparticles. The resistance is measured using the following parameters that can be found in the SCIP tester system:

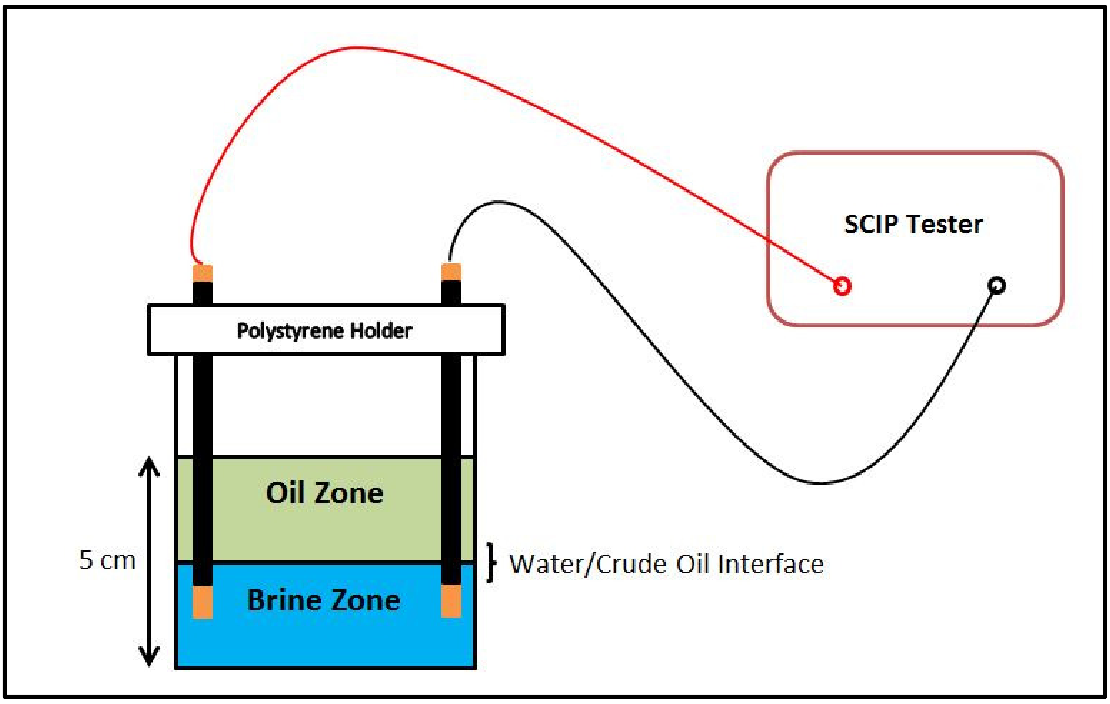

Figure 5: Schematic diagram of resistivity/resistance experiment setup

$$\boldsymbol{R = \rho\, l / A}$$

Where,

R = *resistance (ohms, Ω)*

ρ = *resistivity (ohm meter, Ω m)*

l = *length of conductor (m)*

A = *cross-sectional area of conductor* (m^2)

3.3.4 Zeta Potential Measurement

In the Zeta Potential measurement, the SurPASS Electrokinetic Analyzer for Solid Surface Analysis is used in conducting the measurement. The equipment use is fully automated, which may determine the Zeta Potential measurement accurately.

3.5 Gantt Chart and Key Milestones

No	Detail	FYP 1 Week No.								FYP 2 Week No.													
		8	9	10	11	12	13	14	15	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Preparation Surface-Modified Nanoparticles																						
2	Analysis of Surface-Modified Nanoparticles																						
3	Interface Experimentation																						
4	Resistivity Testing																						
5	Result Analysis and Discussion																						
6	Report Preparation																						

Table 4: Gantt Chart and Key Milestones

Chapter 4: Result and Discussion

4.1 Zeta Potential of Nanoparticles

4.1.1 Zeta Potential of Zinc Oxide without Coating

After the completion of the surface coating of the Zinc Oxide Nanoparticles using Oleic Acid and Silica Dioxide, the samples were sent analysis for the zeta potential to be measured including the Zinc Oxide Nanoparticles without coating. This is conducted to verified and evaluate for the successfulness of surface modifications. The first sample which was tested is the Zinc Oxide without coating as a base case to compare before and after the coating was done. This is to prove that the surface modification has been successfully applied.

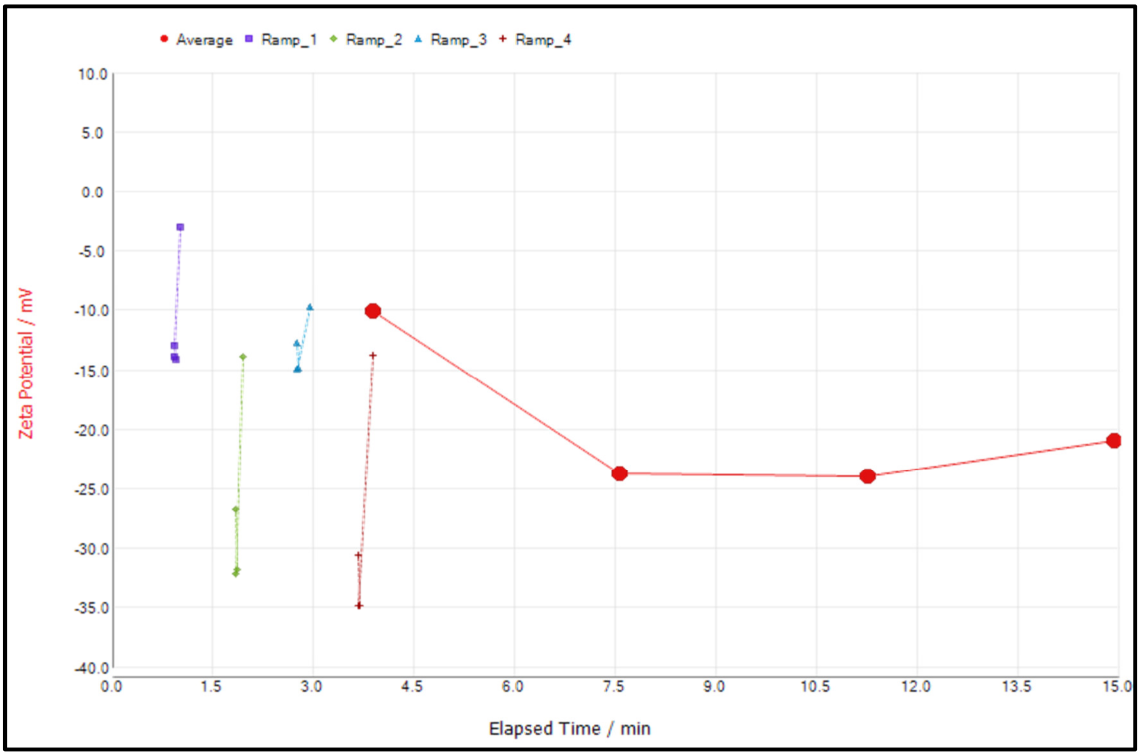

Figure 6: Zinc Oxide without coating Zeta Potential Result

Figure 6 shows the zeta potential of Zinc Oxide without coating measured using SurPASS Electrokinetic Analyzer for Solid Surface Analysis to obtain the plot. From the plot it is observe that the zeta potential has value range of -10mV to -24mV which will act as a base to compare and differentiate before and after the surface modification. The change will prove the successfulness of coating of the Zinc Oxide Nanoparticles.

4.1.2 Zeta Potential of Zinc Oxide with Silica Oxide Coating

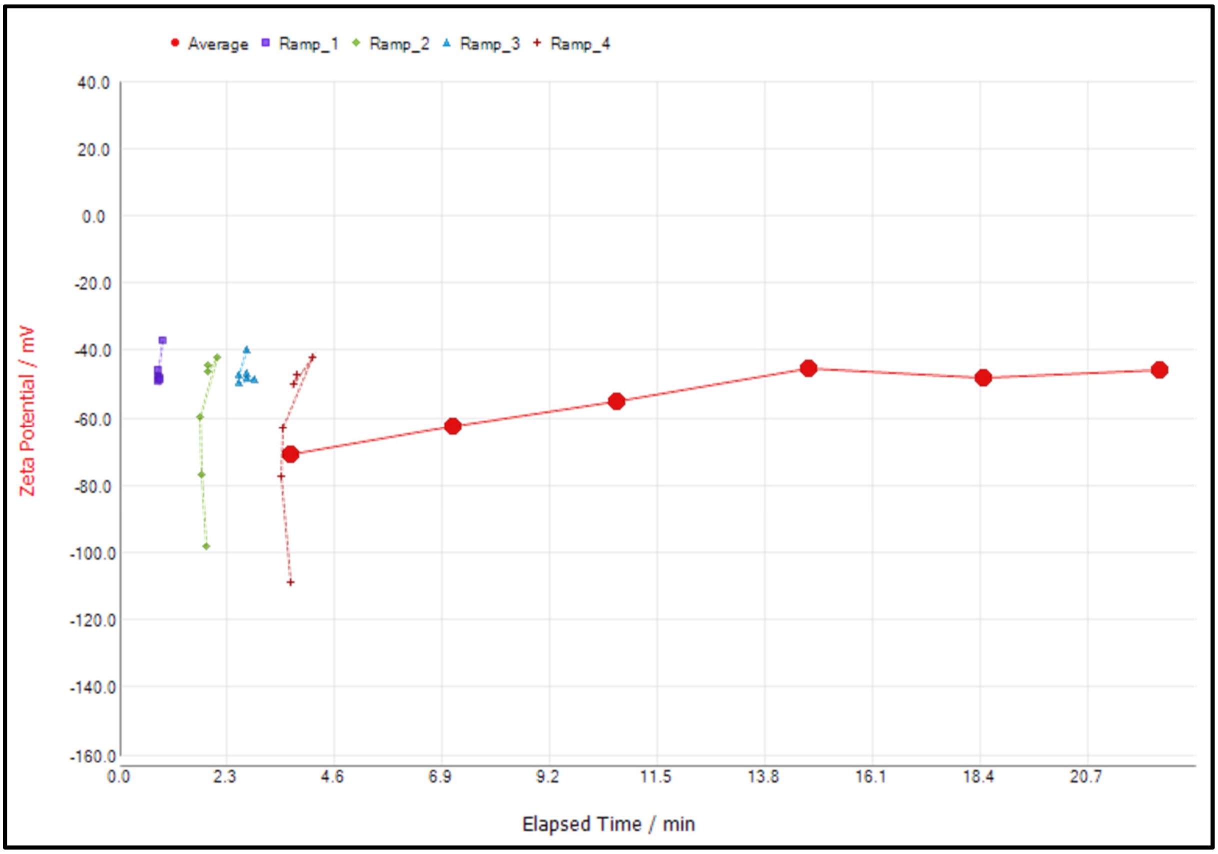

Figure 7: Zinc Oxide with Silica Dioxide Coating Zeta Potential Result

Figure 7 shows the zeta potential of Zinc Oxide with Silica Dioxide coating measured using SurPASS Electrokinetic Analyzer for Solid Surface Analysis to obtain the plot. From the plot it is observe that the zeta potential has value range of -45mV to -71mV which is evidence that the surface of the Zinc Oxide has been modified using Silica Dioxide.

4.1.3 Zeta Potential of Zinc Oxide with Oleic Acid Coating

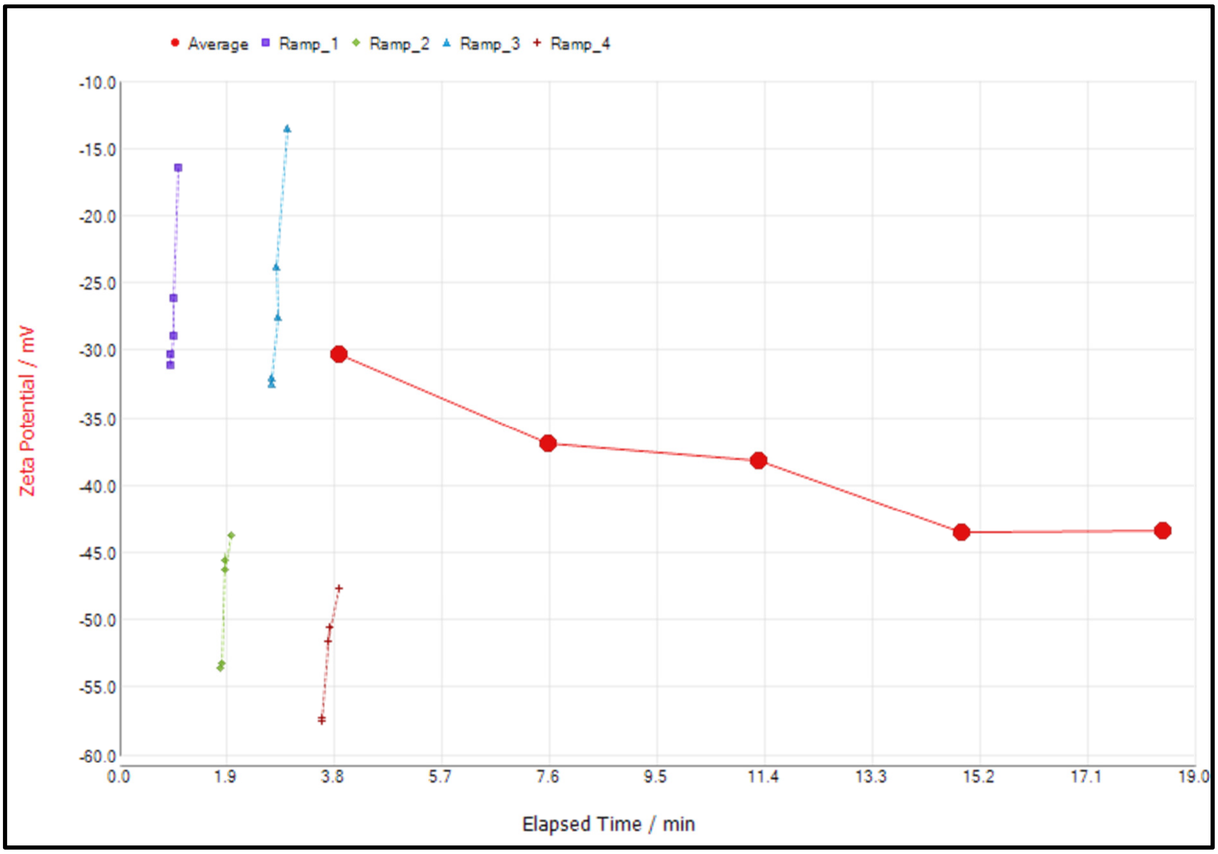

Figure 8: Zinc Oxide with Oleic Acid Coating Zeta Potential Result

Figure 8 shows the zeta potential of Zinc Oxide with Oleic Acid coating measured using SurPASS Electrokinetic Analyzer for Solid Surface Analysis to obtain the plot. From the plot it is observe that the zeta potential has value range of -30mV to -43mV which is evidence that the surface of the Zinc Oxide has been modified using Oleic Acid.

4.1.4 Hydrophobicity Tails of the Oleic Acid

Furthermore, the formation of the hydrophobic tails of the Oleic Acid molecules that is facing outwards forming a nonpolar shell can be seen when immersed with pure water. In figure 9 below, shows that the hydrophobic tail is preventing the Zinc Oxide from mixing with the pure water confirming the successfulness of the surface coating.

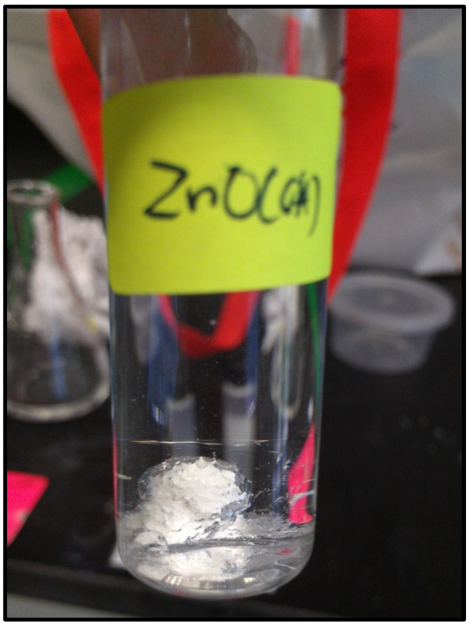

Figure 9: Zinc Oxide with Oleic Acid Coating Immerse in Pure Water

4.2 Observation Analysis

The surface-modified nanoparticles is mixed and stirred in a mixture of 30 000 ppm of brine and different type of crude oil. The types of crude oil use for the experimentation are Miri Light Crude Oil, Kikeh Medium Crude Oil and Castilla Heavy Crude Oil. Observation was done on the mixture particularly on the interface of the brine and the crude oil.

4.2.1 Observation Analysis on Mixture of Light Crude Oil with ZnO (OA)

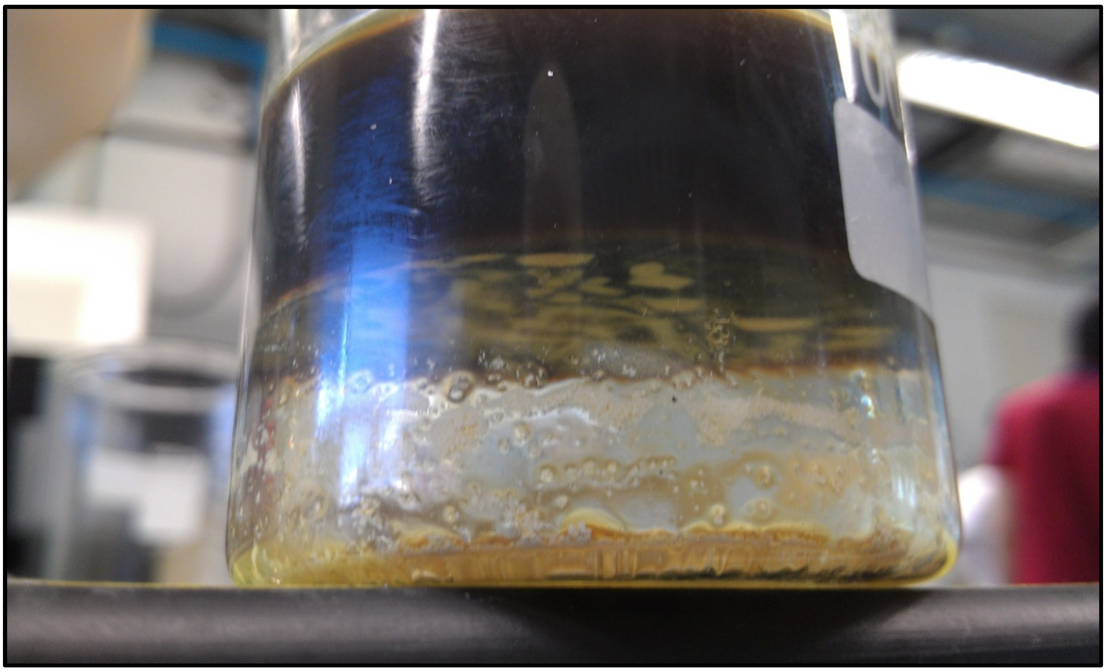

Figure 10: Mixture of Light Crude Oil with ZnO (OA)

Figure 10 shows the observation done at the interface of the mixture of 0.5 wt% Zinc Oxide coated with Oleic Acid in light crude oil. From the observation, it can be seen that some of the nanoparticles shows a positive aggregation at the interface. However, in the brine zone it is also observe that some of the nanoparticles does not aggregate to the interface, either sticking to the walls of the beaker or remaining at the bottom of the beaker. In comparison with previous studies, this mixture did not produce any monolayer as reported in the previous experimentation.

4.2.2 Observation Analysis on Mixture of Light Crude Oil with ZnO (SiO2)

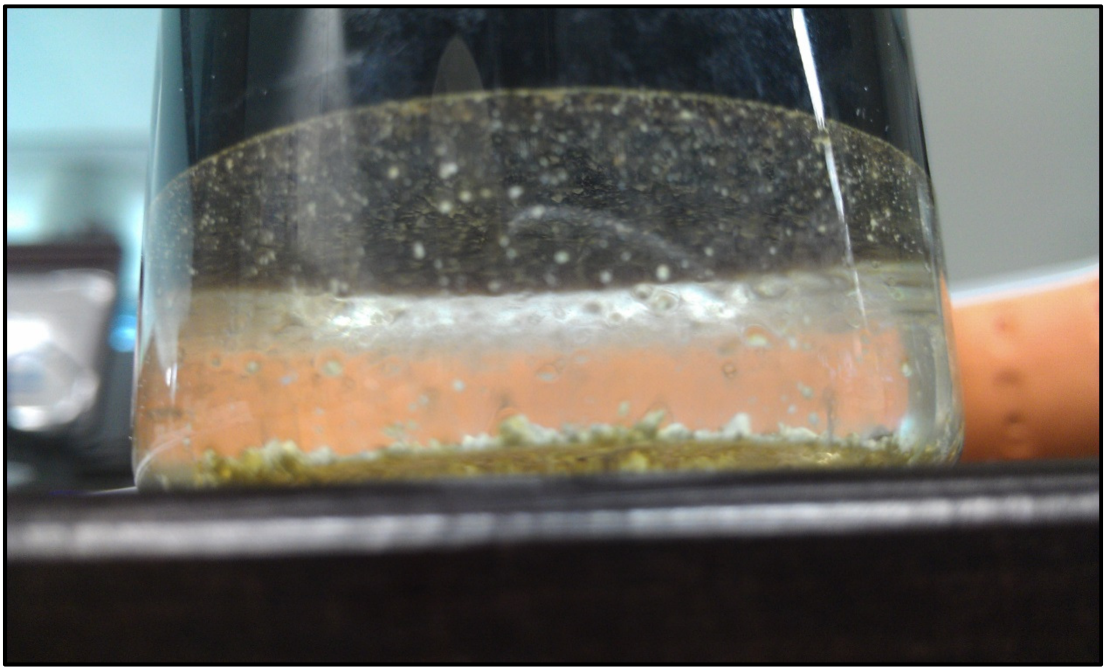

Figure 11: Mixture of Light Crude Oil with ZnO (SiO2)

Figure 11 shows the observation done at the interface of the mixture of 0.5 wt% Zinc Oxide coated with Silica Dioxide in light crude oil. From the observation, it can be seen that the nanoparticles shows little or no aggregation at the interface. The nanoparticles are seen to remain at the bottom of the beaker and some sticking on the side walls of the beaker.

4.2.3 Observation Analysis on Mixture of Medium Crude Oil with ZnO (OA)

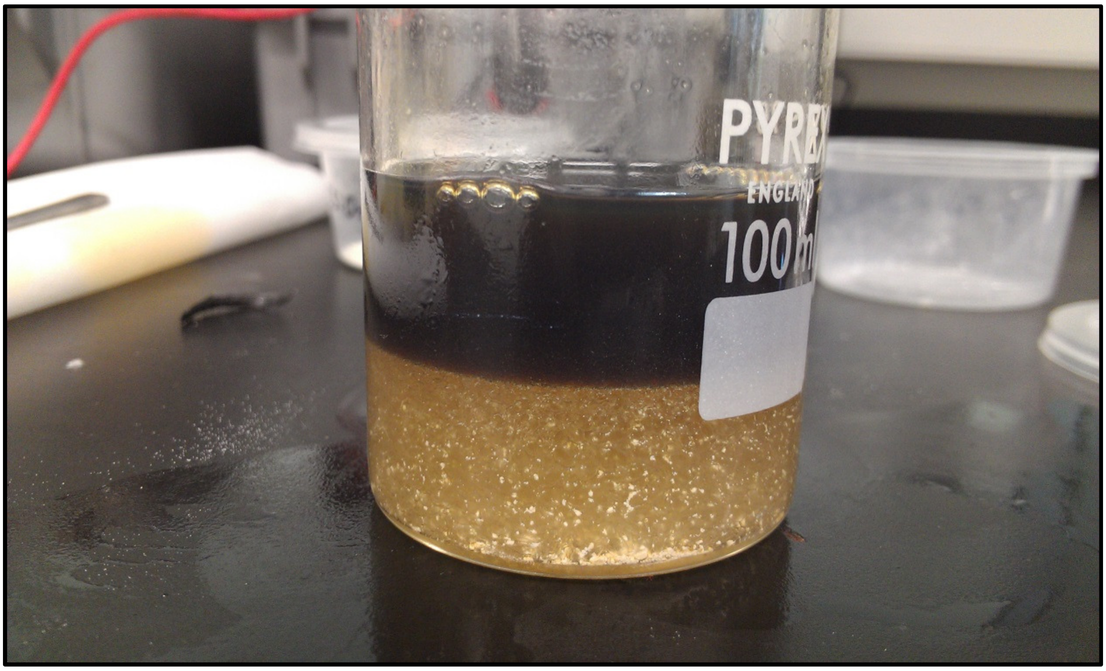

Figure 12: Mixture of Medium Crude Oil with ZnO (OA)

Figure 12 shows the observation done at the interface of the mixture of 0.5 wt% Zinc Oxide coated with Oleic Acid in medium crude oil. From the observation, it can be seen that the mixture of the coated nanoparticles produce an emulsion like substance in the brine zone. During the mixture, the crude oil sticks with the coated nanoparticles which may contribute to emulsion like substance produce in the mixture.

4.2.4 Observation Analysis on Mixture of Medium Crude Oil with ZnO (SiO2)

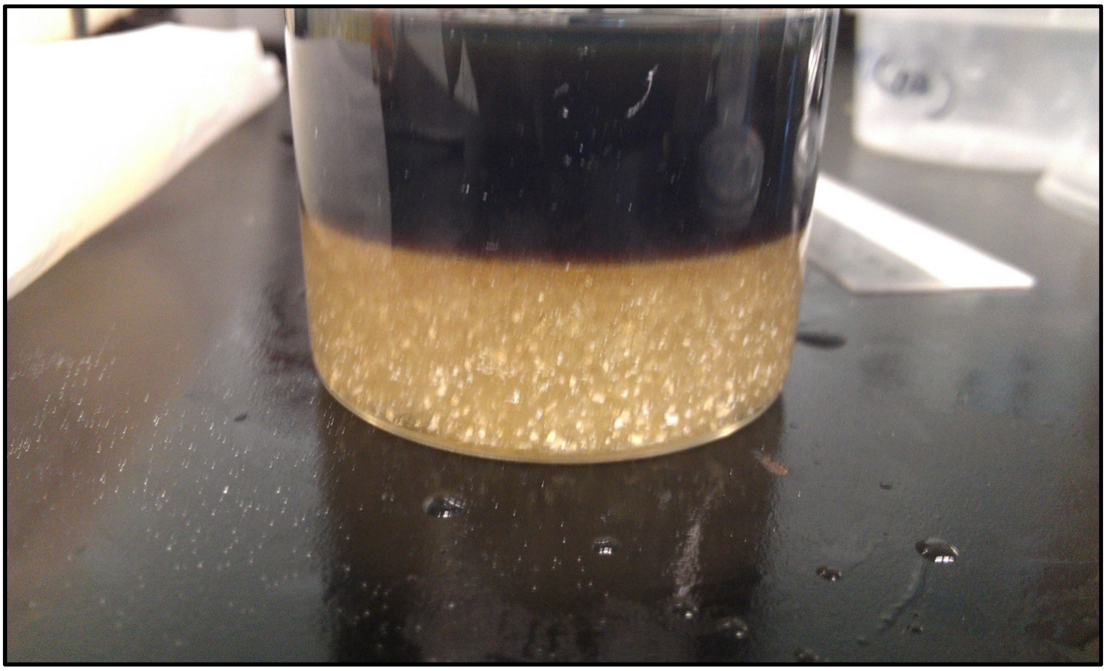

Figure 13: Mixture of Medium Crude Oil with ZnO (SiO2)

Figure 13 shows the observation done at the interface of the mixture of 0.5 wt% Zinc Oxide coated with Silica Dioxide in medium crude oil. From the observation, it can be seen that the mixture of the coated nanoparticles produce an emulsion like substance in the brine zone, again similar to the previous result. During the mixture, the crude oil sticks with the coated nanoparticles which may contribute to emulsion like substance produce in the mixture.

4.2.5 Observation Analysis on Mixture of Heavy Crude Oil with ZnO (OA)

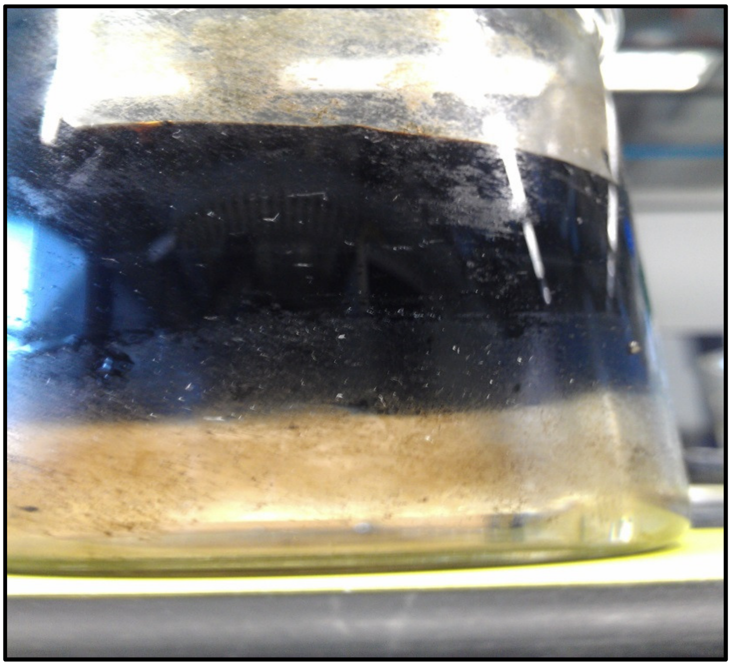

Figure 14: Mixture of Heavy Crude Oil with ZnO (OA)

Figure 14 shows the observation done at the interface of the mixture of 0.5 wt% Zinc Oxide coated with Oleic Acid in heavy crude oil. From the observation, there is no nanoparticle seen in the mixture because, the surface-coated nanoparticles has maintained in the oil zone. The hydrophobic tail that surrounds the nanoparticles assists the nanoparticles to suspend in the oil zone.

4.2.6 Observation Analysis on Mixture of Heavy Crude Oil with ZnO (SiO2)

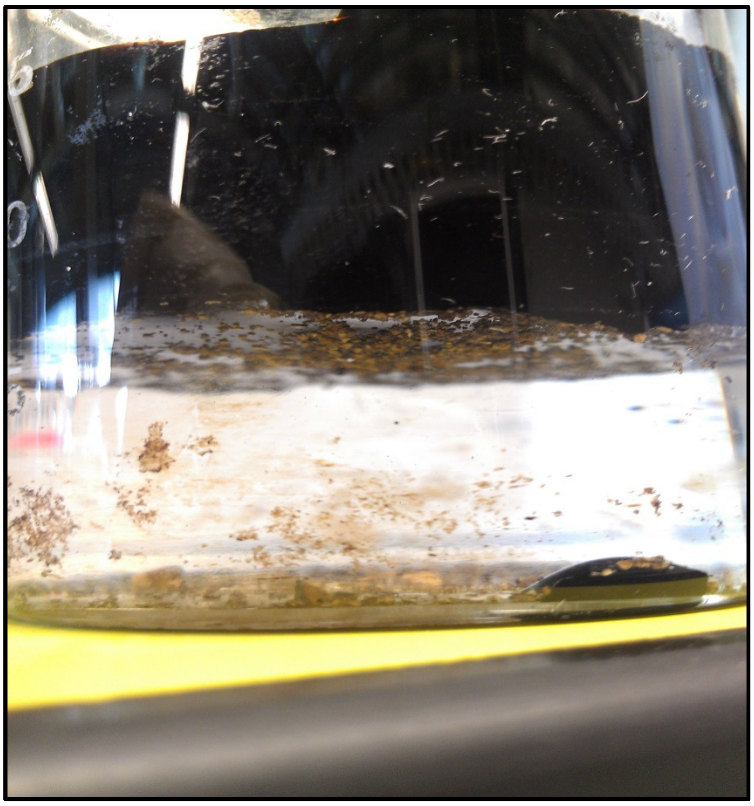

Figure 15: Mixture of Heavy Crude Oil with ZnO (SiO2)

Figure 15 shows the observation done at the interface of the mixture of 0.5 wt% Zinc Oxide coated with Silica Dioxide in heavy crude oil. From the observation, we can see some of the nanoparticles are aggregating at the interface but most of the nanoparticles have fallen to the bottom of the beaker. Since the Silica Dioxide coating is not hydrophobic it does not suspend as Oleic Acid coating does as shown in figure 14.

4.3 Resistivity Measurement at the Interface

After the observation at the interface of the nanoparticles, resistivity experimentation is conducted in the mixture of surface-coated nanoparticles with different type of crude oil. Afterwards, the 0.5 wt% of surface-coated nanoparticles is used in the mixture to measure the changes in resistance. Prior to this experimentation, the resistivity has been measure to acquire the value of resistance in the absence of the coated nanoparticles to obtain a base case for each type of crude oil to compare the value after the addition of the surface-coated nanoparticles.

4.3.1 Resistance Measurement for Mixture of Light Crude Oil with ZnO (OA)

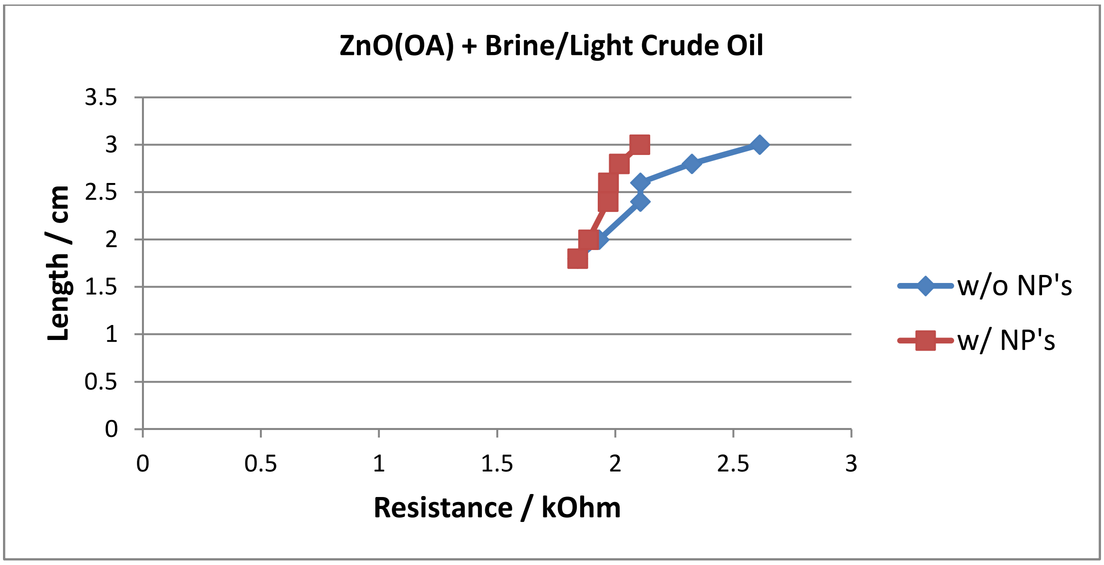

Figure 16: Mixture of Light Crude Oil with ZnO (OA)

Figure 16 shows the resistance measurement in the mixture of light crude oil in the absence and presence of 0.5 wt% Zinc Oxide coated with Oleic Acid. From the figure, it is interpreted that there is a change in resistance can be seen where a lower resistance is obtain in the presence of the nanoparticles. However, the change is not as significance as expected in the beginning of the experimentation.

4.3.2 Resistance Measurement for Mixture of Light Crude Oil with ZnO (SiO2)

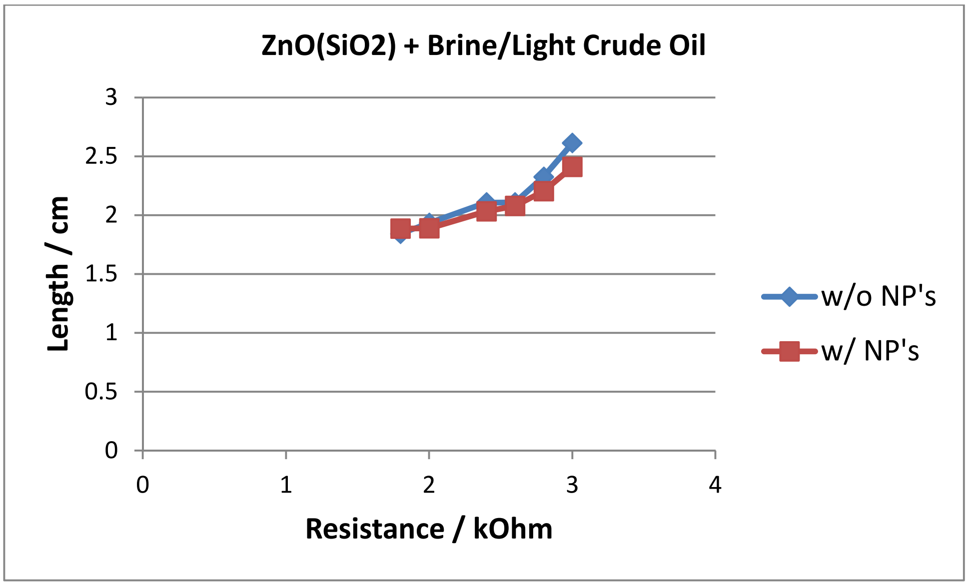

Figure 17: Mixture of Light Crude Oil with ZnO (SiO2)

Figure 17 shows the resistance measurement in the mixture of light crude oil in the absence and presence of 0.5 wt% Zinc Oxide coated with Silica Dioxide. From the figure, it is interpreted that there is a change in resistance which can be seen where a lower resistance is obtain in the presence of the nanoparticles similar when using Zinc Oxide coated with Oleic Acid in light crude oil.

4.3.3 Resistance Measurement for Mixture of Medium Crude Oil with ZnO (OA)

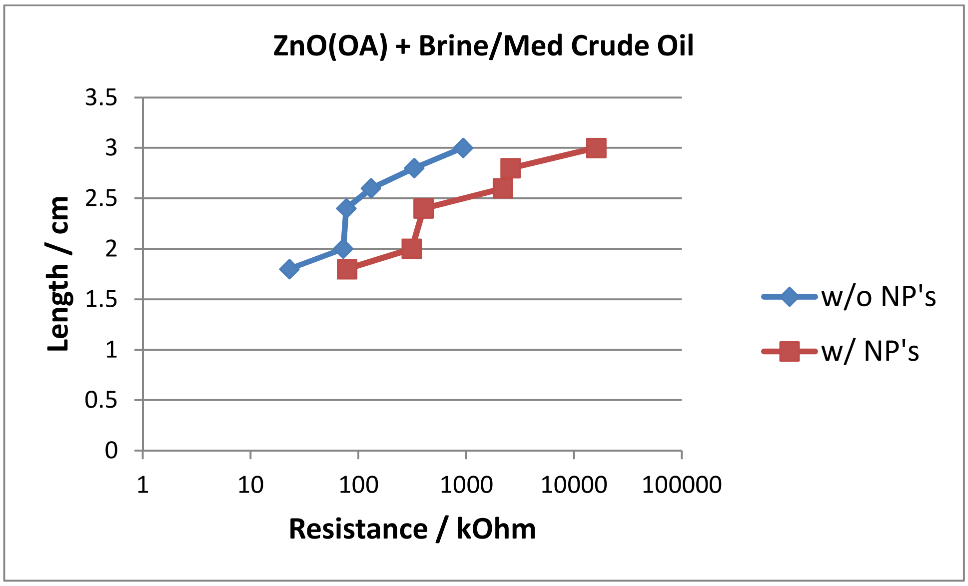

Figure 18: Mixture of Medium Crude Oil with ZnO (OA)

Figure 18 shows the resistance measurement in the mixture of medium crude oil in the absence and presence of 0.5 wt% Zinc Oxide coated with Oleic Acid. From the figure, it is interpreted that there is a significance change in resistance can be seen where a higher resistance is obtain in the presence of the nanoparticles.

4.3.4 Resistance Measurement for Mixture of Medium Crude Oil with ZnO (SiO2)

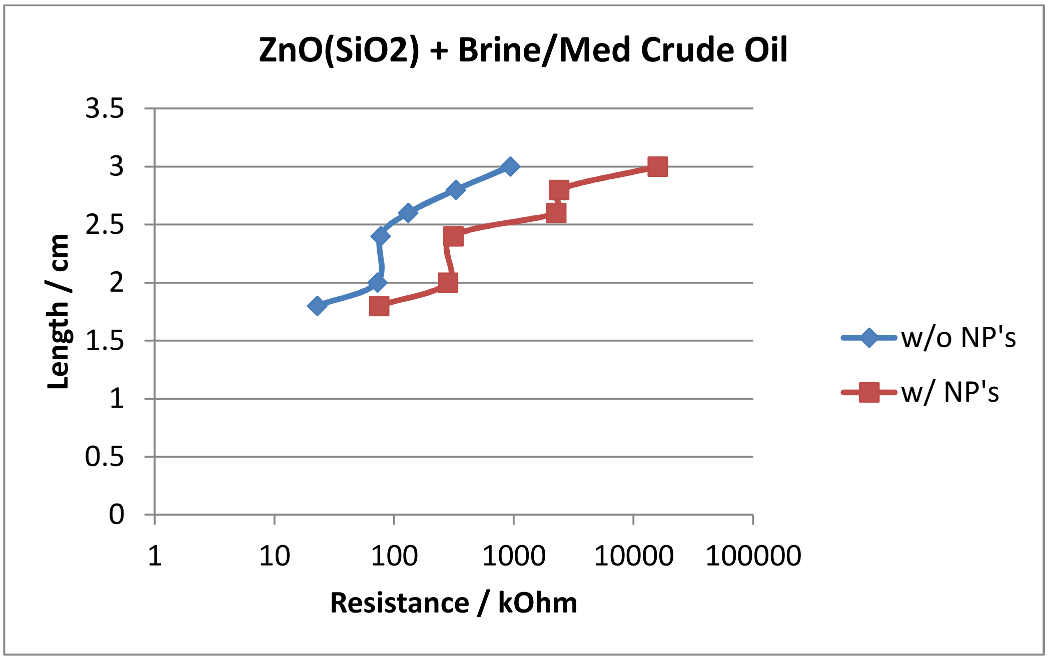

Figure 19: Mixture of Medium Crude Oil with ZnO (SiO2)

Figure 19 shows the resistance measurement in the mixture of medium crude oil in the absence and presence of 0.5 wt% Zinc Oxide coated with Silica Dioxide. From the figure, it is interpreted that there is a significance change in resistance can be seen where a higher resistance is obtain in the presence of the nanoparticles. The result is similar when using Zinc Oxide coated with Oleic Acid in medium crude oil.

4.3.5 Resistance Measurement for Mixture of Heavy Crude Oil with ZnO (OA)

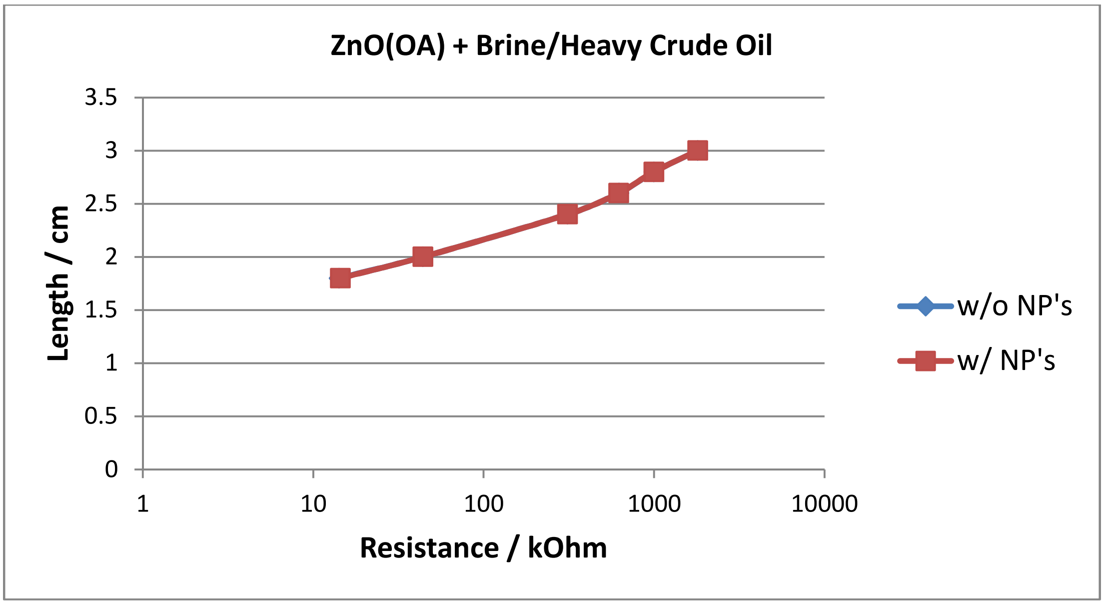

Figure 20: Mixture of Heavy Crude Oil with ZnO (OA)

Figure 20 shows the resistance measurement in the mixture of heavy crude oil in the absence and presence of 0.5 wt% Zinc Oxide coated with Oleic Acid. From the figure, we can observe there are little or no changes in resistivity from the mixture. The measurement of resistance in the oil zone could not be achieved since the crude oil will show infinite resistance in the SCIP testing tool.

4.3.6 Resistance Measurement for Mixture of Heavy Crude Oil with ZnO (SiO2)

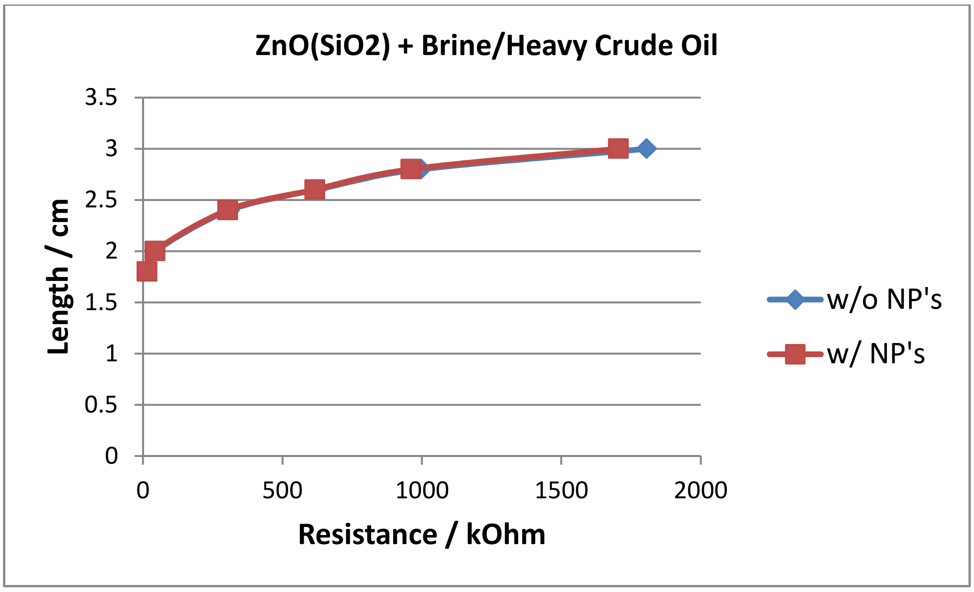

Figure 21: Mixture of Heavy Crude Oil with ZnO (SiO2)

Figure 21 shows the resistance measurement in the mixture of heavy crude oil in the absence and presence of 0.5 wt% Zinc Oxide coated with Oleic Acid. From the figure, it can be seen that a lower resistance is obtain after the addition of the surface-coated nanoparticles.

4.4 Discussion

Three main experimentations has been conducted in this studies which are the Zeta Potential measurement of newly modified nanoparticles, observation at the water/crude oil interface of mixture of surface-coated nanoparticles with different type of crude and the measurement of resistivity in the absence and the presence of the surface-coated nanoparticles.

In theory, the modification of Zinc Oxide nanoparticles surfaces should help further improve the nanoparticles so that, it gives an improved aggregation at the water/crude oil interface. Additionally, the measurement of resistivity changes in the absence and the presence of the surface-modified nanoparticles at the water/crude oil interface should have a significant reduction so that it may assist in the possibility of tracking of the formation flood front. Unfortunately, the result obtained shows otherwise.

During the observation at the interface of the surface-coated nanoparticles at the water/oil interface, it did not show any significant aggregation. No monolayer is form as suggested by previous experimentation. When conducted with different type of crude oil it shows a very different behaviour. In the mixture of surface-coated nanoparticles with medium crude oil, it can be observe that an emulsion like substance is form in the brine zone.

This is may due to the surface-coated nanoparticles sticking to the crude oil and brings it down to the brine zone forming such emulsion. This can be confirmed from the resistivity measurement, whereby an increase of resistance is measured in the brine zone. Both coating of Oleic Acid and Silica Dioxide shows similar behaviour in medium crude oil.

In the mixture of surface-coated nanoparticles with heavy crude oil, the surface-coated nanoparticles were seen to sustain at the oil zone. Further resistivity measurement could not identify the presence of the surface-coated nanoparticles in the oil zone since resistance is already high in the oil zone. In contrast, this does not occur when Zinc Oxide is coated with Silica Dioxide due to the absent of hydrophobic properties of the coating. The measurement of resistance again shows slightly lower reading of resistivity which is insignificant.

Furthermore, the resistivity measurement at the water/ crude oil interface shows that the resistivity changes are not significant; only a slight reduction of resistance was obtained when surface-coated nanoparticles were add to the mixture of different type of crude oil. This can be seen especially in the mixture light crude oil with both Oleic Acid and Silica Dioxide coating and the mixture of heavy crude oil with addition of Zinc Oxide coated with Silica Dioxide. These are the mixture that shows a clear aggregation at the interface when compare to other crude oil. The insignificance in resistance is due to the presence of the coating which neutralizes the outer electron that is responsible in the conductivity of electricity which helps in lowering the resistance in the mixture.

Further investigation in the overall result of this study and with the reference from previous research, it is found that the zeta potential measurement may be one of the factors that contribute to the ability of the nanoparticles to aggregate at the water/crude oil interface. It is observed that a lower value of zeta potential would provide a better aggregation at the interface. This finding may help future works in determining more factors that contribute to the aggregation of nanoparticle at water/crude oil interface.

Chapter 5: Conclusion and Recommendation

5.1 Conclusion

From the objectives of this research, stated in the first chapter of this theses. All three main objectives has been achieved which is to assess the possibility if using surface-modified nanoparticles to assist in the monitoring if the formation flood front.

1. The observation on the interaction of nanoparticles at the water/crude oil interface of surface-modified nanoparticles in different type of crude oil has been carried out and its found that hydrophobicity of the oleic coating did not help in preventing the nanoparticles to fall in to the brine zone

2. The evaluation using Zeta Potential of the synthesized surface-modified nanoparticle for analyzing the stability of the surface-modified nanoparticles has been conducted and from the result, it is confirm the successfulness of the surface modification

3. The measurement of resistivity at water/crude oil interface in the presence and the absence surfaced-modified nanoparticles for the development of a tracer for the flood front has been successfully completed. The result shows insignificant changes in the resistivity due to inability of nanoparticles to aggregate at the water/crude oil interface may be the factor that reduces the conductivity of the nanoparticles

In conclusion, Oleic Acid and Silica Dioxide surface modification for nanoparticles were found not suitable to assist in the waterflood front monitoring unfortunately. This is due to the insignificant aggregation and resistivity difference at the interface.

However, further investigation on the measured zeta potential and based on previous experimentation, it can be observed that a lower (-/+) value of zeta potential would provide a better aggregation at the interface.

5.2 Future Work and Recommendations

As for recommendation for this research, further studies and future works must be conducted to verify the factor that contribute to the aggregation at the water/oil interface. Other method of surface modification should be attempted to achieve better conductivity hence, reducing the resistance while maintaining the aggregation at the water/crude oil interface. Detailed characterization should also be done, in order to fully understand the factor and ability of nanoparticles to aggregate at the interface.

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Appendix

A.1 Resistance Value before and after the addition of Surface-Modified Nanoparticles

	Before	After
Phases	Resistance (kOhm)	Resistance (kOhm)
Crude Oil (5cm)	Infinite	Infinite
Interface (3cm)	2.611	2.104
Interface (2.8cm)	2.324	2.017
Interface (2.6cm)	2.107	1.971
Interface (2.4cm)	2.106	1.969
Brine (2cm)	1.932	1.887
Brine (1.8cm)	1.841	1.841

Mixture of Light Crude Oil with Zno (OA)

	Before	After
Phases	Resistance (kOhm)	Resistance (kOhm)
Crude Oil (5cm)	Infinite	Infinite
Interface (3cm)	2.611	2.409
Interface (2.8cm)	2.324	2.202
Interface (2.6cm)	2.107	2.077
Interface (2.4cm)	2.106	2.032
Brine (2cm)	1.932	1.887
Brine (1.8cm)	1.841	1.885

Mixture of Light Crude Oil with Zno (SiO2)

	Before	After
Phases	Resistance (kOhm)	Resistance (kOhm)
Crude Oil (5cm)	Infinite	Infinite
Interface (3cm)	937.987	16092
Interface (2.8cm)	328.663	2587.261
Interface (2.6cm)	131.263	2195.159
Interface (2.4cm)	77.173	402.686
Brine (2cm)	72.444	312.277
Brine (1.8cm)	22.881	78.342

Mixture of Medium Crude Oil with Zno (OA)

	Before	After
Phases	Resistance (kOhm)	Resistance (kOhm)
Crude Oil (5cm)	Infinite	Infinite
Interface (3cm)	937.987	15893
Interface (2.8cm)	328.663	2385.221
Interface (2.6cm)	131.263	2259.513
Interface (2.4cm)	77.173	312.726
Brine (2cm)	72.444	282.332
Brine (1.8cm)	22.881	75.113

Mixture of Medium Crude Oil with Zno (SiO2)

	Before	After
Phases	Resistance (kOhm)	Resistance (kOhm)
Crude Oil (5cm)	Infinite	Infinite
Interface (3cm)	1805.5	1804.5
Interface (2.8cm)	997.2	996.6
Interface (2.6cm)	621.4	620.6
Interface (2.4cm)	310.6	310.7
Brine (2cm)	43.98	43.965
Brine (1.8cm)	14.205	14.425

Mixture of Heavy Crude Oil with Zno (OA)

	Before	After
Phases	Resistance (kOhm)	Resistance (kOhm)
Crude Oil (5cm)	Infinite	Infinite
Interface (3cm)	1805.5	1704.5
Interface (2.8cm)	997.2	960.6
Interface (2.6cm)	621.4	615.4
Interface (2.4cm)	310.6	303.2
Brine (2cm)	43.98	43.305
Brine (1.8cm)	14.205	14.425

Mixture of Heavy Crude Oil with Zno (SiO2)

A.2 Zeta Potential Value of Nanoparticles

Titration Source	Solute	Concentration [g/l]	pH	Conductivity [mS/m]	Cell Resistance [KOhm]	ζ [mV]	Elapsed Time [min]
Manual	NaCl	5.844	3.77345	1305.782833	1.417963	-10.11	3.8953333
Manual	NaCl	5.844	3.77369	1313.021583	1.41975283	-23.76	7.5675667
Manual	NaCl	5.844	3.77389	1319.376333	1.42436692	-23.92	11.2601
Manual	NaCl	5.844	3.77404	1324.280667	1.42061583	-21.02	14.935717

Zeta Potential Value for Zno (Base)

Titration Source	Solute	Concentration [g/l]	pH	Conductivity [mS/m]	Cell Resistance [KOhm]	ζ [mV]	Elapsed Time [min]
Manual	NaCl	5.844	3.77367	1225.661	1.7553769	-30	3.885183
None	NaCl	5.844	3.77368	1234.341	1.7452608	-38	11.28037
None	NaCl	5.844	3.77381	1238.327	1.7411093	-43	14.86473
None	NaCl	5.844	3.77382	1241.545	1.7342544	-43	18.44573

Zeta Potential Value for Zno (OA)

Titration Source	Solute	Concentration [g/l]	pH	Conductivity [mS/m]	Cell Resistance [KOhm]	ζ [mV]	Elapsed Time [min]
None	NaCl	5.844	3.77269	1266.525417	1.4380254	-71.1	3.66548
None	NaCl	5.844	3.77242	1271.254917	1.4277865	-62.3	7.13493
None	NaCl	5.844	3.7726	1273.632	1.4347099	-55.3	10.6213
None	NaCl	5.844	3.77255	1273.705167	1.4751819	-45.4	14.7363
None	NaCl	5.844	3.77277	1274.749	1.4324638	-48.3	18.466
None	NaCl	5.844	3.77277	1276.535917	1.4284027	-46	22.2599

Zeta Potential Value for Zno (SiO2)