STUDY ON CHARACTERIZATION AND OPTIMIZATION OF HYDROPHOBIC SILICA NANO-PARTICLES FOR OIL-WATER SEPARATION

By

HARVIN KAUR A/P GURCHRAN SINGH

(10663)

SUPERVISOR: PROFESSOR THANABALAN MURUGESAN

Dissertation submitted to the Chemical Engineering Programme

in Partial Fulfilment of the Requirements

for the Bachelor of Engineering (Hons) Degree in Chemical Engineering

on 5th of January 2012

Universiti Teknologi Petronas

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

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.

(HARVIN KAUR A/P GURCHRAN SINGH)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

SEPTEMBER, 2011

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Oil spills, Marine pollution and Environmental pollution are major problems especially in today's world. Therefore, there is a need of finding a new method to enhance the existed method of removing hydrocarbons, which is more effective and reliable. Through the researchers being done, there are a few methods that can be improved and the most promising one is the separation process using hydrophobic silica nano-particles. The principal scope of this research is to investigate and understand systematically how the synthesis parameters, structure and modification of silica nanoparticles affect it is properties and ability to absorb oil from water based on the experimental outcome of the modified silica nanoparticles. Thus, the structure of the synthesized silica nanoparticles was varied systematically to understand the effect on thermo physical properties and absorption of oil. In chapter one, the author talks about the Introduction to the research with the Background of the Project and also the Scope of Study where a brief description was given on Silica Nano-Particles. There are a few objectives to this research which are to Synthesis and Characterize of Silica Nano-Particles and to conduct the Experiment on Oil-Water Separation and Optimization for Oil Absorbed. After that, in Chapter two, the author talks about the Literature Review for the research. In this part, there were a lot of references taken and a few journals and books were read to support the research that was conducted. Next, in Chapter 3, the author talks about the methodology of how the Synthesis and Characterization of the Silica Nano-Particles is done. The methodology of the Oil-Water Separation experiment is also been shown in that section. In Chapter 4, the author talks about the Results that were obtained from the Material Characterization, Experiment and Optimization for Oil Absorbed and the author has discussed what has been accomplished from all these three parts. Last but not least, in Chapter 5, the author talks about the Conclusion and Recommendation about this research. In this part, the Conclusion summarizes this whole report and the Recommendation talks about how to improve this research in the future. Thus, this study is aimed at investigating the efficiency of silica nano-particles can be simply improved by its surface modification with selected hydrophobic organic molecules in the specific processes.

ACKNOWLEDGEMENT

CHAPTER 1: INTRODUCTION

1.1 Background of Study

A serious problem which long has plagued industrial and environmental concern is the removal of hydrocarbons, particularly oil, from unwanted areas into or unto which it has been discharged. Of particular concerns is the removal of discharged oil from water or shore areas which occurs as a result, for example, of oil tankers accidents at sera or mishaps at the loading or unloading of oil from these tankers at port. Nowadays there is a gradual increase in marine pollution due to many factors such as: high demand for oil to meet the multiplex human consumption and multitudinous industrial needs, the large scale industrialization, increasing of population in many parts of the world, increase of petroleum industries and increase of oil transportation and other hazardous materials[1].

An oil spill is a release of a liquid petroleum hydrocarbon into the environment due to human activity, and is a form of marine pollution which can affect marine life. Other occasions where hydrocarbon removal is of concern range from problems such as the discharge of oil at areas around oil wells and oil storage facilities or the cleaning of surfaces in which oil was stored (e.g. on-shore storage tanks, holds of tankers, etc.) to problems such as the discharge or leaking of oil from vehicles onto roads or driveway surfaces. Furthermore, oil-water emulsions which are used, for example, as cutting fluids require separation of oil from the water prior to disposal.

Table 1 : Previous Oil Spills accidents

Spill / Tanker	Location	Date	Tons of crude oil
Gulf War oil spill	Iraq, Persian Gulf and Kuwait	January 19, 1991 -January 28, 1991	818,000– 1,091,000
Deepwater Horizon	United States, Gulf of Mexico	April 20, 2010 – July 15, 2010	560,000-585,000

Environmental pollution has become a significant threat to the world in which we life and the environmental regulation are increasingly stringent every day .The need for removing oil spill leads to develop arrange of materials for cleaning up oil from oil impacted areas. The varieties of oil source make it difficult to select the appropriate oil spill cleanup which depend on the type of oil, spill, location and weather conditions[2].A number of solutions have been proposed for dealing with the problem of removing hydrocarbons from unwanted areas. One of these solutions involves the use of bacteria to degrade the hydrocarbons. However, such methods are expensive, raise important environmental concerns, and are often ineffective in cold weather environments.

Another solution to the problem lies in the use of absorbents which are intended to remove the hydrocarbons from unwanted areas by the use of physical forces rather than chemical break down of the hydrocarbons, i.e. where it is drawn into the absorbent material in much the same way water is drawn into the sponge. A lot of examples for absorbents of this type are found in the literature. Some of the limitations of those examples mentioned include prohibitive cost, ineffectiveness in extreme environmental conditions, tackiness of the material after it is saturated with oil, retention of oil in the absorbent until the absorbent is removed from the water, and ineffective or temporary hydrophobic characteristics.

In order to effectively remove hydrocarbons from water it is necessary that the absorbent absorb only the hydrocarbon and not the water. That is, the material should be both oleophilic and hydrophobic. Fine particulate silica has been known to exhibit both of these properties. It can be treated to make it hydrophobic. But, upon standing in water for a number of hours, the silica loses its hydrophobicity, becomes hydrophilic, enters the water, leaving the oil floating on top. Another problem is that after the treated silica is exposed to and has absorbed the hydrocarbons, the material does not agglomerate. Thus, it is difficult, if not impossible, to recover the saturated material without the use of very fine mesh screens.

1.2 Problem Statement

In the process to clarify the purpose of the research was being carried out, the problem statement are divided into two sections:

1.2.1 Problem Identification

The separation of oil and water is highly demanded right now as there are many areas involved with this matter. Areas such as oil and gas industry, oil pollution problem and water treatment system need a very effective oil and water separation technique to save money and time. It is true that there are quite a number of existed conventional methods, but for this research, I would like to see how efficient hydrophobic silica nano-particles are. Therefore, there is a need of finding a new method to enhance the existed method, which is effective.

It has been theoretically studied that the efficiency of silica nano-particles can be simply improved by its surface modification with selected hydrophobic organic molecules in the specific processes. With respect to that, the author has been decided on proving those theoretical studies and finding the best metal oxide which led to that improved silica nano-particles in the course of lab experimentation.

1.2.2 Significant of Project

The aim of this research is to understand and calculate the amount of oil absorbed while conducting the Oil-Water Separation. In order to meet the time frame of the project, the author has decided to fix two of the parameters which are pressure and concentration. Temperature, Density and the Oil Absorbed are manipulated variables and a better study can be conducted on the behavior of the Silica-Titanium nano-particles under various conditions.

5

One relatively new application is the use of hydrophobic absorbent for oil spill cleanup. These materials have been considered and used commercially in oil spill cleanup. Silica nanoparticles synthesized via sol gel process can achieve unique properties such as; high purity, small size of the particles, high surface area, high thermal and mechanical stability but the most disadvantages of silica nanoparticles produced by sol gel process.

Silica nanoparticles with hydrophilic nature absorb oil but become deactivated with co-absorption of water due to the present of hydroxyl group at their surface which reacts with water by hydrogen bond. The advantage of silica nanoparticles modification is to convert them from hydrophilic to hydrophobic to increase their ability to absorb oil in water-oil environment. Liquid modification of silica nanoparticles by doping with different percent of titanium sol to replace hydroxyl groups "which exist at silica nanoparticles surface in silica sol" with metal oxide (TiO_2) by covalent bond between these oxides and silica.

1.3 Objective

The main objective of this research is to investigate the effect of the amount of absorbent and effect of temperature on absorption of oil.

There are also a few other objectives which are:

- To prepare the surface modified silica nano-particles using the sol-gel method for Titanium 1%, Titanium 3% and Titanium 5%.
- To Characterize the finished product using a FTIR, FESEM, TGA, XRD, XRF, BET and SEM.
- To conduct the Experiments on Oil-Water Separation and Optimize the Oil Absorbed.

1.4 Scope of Study

For the scope of study, the author will synthesis the surface modified hydrophobic silica nano-particles with the selected hydrophobic substances. The characterization

process of the silica nano-particles will then take place. After that, at the Temperature of 25°C, we will measure the density for different concentrations of Silica-Titanium 1%, Silica-Titanium 3% and Silica-Titanium 5%. The last experiment will be conducted at different Temperatures of 35°C and 45°C. The weight of the silica nanoparticles will be varied at 0.5g, 1.0g and 1.5g. Experiments will be conducted to use different Oil Percentages which are 10%, 30%, 50%, 70% and 90%.Five different parameters have been chosen to conduct the study. Pressure will be fixed throughout the experiment to compare the results of each study that will be carried out. The scope of the study will be on the density trend of oil-water separation at fixed high pressure, three different concentrations, and two different high temperatures.

1.4.1 The relevancy of the Project

This project will focus on the topic separation of oil and water at different concentrations and temperature conditions. This topic is related to the course of Separation Process in the chapter of Absorption, plus the knowledge of Chemical Engineering Fluid Mechanics, Organic Chemistry and Physical Chemistry is also needed to perform research for this project.

1.4.2 Feasibility of the project within the scope and time frame.

The project is divided into four sections. Section one will basically be on finding, collecting, and reading of journals, technical papers, and books of the research topic. In this section one, the author will synthesize the silica nano-particles. The second section of the project will be mainly on characterizing the hydrophobic silica nano-particles. The third section of the project is the experiment on oil water separation and the amount of oil that can be absorbed by the hydrophobic silica nano-particles. The last section will then be done to optimize the Oil absorbed to achieve the best Optimization rate.

CHAPTER 2: LITERATURE REVIEW

2.1 Separation of Oil and Water

In order to separate oil from water, it is necessary to understand first about the structure and properties of both two substances. The separation process maybe looks quite simple as oil and water are different in terms of their density. But in the real situation, this process requires more than just a difference in density to achieve the best result. Other properties also have to be considered and most importantly are the effect of the structure of each of the substances to the process. Therefore, the better understanding in the structure and properties of oil and water will help a lot in reaching this project's objective.

As the basis of the project, fine particle sized treated hydrophobic silica is added to water which contains oil. The silica nanoparticles absorb the oil and the silica/oil mixture floats on top of the water where it can be scooped off or otherwise substantially separated from the water. The oil and silica may then be conveniently separated by placed back into water and allowed to stand for an extended period of time until the silica loses its hydrophobicity, becomes hydrophilic, and goes into the water phase leaving the oil floating on the water. The oil may then be removed for further handling and then silica may then be separated from the water for further handling.

The expression "oil" is meant to include liquid hydrocarbons, e.g. gasoline, kerosene, fuel oil, crude oil, paraffinic oil, vegetable oils, and the like and includes such water-immiscible liquids such as xylene, toluene, styrene, alkylbenzenes, naphtha, naphthenic compounds, liquid organic polymers and the like. The water, which contains the oil desired to be separated, may be a river, lake, effluent ditch, bay, holding tank or process stream. Water containing dissolved ingredients and saline waters, e.g., brines, seawater, estuaries, and the like can also be considered.

The water, which contains the oil desired to be separated, may be a river, lake, or process stream. Waters containing dissolved ingredients and saline waters.

The ratio of oil to water is not particularly significant except that there should be enough of one with the other to be considered as being something more than "insignificant" for the present invention to be economically practical. In instance where there is a relatively small amount of water to oil, a water phase may form at the bottom; this water layer may be drawn off, generally along with a small amount of the oil, and then the so-removed water layer may be treated to remove any oil which may have been drawn off the water. In most instances, it is desired to remove as much oil from the water as it is reasonably possible; in these cases some water may be taken along with the silica/oil mixture. This is not generally a problem because the convenient manner of separating the oil from the silica involves adding enough water so that it will take up the silica when the silica reverts from hydrophobic to hydrophilic, allowing the oil to remain floating of top of the water.

2.1.1 Water

Water (H_2O) is often perceived to be ordinary as it is transparent, odorless, tasteless and ubiquitous. It is the simplest compound of the two most reactive elements, consisting of just two hydrogen atoms attached to single oxygen atoms. Indeed, very few molecules are smaller or lighter. Liquid water, however, is the most extraordinary substance. Various other properties of water, such as its high specific heat, are due to these hydrogen bonds. As the temperature of water are lowered, clusters of molecules form through hydrogen bonding, with each molecule being linked to others by up to four hydrogen bonds, each oxygen atom tends to surround itself with four hydrogen atoms in a tetrahedral arrangements. Hexagonal rings of oxygen atoms are formed in this way, with alternate atoms in either a higher or lower plane than their neighbors to create a kinked three-dimensional structure.
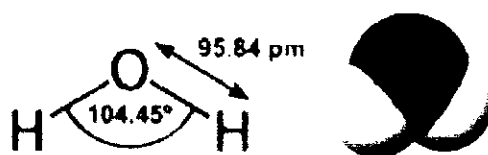
Figure 1: The molecular structure of Water

2.1.2 Oil

Lipids consist of numerous fatlike chemical compounds that are insoluble in water but soluble in organic solvents. Lipid compounds include monoglycerides, diglycerides, triglycerides, phosphatides, cerebrosides, sterols, terpenes, fatty alcohols and fatty acids. Dietary fats supply energy, carry fat-soluble vitamins (A, D, E, K), and are a source of antioxidants and bioactive compounds. Fats are also incorporated as structural components of the brain and cell membranes.

Fatty acids consist of the elements carbon (C), hydrogen (H) and oxygen (O) arranged as a carbon chain skeleton with a carboxyl group (-COOH) at one end. Saturated fatty acids (SFAs) have all the hydrogen that the carbon atoms can hold, and therefore, have no double bonds between the carbons.

2.1.3 Paraffin Oil

In chemistry, **paraffin** is a term that can be used from "alkane", indicating hydrocarbons with the general formula C_nH_{2n+2}. **Paraffin wax** refers to a mixture of alkanes that falls within the $20 \leq n \leq 40$ range; they are found in the solid state at room temperature and begin to enter the liquid phase past approximately 37°C.

The simplest paraffin molecule is that of methane, CH_4, a gas at room temperature. Heavier members of the series, such as octane, C_8H_{18}, and mineral oil appear as liquids at room temperature. The solid forms of

paraffin, called *paraffin wax*, are from the heaviest molecules from $C_{20}H_{42}$ to $C_{40}H_{82}$.

2.1.4 Hydrophobic Effects

The hydrophobic effect is the property that non-polar molecules tend to form intermolecular aggregates in aqueous medium and analogous intramolecular interactions. The name arises from the combination of water in Attic Greek hydro- and for fear phobos, which describes the apparent repulsion between water and hydrocarbons. At the macroscopic level, the hydrophobic effect is apparent when oil and water are mixed together and form separate layers.

2.1.5 Oleophilic Effect

The oleophilic effect is actually the properties of a substance where it has a tendency to absorb oil more than water. Based on the above findings, the best substance to be used in the water treatment process should consist of both the hydrophobic and also the oleophilic behavior to attain effective separation of oil and water.

2.1.6 Surface Modified Silica Nano-Particles

Surface modified silica nano-particles are basically the ordinary silica in nano particle size which has undergone the synthesized process with hydrophobic organic molecules. With this synthesized process which is the grafting of the silica nano, the hydrophobicity characteristics will be achieved. As has been stated earlier on, the hydrophobicity together with oleophilicity is two characteristics that crucial in developing more effective absorbent material.

11

2.1.7 Silica

Silica or silicon dioxide (from the Latin silex), is an oxide of silicon with a chemical formula of SIO_2 and has been known for its hardness since antiquity. Silica is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms. It is a principal component of most types of glass and substances such as concrete. Silica is the most abundant mineral in the earth's crust.

SiO_2 has a number of distinct crystalline forms in addition to amorphous forms. With the exception of stishovite and fibrous silica, all of the crystalline forms involve tetrahedral SiO_4 units linked together by shared vertices in different arrangements. Silicon-oxygen bond lengths vary between the different crystal forms.

Sand consists of small grains or particles of mineral and rock fragments. Although these grains may be of any mineral composition, the dominant component of sand is the mineral quartz, which is composed of silica. Other components may include aluminium, feldspar and iron-bearing minerals. Sand with particularly high silica levels that is used for purposes other than construction is referred to as silica sand or industrial sand. Industrial uses of silica sand depends on its purity and physical characteristics. Some of the more important physical properties are: grain size and distribution, shape, sphericity, and grain strength.

2.1.8 Standard curves (Density vs. Oil Percentage) for Temperatures: 25°C, 35°C and 45°C.
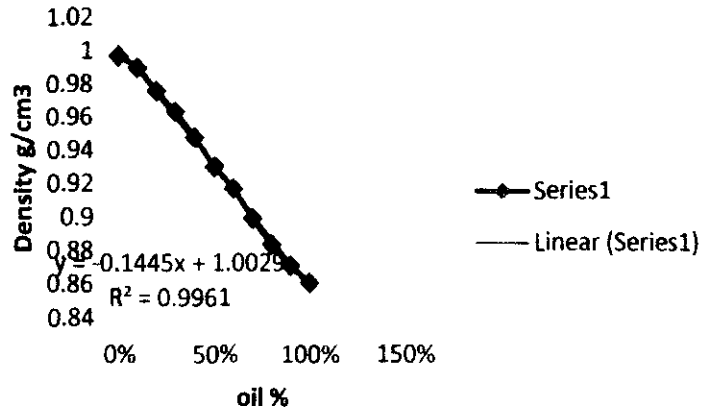
Figure 2: Standard curve for 25 °C
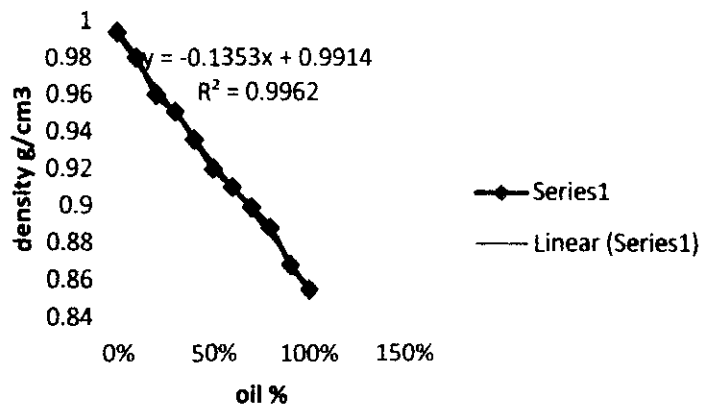
Figure 3: Standard curve for 35 °C
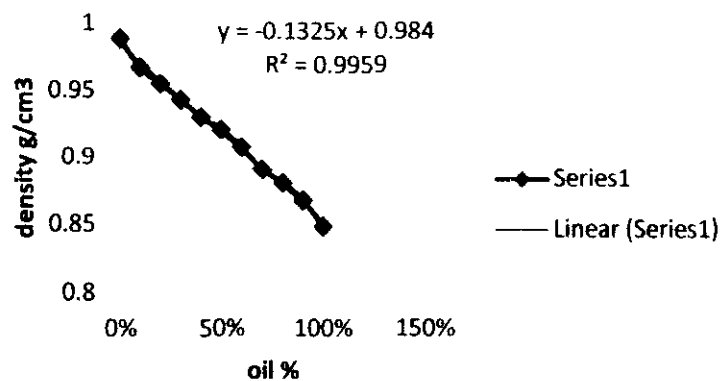
Figure 4: Standard curve for 45 °C

2.2   Sol-Gel Method

The sol-gel process, also known as chemical solution deposition, is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Sol–gel is one of the most suitable process for the preparation of nanoparticles because it allows to control practically all variables correlated to the particles: size, shape, porosity, density, purity, functional groups, active sites, morphology and so on [3]. Sols are dispersions of colloidal particles with diameters of 1-100nm in a liquid. A gel is an organized, rigid network with pores of sub micrometer dimensions and polymeric chains with average length greater than a micrometer. The "gel" embraces a variety of combinations of substances.

2.2.1 Hydrolysis and condensation reaction

In the formation of silica particles using a tetra alkoxysilane, the synthesis proceeds via hydrolysis promoted by a catalyst in the presence of a low molecular weight alcohol. Equation 1 shows the formation of silanol groups from the hydrolysis of tetra alkoxysilane[4].

$$\text{Hydrolysis} \quad Si(OC_2H_5)_4 + H_2O \xrightarrow{\quad OH^- \quad} Si(OH)_4 + C_2H_5OH$$

$$\text{Condensation} \quad Si(OH)_4 + Si(OH)_4 \xrightarrow{\quad OH^- \quad} Si\text{-}O\text{-}Si + H_2O$$

$$\text{Condensation} \quad Si(OH)_4 + Si(OC_2H_5) \xrightarrow{\quad OH^- \quad} Si\text{-}O\text{-}Si + C_2H_5OH$$
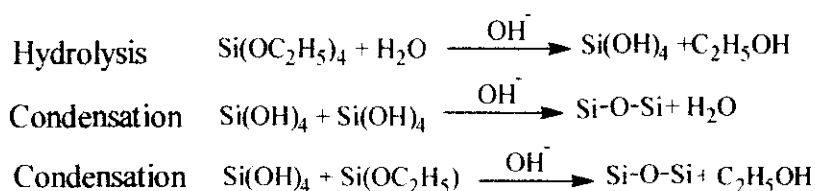
Alkoxy substituent groups on the silicon atom are fewer electrons withdrawing and increase the steric hindrance of the attacking nucleophile, resulting in slower hydrolysis of the silane molecule when compared with hydroxyl substituents. As a result, after the loss of each alkoxy group, the rate of the hydrolysis reaction increases. The hydrolyzed silica then proceeds through a condensation reaction to produce a SiO_2 network by either silanol-silanol condensation or silanol-ether condensation. The poor reactivity of silicon is generally affected by using acid or base catalysts. Slower hydrolysis and faster condensation were observed in the case of base catalysis leading to

14

compact colloidal particles. While the reaction occurs through an acid – catalysis lead to faster hydrolysis and open polymer structure [5].

The hydrolysis and condensation reactions in the sol-gel process can be influence by many factors which include the water/silane ratio, catalyst, temperature, and the nature of solvent.A dried gel contains a very large concentration of chemisorbed hydroxyls on the surface of the pores. A stabilized gel can be formed by thermal treatment in the range of 500-800 °C desorbs the hydroxyls and thereby decreases the contact angle and the sensitivity of the gel to rehydration stresses[6].

The goal of sol-gel processing is to control the structure of a material on a nanometer scale from the earliest stages of processing. For pure silica powders, fibers, and even monoliths this goal has been achieved. The potential of enhanced properties due to ultra-structural processing, control of higher purity, and greater homogeneity has been realized using sol gel. Other engineering advantages of the lower temperature chemically based sol-gel processing such as net-shape casting, fiber pulling, and film coating have also reached economic potential.

2.2.2 Modification of silica nanoparticles

The chemical properties of the silica surface are mainly determined by the various silanol and siloxane groups that are present on the external as well as the internal structure.The structure of silica nanoparticles showed three dimensional networks. Silanol and siloxane groups are created on the silica surface, leading to hydrophilic nature of the particles. The surfaces of the silica are typically terminated with three silanol types: free or isolated silanols, hydrogen-bonded or vicinal silanols and geminalsilanols.These bonds hold individual silica particles together and the aggregates remain intact even under the best mixing conditions.

The hydroxyl groups on the surface of silica particles can be easily tailored with organic compounds or polymers. Functionalization of mesoporous silica matrix with polymers, metals, semiconductors and metal oxides has received considerable recognition because of their excellent catalytic, opt electrical, chemical and environmental properties. The most convenient technique for silica surface functionalization is the doping of sol-gel synthesized silica matrix with metal nanoparticles. These metal doped sol-gel materials are used extensively in catalytic, optical and sensor applications. It is also possible to modify the acid–basic properties on the active sites on the particle surface [7]. Sol–gel technology has opened the possibility for producing ceramic nanoparticles with large surface area and a wide variety of active sites on their surface, particularly appropriated for the adsorption of metal ions, optical devices, fibers and thin film.

Addition of metal salts (nitrate, chloride, and sulfate) directly to the hydrolyzed sol mixtures of tetraethyl-orthosilicate (TEOS), tetramethylorthosilicate (TMOS), to form gels. The gels thus formed are then subjected to high temperatures to reduce the metal salts to the respective metal nanoparticles. Some of the particles synthesized using this method tends to precipitate out of the silica matrix. This causes a decrease in metal loading, which in turn causes loss in catalytic efficiency.

2.2.3 Silica nanoparticles characterization

Many techniques are used for characterization of particular properties of nanocomposites. To understand structure-property relationships, some characterization techniques are employed. The characterization methods used in the analysis of the chemical structure, microstructure and morphology, as well as the physical properties, of the nanocomposites are varied.

16

The properties of silica nanoparticles strongly depend on their composition, the size of the particles, interfacial interaction. The interfacial interaction between silica nanoparticles and the modifier (which depends on the preparative procedure) strongly affects the chemical, mechanical, thermal, and other properties of the nanocomposites. The internal surfaces are critical in determining the properties of nanofilled materials since silica nanoparticles have high surface area-to-volume ratio, particularly when the size decreases below 100 nm. The interaction zone has significant impact on properties of silica nanoparticles. Therefore different types of characterization have been used to clarify silica nanoparticles properties. There are 8 types of Characterization for Silica Nano-Particles such as *Fourier transmission infrared (FTIR), X-ray diffraction (XRD), X-ray fluorescence (XRF), Silica nanoparticles morphology (SEM), Field Emission Scanning Electron Microscopy (FESEM), Transmission electron microscopy (TEM),Surface area and pore size analyzer (BET)*and *Thermal gravimetric analysis (TGA)*. The details of each method are shown in the Discussion section. Moreover, the Application of the Modified Silica Nano-Particles is also shown in the Appendix section.

CHAPTER 3: METHODOLOGY

3.1 Research Methodology

Different findings and methodologies are gathered from the research work of other researchers and to be incorporated in this project. First and foremost, various journals and technical papers were read through the get the general understanding on the project. It is also needed to identify the objective of this project and to come up with a proven method to run the experiment next semester.

This methodology part can be divided into three categories which are:

- Synthesis of the Hydrophobic Silica Nano-Particles with Titanium 1%, Titanium 3% and Titanium 5% using Sol-Gel Process.

- Characterization using XRF, XRD, TGA, FTIR, TEM, FESEM and BET

- Experiment :

1. Rate of Oil Absorption using the different concentration of Silica-Titanium.

2. Rate of Oil Absorption based on the effect of Temperature.

3. Rate of Oil Absorption based on the effect of Oil Percentage.

4. Rate of Oil Absorption based on the effect of mass of Silica-Titanium.

- Optimizing the Oil Absorbed to get the best combination to achieve the highest Oil Absorbed rate using the Box Behnken software.

For last semester (FYP I), I have completed the Synthesis of the Hydrophobic Silica Nano-Particles with Titanium 1%, Titanium 3% and Titanium 5% using the Sol-Gel Process. After that, I have also completed the Characterization of the Silica-Titanium 1%, 3% and 5% that I have developed using XRF, FTIR and BET. I have attached the results of the Characterization in the results section.

For this semester (FYP II), I have completed the Characterization of the Silica-Titanium 1%, 3% and 5% using XRD, TGA, TEM and FESEM. All the

Characterization has been done using the Material Characterization in the Mechanical Lab at Block 17. Moreover, I have also completed the Experiment for oil-water separation and graphs. To complete my whole Final Year Project (FYP), I have also analyzed the Oil Absorbed for each experiment and then optimized the results into the Box Behken software to get the best combination of parameters that can achieve the highest Oil Absorbed rate.

3.2 Project Activities

3.2.1 Methodology for the Synthesis of the Hydrophobic Silica Nano-Particles with Titanium 1%, Titanium 3% and Titanium 5% using Sol-Gel Process

Liquid Modification of silica nanoparticles

Silica nanoparticles are commercially available and they can also be synthesized in the laboratory using sol gel process. The chemical properties of silica surface are mainly determined by the various silanol and siloxane groups present on silica nanoparticles surface. The hydroxyl groups onthe surface of silica nanoparticles can be easily tailored with inorganic or organic compounds. Modifications of silica nanoparticles using metal alkoxide or silane reagent are the most convenient technique for silica surface functionalization[8].

Modification of silica nanoparticles using metal oxide as inorganic modifiers

To synthesize silica sol, tetraethoxyorthosilicate (TEOS) was used as the starting materials. Hydrolysis of the TEOS was carried out under base catalyzed conditions and ammonia was used as the base. The hydrolysis ratio between water and TEOS was 2.The hydrolysis reaction (Eq. 1), through the addition of water, replaces alkoxide groups (OC_2H_5) with hydroxyl groups (OH^-). Subsequently, condensation reactions (Eq. 2) involving the silanol groups (Si-OH) produce siloxane bonds (Si-O-Si).

Hydrolysis $\quad Si(OC_2H_5)_4 + H_2O \xrightarrow{\ OH^- \ } Si(OH)_4 + C_2H_5OH$

Condensation $\quad Si(OH)_4 + Si(OH)_4 \xrightarrow{\ OH^- \ } Si-O-Si + H_2O$

Condensation $\quad Si(OH)_4 + Si(OC_2H_5) \xrightarrow{\ OH^- \ } Si-O-Si + C_2H_5OH$
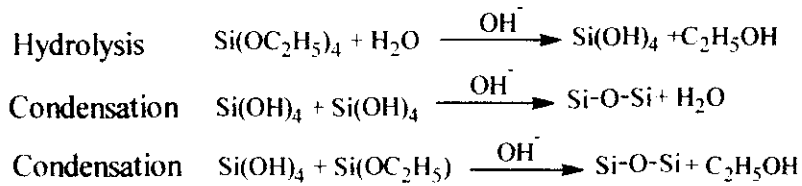
The base catalyst reaction mechanism of silica sol shown below[8]:
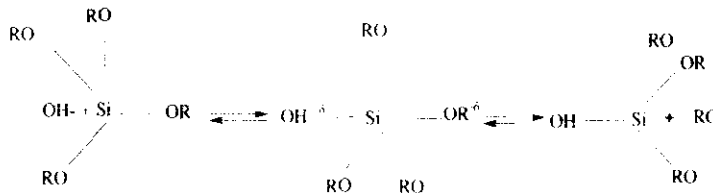
Figure 5: Base catalyst reaction

Silica sols were synthesized and kept at room temperature for 20 minutes. They modified with three different percent (1%, 3% and 5%) of sols. Titanium sols were used as inorganic modifiers.

The modified sols were stirred at 100 rpm for 1hour and kept at room temperature for 24 hours, they dried at 105 °C and grinded with agate mortar to produce modified silica nanoparticles.

$$n\ Si-OH + MX_m \longrightarrow (Sio)_m\text{-}M_{m\text{-}n} + nHX$$

Table 2: Composition of silica sol

TEOS mL	NH$_3$mL	H$_2$O mL
2.765	0.237	5.5

Synthesis of Titanium sol

Titanium tetrapropoxide (30 ml) were mixed with 100 ml of ethanol. The mixture was stirred for 30 min followed by sonication (30 min) then 24 ml of distilled water was added at rate of 1 ml /min with continuous stirring [9]. The mixture was kept in oven at 95 °C for 24 hours to produce titanium oxide.

$$(RO)_3 - Ti - OR + H_2O \rightleftharpoons (RO)_3 - Ti - O - H + R - OH$$

$$(RO)_3 - Ti - O - H + R - OH \rightleftharpoons (RO)_3 - Ti - O - Ti(RO)_3 + H_2O$$

$$Si-OH + TiO_2 \longrightarrow (SiO)- Ti + H_2O$$
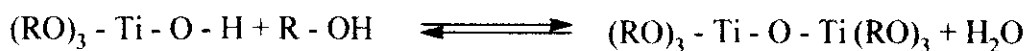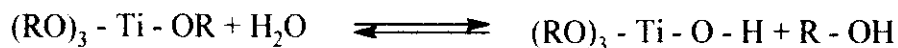
Table 3 : Percent of titanium sol added to silica sols

Percent %	Amount of titanium sol mL
1	0.02765
3	0.0829
5	0.138

3.2.2.1 Methodology For Characterization Using XRF, FTIR And BET

Silica nanoparticles have been the subject of extensive research. There is a number of literature reports of various analytical techniques used to characterize these particles after modification. The characterization studies improve the understanding of the process involved and the final properties of the resultant composites. I have completed the Characterization on **Fourier Transform infrared (FTIR), X-Ray Fluorescence (XRF) and Surface area of silica nanoparticle (BET), X-Ray Diffraction (XRD), Thermo Gravimetric Analysis (TGA), Transmission Electron Microscopy (TEM) and Field Emission Scanning Microscopy (FESEM).**The details on the importance the characterization has been explained in Literature Review part and the results and discussion can be found in Chapter 4.

3.2.2.2 Experiment For Oil-Water Separation :

Temperature: 25°C, 35°C and 45°C

Percentage of Titanium: 1%, 3% and 5%

Silica-Titanium: 0.5g, 1.0g and 1.5g

Oil percentage: 10%, 30%, 50%, 70% and 90%

Rate of Oil Absorption using the different concentration of Silica-Titanium.

Five mixtures of paraffin oil and distilled water (90%, 70%, 50%, 30%, 10% oil) were prepared as shown in table below and stirred at 250 rpm for 5 minutes. Then 0.5 g of silica nanoparticles modified with 1% titanium were added to the mixture and the density was measured every hour using portable densitometer (5 ml). At least three independent measurements were taken for each sample every hour to ensure the effectiveness of the measurement.

Increasing the density of the mixture with the time shows the adsorption of paraffin oil from the mixture by silica titanium nanoparticles. This is taken at room temperature of 25°C.

Table 4: Five samples with different ratio between paraffin oil and water

Sample	Oil %	Paraffin oil ml	Water ml
1	10	1	9
2	30	3	7
3	50	5	5
4	70	7	3
5	90	9	1

Rate of Oil Absorption based on the effect of Temperature.

The effect of temperatures (25°C, 35 °C and 45 °C) on adsorption of paraffin oil from oil water environment was studied for silica nanoparticles modified with 5% titanium. Five samples of paraffin oil and water were prepared and kept in required temperature (25°C, 35 °C or 45 °C) in water path and stirred at 250 rpm. The temperature were monitored by two thermometer one for the water path and the other the paraffin oil and water.

22

When the temperature of the mixture reaches the required temperature, 0.5 g of modified silica nanoparticles with titanium (5%) were added individually to paraffin oil and water mixtures (90%, 70%, 50%, 30%, 10% oil).

The densities of the mixtures were measured every hour using portable densitometer. At least three independent measurements were taken for each sample to assure the effectiveness of the measurement.

Rate of Oil Absorption based on the effect of weight of Silica-Titanium.

Five mixtures of paraffin oil and distilled water (90%, 70%, 50%, 30%, 10% oil) were prepared as shown in table below and stirred at 250 rpm for 5 minutes. Then 0.5 g of silica nanoparticles modified with 1% titanium were added to the mixture and the density was measured every hour using portable densitometer (5 ml). At least three independent measurements were taken for each sample every hour to ensure the effectiveness of the measurement. After that, the weight of silica nanoparticles will be varied at 1.0g and 1.5g.

Increasing the density of the mixture with the time shows the adsorption of paraffin oil from the mixture by silica titanium nanoparticles. This is taken at room temperature of 25°C, 35°C and 45°C.

Rate of Oil Absorption based on the Percentage of Oil.

Five mixtures of paraffin oil and distilled water (90%, 70%, 50%, 30%, 10% oil) were prepared as shown in table below and stirred at 250 rpm for 5 minutes. Then 0.5 g of silica nanoparticles modified with 1% titanium were added to the mixture and the density was measured every hour using portable densitometer (5 ml). At least three independent measurements were taken for each sample every hour to ensure the effectiveness of the measurement. All experiments are done using all the 5 different percentage of oil.

23

3.2   Tools Required

i)   Paraffin oil

ii)   Distilled Water

iii)   Acetone

iv)   Thermometer

v)   Magnetic Stirrer

vi)   Oven

vii)   Retort Stand

viii)   Glass beaker

ix)   Equipment for Characterization of materials
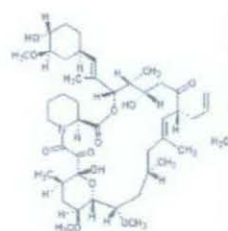
Figure 6: Tools required for Experiment

3.3   Key Milestones & Gantt Chart

Processes

Milestones ★

No	Detail/Week	1	2	3	4	5	6	7	Mid Semester Break	8	9	10	11	12	13	14	15
1	Project Work Continues																
2	Submission of Progress Report									★							
3	Project Work Continues																
4	Pre - SEDEX												★				
5	Submission of Draft Report													★			
6	Submission of Dissertation (soft bound)														★		
7	Submission of Technical Paper														★		
8	Oral Presentation															★	
9	Submission of Project Dissertation (Hard Bound)																★

CHAPTER 4: RESULTS AND DISCUSSION

4.1 RESULTS

4.1.1 RESULTS FOR CHARACTERIZATION

Fourier transmission infrared (FTIR)
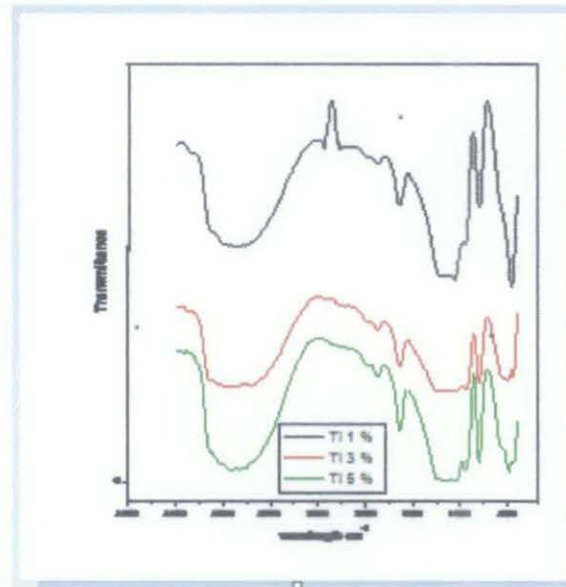
Figure 7: FTIR Results for Silica-Titanium 1%, 3% and 5%

X-ray fluorescence (XRF)

Table 5 : XRF for the Silica Sols

Sample	Si KCps	O KCps	Ti KCps
1% Ti	46.7	53	-
3% Ti	46.3	53	0.394
5% Ti	46.3	53	0.53

The amount of Ti is correct based on the XRF Material Characterization.

Surface area and pore size analyzer (BET)

BET Surface:

Pure Silica : 303.6973 m^2/g

Ti 1% : 77.9345 m^2/g

Ti 3% : 31.4268 m^2/g

Ti 5% : 31.0351 m^2/g

Field Emission Scanning Electron Microscopy (FESEM)
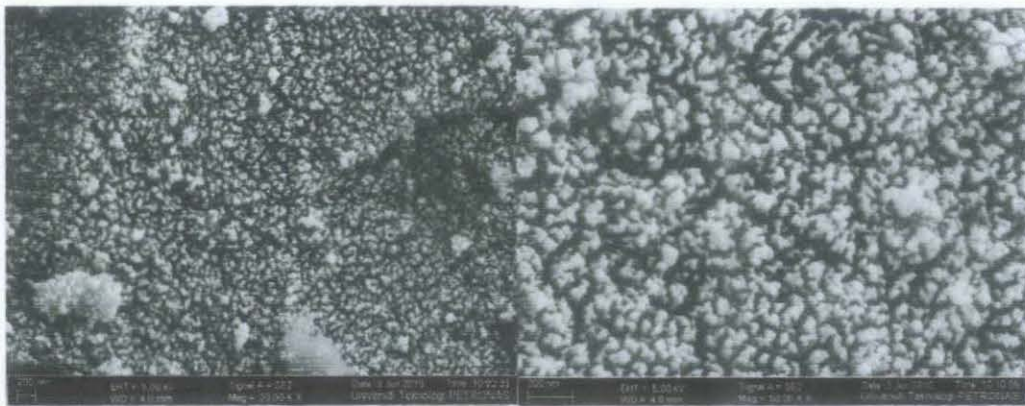
Figure 8: FESEM for Silica Pure
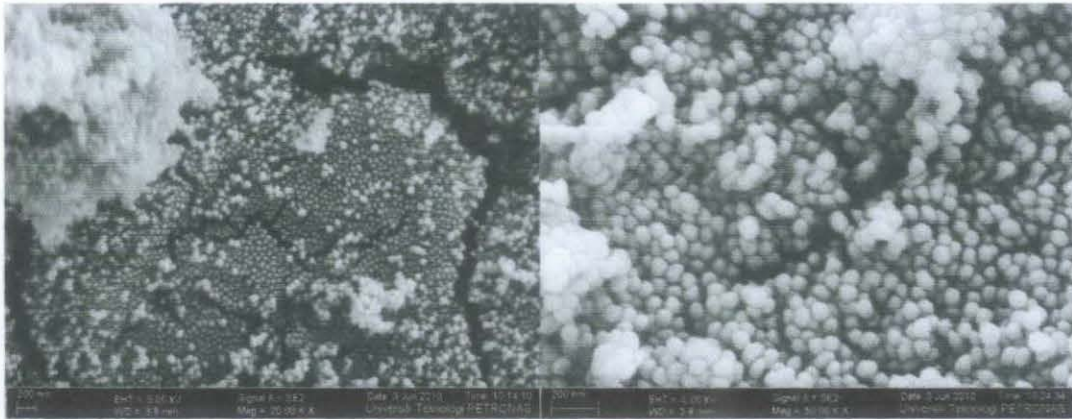
Figure 9: FESEM for Silica-Titanium 1%
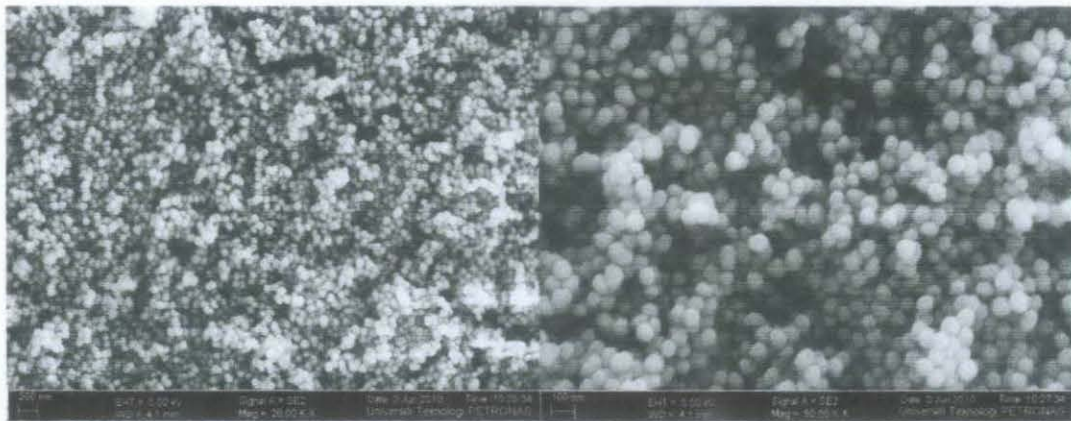
Figure 10: FESEM for Silica-Titanium 3%
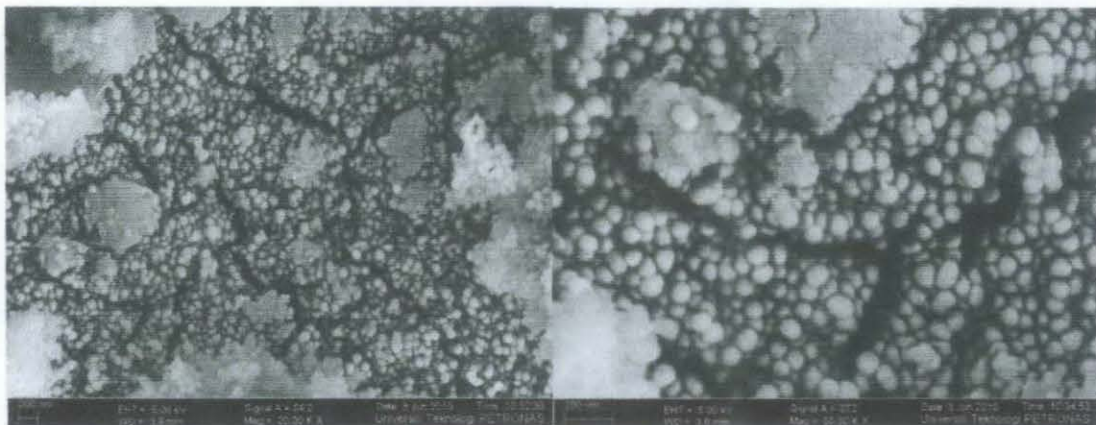
Figure 11: FESEM for Silica-Titanium 5%

26

X-ray diffraction (XRD)

Silica pure
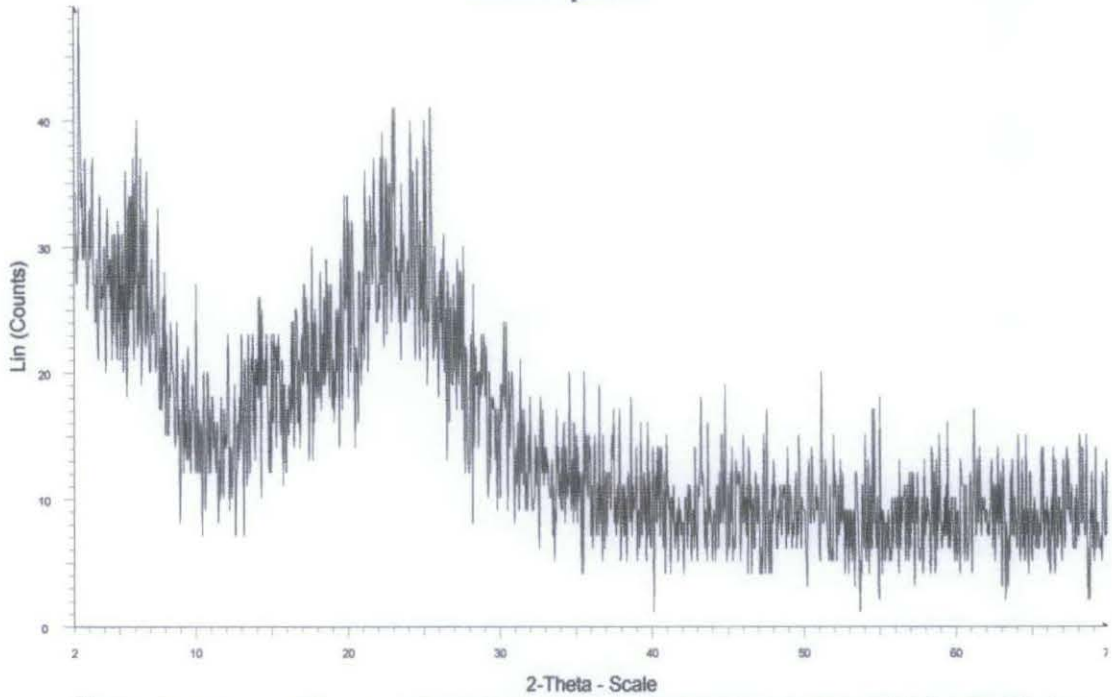
Silica pure - File: Silica pure.raw - Type: 2Th/Th locked - Start: 2.000 ° - End: 70.000 ° - Step: 0.050 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 1304669696 s - 2-Theta: 2.000 ° - Theta: 1
Operations: Import

Silica-Titanium 1%
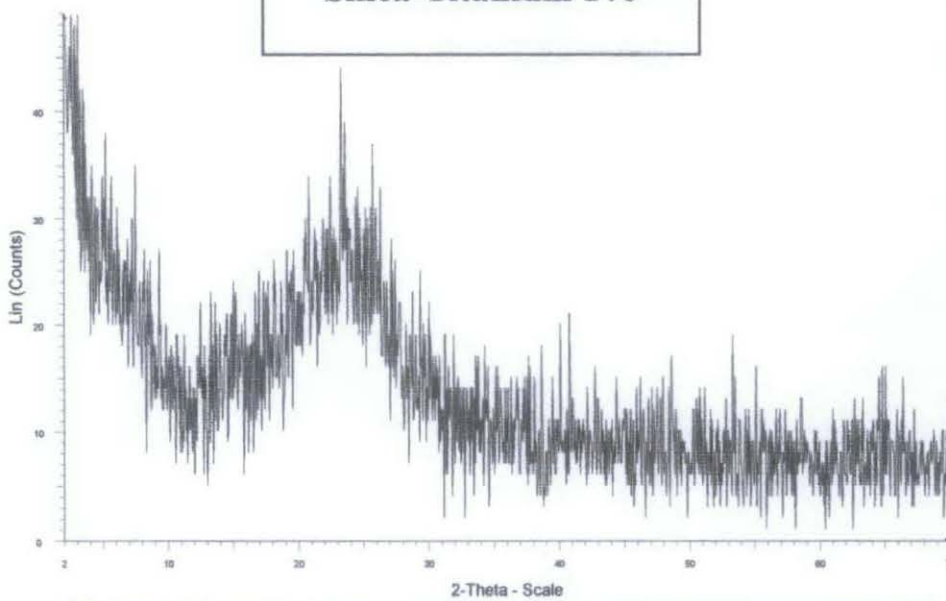
Silica Aluminium 1% - File: Silica Aluminium 1%.raw - Type: 2Th/Th locked - Start: 2.000 ° - End: 70.000 ° - Step: 0.050 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 1304699456 s - 2-Thet
Operations: Import
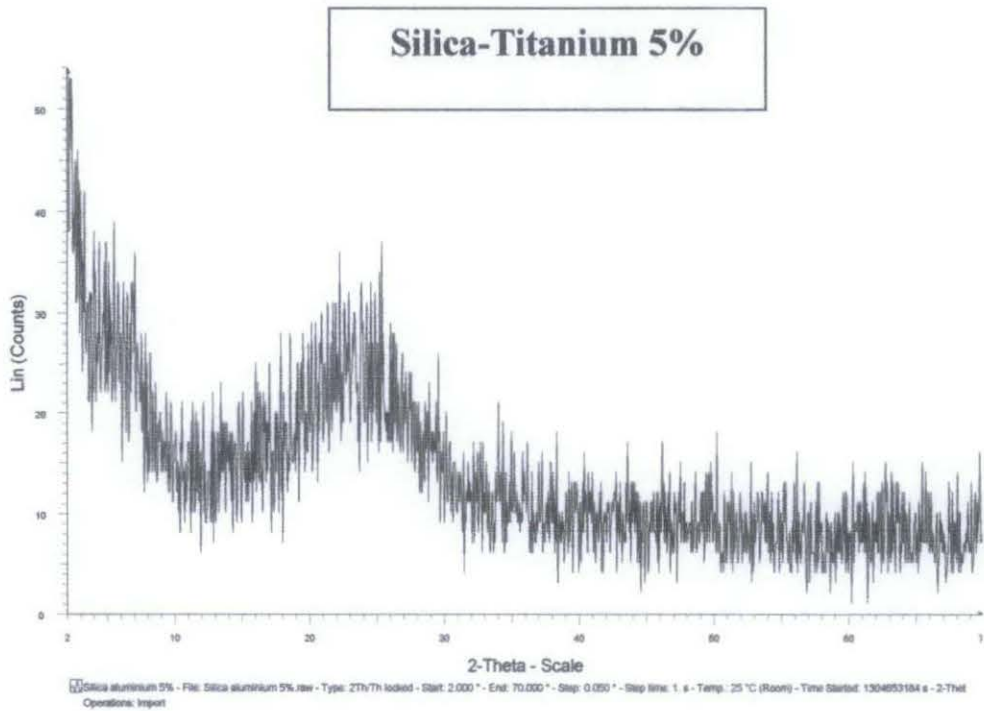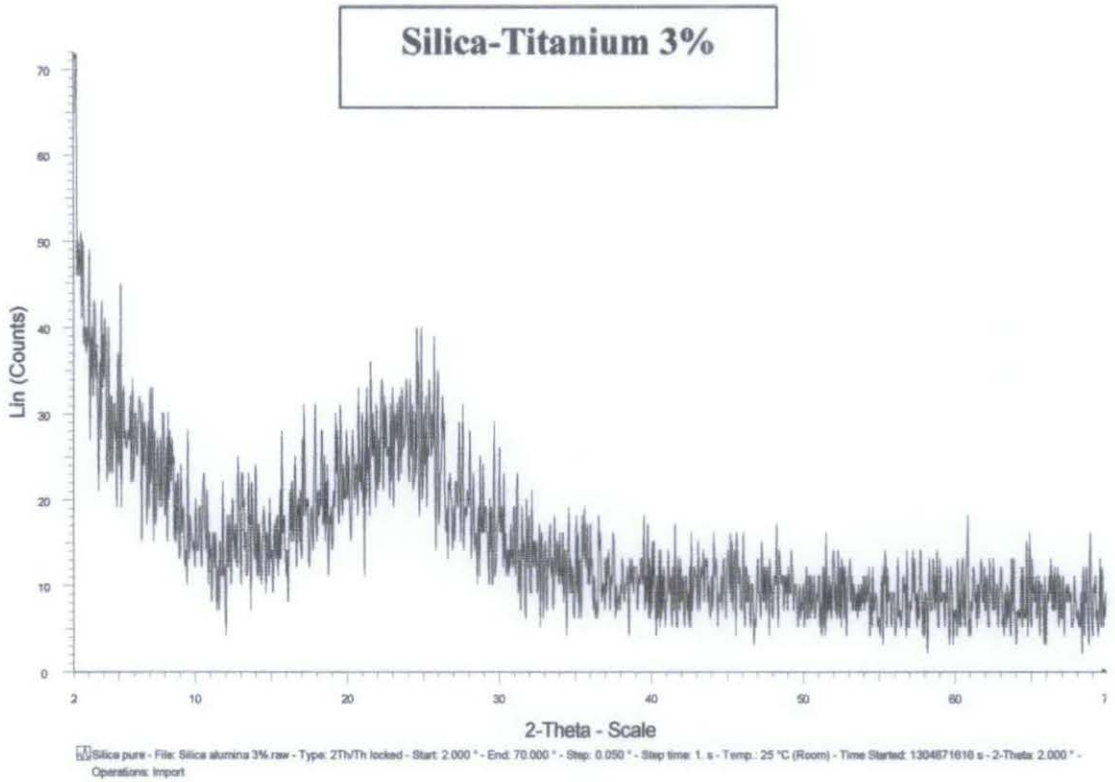
Figure 12: XRD of Silica Pure, Silica-Titanium 1%, 3% and 5%
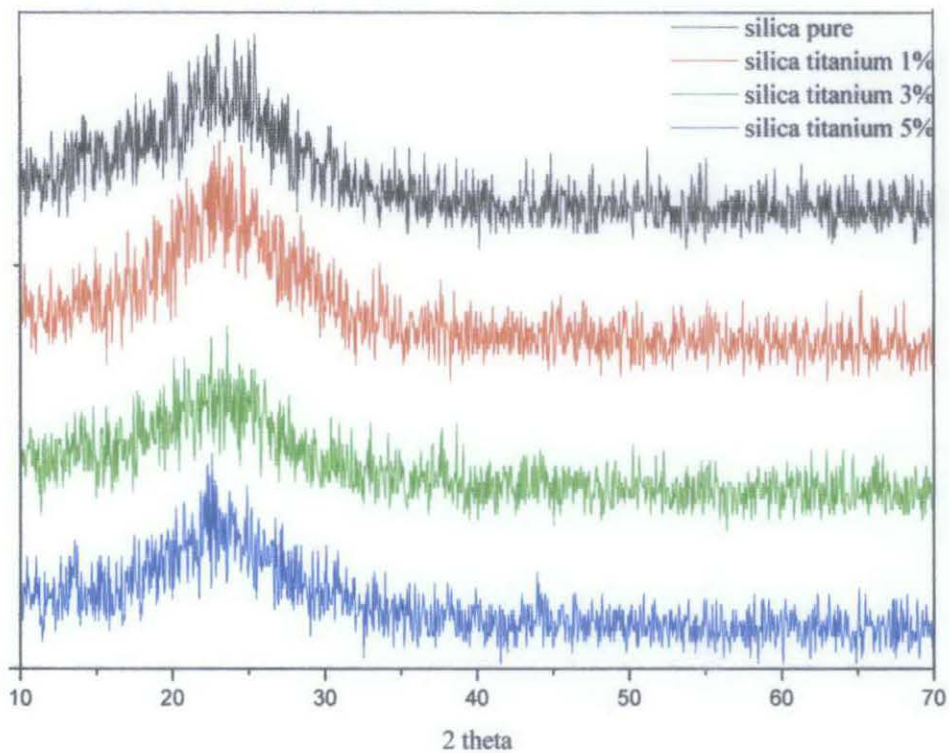
Figure 13: XRD comparison before Pure Silica and the 3 silica sols

Transmission electron microscopy (TEM)
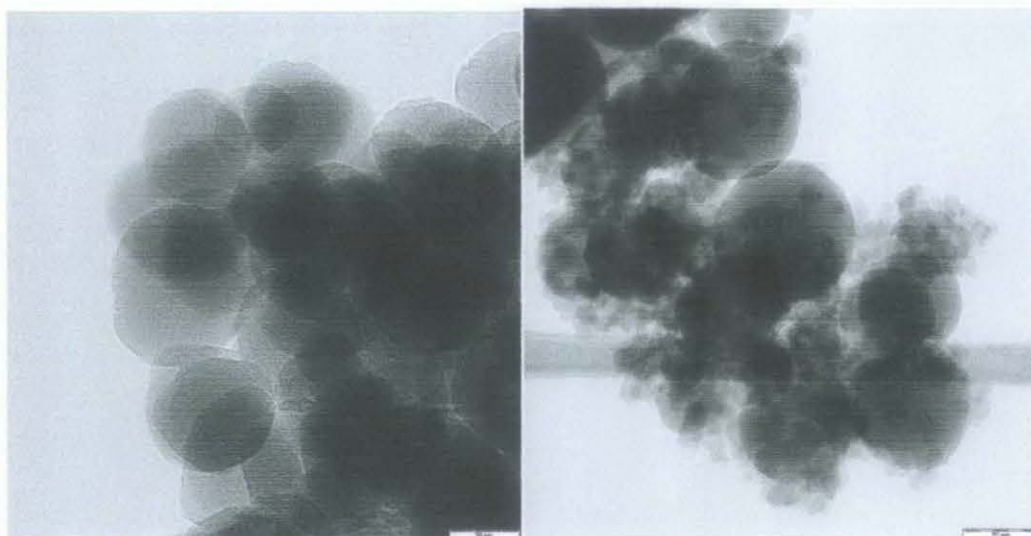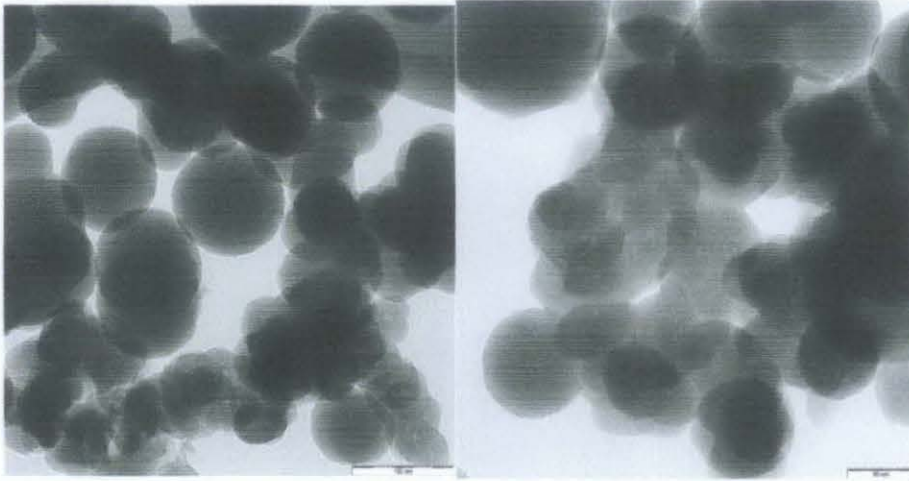
Figure 14: TEM of the Silica Sols

Thermal gravimetric analysis (TGA)

Silica Pure
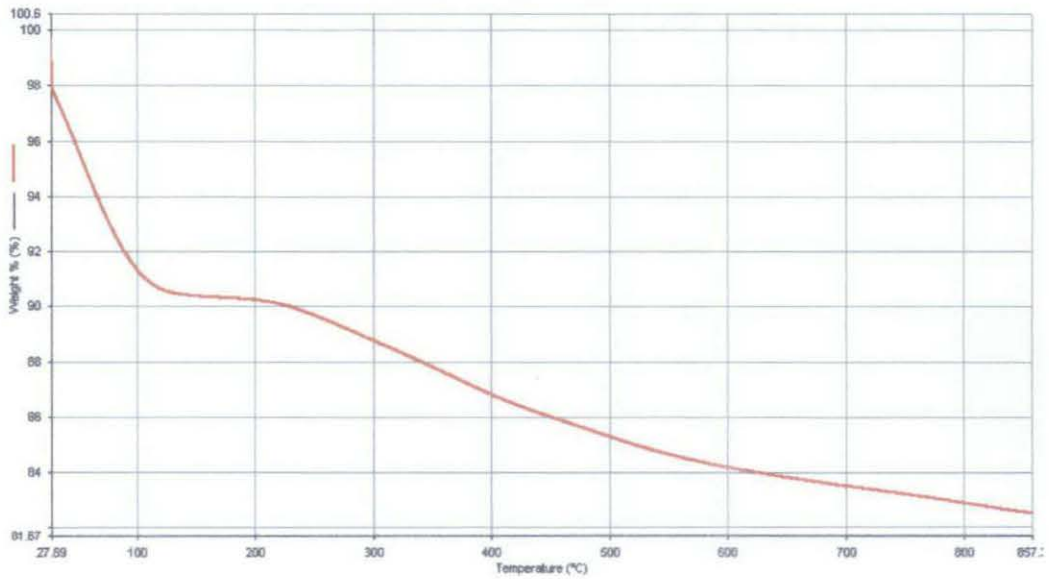
Figure 15: TGA of Silica Pure

Silica Titanium 1%
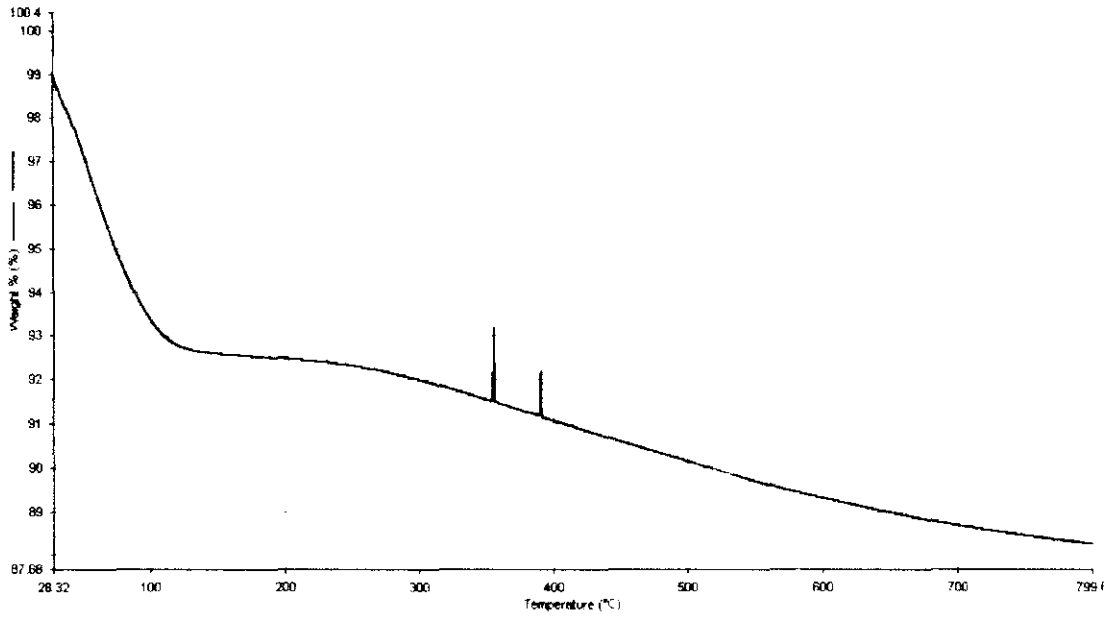
Figure 16: TGA of Silica-Titanium 1%
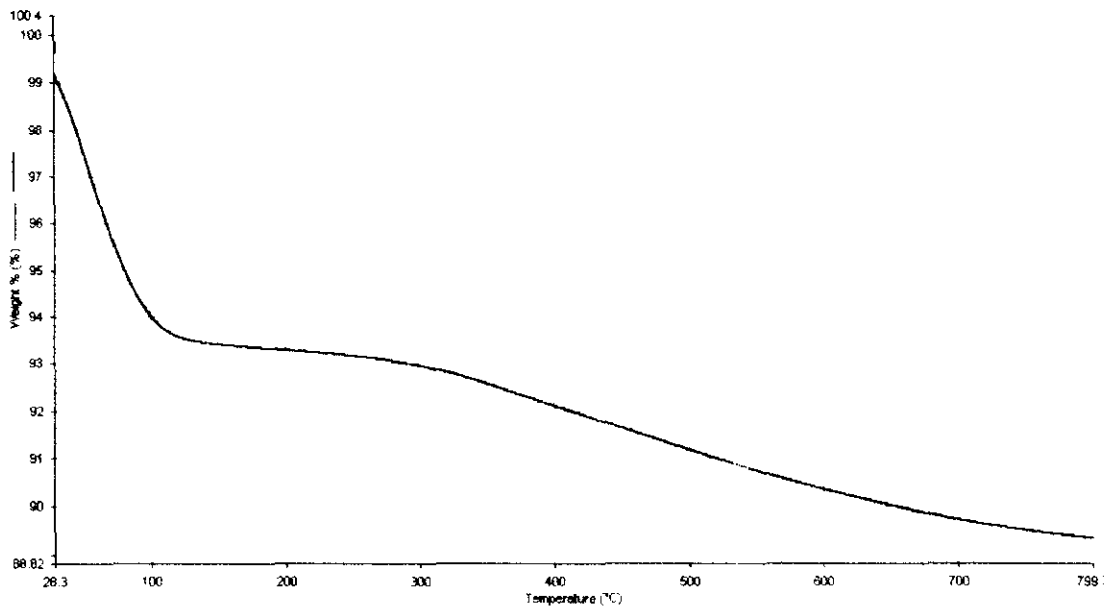
Silica Titanium 3%

Figure 17: TGA of Silica-Titanium 3%

Silica Titanium 5%
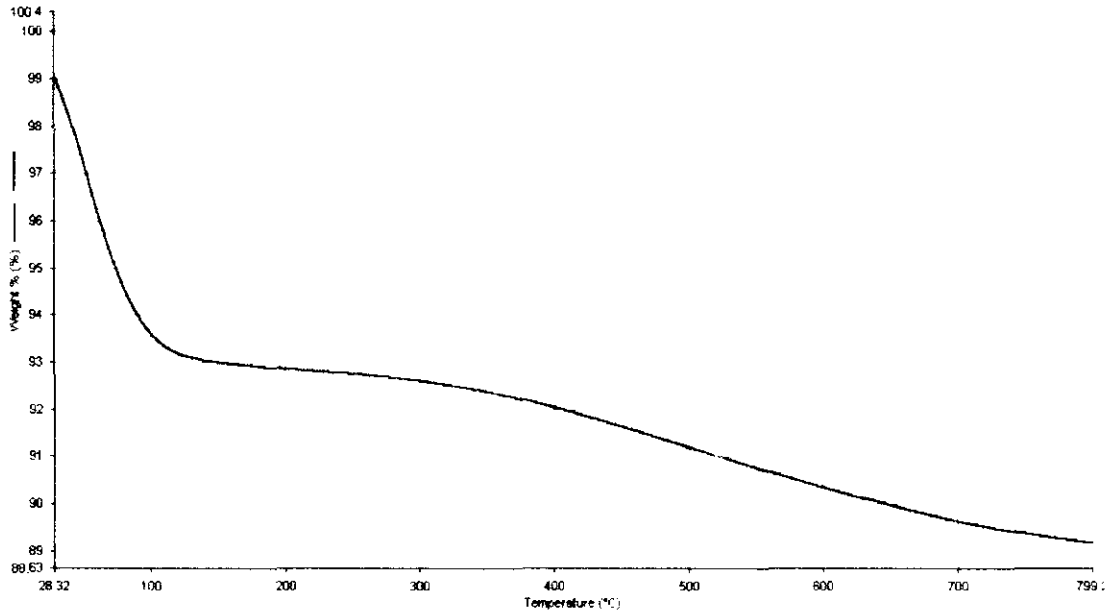
Figure 18: TGA of Silica-Titanium 5%

4.1.2 RESULTS FOR EXPERIMENT
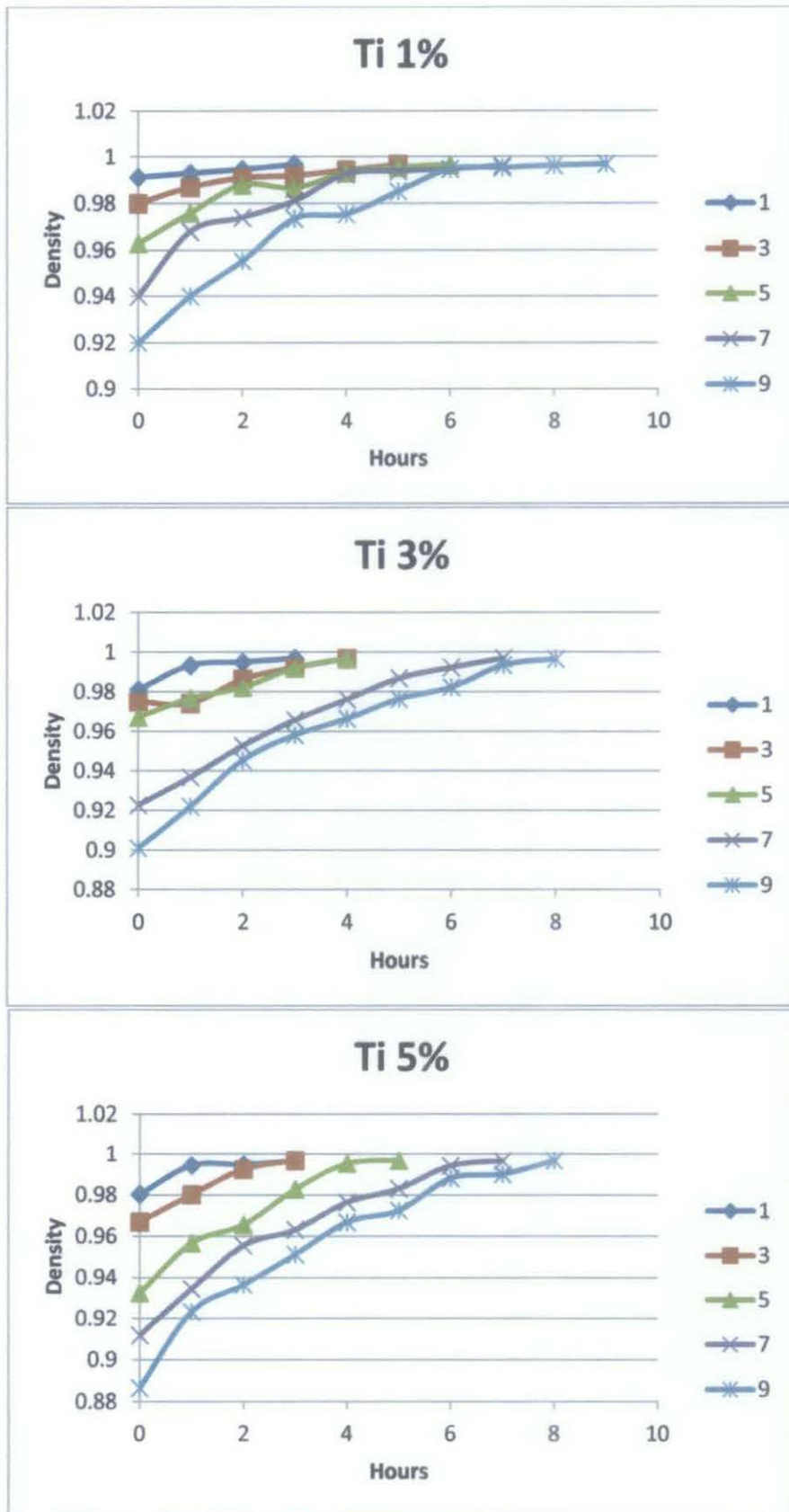
Figure 19: Results for Temperature 25 °C and Silica-Titanium 0.5g
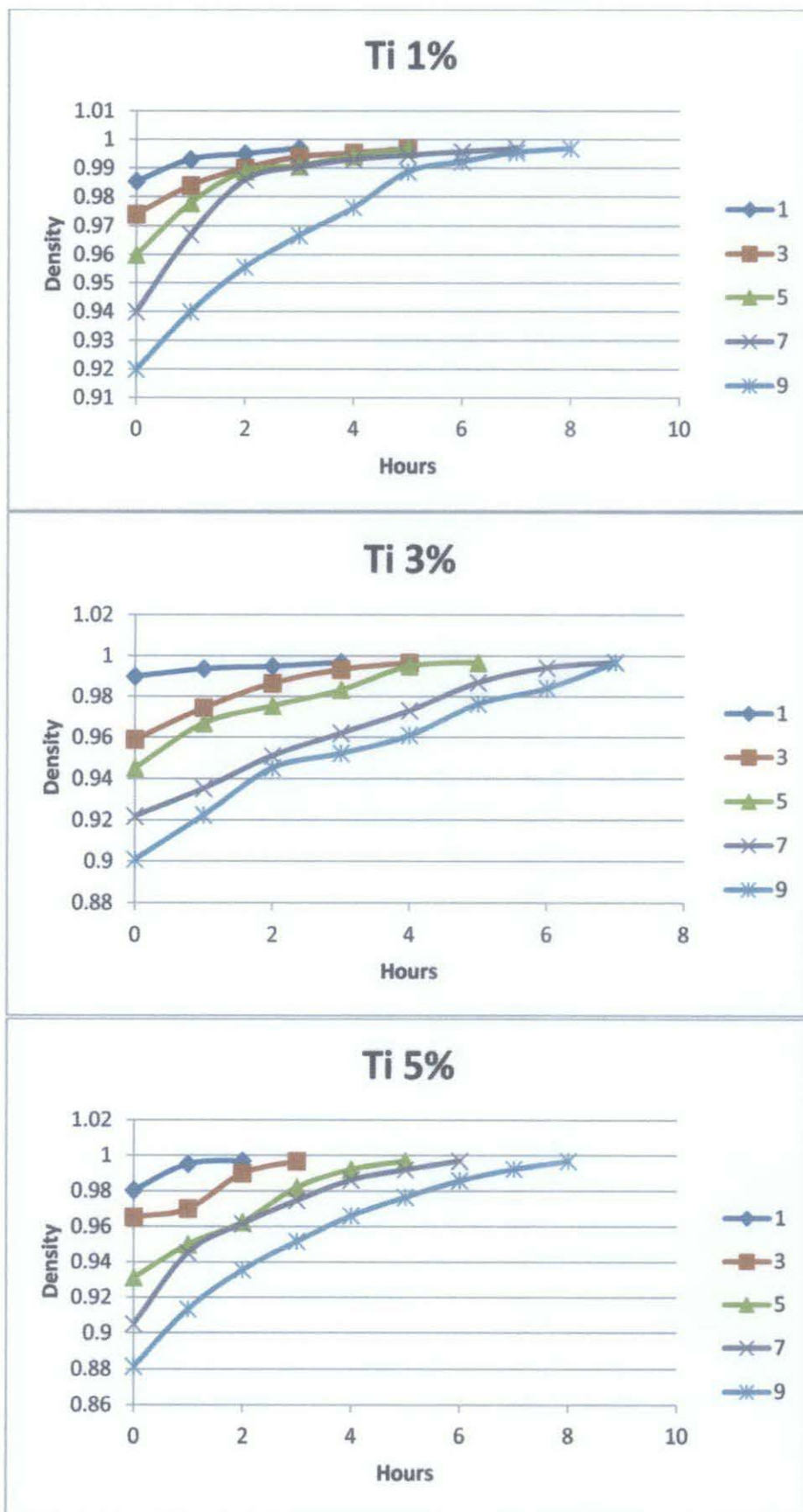
Figure 20: Results for Temperature 25 °C and Silica-Titanium 1.0g
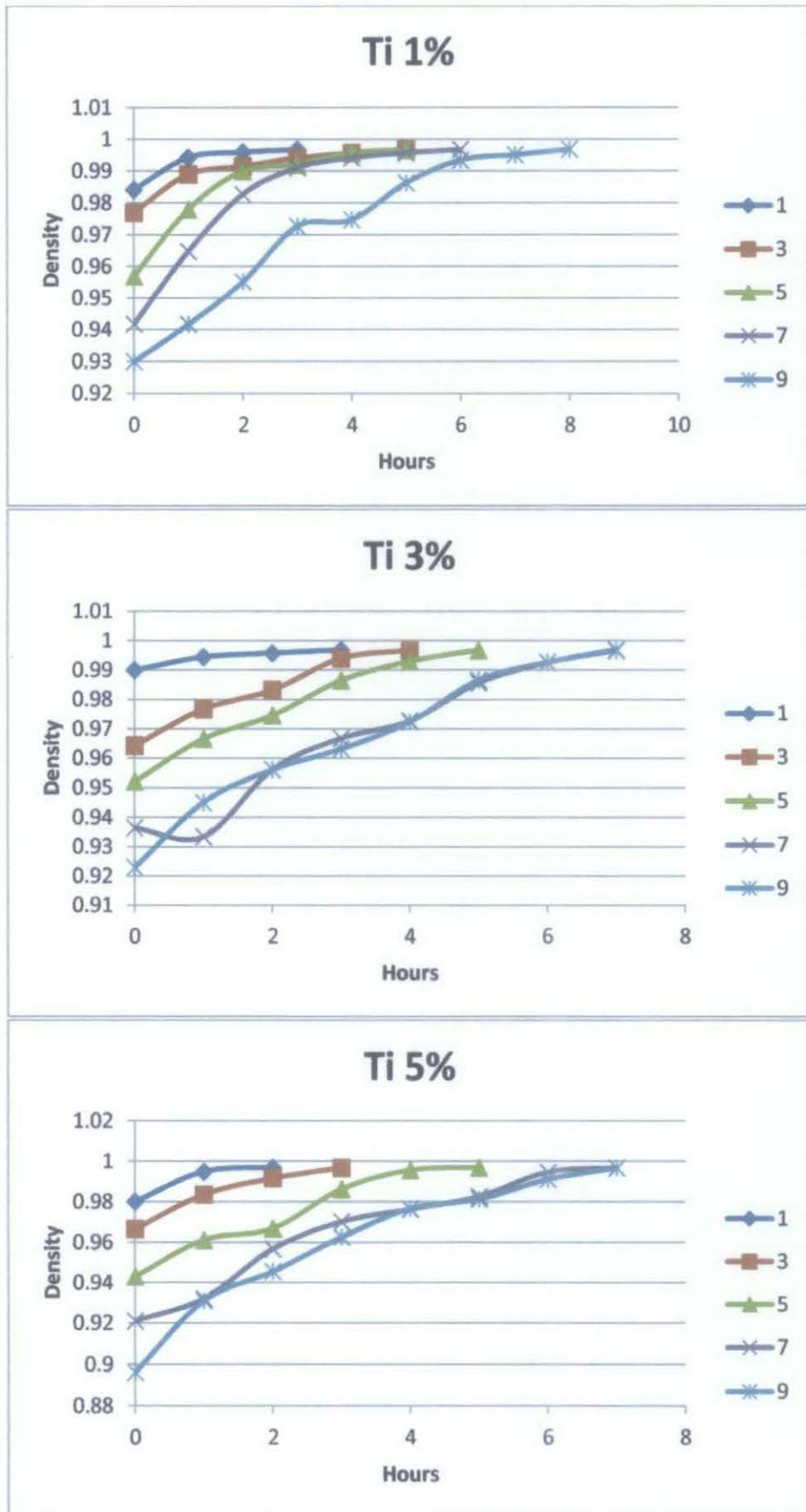
Figure 21: Results for Temperature 25 °C and Silica-Titanium 1.5g
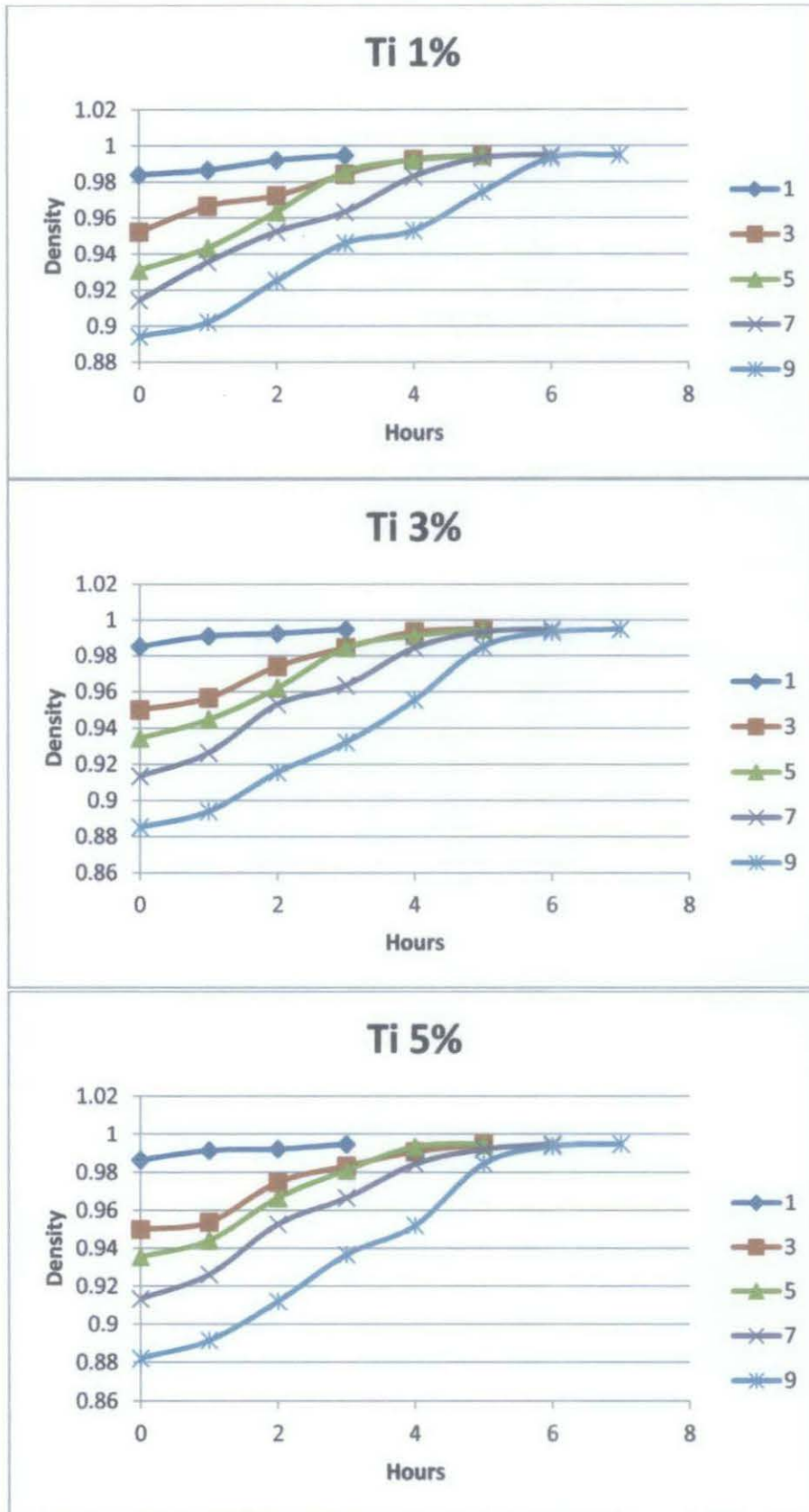
Figure 22: Results for Temperature 35 °C and Silica-Titanium 0.5g
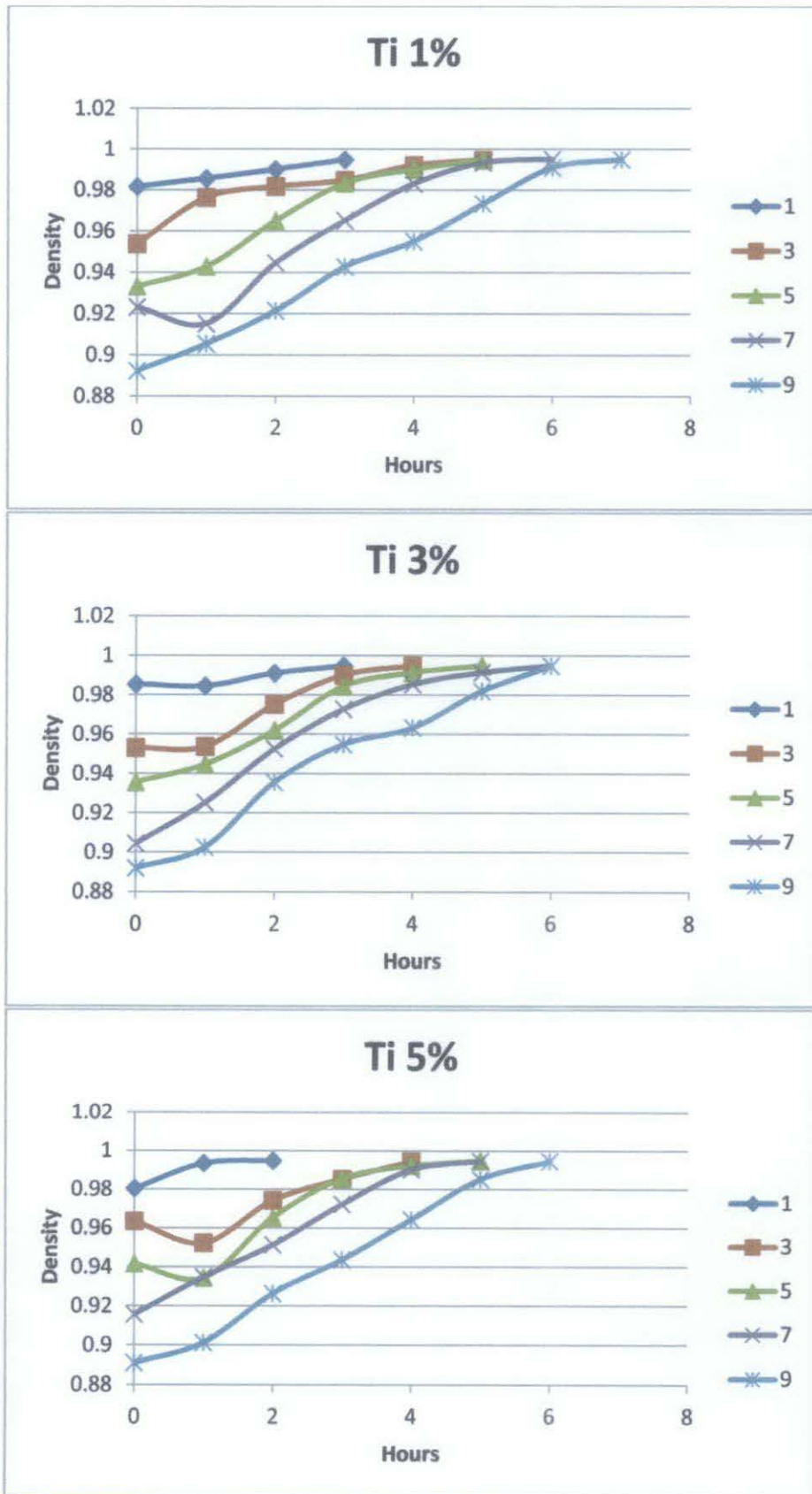
Figure 23: Results for Temperature 35 °C and Silica-Titanium 1.0g
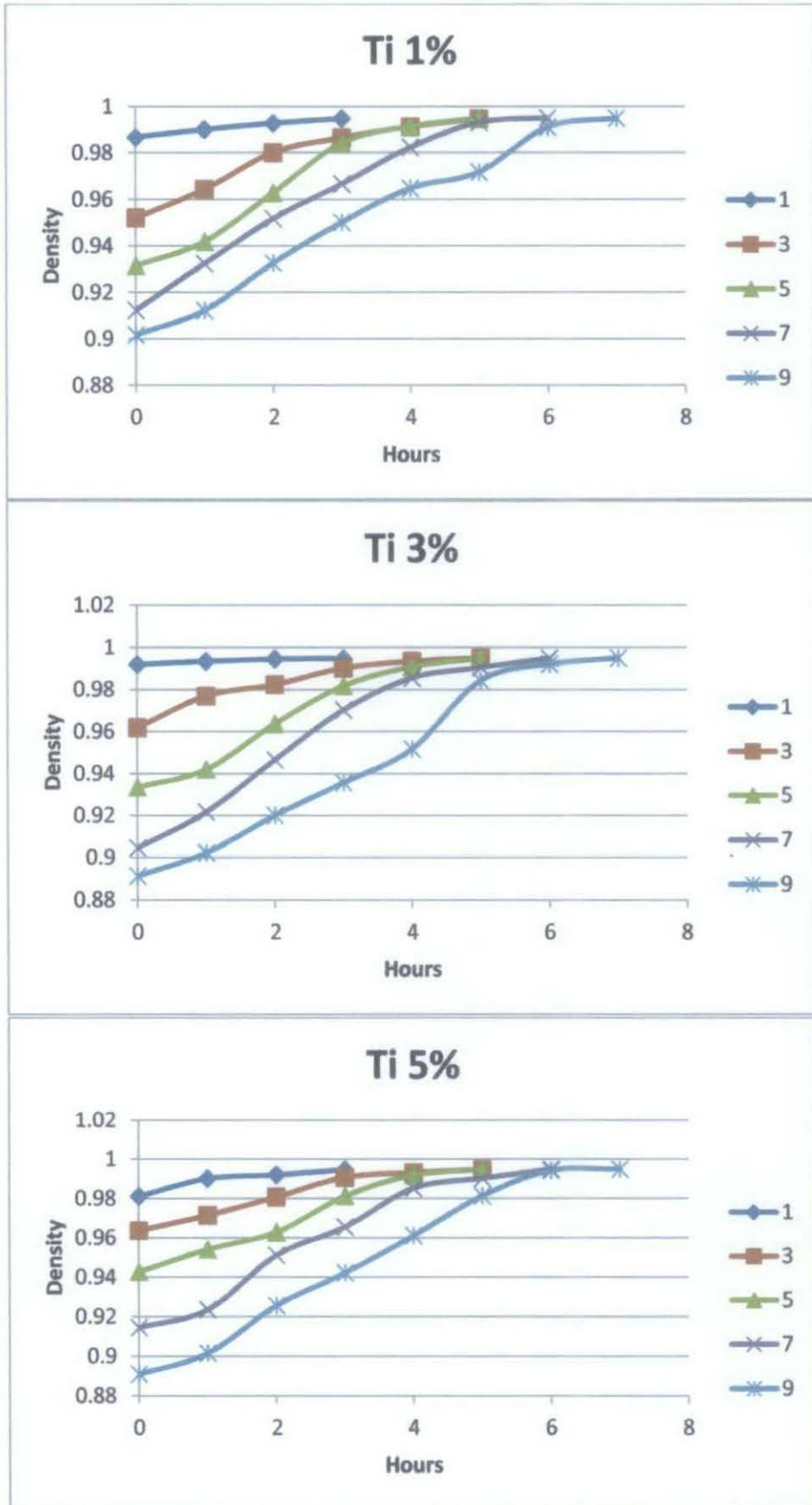
Figure 24: Results for Temperature 35 °C and Silica-Titanium 1.5g
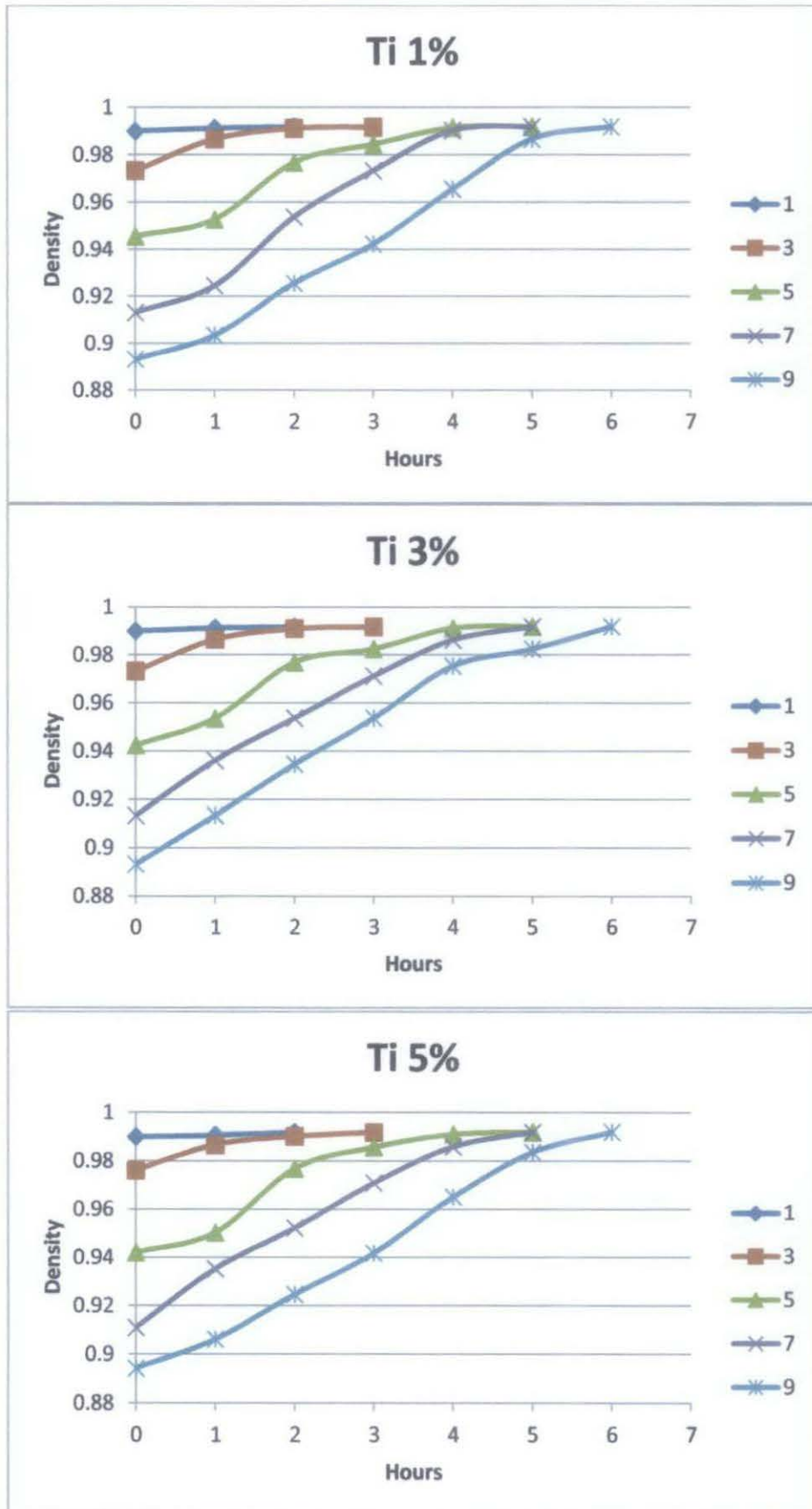
Figure 25:Results for Temperature 45 °C and Silica-Titanium 0.5g
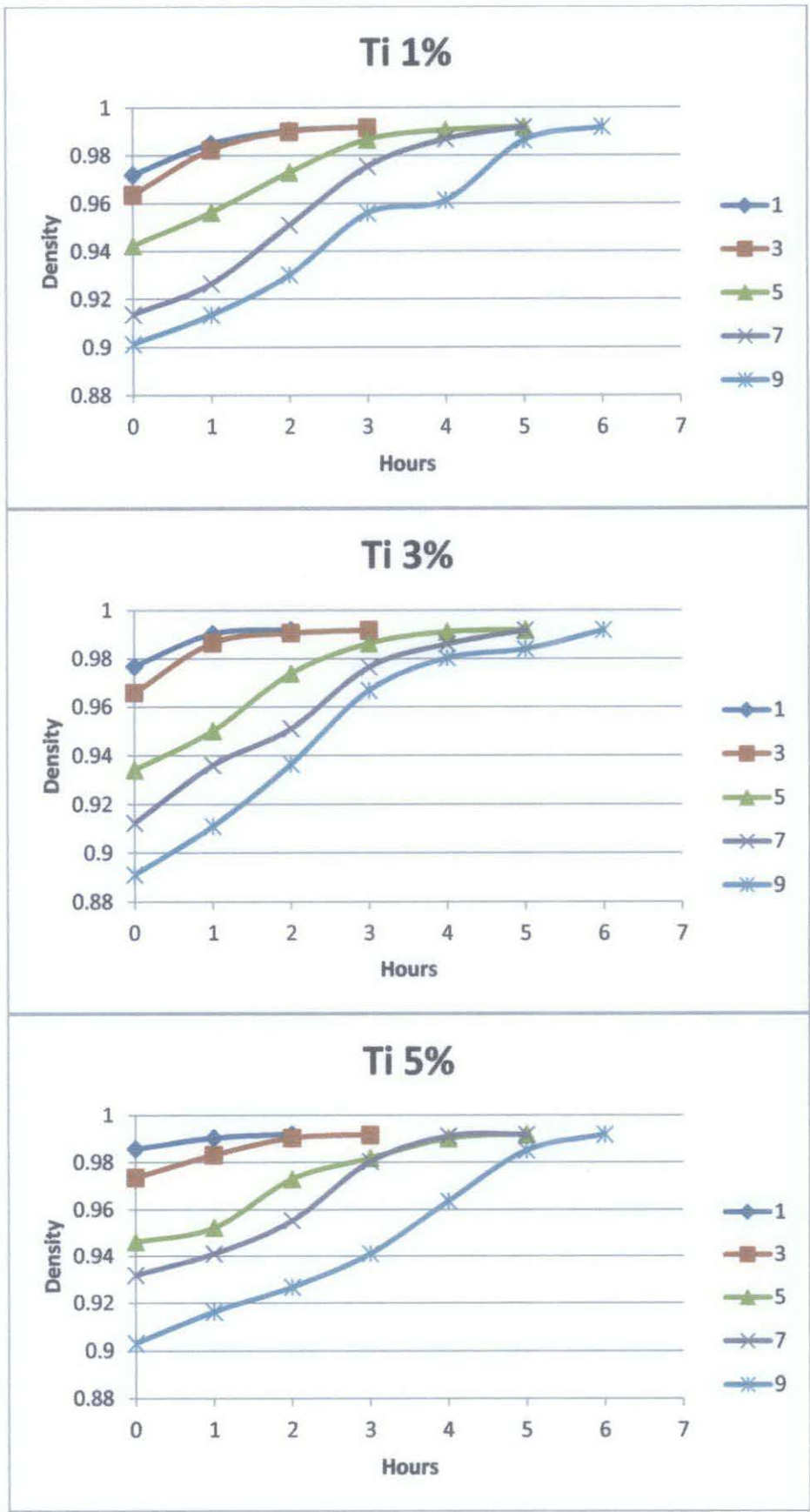
Figure 26: Results for Temperature 45 °C and Silica-Titanium 1.0g
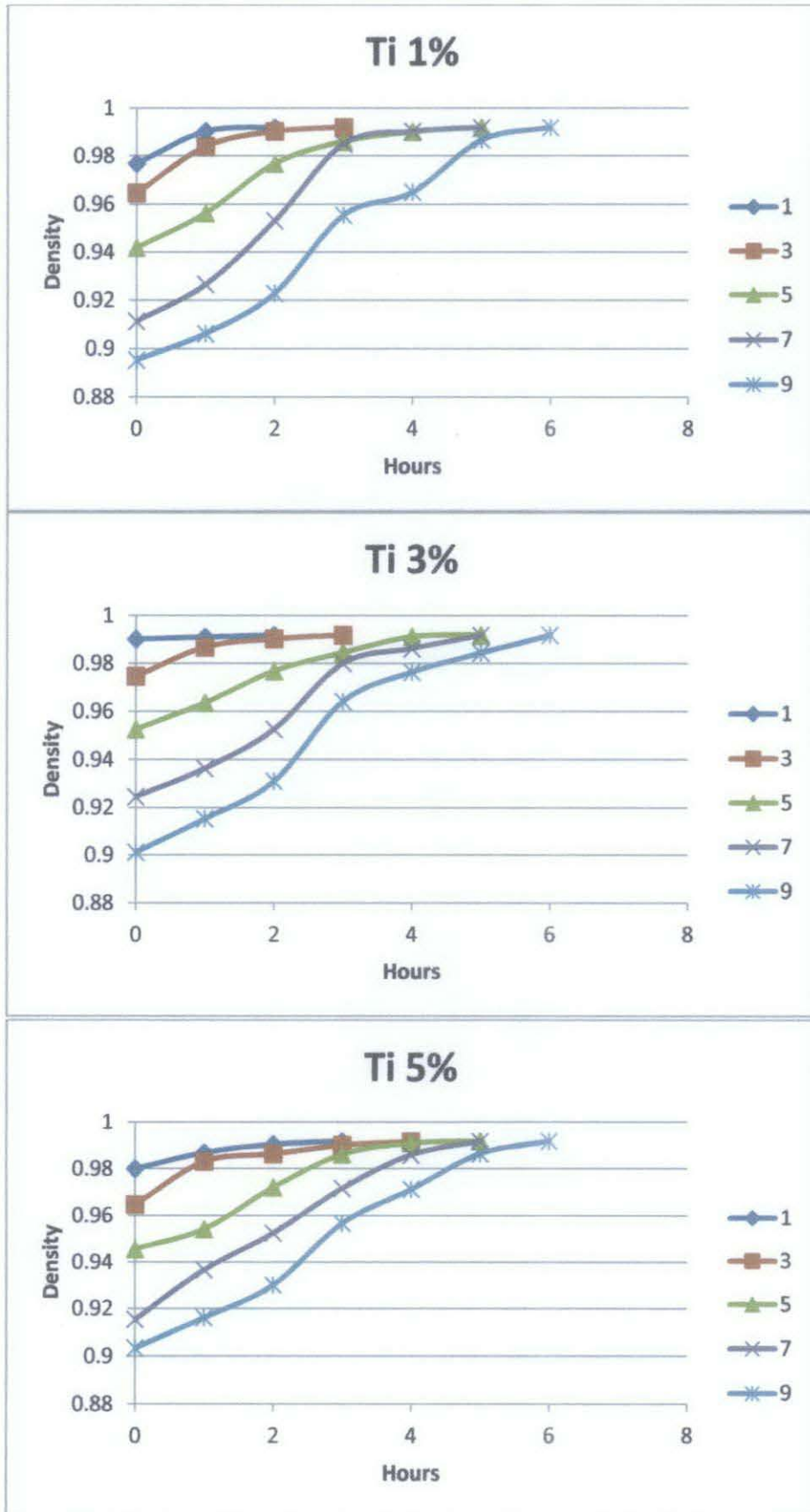
Figure 27: Results for Temperature 45 °C and Silica-Titanium 1.5g

4.1.3 OPTIMIZATION ON OIL ABSORBED

To complete my whole Final Year Project (FYP), I have analyzed the Oil Absorbed for each experiment and then optimized the results into the Box Behnken software to get the best combination of parameters that can achieve the highest Oil Absorbed rate. After doing that, I have compared the data that I have obtained from the experimental work and also from the software.

After calculating all the Oil Absorbed values, I have keyed it into the software at each parameter. From there, the Box Behnken software analyzes the experiment to obtain the following:

Analysis of Variance for Oil absorbed

Table 6 : ANOVA Table

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:Titanium percent	382.279	1	382.279	104.14	0.0000
B:Oil percentage	20429.8	1	20429.8	5565.28	0.0000
C:Temperature	183.535	1	183.535	50.00	0.0000
D:Silica	59.5708	1	59.5708	16.23	0.0001
AA	9.67556	1	9.67556	2.64	0.1066
AB	483.864	1	483.864	131.81	0.0000
AC	27.1216	1	27.1216	7.39	0.0074
AD	51.8671	1	51.8671	14.13	0.0002
BB	1980.35	1	1980.35	539.47	0.0000
BC	214.97	1	214.97	58.56	0.0000
BD	99.5225	1	99.5225	27.11	0.0000
CC	2.15927	1	2.15927	0.59	0.4444
CD	1.82087	1	1.82087	0.50	0.4824
DD	6.39809	1	6.39809	1.74	0.1888
blocks	4.72269	1	4.72269	1.29	0.2586
Total error	535.955	146	3.67093		
Total (corr.)	24473.6	161			

42

R-squared = 97.8101 percent

R-squared (adjusted for d.f.) = 97.6015 percent

Standard Error of Est. = 1.91597

Mean absolute error = 1.16325

Durbin-Watson statistic = 1.98425 (P=0.4603)

Lag 1 residual autocorrelation = 0.00500779

Regression coeffs.for Oil absorbed

Table 7: Regression Coefficients

Coefficient	Estimate
constant	63.1346
A:Titanium percent	-2.00859
B:Oil percentage	-9.97017
C:Temperature	-0.578043
D:Silica	4.71146
AA	-0.129606
AB	0.324045
AC	0.0306875
AD	-0.84875
BB	0.463553
BC	0.0431979
BD	-0.587847
CC	0.00244907
CD	-0.0318056
DD	1.6863

This pane displays the regression equation which has been fitted to the data. The equation of the fitted model is:

Oil absorbed = 63.1346 - 2.00859*Titanium percent - 9.97017*Oil percentage - 0.578043*Temperature + 4.71146*Silica - 0.129606*Titanium percent^2 + 0.324045*Titanium percent*Oil percentage + 0.0306875*Titanium percent*Temperature - 0.84875*Titanium percent*Silica + 0.463553*Oil percentage^2 + 0.0431979*Oil percentage*Temperature - 0.587847*Oil percentage*Silica + 0.00244907*Temperature^2 - 0.0318056*Temperature*Silica + 1.6863*Silica^2

where the values of the variables are specified in their original units.

43

Path of Steepest Ascent for Oil absorbed

Table 8: Steepest Ascent Table

Titanium percent	Oil percentage	Temperature	Silica	Predicted Oil absorbed
(%)	(%)	(Celcius)	(gram)	(%)
3.0	5.0	35.0	1.0	15.8906
4.0	16.2356	38.7635	0.852262	40.7689
5.0	27.8251	42.5394	0.704249	202.607
6.0	39.6645	46.2818	0.560974	510.095
7.0	51.591	50.0115	0.419488	964.994
8.0	63.5621	53.7344	0.278957	1568.04

This pane displays the path of steepest ascent (or descent). This is the path from the center of the current experimental region along which the estimated response changes most quickly for the smallest change in the experimental factors. It indicates good locations to run additional experiments if your goal is to increase or decrease Oil absorbed. Currently, 6 points have been generated by changing Titanium percent in increments of 1.0 %.

Optimize Response
Goal: maximize Oil absorbed

Optimum value = 48.2544

Table 9: Optimization Table

Factor	Low	High	Optimum
Titanium percent	1.0	5.0	5.0
Oil percentage	1.0	9.0	1.0
Temperature	25.0	45.0	25.0
Silica	0.5	1.5	1.5

This table shows the combination of factor levels which maximizes Oil absorbed over the indicated region.

4.2 ANALYSIS AND DISCUSSION

4.2.1 Discussion on Material Characterization

Fourier transmission infrared (FTIR)

The chemical structure of silica nanoparticles is generally identified by FTIR spectra. Fourier transformation infrared (FTIR) spectrometryis widely used to prove the formation of silica nanoparticles especially for those prepared by the sol-gel reaction, in which process a silica network can be formed . The FTIR will basically detect the vibration characteristics of silica groups in the sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, the silica group will absorb the infrared radiation and resulted in the emerging of the peaks in the plot. The characterization of the silica sol is being done to ensure the existence of the silica component in it. From the figure in the results section, it can be seen that a few peaks emerged which indicates that the silica sols contains the different amounts of silica-titanium.

X-ray fluorescence (XRF)

X-ray fluorescence technology provides one of the simplest, most accurate and most economic analytical methods for determination of minor and major elemental composition of materials. From the data shown in the table, it is proven that the composition for Silica-Titanium 1%, Silica-Titanium 3% and Silica-Titanium 5% is correct with the right amount of Titanium.

Surface area and pore size analyzer (BET)

Several techniques were applied to determine the surface area for the solid materials. Surface analysis of silica nanoparticles were performed by nitrogen sorption isotherms. The surface area is usually described by the gas adsorption or desorption isotherms. From the BET Material Characterization, The surface area of the Silica

Sols are determined. As one can see, the surface area for the pure silica is the most and it reduces as more Titanium is added.

Field Emission Scanning Electron Microscopy (FESEM)

Scanning electron microscopy is one of the most essential techniques used to determine the surface properties of silica nanoparticles. SEM is used to determine the morphological change by scanning the sample with a high-energy beam of electrons. The basic components of the field emission scanning electron microscopy are lens system, the electron gum, the electron collector, the photo-recording cathode ray tube, and the associated electronics. The figures in the results section shows the morphological change between a silica pure material and silica-titanium.

X-ray diffraction (XRD)

Every crystalline substance produced its own XRD pattern, which because it is dependent on the internal structure, which is the characteristic of a specific substance. Using the XRD, the concentration or the amount of a component can be detected using the X-ray to diffract the internal structure of the component in all possible concentrations. In the figures, it shows the differences of the XRD plots for Silica Pure, Silica-Titanium 1%, Silica-Titanium 3% and Silica-Titanium 5%.

Transmission electron microscopy (TEM)

Transmission electron microscope is one of the most common and powerful system to characterize the nano materials, mainly when the determination of the particle shape and size is important. Silica nanoparticles is trans illuminated by a beam of accelerated electrons with an energy of 50-200 keV in vacuum system, illumination system, a specimen stage, an objective lens system, the magnification system, the data recording system, and the chemical analysis system. In the results section, one is able to see the particle shape and size of Silica Pure, Silica-Titanium 1%, Silica-Titanium 3% and Silica-Titanium 5%.

Thermal gravimetric analysis (TGA)

Thermo gravimetric analysis (TGA) is a technique in which changes in weight of a specimen are recorded as a function of temperature by heating the specimen in air or in a controlled atmosphere such as nitrogen. TGA is one of the most common techniques used to investigate a material's thermal stability by monitoring the weight change as the results of specimen heating. The analysis involves heating a known mass of sample in an inert gas or oxidizing atmosphere and measuring the mass change over specific temperature ranges to provide indications of the sample thermal stability. Based on the results, one can see that for Silica Pure, the weight starts changing at around 200°C but for the Silica-Titanium compounds its starts to change at around 300°C. This shows the thermal stability of the compounds that it can reach up to that temperature.

4.2.2 Discussion for the Oil-Water Separation

All the densities have been recorded per hour and the graphs of density vs. hour have been plotted. From the graphs, we can see that as the concentration of Silica-Titanium increases from 1% to 5%. As the Oil Concentration increases, it takes a longer time for the solution to reach the density of pure water. At the temperature 25°C, the density of pure water is 0.997. At temperature of 35°C, the density of pure water is 0.995 and for 45°C, it is 0.992. This is based on the calibration curve that I have done and obtained which is in the Literature Review section. For the Silica-Titanium, it is observed that the experiment conducted with 1.5g takes up a shorter time to reach the density of pure water as compared to 1.0g and 0.5g.

The Tables with all the raw data are attached in the Appendices section. In Figure 19, it is the Results for Temperature 25 °C, Silica-Titanium 0.5g. From the

47

graphs it can be seen that as the percentage of Titanium increases, it makes it easier to obtain the density of water faster as the absorbent is more hydrophobic as compared to the rest. In Figure 20, it is the Results for Temperature 25 °C and Silica-Titanium 1.0g. From those graphs, it can be seen that since the Silica-Titanium is now 1.0g, it takes a faster time to reach the density of water. In Figure 21, it is the Results for Temperature 25 °C and Silica-Titanium 1.5g. From the graphs, it is observed that for Silica-Titanium 1.5g, it takes a faster time to reach the density of water as compared to Silica-Titanium 1.0g and Silica-Titanium 0.5g.This is because the surface area shown by the BET Characterization for 1.5g is higher than 0.5g and 1.0g and that allows it to absorb more hydrocarbon.

In Figure 22, 23 and 24, it is Results for Temperature 35 °C and Silica-Titanium 0.5g, Results for Temperature 35 °C and Silica-Titanium 1.0g and Results for Temperature 35 °C and Silica-Titanium 1.5g, respectively. The Temperature is now higher as compared to the graphs produced in Figure 19, 20 and 21. From all these 9 graphs, it is noticed that as the temperature increases, it takes a longer time to reach the density of water. The density of water now becomes 0.995 based on the calibration curve that I have obtained.

In Figure 25, 26 and 27, it is Results for Temperature 45 °C and Silica-Titanium 0.5g, Results for Temperature 45 °C and Silica-Titanium 1.0g and Results for Temperature 45 °C and Silica-Titanium 1.5g. The temperature now becomes even higher as compared to the others. From the graphs, it can be seen that now that it takes a much longer time to achieve the density of water which is 0.992.

After obtaining the density using the densitometer, we have to calculate the amount of Oil absorbed. To calculate the amount of oil absorb from each sample with the time, standard curves were plotted using different sample densities of paraffin oil and water (0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100% oil). The parameters varied in this experiment are:

The slope and intercept of the linear equation below of the standard curves were used to calculate the amount of oil absorbed:

From the straight line equation

$$y = mx + c$$

$$x = \frac{y - c}{m}$$

Where

y: is the density

x: is the weight fraction

m: is the slope of the line

C: is the constant

The percent of oil absorb $= 1 - x$

The weight of oil absorb (g) = percent of oil absorb/the weight of oil in the sample

The oil absorb % = (weight of oil absorb (g)/ the weight of oil in the sample)*100

(All the Oil Absorbed values are in the Appendices section)

For example:

49
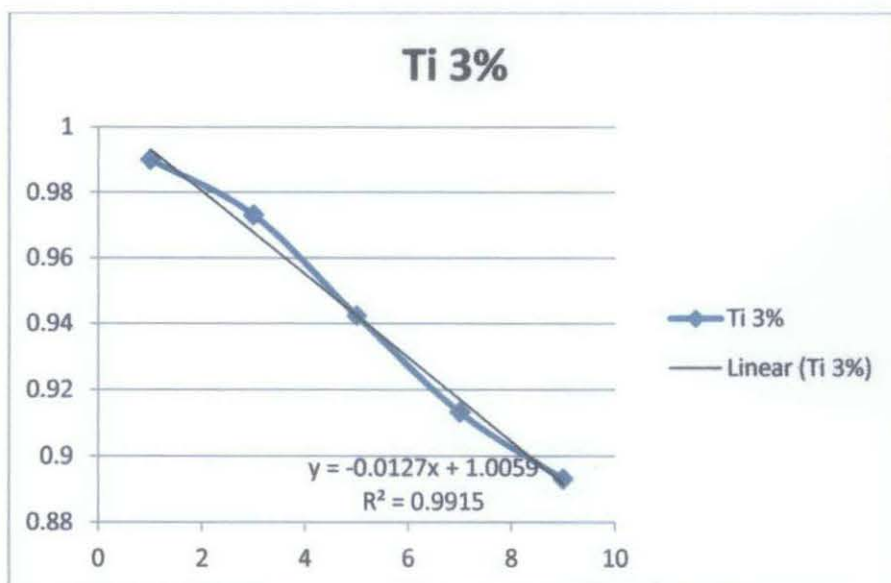
The particular density vs. the weight fraction is plotted in the graph. From there, we obtain a linear equation line which is

$Y = -0.0127x + 1.0059$

$X = \dfrac{y-1.0059}{-0.0127}$

$Y = 0.9769$, thus $x = 2.2835$

Then we put in the values of the density to obtain the particular weight fraction. From there we use, The percent of oil absorb $= 1 - x$

$1 - 2.2835 = -1.2835$

percent of oil absorb/the weight of oil in the sample

$1.2835/5.00 = 0.2567$

$0.2567/5 = 0.05134$

$0.05134 \times 100 = 5.13\%$ within the 1st hour

Comparing Silica-Titanium 1%, Silica-Titanium 3% and Silica-Titanium 5% at a constant Temperature of 25 °C.

Silica-Titanium 1%
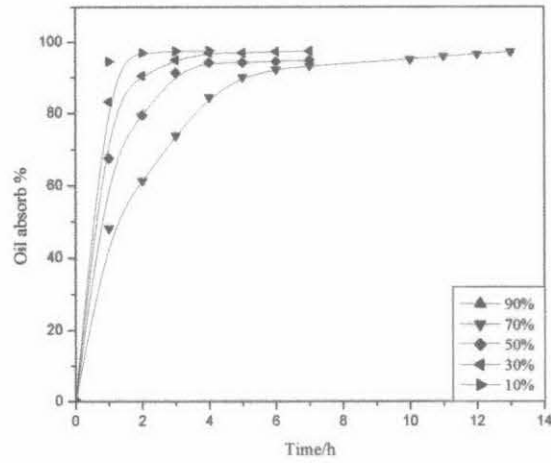
Figure 28: Silica Titanium Oil Absorbed vs. Time

Silica-Titanium 3%
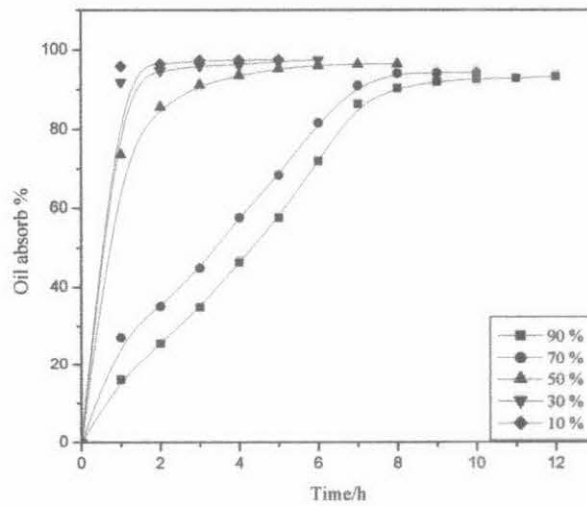
Figure 29: Silica Titanium 3% Oil Absorbed vs. Time

Silica-Titanium 5%

51
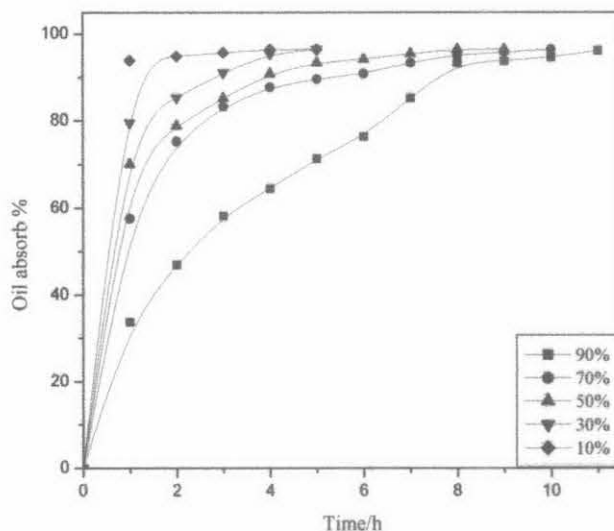
Figure 30: Silica Titanium 5% Oil Absorbed vs. Time

From the graphs above, we can see that for Silica-Titanium 5%, it takes a shorter time to reach the density of water which is 0.997. This is because as there is more Titanium (from metal oxide) in the oil-water environment, the hydrophobicity will be more and that helps to absorb more oil. For Silica-Titanium 5%, it takes about maximum 11 hours to absorb, as compared to Silica-Titanium 1% and Silica-Titanium 3% which takes 13 hours and 12 hours respectively. As the Temperature is 25°C, the viscosity of the oil is high and therefore absorption is higher. [4]

Comparison of Silica-Titanium 5% at different Temperatures which are 25 °C, 35 °C and 45 °C.
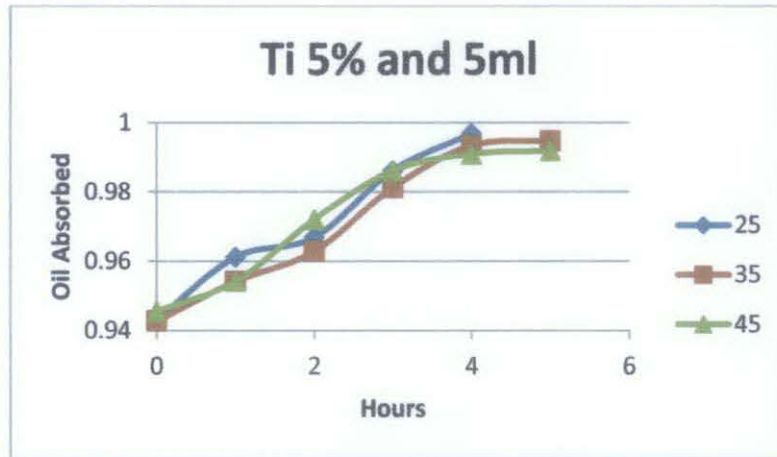
Figure 31: Comparison of different Temperatures

Based on the graph above, as the Temperature increases, it takes a longer time for the oil to get absorbed. Thus, the viscosity of the oil reduces and that is when the Oil starts to come out from the pores. As that happens, the absorption rate reduces because the desorption of the oil from the pores increases.

From the graphs, we can see that for Ti 1%, it takes a longer time to reach the density of water as compared to Titanium 3%. This is because the as more metal – oxide is mixed synthesized together with the Titanium, it makes it more hydrophobic. Thus, it makes it faster for the material to absorb the oil as compared to water. The advantage of adding absorbent materials to oil spill is changing the phase from liquid to semi solid phase which make the removal of absorbent and oil easier[18]

4.2.3 Discussion for the Optimization

Box-Behnken Design is defined as a set of experimental designs for response surface methodology that has points at center and the midpoint of each side. Devised by George E. P. Box and Donald Behnken in 1960, these are designed to achieve goals such as:

a. each factor, or independent variable, is placed at one of three equally spaced values,

b. the design should be sufficient to fit a quadratic model, that is, one containing squared terms and products of two factors,

c. the ratio of the number of experimental points to the number of coefficients in the quadratic model should be reasonable and the estimation variance should more or less depend only on the distance from the centre, and should not vary too much inside the smallest (hyper) cube containing the experimental points.[17]

Based on the ANOVA Table obtained, the table partitions the variability in Oil absorbed into separate pieces for each of the effects. It then tests the statistical significance of each effect by comparing the mean square against an estimate of the experimental error. In this case, 10 effects have P-values less than 0.05, indicating that they are significantly different from zero at the 95.0% confidence level.

The R-Squared statistic indicates that the model as fitted explains 97.8101% of the variability in Oil absorbed. The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 97.6015%. The standard error of the estimate shows the standard deviation of the residuals to be 1.91597. The mean absolute error (MAE) of 1.16325 is the average value of the residuals. The Durbin-Watson (DW) statistic tests the residuals to determine if there is any significant correlation based on the order in which they occur in your data file. Since the P-value is greater than 5.0%, there is no indication of serial autocorrelation in the residuals at the 5.0% significance level.

The formula to obtain the Oil Absorbed based on the software is given as below:

Oil absorbed = 63.1346 - 2.00859*Titanium percent - 9.97017*Oil percentage - 0.578043*Temperature + 4.71146*Silica - 0.129606*Titanium percent^2 + 0.324045*Titanium percent*Oil percentage + 0.0306875*Titanium percent*Temperature - 0.84875*Titanium percent*Silica + 0.463553*Oil percentage^2 + 0.0431979*Oil percentage*Temperature - 0.587847*Oil percentage*Silica + 0.00244907*Temperature^2 - 0.0318056*Temperature*Silica + 1.6863*Silica^2

The parameter that gives the highest rate of Absorption at the 3rd hour is when:
Optimum value = 48.2544

Table 10: Optimization Table

Factor	Optimum
Titanium percent	5.0
Oil percentage	1.0
Temperature	25.0
Silica	1.5

Based on the results from the Software, it can be seen that the highest rate of optimization is the same as the results obtain by the experiment. This shows that when the temperature is 25°C the viscosity of the oil is high and therefore it makes it easier to absorb the hydrocarbon. This shows that the results that I have obtained are correct and validated.

CHAPTER 5: CONCLUSION & RECOMMENDATION

5.1 CONCLUSION

To conclude this report, it is best to say that the objectives of the project are successfully achieved although there are quite a few obstacles that I have faced. Despite the problems, the project has been able to carry through and has finished in the given period of time.

In this project there are four sections which have been completed which is doing the Synthesis of the Silica Nano-Particles with different percentage of Titanium, Characterization the Surface Modified Silica-Titanium, completing the experiment on Oil-Water Separation and last but not least completing the Optimization on Oil Absorbed. The density has been recorded using the densitometer to achieve the density of pure water. This shows that all the oil has been absorbed and there is no hydrocarbon left.

Sol–gel technology has opened the possibility for producing ceramic nanoparticles with large surface area and a wide variety of active sites on their surface, particularly appropriated for the adsorption of metal ions, optical devices, fibers and thin film. Due to the hydrophilic nature of silica nanoparticles there are some important methods to modify it to become Hydrophobic Silica Nano-Particles and that is why Metal Oxides are added.

The Synthesis of the Titanium sols was done using the Hydrolysis and Condensation reaction and after that the Characterization of the Silica Nano-Particles provides information on the Morphology and Properties of the Material itself. Last but not least, the Experiment on Oil-Water Separation has been conducted, the results have been achieved. Moreover, I have also analyzed the Oil Absorbed for each experiment and then optimized the results into the Box Behnken software to get the best combination of parameters that can achieve the highest Oil Absorbed rate.

The calculation of the amount of oil absorbed is done to test the efficiency of the Silica Modified Nano-Particles. This experiment is then done at three different

57

temperatures. One of the parameters which is pressure will remain constant throughout the experiment. Whereas, the other two parameters which are Concentration and Temperature will be varied to understand the efficiency of the Silica Nano-Particles behavior for Oil-Water Separation under different conditions.

Once the experimental data such as the density is obtained, the amount of oil absorbed can be calculated. To calculate the amount of oil absorb from each sample with the time, standard curves were plotted using different sample densities of paraffin oil and water (0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100% oil). The slope and intercept of the linear equation of the standard curves were used to calculate the amount of oil absorbed. This shows the efficiency of the Surface Modified Silica Nano-Particles with Titanium 1%, Titanium 3% and Titanium 5%.

The last part is the Optimization of Oil Absorbed by the Box Behnken software. This has been done and the results from the optimization have matched the results that I have obtained from the Box Behnken software. This shows that the results were correct and it fits my Literature Review.

5.2 RECOMMENDATIONS AND FUTURE WORK

This study can be extended by taking into account the different metal oxides such as Alumina and Zirconium. This will show that there can be a wide range of Silica Nano-Particles to remove Hydrocarbons from oil spills. If this study can prove that other metal oxides can remove hydrocarbons, this will be much convenient and cost effective for Oil and Water to be separated. This study can also be taken one step further into removing oil from High Temperature and High Pressure conditions.

Although oil is important for modern industrial life, under control, it is efficient, versatile, and productive it is production and transportation have their negative side. Plus, once this experimental study achieves its objective, a proper study in detail can be done as a new way of removing hydrocarbons from unwanted areas using Hydrophobic Silica Nano-Particles. Various tests can be conducted and this particular study will be very beneficial to the drilling fluids and operating

companies that deal with oil and gas out there. It will certainly enable them to

operate   with   crude   oil   under   extreme   conditions.

REFERENCES

Abedajo, M.O., Frost, R.L., Kloprogge, J.T., Carmody, O., and Kokot, S. (2003). Porous materials for oil spill cleanup: A review of synthesis and absorbing properties. *Journal on Porous materials, vol. 10*, 159-170.

Assink, R.A., and Prabakar, S. (1997). Hydrolisis and condensation kinetics of two component organically modified silica sols. *Journal of Non-Crystalline Solids*, 39-48.

Brinker, C.J. and Scherer, G.W. (1990). *Sol-gel science: The physics and chemistry of sol-gel processing.* Washington D.C.: Academic Pr.

Donald, W. (1977). *Patent No. 4054689.* USA.

Donald, W. (1979). *Patent No. 4151078.* USA.

Hench, L.L. and West, J.K. (1990). The sol-gel process. *Chemical Reviews*, 33-72.

James, F. and Edward, F. (1991). *Patent No. 5037557.* New York, USA.

Jeffrey, B. C. and George, S. W. (1990). *Sol-gel science.* Gulf Professional Publishing.

Lopez, T.M., Avnir, D. and Aegerter, M.A. (2003). *Emerging fields in sol-gel science and technology.* Netherlands: Kluwer Academic Publishers.

Medina, M., Tapia, J., Pacheco, S., Espinosa, M. and Rodriguez, R. (2010). Adsorption of lead ions in aqueous solution using silica-alumina nanoparticles. *Journal of non-crytalline solids, vol. 356*, 383-387.

Phys, J. (n.d.). *Conf. Ser. 26 371.* Retrieved June 14, 2011, from Iopscience: http://iopscience.iop.org/1742-6596/26/1/090

Teas, C., Kalligeros, S., Zanikos, F., Stournas, S., Lois, E. and Anastopoulos, G. (2001). Investigation of the effectiveness of absorbent materials in oil spills clean up. *Desalination*, 259-264.

Ventikos, N.P., Vergetis, E., Psaraftis, H.N. and Triantafyllou, G. (2004). A high level synthesis of oil spill response equipment and countermeasures. *Journal of hazardous materials*, 51-58.

Xiaohong, L., Zhi, C., Liu, F., Zhang, Z. and Dang, H. (2005). *A Novel method of Preparation of Superhydrophobic Nano-silica in Aqueous Solution.*

Yang, Z. and Lin, Y.S. (2000). Sol-gel synthesis of silicalite-alumina granules. *Industrial and engineering chemistry research*, 4944-4948.

Zou, H., Wu, S. and Shen, J. (1990). Polymer/silica nanocomposites: Preparation, Characterization, properties and applications. *Chemical Reviews*, 3893-3957.

APPENDICES

Table 11: Results for Temperature 25 °C, Silica-Titanium 0.5g and Percentage of Titanium: 1%

Ti 1%   0.5g

	Oil (ml)	Water (ml)	Hours 0	1	2	3	4	5	6	7	8	9
Density	1	9	0.9913	0.993	0.9947	0.9968						
Density	3	7	0.98	0.987	0.991	0.992	0.9944	0.9967				
Density	5	5	0.963	0.976	0.988	0.9867	0.9932	0.9955	0.9966			
Density	7	3	0.94	0.968	0.974	0.9811	0.9926	0.9939	0.9948	0.9962		
Density	9	1	0.92	0.94	0.9553	0.9735	0.9755	0.9852	0.9948	0.9954	0.9964	0.9969

Table 12: Results for Temperature 25 °C, Silica-Titanium 0.5g and Percentage of Titanium: 3%

Ti 3%

	Oil (ml)	Water (ml)	Hours 0	1	2	3	4	5	6	7	8
Density	1	9	0.9812	0.9934	0.995	0.9969					
Density	3	7	0.975	0.9742	0.9865	0.9923	0.9967				
Density	5	5	0.9452	0.9672	0.9768	0.9823	0.9922	0.9968			
Density	7	3	0.9228	0.9369	0.9527	0.9658	0.9763	0.987	0.9924	0.997	
Density	9	1	0.901	0.9221	0.9454	0.9581	0.9665	0.9765	0.9825	0.9936	0.9967

Table 13: Results for Temperature 25 °C, Silica-Titanium 0.5g and Percentage of Titanium: 5%

Ti 5%

	Oil (ml)	Water (ml)	Hours 0	1	2	3	4	5	6	7	8
Density	1	9	0.9804	0.9945	0.995	0.9969					
Density	3	7	0.9669	0.9801	0.9925	0.9968					
Density	5	5	0.9325	0.9567	0.9656	0.9828	0.9954	0.9969			
Density	7	3	0.912	0.9345	0.9555	0.9632	0.9764	0.9831	0.9943	0.9967	
Density	9	1	0.8865	0.9233	0.9365	0.9512	0.9668	0.9725	0.9881	0.9902	0.9968

Table 14: Results for Temperature 25 °C, Silica-Titanium 1.0g and Percentage of Titanium: 1%

Ti 1%   1.0g

	Oil (ml)	Water (ml)	Hours 0	1	2	3	4	5	6	7	8
Density	1	9	0.9855	0.993	0.995	0.9969					
Density	3	7	0.974	0.984	0.99	0.9939	0.9953	0.9968			
Density	5	5	0.96	0.978	0.989	0.9908	0.9943	0.9967			
Density	7	3	0.94	0.967	0.986	0.9905	0.993	0.9945	0.9957	0.9968	
Density	9	1	0.92	0.94	0.9556	0.9667	0.9764	0.9888	0.9923	0.9955	0.9969

Table 15: Results for Temperature 25 °C, Silica-Titanium 1.0g and Percentage of Titanium: 3%

Ti 3%

	Oil (ml)	Water (ml)	Hours 0	1	2	3	4	5	6	7
Density	1	9	0.99	0.9937	0.995	0.9969				
Density	3	7	0.959	0.9745	0.9866	0.9934	0.9967			
Density	5	5	0.9452	0.9669	0.9755	0.9834	0.9951	0.9968		
Density	7	3	0.922	0.9354	0.9511	0.9621	0.9732	0.987	0.9943	0.997
Density	9	1	0.901	0.9225	0.9452	0.9523	0.9611	0.9765	0.9843	0.9968

Table 16: Results for Temperature 25 °C, Silica-Titanium 1.0g and Percentage of Titanium: 5%

Ti 5%

	Oil (ml)	Water (ml)	Hours 0	1	2	3	4	5	6	7	8
Density	1	9	0.9804	0.9952	0.9969						
Density	3	7	0.9654	0.9701	0.99	0.9967					
Density	5	5	0.9312	0.95	0.9626	0.982	0.9921	0.9969			
Density	7	3	0.905	0.9453	0.9617	0.9748	0.9862	0.992	0.9969		
Density	9	1	0.8815	0.9134	0.9356	0.9518	0.9662	0.9766	0.9858	0.9923	0.9968

Table 20: Results for Temperature 35 °C, Silica-Titanium 0.5g and Percentage of Titanium: 1%

Ti 1%			Hours							
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6	7
Density	1	9	0.9841	0.9867	0.9921	0.9948				
Density	3	7	0.9523	0.9666	0.9724	0.9844	0.9925	0.9947		
Density	5	5	0.9311	0.9435	0.9634	0.9856	0.9921	0.9949		
Density	7	3	0.9144	0.9356	0.9524	0.9634	0.9831	0.9934	0.995	
Density	9	1	0.8944	0.9023	0.9254	0.9462	0.9532	0.9745	0.9934	0.995

Table 21: Results for Temperature 25 °C, Silica-Titanium 0.5g and Percentage of Titanium: 3%

Ti 3%			Hours							
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6	7
Density	1	9	0.9852	0.991	0.9925	0.9948				
Density	3	7	0.95	0.9567	0.9741	0.9846	0.9935	0.995		
Density	5	5	0.9345	0.9448	0.9621	0.9845	0.9914	0.9949		
Density	7	3	0.9135	0.9264	0.9531	0.9636	0.9844	0.9934	0.9949	
Density	9	1	0.8854	0.8941	0.9157	0.9323	0.9556	0.9852	0.9933	0.995

Table 22: Results for Temperature 25 °C, Silica-Titanium 0.5g and Percentage of Titanium: 5%

Ti 5%	T= 35	0.5g								
			Hours							
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6	7
Density	1	9	0.9865	0.9915	0.9923	0.9948				
Density	3	7	0.95	0.9539	0.9748	0.9833	0.9909	0.9947		
Density	5	5	0.9355	0.9442	0.9666	0.9812	0.9935	0.9949		
Density	7	3	0.9135	0.9262	0.9528	0.9667	0.9844	0.9922	0.9949	
Density	9	1	0.8822	0.8916	0.9121	0.9367	0.9522	0.9846	0.9938	0.995

Table 23: Results for Temperature 35 °C, Silica-Titanium 1.0g and Percentage of Titanium: 1%

Ti 1%			Hours							
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6	7
Density	1	9	0.9816	0.9856	0.9901	0.9948				
Density	3	7	0.9538	0.9763	0.9817	0.9848	0.9921	0.9947		
Density	5	5	0.9334	0.9429	0.9651	0.9834	0.9902	0.9949		
Density	7	3	0.9232	0.9152	0.9446	0.9652	0.9831	0.9934	0.995	
Density	9	1	0.8923	0.9054	0.9215	0.9428	0.9551	0.9733	0.991	0.995

Table 24: Results for Temperature 35 °C, Silica-Titanium 1.0g and Percentage of Titanium: 3%

Ti 3%			Hours							
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6	7
Density	1	9	0.9855	0.9846	0.9911	0.9948				
Density	3	7	0.9532	0.9538	0.9752	0.9902	0.9948			
Density	5	5	0.9357	0.9448	0.9621	0.9845	0.9914	0.9949		
Density	7	3	0.9046	0.9253	0.9526	0.9728	0.9854	0.9915	0.9949	
Density	9	1	0.8922	0.9027	0.9357	0.9549	0.9634	0.982	0.9947	

Table 25: Results for Temperature 35 °C, Silica-Titanium 1.0g and Percentage of Titanium: 5%

Ti 5%	T= 35	1.0g								
			Hours							
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6	7
Density	1	9	0.9805	0.9936	0.9949					
Density	3	7	0.9635	0.9523	0.9743	0.9854	0.9946			
Density	5	5	0.9417	0.9344	0.9654	0.9857	0.9923	0.9949		
Density	7	3	0.9157	0.9348	0.9514	0.9723	0.9903	0.9948		
Density	9	1	0.8911	0.9013	0.9264	0.9437	0.9643	0.9853	0.9947	

Table 26: Results for Temperature 35 °C, Silica-Titanium 1.5g and Percentage of Titanium: 1%

Ti 1%	Oil (ml)	Water (ml)	Hours 0	1	2	3	4	5	6	7
Density	1	9	0.9867	0.9901	0.9928	0.9949				
Density	3	7	0.9521	0.9643	0.9801	0.9865	0.9913	0.9947		
Density	5	5	0.9315	0.9419	0.9629	0.9842	0.9915	0.9949		
Density	7	3	0.9124	0.9325	0.9518	0.9667	0.9824	0.9932	0.995	
Density	9	1	0.9018	0.9123	0.9327	0.9502	0.9648	0.9718	0.9911	0.995

Table 27: Results for Temperature 35 °C, Silica-Titanium 1.5g and Percentage of Titanium: 3%

Ti 3%	Oil (ml)	Water (ml)	Hours 0	1	2	3	4	5	6	7
Density	1	9	0.992	0.9935	0.9946	0.9948				
Density	3	7	0.9619	0.9769	0.9824	0.9902	0.9935	0.995		
Density	5	5	0.9336	0.9421	0.9637	0.9818	0.9909	0.9949		
Density	7	3	0.9046	0.9217	0.9467	0.9703	0.9856	0.9906	0.9949	
Density	9	1	0.8913	0.9023	0.9201	0.9357	0.9518	0.9843	0.9922	0.995

Table 28: Results for Temperature 35 °C, Silica-Titanium 1.5g and Percentage of Titanium: 5%

Ti 5% T= 35

	Oil (ml)	Water (ml)	Hours 0	1	2	3	4	5	6	7
Density	1	9	0.9812	0.9902	0.9921	0.9948				
Density	3	7	0.9637	0.9715	0.9808	0.9907	0.9932	0.9947		
Density	5	5	0.9428	0.9542	0.9629	0.9813	0.9919	0.9948		
Density	7	3	0.9145	0.9236	0.9512	0.9656	0.9853	0.9903	0.9949	
Density	9	1	0.8911	0.9016	0.9257	0.9423	0.9612	0.9814	0.9943	0.995

Table 29: Results for Temperature 45 °C, Silica-Titanium 0.5g and Percentage of Titanium: 1%

| Ti 1% | | T= 45 | | | | | | | |

			Hours						
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6
Density	1	9	0.99	0.9912	0.9918				
Density	3	7	0.9734	0.9867	0.9912	0.9917			
Density	5	5	0.9456	0.9527	0.9769	0.9845	0.9916	0.9919	
Density	7	3	0.9132	0.9246	0.9537	0.9734	0.9903	0.9918	
Density	9	1	0.8933	0.9035	0.9257	0.9423	0.9656	0.9867	0.9919

Table 30: Results for Temperature 45 °C, Silica-Titanium 0.5g and Percentage of Titanium: 3%

| Ti 3% | | T= 45 | | | | | | | |

			Hours						
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6
Density	1	9	0.9901	0.9913	0.9918				
Density	3	7	0.9732	0.9865	0.9911	0.9918			
Density	5	5	0.9425	0.9536	0.9769	0.9825	0.9913	0.9919	
Density	7	3	0.9133	0.9362	0.9537	0.9712	0.9863	0.9918	
Density	9	1	0.8932	0.9134	0.9346	0.9537	0.9754	0.9825	0.9919

Table 31: Results for Temperature 45 °C, Silica-Titanium 0.5g and Percentage of Titanium: 5%

| Ti 5% | | T= 45 | | | | | | | |

			Hours						
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6
Density	1	9	0.99	0.9906	0.9918				
Density	3	7	0.9762	0.9866	0.9901	0.9917			
Density	5	5	0.9421	0.9503	0.9769	0.9857	0.991	0.9919	
Density	7	3	0.911	0.9353	0.9522	0.971	0.9859	0.9918	
Density	9	1	0.8943	0.9062	0.9247	0.9418	0.9651	0.9836	0.9919

Table 32: Results for Temperature 45 °C, Silica-Titanium 1.0g and Percentage of Titanium: 1%

| Ti 1% | T= 45 | | | | | | | | |

			Hours						
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6
Density	1	9	0.9721	0.9849	0.9905	0.9918			
Density	3	7	0.9638	0.9823	0.99	0.9917			
Density	5	5	0.9425	0.9564	0.9731	0.9867	0.9906	0.9919	
Density	7	3	0.9137	0.9265	0.9512	0.9755	0.9869	0.9918	
Density	9	1	0.9014	0.9135	0.9302	0.9561	0.9614	0.9863	0.9919

Table 33: Results for Temperature 45 °C, Silica-Titanium 1.0g and Percentage of Titanium: 3%

| Ti 3% | T= 45 | | | | | | | | |

			Hours						
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6
Density	1	9	0.9768	0.9903	0.9918				
Density	3	7	0.9658	0.9866	0.9907	0.9918			
Density	5	5	0.9343	0.9501	0.9738	0.9864	0.9912	0.9919	
Density	7	3	0.9124	0.9361	0.9511	0.9765	0.9862	0.9918	
Density	9	1	0.8912	0.9111	0.9366	0.9668	0.9803	0.9841	0.9919

Table 34: Results for Temperature 45 °C, Silica-Titanium 1.0g and Percentage of Titanium: 5%

| Ti 5% | T= 45 | | | | | | | | |

			Hours						
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6
Density	1	9	0.9858	0.9904	0.9919				
Density	3	7	0.9736	0.9832	0.9904	0.9917			
Density	5	5	0.9461	0.9523	0.973	0.9818	0.9902	0.9919	
Density	7	3	0.9319	0.9411	0.9553	0.9804	0.9912	0.9918	
Density	9	1	0.9032	0.9163	0.9268	0.9411	0.9636	0.9851	0.9919

Table 35: Results for Temperature 45 °C, Silica-Titanium 1.5g and Percentage of Titanium: 1%

Ti 1%	T= 45								
			Hours						
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6
Density	1	9	0.9769	0.9903	0.9918				
Density	3	7	0.9647	0.984	0.9903	0.9919			
Density	5	5	0.9418	0.9564	0.9769	0.9861	0.9901	0.9919	
Density	7	3	0.9113	0.9265	0.9532	0.9851	0.9903	0.9918	
Density	9	1	0.8954	0.9063	0.9228	0.9555	0.9651	0.9867	0.9919

Table 36: Results for Temperature 45 °C, Silica-Titanium 1.5g and Percentage of Titanium: 3%

Ti 3%	T= 45								
			Hours						
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6
Density	1	9	0.9902	0.991	0.9918				
Density	3	7	0.9747	0.9868	0.9903	0.9918			
Density	5	5	0.9527	0.9636	0.9769	0.9846	0.9912	0.9919	
Density	7	3	0.9246	0.9364	0.9526	0.9801	0.9863	0.9918	
Density	9	1	0.9012	0.9154	0.9311	0.9642	0.9765	0.9845	0.9919

Table 37: Results for Temperature 45 °C, Silica-Titanium 1.5g and Percentage of Titanium: 5%

Ti 5%	T= 45								
			Hours						
	Oil (ml)	Water (ml)	0	1	2	3	4	5	6
Density	1	9	0.9801	0.9869	0.9905	0.9918			
Density	3	7	0.9647	0.9831	0.9864	0.9901	0.9917		
Density	5	5	0.9456	0.9542	0.9721	0.9862	0.991	0.9919	
Density	7	3	0.9154	0.9366	0.9525	0.9717	0.986	0.9918	
Density	9	1	0.9034	0.9162	0.9301	0.9567	0.9713	0.9865	0.9919

Titanium percent	Oil percentage	Temperature	Silica	Oil absorbed
%	%	Celcius	gram	%
1	1	25	0.5	41.2
5	1	45	1	29.5
1	9	45	0.5	9.77
1	1	25	1.5	48.72
3	9	25	0.5	10.09
3	5	35	0.5	15.73
3	9	45	1	9.91
3	5	25	1	15.26
5	1	35	0.5	30.52
5	5	25	1	16.5
1	9	45	1.5	9.82
5	1	25	1.5	37.38
3	9	25	1	9.76
3	5	25	0.5	17
3	1	35	1	36.44
5	5	25	0.5	14.09
1	5	35	1	17.26
5	5	45	1.5	12.57
5	5	35	1	14.94
1	1	35	1	40.62
5	5	35	1.5	14.5
5	9	45	1	10.34
3	9	45	1.5	10.08
1	1	45	0.5	34.92
1	1	35	1.5	47.24
5	9	45	0.5	12.55

Titanium percent	Oil percentage	Temperature	Silica	Oil absorbed
%	%	Celcius	gram	%
1	1	45	1.5	40.74
3	5	45	1	14.71
3	1	35	1.5	39.13
3	5	45	0.5	15.97
5	1	25	0.5	31.4
1	9	45	1	7.72
5	9	35	1.5	8.03
1	5	45	0.5	15.18
5	9	25	1.5	7.15
5	9	45	1.5	9.66
3	5	35	1.5	17.02
3	9	35	1	9
1	9	25	1	7.25
3	5	35	1	15.42
5	9	35	1	10.14
3	5	25	1.5	19.49
3	1	45	1	34.39
1	1	45	1	38.04
3	5	45	1.5	14.6
1	9	35	1	8.16
1	9	25	0.5	7.23
5	5	45	1	12.85
1	5	45	1.5	17.63
1	5	35	1.5	18.02
1	5	25	0.5	14.24
5	5	35	0.5	15.28

Titanium percent	Oil percentage	Temperature	Silica	Oil absorbed
%	%	Celcius	gram	%
3	1	25	0.5	39.38
5	9	25	0.5	9.97
3	1	25	1	40.33
3	1	45	1.5	35.96
3	1	25	1.5	43.32
5	1	35	1	30.09
3	9	35	0.5	9.99
1	5	25	1.5	20.56
3	1	35	0.5	36.44
1	9	25	1.5	9.72
3	9	45	0.5	9.72
5	5	45	0.5	13.25
1	9	35	0.5	9.55
1	5	25	1	18.93
1	9	35	1.5	9.05
5	9	25	1	9.85
5	1	25	1	34.01
5	9	35	0.5	10.07
1	5	35	0.5	17.47
5	1	45	0.5	29.03
5	1	45	1.5	30.77
1	1	25	1	45.96
1	5	45	1	14.38
3	1	45	0.5	31.41
3	9	35	1.5	9.3
1	1	35	0.5	39.54

Titanium percent	Oil percentage	Temperature	Silica	Oil absorbed
%	%	Celcius	gram	%
3	9	25	1.5	9.54
5	5	25	1.5	15.36
5	1	35	1.5	33.7
5	9	25	1	9.85
1	1	25	1.5	51.72
1	9	25	0.5	10.23
5	1	25	1.5	35.38
1	1	35	0.5	39.54
3	9	35	0.5	9.99
5	5	45	0.5	16.25
3	5	35	0.5	10.73
3	9	45	0.5	11.72
1	1	45	1	38.04
3	1	45	1.5	35.96
1	5	25	1.5	21.56
1	9	35	0.5	9.55
1	5	35	0.5	17.47
5	9	35	1	10.14
5	5	35	0.5	15.28
3	1	25	1.5	45.32
1	9	45	1.5	9.82
5	9	45	1.5	9.66
5	9	45	0.5	9.63
1	5	25	1	18.93
3	9	45	1	9.91
3	5	25	1.5	16.49

Titanium percent	Oil percentage	Temperature	Silica	Oil absorbed
%	%	Celcius	gram	%
1	9	35	1.5	9.05
1	1	35	1.5	46.24
1	5	25	0.5	18.24
3	9	25	1.5	9.54
1	1	35	1	40.62
5	5	25	1	16.5
5	9	45	1	10.34
1	9	25	1.5	9.72
1	1	45	0.5	29.92
3	1	45	1	38.39
1	1	25	1	40.96
5	1	35	0.5	32.52
1	1	45	1.5	40.74
3	5	45	1	16.71
3	1	25	0.5	50.38
3	5	35	1	15.42
5	9	35	0.5	10.07
3	1	35	0.5	36.44
1	5	45	0.5	15.18
5	1	45	1	35.92
5	5	35	1	14.94
5	1	25	1	31.01
3	5	45	0.5	15.97
5	5	45	1	16.85
5	9	35	1.5	10.03
3	5	35	1.5	17.02

Titanium percent	Oil percentage	Temperature	Silica	Oil absorbed
%	%	Celcius	gram	%
3	1	35	1.5	40.13
5	1	35	1.5	28.7
3	1	25	1	36.33
5	1	45	1.5	30.77
5	5	25	0.5	17.09
1	1	25	0.5	42.05
5	1	25	0.5	33.4
3	9	25	1	9.76
1	5	35	1	17.26
3	9	35	1.5	9.3
5	5	25	1.5	15.36
5	9	25	1.5	10.15
5	5	45	1.5	14.57
3	1	45	0.5	32.41
1	9	35	1	10.16
5	1	35	1	30.09
3	9	35	1	9.31
3	9	25	0.5	10.09
3	5	25	1	15.26
1	5	45	1	14.38
3	5	25	0.5	16
3	5	45	1.5	14.6
5	9	25	0.5	9.97
5	1	45	0.5	27.03
3	9	45	1.5	10.08
1	5	45	1.5	14.63

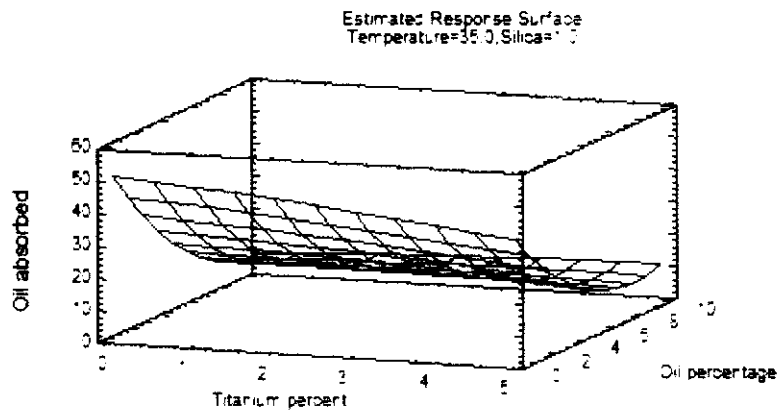| Titanium percent	Oil percentage	Temperature	Silica	Oil absorbed
%	%	Celcius	gram	%
3	1	35	1	36.44
1	9	45	0.5	9.77
1	9	25	1	10.25
1	9	45	1	9.72
5	5	35	1.5	14.5
1	5	35	1.5	18.02

Response Plots

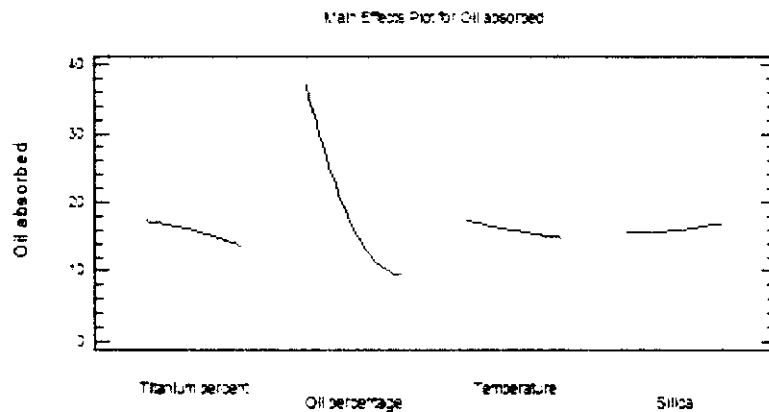**Figure 32: Response Plot for Optimization**

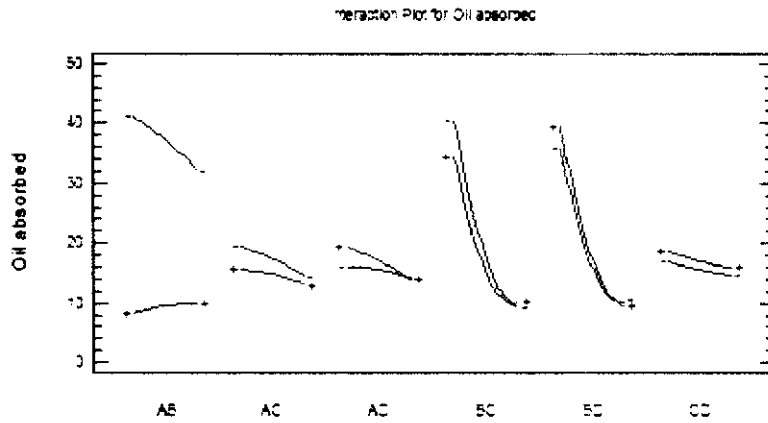**Figure 33 : Main Effects Plot**

Figure 34: Interaction Plot

Estimation Results for Oil absorbed

Row	Observed Value	Fitted Value	Lower 95.0% CL for Mean	Upper 95.0% CL for Mean
1	41.2	42.2313	40.7891	43.6735
2	29.5	29.7253	28.5077	30.9429
3	9.77	8.37389	6.93168	9.8161
4	48.72	48.0836	46.6414	49.5258
5	10.09	9.89912	8.68153	11.1167
6	15.73	15.3987	14.4579	16.3395
7	9.91	10.0522	9.01091	11.0934
8	15.26	17.2683	16.3275	18.2091
9	30.52	31.2501	30.0325	32.4677
10	16.5	14.2548	13.2135	15.296
11	9.82	8.88731	7.44511	10.3295
12	37.38	36.2111	34.7689	37.6533
13	9.76	9.20356	8.1623	10.2448
14	17.0	16.7882	15.7469	17.8295
15	36.44	36.8904	35.9496	37.8312
16	14.09	14.6234	13.4058	15.841
17	17.26	17.0828	16.142	18.0236
18	12.57	13.0315	11.8139	14.2491
19	14.94	13.32	12.3792	14.2608
20	40.62	40.8457	39.8044	41.887
21	14.5	13.6355	12.5942	14.6768
22	10.34	10.8585	9.64088	12.0761
23	10.08	9.88171	8.66412	11.0993
24	34.92	35.2588	33.8166	36.701
25	47.24	44.0344	42.8168	45.252
26	12.55	12.7208	11.2786	14.163
27	40.74	40.475	39.0328	41.9172
28	14.71	14.6611	13.7203	15.6019
29	39.13	39.2303	38.1891	40.2716
30	15.97	14.499	13.4578	15.5403
31	31.4	33.7538	32.3116	35.196
32	7.72	8.20903	6.99144	9.42662
33	8.03	8.71532	7.49773	9.93292
34	15.18	14.3995	13.1819	15.6171
35	7.15	8.0812	6.639	9.52341
36	9.66	9.83926	8.39705	11.2815
37	17.02	16.8841	15.9433	17.8249
38	9.0	9.38296	8.44217	10.3238
39	7.25	8.58792	7.37033	9.80551
40	15.42	15.7198	14.779	16.6606
41	10.14	9.57551	8.53424	10.6168

42	19.49	18.5916	17.5504	19.6329
43	34.39	34.1038	33.0625	35.145
44	38.04	37.4453	36.2277	38.6629
45	14.6	15.6663	14.6251	16.7076
46	8.16	8.15356	7.1123	9.19483
47	7.23	8.43472	6.99251	9.87693
48	12.85	12.875	11.8338	13.9163
49	17.63	17.2643	16.0467	18.4819
50	18.02	19.0958	18.0545	20.1371
51	14.24	17.9162	16.6986	19.1337
52	15.28	13.8476	12.8064	14.8889
53	39.38	38.511	37.2934	39.7286
54	9.97	10.3267	8.88446	11.7689
55	40.33	40.1668	39.1255	41.2081
56	35.96	36.2847	35.0671	37.5023
57	43.32	42.6658	41.4482	43.8834
58	30.09	31.8982	30.8569	32.9395
59	9.99	10.2375	9.19628	11.2788
60	20.56	21.4171	20.1995	22.6347
61	36.44	35.3936	34.3523	36.4348
62	9.72	9.58426	8.14205	11.0265
63	9.72	11.0658	9.8482	12.2834
64	13.25	13.5617	12.3441	14.7793
65	9.55	8.1594	6.94181	9.37699
66	18.93	19.245	18.2038	20.2863
67	9.05	8.99088	7.77329	10.2085
68	9.85	8.78236	7.56477	9.99995
69	34.01	34.5609	33.3433	35.7785
70	10.07	11.2788	10.0613	12.4964
71	17.47	15.9129	14.8716	16.9542
72	29.03	29.2363	27.7941	30.6785
73	30.77	31.0575	29.6153	32.4997
74	45.96	44.7359	43.5183	45.9535
75	14.38	15.4103	14.3691	16.4516
76	31.41	32.766	31.5484	33.9836
77	9.3	9.37153	8.33026	10.4128
78	39.54	38.5001	37.2825	39.7177
79	9.54	9.35116	8.13357	10.5687
80	15.36	14.7293	13.5117	15.9469
81	33.7	33.3894	32.1718	34.607
82	9.85	9.12384	7.90625	10.3414
83	51.72	48.4251	46.9829	49.8673
84	10.23	8.7762	7.334	10.2184
85	35.38	36.5526	35.1104	37.9948
86	39.54	38.8416	37.624	40.0592

87	9.99	10.579	9.53776	11.6203
88	16.25	13.9032	12.6856	15.1208
89	10.73	15.7402	14.7994	16.681
90	11.72	11.4073	10.1897	12.6249
91	38.04	37.7868	36.5692	39.0044
92	35.96	36.6262	35.4086	37.8437
93	21.56	21.7586	20.541	22.9762
94	9.55	8.50088	7.28329	9.71847
95	17.47	16.2544	15.2131	17.2957
96	10.14	9.91699	8.87572	10.9583
97	15.28	14.1891	13.1479	15.2304
98	45.32	43.0073	41.7897	44.2249
99	9.82	9.2288	7.78659	10.671
100	9.66	10.1807	8.73853	11.6229
101	9.63	13.0623	11.6201	14.5045
102	18.93	19.5865	18.5453	20.6278
103	9.91	10.3937	9.35239	11.4349
104	16.49	18.9331	17.8918	19.9744
105	9.05	9.33236	8.11477	10.55
106	46.24	44.3759	43.1583	45.5935
107	18.24	18.2576	17.04	19.4752
108	9.54	9.69264	8.47505	10.9102
109	40.62	41.1872	40.1459	42.2284
110	16.5	14.5962	13.555	15.6375
111	10.34	11.2	9.98236	12.4175
112	9.72	9.92574	8.48353	11.3679
113	29.92	35.6003	34.1581	37.0425
114	38.39	34.4452	33.404	35.4865
115	40.96	45.0774	43.8598	46.295
116	32.52	31.5916	30.374	32.8092
117	40.74	40.8165	39.3743	42.2587
118	16.71	15.0026	14.0618	15.9434
119	50.38	38.8525	37.6349	40.07
120	15.42	16.0613	15.1205	17.0021
121	10.07	11.6203	10.4027	12.8379
122	36.44	35.735	34.6938	36.7763
123	15.18	14.741	13.5234	15.9586
124	35.92	30.0668	28.8492	31.2844
125	14.94	13.6615	12.7207	14.6023
126	31.01	34.9024	33.6848	36.12
127	15.97	14.8405	13.7992	15.8818
128	16.85	13.2165	12.1753	14.2578
129	10.03	9.05681	7.83921	10.2744
130	17.02	17.2256	16.2848	18.1663
131	40.13	39.5718	38.5305	40.6131

132	28.7	33.7309	32.5133	34.9485
133	36.33	40.5083	39.467	41.5496
134	30.77	31.399	29.9568	32.8412
135	17.09	14.9649	13.7473	16.1825
136	42.05	42.5728	41.1306	44.015
137	33.4	34.0953	32.6531	35.5375
138	9.76	9.54505	8.50378	10.5863
139	17.26	17.4243	16.4835	18.3651
140	9.3	9.71301	8.67174	10.7543
141	15.36	15.0708	13.8532	16.2884
142	10.15	8.42269	6.98048	9.86489
143	14.57	13.373	12.1554	14.5906
144	32.41	33.1075	31.8899	34.325
145	10.16	8.49505	7.45378	9.53631
146	30.09	32.2397	31.1984	33.2809
147	9.31	9.72444	8.78365	10.6652
148	10.09	10.2406	9.02301	11.4582
149	15.26	17.6098	16.669	18.5506
150	14.38	15.7518	14.7105	16.7931
151	16.0	17.1297	16.0884	18.1709
152	14.6	16.0078	14.9666	17.0491
153	9.97	10.6681	9.22594	12.1104
154	27.03	29.5778	28.1356	31.02
155	10.08	10.2232	9.0056	11.4408
156	14.63	17.6058	16.3882	18.8234
157	36.44	37.2319	36.2911	38.1726
158	9.77	8.71537	7.27316	10.1576
159	10.25	8.9294	7.71181	10.147
160	9.72	8.55051	7.33292	9.7681
161	14.5	13.977	12.9357	15.0183
162	18.02	19.4373	18.396	20.4785

This table contains information about values of Oil absorbed generated using the fitted model. The table includes:

(1) the observed value of Oil absorbed (if any)

(2) the predicted value of Oil absorbed using the fitted model

(3) 95.0% confidence limits for the mean response

Each item corresponds to the values of the experimental factors in a specific row of your data file. To generate forecasts for additional combinations of the factors, add additional

rows to the bottom of your data file. In each new row, enter values for the experimental factors but leave the cell for the response empty. When you return to this pane, forecasts will be added to the table for the new rows, but the model will be unaffected.