Influence of pH on the Stability Characteristics of Nanofluids for Heat Transfer Applications

By

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14535

Dissertation submitted in partial fulfilment of

the requirement for the

Bachelor of Engineering (Hons)

Chemical Engineering

FYP II September 2014

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CERTIFICATION OF ORIGINALITY

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

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RAFYHADI BIN JUNAEDI

ABSTRACT

Nanofluids have been in intense researches for the past few years with the great potential to improve the efficiency of heat transfer fluids. Knowledge of sediment behaviours of nanofluids give great significances towards the stability of nano-suspensions. This work focuses on the sedimentation behaviours of alumina and zinc oxide nanoparticles in different proportion of ethanol-water binary mixtures. Nanoparticles of 40 nm were used in this project. Under different pH values, the sediment heights with respect to time were measured by visualization method in batch sedimentation. Analysis of TEM, FTIR, zeta potential and particle size distribution were performed to study the influence of pH on the nanofluids. The results showed that in certain ethanol-water proportions, the stability of alumina nanofluids was highly dependent on pH values. The highest stability of the alumina nanofluids can be achieved at the optimal pH value. Whereas pH was found to have insignificant effects on the stability of zinc oxide nanofluids.

ACKNOWLEGMENT

I would like to express my deepest gratitude to the Chemical Engineering department of Universiti Teknologi PETRONAS (UTP) for providing the chance to undertake this remarkable Final Year Project (FYP). My knowledge and skills has been put to a test after completing various kinds of project during my five years intensive chemical engineering course. This course has a good coverage on the overall chemical engineering programme whereby a student with any majors has been assigned with different scope of the study thus contribute the effort and knowledge towards achieving a project goal.

Most important, a very special note thanks to my supervisor Dr Rajashekar Pendyala, who was always willing to assist and provided good support throughout the project completion. Your excellent support, patience and effective guidance have helped my project to completion. Nevertheless, I also would like to thank to my Mr Suhaib Umer Ilyas, phD Student in UTP for guidances from the beginning of the project. I would like to thank to FYP1 and FYP2 coordinators, Dr Maziyar Sabet and Dr Asna respectively for arranging various seminars as support and knowledge to assist the group in the project. The seminars were indeed very helpful and insightful to us.

Besides that, I would also like to take this opportunity to express my deepest thanks to all laboratory technicians who had given guidance in completing this project experiment. Last but not least my heartfelt gratitude goes to my family and friends for providing me continuous support throughout the duration of this project.

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CHAPTER 1

INTRODUCTION

1.0 Background

Thermal Properties of liquids play a decisive role in heat transfer application such as heating and cooling. Thermal conductivity of a fluid is an important property that decides its corresponding heat transfer performance. Conventional heat transfer fluids such as water have poor thermal conductivity which limit their performance in high heat transfer application. Scientists have attempt to enhance the heat transfer performance by using solid additive which now well known as nanofluids.

Nanofluid is a new class of engineering material consisting nanometer-sized particles with dimension less than 100nm dispersed in conventional base fluids. It is a solid and liquid composite material and the typical nanoparticles include metals, oxides, carbides, nitrides or carbon nanotubes whereas the common used base fluids are water, ethylene glycol and ethanol.

Nowadays, nanofluids are regard regarded as promising heat transfer fluids due to their high thermal conductivity. The basic idea is that, when the nanoparticles which have higher thermal conductivity than the base fluids are added together, the effective thermal conductivity of the suspension can be increased and because of that advantage, nanofluids have a great potential to replace conventional heat transfer fluids in many heat transfer applications.

1.1 Problem Statement

In an age of increasing heat fluxes and power loads in heat transfer application in medical field, power electronics, micromechanics, transportation, heating, ventilating and air conditioning, better heat transfer fluids are necessary to enhance heat dissipation, improve energy efficiency and lengthen device lifetime. Thus, to meet these increasing thermal management needs, the heat transfer efficiency of the conventional fluids such as water, ethylene glycol, and ethanol must be improved.

Nanofluids offer higher thermal conductivity performance than the conventional heat transfer fluids. Despite having that great potential, the stability of nanofluids still being an issue nowadays especially on how to effectively control the coagulation of nanoparticles in the base fluids.

The main reason for the coagulation is due to the high surface energy of the nanoparticles which causes the particles difficult to disperse in the base fluid. Significant amounts of experiment as well as theoretical research were conducted to investigate the factors to stabilize nanofluids by well-dispersing the nanoparticles. Some of the identified factors are particle size, temperature, dispersant, base fluids selection and mixing methods.

Previous studies shown that stability of nanoparticle in aqueous base fluids is highly dependent on pH. This project is to investigate effect of pH on the stability of nanoparticles in binary mixture.

1.2 Objectives and Scope of Study

The following are the objectives of the study:

i. To investigate settling behaviors of alumina and zinc oxide in different ethanol – water concentration and different pH values by using sedimentation analysis
ii. To investigate effect of pH on the particles size by using Particle Size Analyzer.
iii. To identify an optimum pH value that give the highest absolute value of zeta potential
iv. To compare agglomeration of the particles in natural condition and in the optimum pH condition

The study is limited only to investigate the influence of pH on the stability characteristics of the nanofluids because of the time constrain. The sedimentation of the nanofluids take days to be monitored and there are number of nano-suspensions to be evaluated. The study is delaminated to the following scopes:

i. Preparation of the nanofluids.

   Prior to the experiment, is to decide suitable concentration of hydrochloric acid and sodium hydroxide to be used by utilizing FTIR analysis. Then, the range of pH will be chosen based on the selected concentrations. The best sequence to prepare the nano-suspensions are selected based on literature reviews.

ii. Evaluation of the influence of pH on the stability of nanofluids.

   Zeta potential is selected as a quantification to evaluate the influence of pH by using. Sediment analysis is selected to study settling behavior of the nanofluids by plotting the sediment ratio over time. The sediment analysis will be carried out in at least 1 week. The purpose of the evaluation is to find the optimum pH condition at which the nano-suspensions are most stable.

CHAPTER 2

LITERATURE REVIEW

2.1 Concept of Nanofluids

The term "nanofluids" refer to a solid-liquid mixture which consists of nanoparticles which are dispersed in base fluids and the particles are very small with their smallest dimension usually less than 100nm. The typical particles are metals, oxides, carbides, nitrides and carbon nanotube (Rao, 2010). According to Kostic (2006), the common base fluids or dispersion medium are water, oil, ethylene-glycol mixture, refrigerant, polymer solutions, bio-fluids and others.

Together with the rapid increasing in thermal load especially in fields of microelectronics, automobiles, micromechanics, instrumentation, heating, ventilating and air conditioning, the needs for the high performance heat transfer fluid becoming a great demand. This is because the low thermal conductivity of conventional heat transfer fluids become the limitation in the cooling or heating performance (Li et al., 2008). Thus, the conventional heat transfer fluids such as engine oil, glycol and water which have poor thermo-physical properties are not suitable to meet the growing demand.

There is therefore, nanofluids which is an advanced cooling and innovative heat transfer fluids are needed to warrant the demand for the heat transfer applications. It was proven that nanoparticles with higher thermal conductivity than their base fluid can increase the effective thermal conductivity of suspension.

Based on the figure 1 below, at room temperature, metallic solids have higher thermal conductivity than fluids e.g. Copper at room temperature has thermal conductivity about 700 times greater than that of water and about 300 times greater than engine oil

(Choi, Zhang, Keblinski, 2004). Thus, it can be expected that the thermal conductivity would be higher for fluids containing suspended metallic or nonmetallic (oxide).

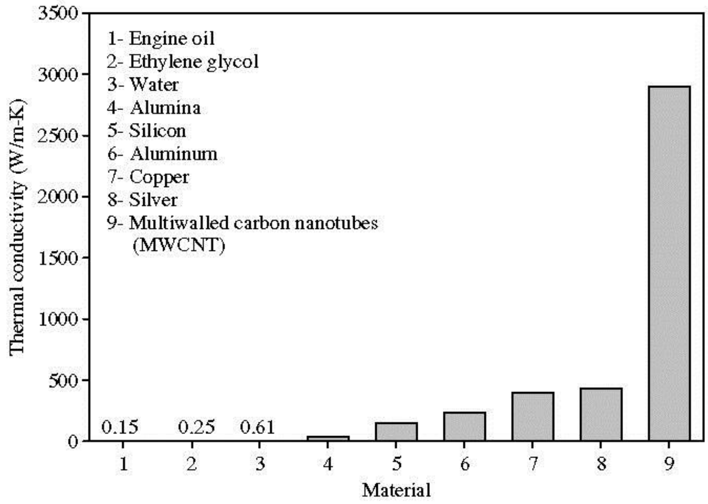


Figure 1: Thermal conductivity of typical materials at 300 K – Choi et al.

2.2 Nanofluids in Heat Transfer Applications

According Putnam et al. (2006), low concentration of water have larger effect on the thermal conductivity of ethanol-water mixtures than predicted by effective medium theory. As an example, a 2% volume concentration of water increases the thermal conductivity of ethanol by approximately 6% while prediction of the symmetric effective medium theory predicts an increase of only approximately 3%.

The following are the potential applications of ethanol based nanofluids:

i. Combustion

Ethanol based nanofluid can be used in combustion process to speed up ignition process. This was evidenced by Allen et al. (2011) who used an aerosol shock tube and find out that addition of 2% by weight of aluminum in ethanol can reduce the ignition delay by 32%. The nanofluid has better suspension quality because ethanol is a polar and hydrophilic liquid. Therefore, good nanoparticle suspension with hydrophilic oxide surface in ethanol can be maintained

ii. Solar application

Ethanol based nanofluids have potential to convert light energy to thermal energy by radiation adsorption. According to Gan and Qiao (2012) radiation adsorption can be enhanced by adding a small amount of nanoparticle such as aluminum to a base fluid ethanol.

The following are the applications of water based nanofluids:

i. Coolant in transportations

According to Murshed et al. (2008) nonofluids would allow for smaller and lighter engines, radiators, pumps and other components because better thermal conductivity of the nanofluids result in smaller coolant management system.

ii. Electronic liquid cooling system

Nguyen et al. (2007) found out that inclusion of nanoparticles into base fluid water resulted in considerable enhancement of the cooling convective heat transfer coefficient inside a closed system for cooling of microprocessors and other electronic components

2.3 Method of Preparation of Nanofluids

There are two known techniques to prepare nanofluids; two-step and single step preparation methods

According to Yu and Xie (2012), two-step method is the most widely used method to prepare nanofluids. The nanoparticles used in this method are first produced as dry powders by mean of chemical or physical methods. In the second processing step, the nanosized powder will be dispersed into a base fluid with the help of intensive magnetic force agitation, ultrasonic agitation homogenizing, ball milling and high-shear mixing. The two-step method is the most economic method because nanopowder synthesis techniques have already been scaled up to industrial production levels.

Li et al. (2009) define the single step method as a process combines the preparation and synthesis of nanofluids in which the nanoparticles are directly prepared via physical vapor deposition technique or liquid chemical method. The drying, storage, transportation and dispersion of nanoparticles are avoided in the single step method.

Thus, the agglomeration of nanoparticles is minimized and the stability id fluids is increased

2.4 pH Adjustment Using Hydrochloric Acid and Sodium Hydroxide

One of the important key issues is the production of undesired side products thereby leading to poor quality of synthesized nanofluids (Wang & Fan, 2010). In this experiment, side products are possible from the addition of hydrochloric acid and sodium hydroxide for the pH adjustment. The side products give effects to the stability of the nanofluids and therefore have to be avoided.

According to Williams and Bost (1936), although ethanol is regarded as a neutral liquid like water, in certain type of reactions, it acts as a weak acid and weak base. They claimed that sodium ethoxide is produced by refluxing ethanol and sodium hydroxide. However, the reflux heat under which the reaction occurred is not specified by Williams and Bost.

$$C_2H_5OH + NaOH \rightarrow C_2H_5ONa + H_2O$$

Szmant (1989) made a claim that the reaction of ethanol and concentrated hydrochloric acid occurs smoothly and potentially more convenient when carried out in a small scale. According to Bond and Hughes (2013), ethanol does not react with hydrochloric acid which is contradicts with the claim made by Szmant. The equation describing the reaction between ethanol and hydrochloric acid.

$$C_2H_5OH + Hcl \rightarrow C_2H_5Cl + H_2O\text{L}$$

Therefore, diluted sodium hydroxide and hydrochloric acid are selected for the pH adjustment as Szmant claimed that concentrated acid reacts with ethanol. Fourier Transform Infrared Spectroscopy (FTIR) is used to confirm any reaction when adding 0.01, 0.05 and 1.0 M of hydrochloric acid and sodium hydroxide.

2.5 The Stability Evaluation Methods: Zeta Potential Analysis

Murkherjee and Paria (2013) have defined zeta potential as the difference between the dispersion medium and the stationary fluid layer which attached to the particles. The zeta potential indicates the degree of repulsion between adjacent and similar charged particles in dispersion. Thus, colloid with high absolute values of zeta potential are electrically stabilized while colloids with low zeta potentials tends to coagulate.

Kim et al. (2009) prepared gold-water nanofluid with an outstanding stability after one month with no dispersants were observed due to a large negative zeta potential of gold nanoparticles in water. Micro-electrophoresis zeta potential analyzer was used to measure the zeta potential.

Zhu et al. (2009) found out that the study of electrophoretic behavior by measurement of the zeta potential is important for understanding the dispersion behavior of naofluids. In the experiment, zeta potential of alumina-water nanofluids was measured under different pH and sodium dodecylbenzene sulfonate (SDBS) concentration. Malvern ZS Nano S analyzer (Malvern Instrument Inc., Londan, UK) was used to measure the zeta potential.

2.6 The Stability Evaluation Methods: Sedimentation Method

According to Wei and Wang (2010), sedimentation method is the most elementary method to evaluate the stability of nanofluids. A field of external force is applied to start the sedimentation of nanoparticles in nanofluids. The height of sediment, volume of sediment or the weight of sediment indicates the stability of nanofluids. Nanofluids are considered to be stable if the concentration of supernatant particles remains constant over time. Use of camera has proven to be an appropriate aid to capture sedimentation photographs to observe the stability of nanofluids (Wei et al., 2009)

According to Ilyas et al. (2013) settling behavior of solid liquid mixtures can be classified into three different classes – flocculation, dispersion and mixed settling. In flocculated sedimentation which occurs in high concentration of solid, clumps are formed as the particles stick together and then settle down. Dispersed sedimentation occurs in very low solid concentrations in which the individual particles settle independently. In mixed sedimentation, particles settling follow both flocculated and dispersed trend simultaneously.

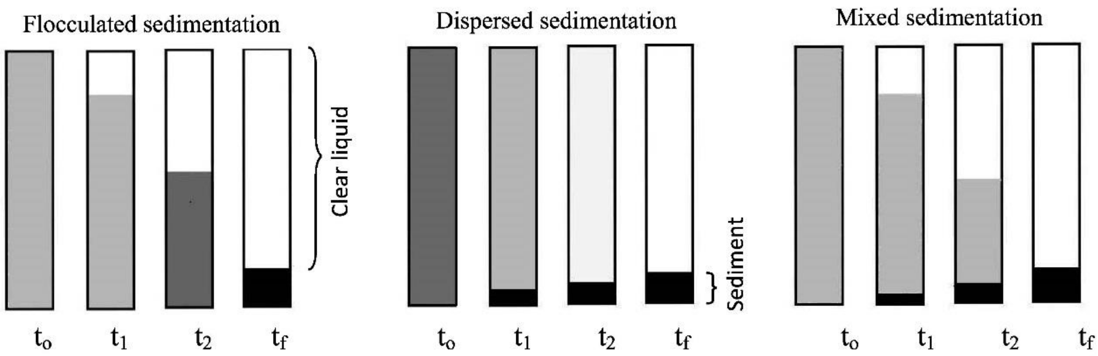


Figure 2: Three different types of settling behavior of suspensions with solid particles at different time intervals (Ilyas et al., 2013)

2.7 Influence of pH on the Stability of Nanofluids

According to Mukherjee and Paria (2013) stability of a nanofluid is directly related to electro-kinetic properties and therefore, pH control can increase the stability due to strong repulsive force. The strong force prevents the nanoparticle from coagulate by dispersing them in the base fluids.

Based on Lee et al. (2006) as the pH goes away from point zero charge (PZC), the surface charge increases because of more frequent attacks onto the surface of hydroxyl groups by potential-determining ions like H^+ and OH^-, resulting to an increase in zeta potential.

When nanoparticles are dispersed in a base fluid, the state of the nanoparticles is determined by the interaction between the particles and the base fluid. The stability of a colloid fluid is determined by the summation of attraction and repulsion force. The van der Waals forces will prevail in case the energy barrier is insufficient to prevent the system from achieving a lower energy state and this will cause the particles to aggregate and settle out of the base fluid. (Cosgrove, 2010).

Qi et al. (2010) state that the higher the particle charge potential, the more stable is the nanofluid and generally nanofluids are kinetically stable systems as the particles able to move over a small distance and because the particles undergoing Brownian motion where van der Waals attraction prevails, the aggregation occurs.

According to Zhang et al. (2010), if the surface charge is not high enough, there will be no barrier and the particles will aggregate to form different secondary structure. The forming of the structure causing the energy balance change due to the change in particle size. The system will be stable in an intermediate state where the particles remain suspended at some small-sized secondary structure.

Huang et al. (2009) conducted an experiment to investigate the influence of pH by using hydrochloric acid and sodium hydroxide to control pH of the suspension of alumina and Zinc Oxide in water. They found that the greater the zeta potential and absorbency, the higher the particle concentration in the suspension and hence the more stable the suspension is.

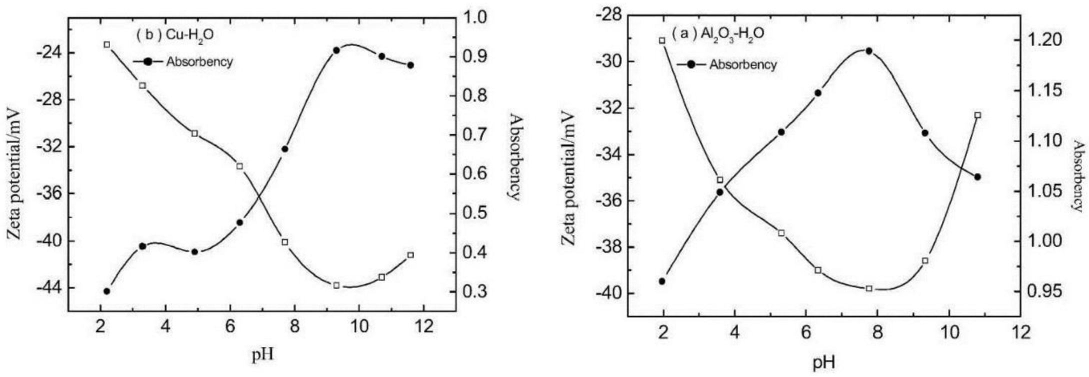


Figure 3: Effect of pH on zeta potential of nano-suspensions with SDBS dispersants. Huang et al. (2009)

The above figures show the experimental results obtained from the experiment. As pH increases the absolute value of zeta potential increases, hence the electrostatic and the particles repulsion force become greater to prevent the attraction and collision caused by Brownian motion. From the figures, $pH_{alumina}$~8.0 and pH_{copper}~9.5 are recorded as the optimum pH in the experiment.

Gowda et al. (2010) conducted a study on the effects of particle surface charge, species, and concentration and dispersion method on thermal conductivity of nanofluids. Alumina and copper oxides are disperse in ethylene glycol and deionized water. They agreed that surface charge is a critical factor for the stabilization of colloidal solutions. In this study, they relate the pH with the change of particle numbers and size increase. One consequence of the agglomeration is the reduction of particle numbers in the suspension and size increase (cluster structures) of particles which will shorten heat conduction path thus increase the thermal conductivity. In the same time, the size increase of particles reduces the particle motion of the fluid to promote more heat transfer. These two heat transfer mechanisms will compete each other to decide the thermal conductivity enhancement.

Wankam et al (2011) have studied the effect of pH on heat transfer nanofluids containing ZrO_2 and TiO_2 nanoparticles. Significant enhancement of thermal conductivity of the nanofluids are observed near the isoelectric point (IEP). The experimental results indicate the stabilities of these nanofluids are affected by pH values. The reasonable justification is that at the IEP, the repulsive forces of the metal oxides are zero, tend to be unstable, form cluster and finally agglomerate together at the corresponding pH value. The IEP is a pH value at which the nanoparticles carry no electrical charges at the corresponding pH value

The latest study conducted by Iranidokht shows that pH variation led into variation of thermal conductivity of mixed nanofluid. The study is to investigate thermal conductivity of mixed nanofluids under controlled pH condition. Ethylene glycol was used as the base fluid to disperse the combination of the two nanoparticles; Titanium Dioxide – Copper and Titanium Dioxide - Alumina. The results show the thermal conductivity of all single particle nanofluids and mixed nanofluids are dependent on their pH values. There was a great different between the experimental thermal conductivity of the mixed nanofluids and the estimated one. By changing the pH, this difference decreased to minimum

In conclusion, based on the literature reviews, it is proved that the stability characteristic of nanofluids is highly dependent on the pH of the suspension. A mixture of ethanol-water will be a suitable choice of base fluid to be used to investigate the influence of pH on the stability of the nanofluid because the mixture has not yet been studied and investigated in previous literatures. Based on the literature, two steps preparation method will be used to prepare the nanofluid in this study.

CHAPTER 3

METHODOLOGY

3.1 Project Flow

i. **Literature Review**
Critical analysis on influence of pH on nanofluids stability is carried out from numbers of comprehensive and up-to-date literature review

ii. **Experiment**
A comprehensive, high achievable and extremely appropriate methodology is develop to carry out the experiment by considering existing constrains.

iii. **Data Collection & Analysis**
Important result is presented in the text and critically analyzed with respect to the theory. Result presented is sufficient to meet objectives and presented professionally

iv. **Conclusion**
Conclusions are made logical and related to the objectives, clearly evaluate the significance and quality of results

3.2 Gantt Chart

Refer appendix 1 for the project schedule, timeline and milestones.

3.3 Experimental Methodology

3.3.1 Chemicals Required

Table 1: Chemicals Used and the Properties

Chemicals	**Properties**
Alumina Powder	Melting Point: 2040 ℃ Boiling Point: 2980℃ Density:3.97 g/cm^3 Size: 40 nm
Zinc Oxide Powder	Melting Point: 1975 ℃ Boiling Point: 2360℃ Density: 5.6 g/cm^3 Size: 40 nm
Deionized Water	Millipore quality water
Ethanol	Melting Point: -114 ℃ Boiling Point: 78.37℃ Density: 3.97 g/cm^3 Miscible in water.
Hydrochloric Acid	Melting Point: -35 ℃ Boiling Point: 57℃ Density:1.49 g/cm^3 Concentration: 0.01M to 1.0M Solubility in water and ethanol: Miscible
Sodium Hydroxide	Melting Point: 681 ℃ Boiling Point: 145℃ Density:2.31 g/cm^3 Concentration: 0.01M to 1.0M Solubility in water and ethanol: Miscible

3.3.2 Instruments and Equipment

Glass Materials	15 ml test tubes, beakers and measuring cylinders – To prepare nanofluids samples
Instruments	PH meter to control pH variation Bath Sonicator to disperse nanoparticles
Characterization Equipment	• Fourier Transform Infra-Red Spectrometer (FTIR) FTIR analysis is an analytical technique to identify organic materials by providing information on chemical bonds and molecular structure. It will be used to confirm that no side reaction would happen when adding nanoparticles, hydrochloric acid and sodium hydroxide into ethanol-water binary mixture • Transmission Electron Microscope (TEM) A high-resolution imaging technique provides information on the morphology of the nanofluid to observe the agglomeration inside the nanofluid and to approximately measure the cluster particle size. The model used is Model Zeiss Libra 200FE. • Particle Size Analyzer (PSA) PSA modelled Malvern is used to determine the size of particles and zeta potential for the suspensions. The model used is The Zetasizer Nano ZS by Malvern.

3.3.3 Preparation of the Nanofluids

In this experiment two-step method will be used to prepare the nanofluid samples as described in detailed by Yue and Xie (2012). 1 wt% of alumina and zinc oxide particles are mixed with different concentration of ethanol – water mixture. The suspensions are for 3 hours by using bath sonicator. Suitable concentration of hydrochloric acid and sodium hydroxide are selected to adjust the pH of nano-suspensions.

The concentration selected must not form any side products when added to the nano-suspensions. FTIR analysis will be carried out to confirm any side products are formed. Then, the pH range for the nano-suspension are chosen based on the selected concentrations. The table below shows the list of variables for the experiment.

Table 2: List of Variables

Variables	Parameters
Controlled Variables	Sonication frequency and time. Concentration of the alumina and zinc oxide.
Independent Variable	Concentration of ethanol and water. PH value of the nanofluid samples.
Dependent Varibales	Sedimentation time for the nanofluid samples Reading of zeta potential

3.3.4 Evaluation on Influence of pH on the Stability of the Nanofluids.

The pH values for the samples are varied in range 2 to 14. Hydrochloric acid is added in order to obtain pH below than 7 and Sodium Hydroxide is added to get higher pH value than 7. The acid or base is added slowly and carefully into the samples and the pH meter is used to measure the pH values of the samples. In case of any excessive addition of acid or base which exceed the target pH value, a new sample must be prepared.

After the addition of hydrochloric acid and sodium hydroxide, a few samples will be tested using FTIR to examine any reaction of the acid and base with the sample. After the reaction confirmation, zeta sizer will be used to obtain zeta potential for each samples. TEM is utilized to get precise and clear image on the agglomeration of the nanofluids.

Following the characterization of the samples, sedimentation analysis is carried out. The samples are evaluate by observing the sedimentation of nanoparticles and photographs will be taken from time to time to follow the sedimentation progress for each samples. The analysis is time consuming because, some samples take long time to show the agglomeration of the nanoparticles.

The following flow diagram summarizes the procedure steps of the experiment.

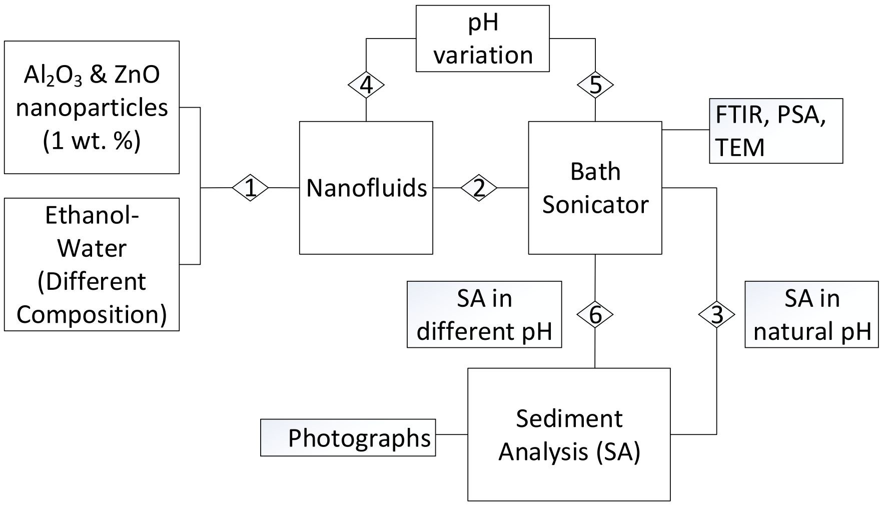


Figure 4: Flow diagram of the experimental procedure

1. Alumina and zinc oxide particles are mixed with different compositions of ethanol – water solution.
2. The nanofluid samples then are sonicated for 30 minutes by using bath sonicator.
3. In the initial stage, the pH of the samples are not varied (natural pH condition). The sediment analysis is carried out in one week.
4. In the second stage, the pH of the samples are varied to 2.5, 4.0, 8.5 and 10.
5. Prior to pH adjustment, FTIR analysis is carried out to confirm that no reaction is occurred when adding sodium hydroxide and hydrochloric acid to the suspensions
6. Sediment analysis is carried out on after the samples are solicited. Comparisons are made with the natural condition samples. Optimum pH values which give the best sediment height are tested using PSA and TEM

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Fourier Transform Infrared Spectroscopy (FTIR)

In the preparation of nanofluids, side products should not be formed under any circumstances. Side products affect the stability of nanofluid by forming undesired sedimentation. Thus, a sequence of FTIR analysis was carried out to check on any side products were formed after adding nanoparticles, hydrochloric acid and sodium hydroxide.

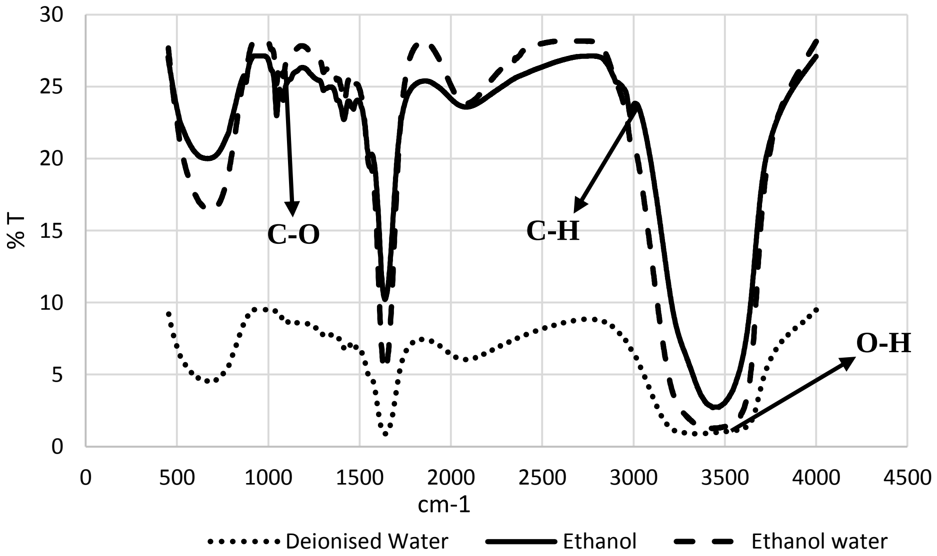


Figure 5: Spectra of deionized water, ethanol and ethanol-water mixture

The figure 5 above shows that no new peaks w formed when ethanol is mixed with deionized water. The spectrum of ethanol – water mixture than is compared to that after adding alumina and zinc oxide.

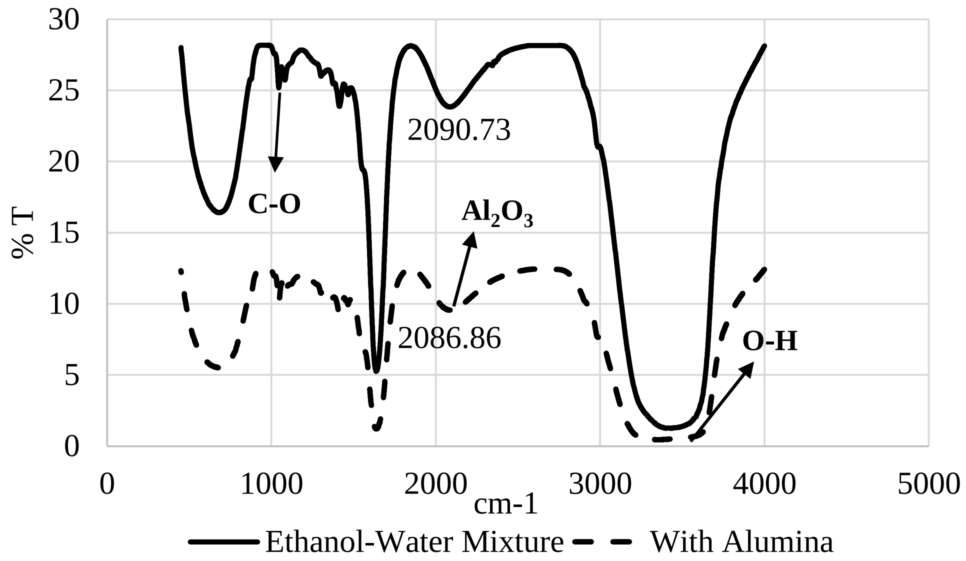


Figure 6: Spectra of ethanol-water mixture and alumina suspension

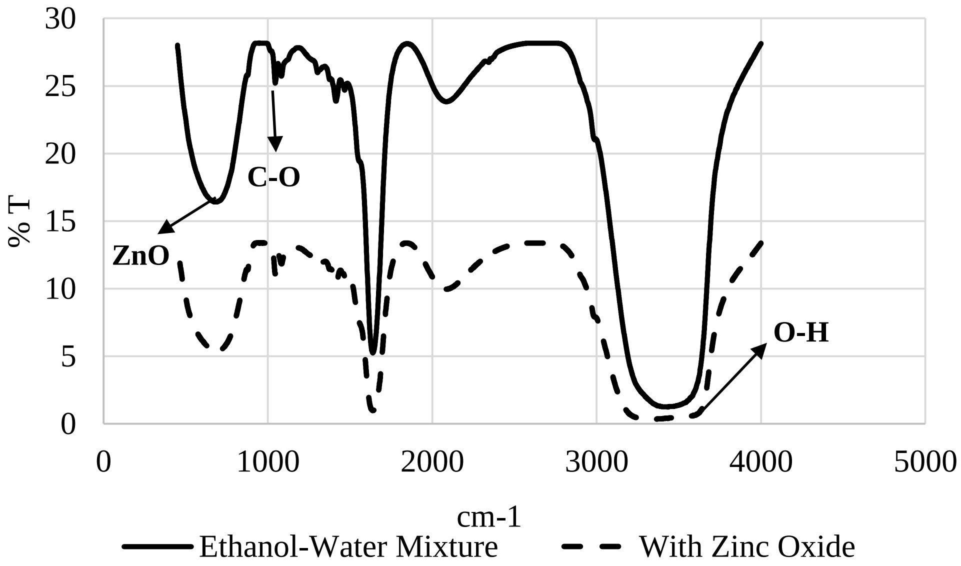


Figure 7: Spectra of ethanol-water mixture and zinc oxide suspension

Figure 6 and figure 7 show the peaks of alumina and zinc oxides suspensions are the same as that of ethanol – water mixture. No emergence of new peaks are observed and therefore no side reaction has occurred after adding the particles into water – ethanol mixture. The spectra of alumina and zinc oxide suspension are then compared with that after adding 1.0 M of hydrochloric acid and sodium hydroxide.

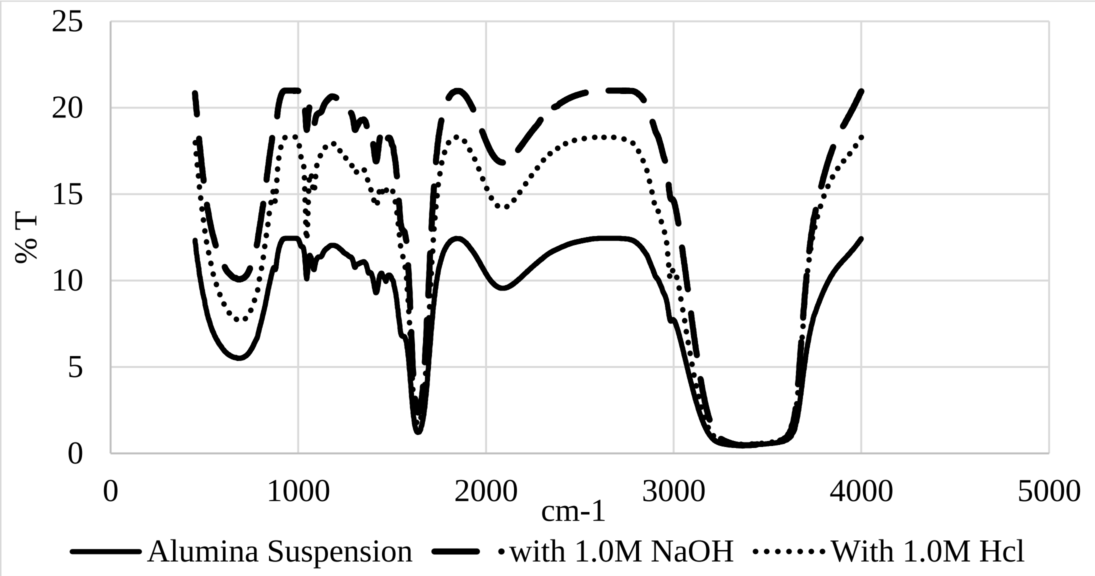


Figure 8: Spectra of alumina suspension and with 1.0M of Hcl and NaoH

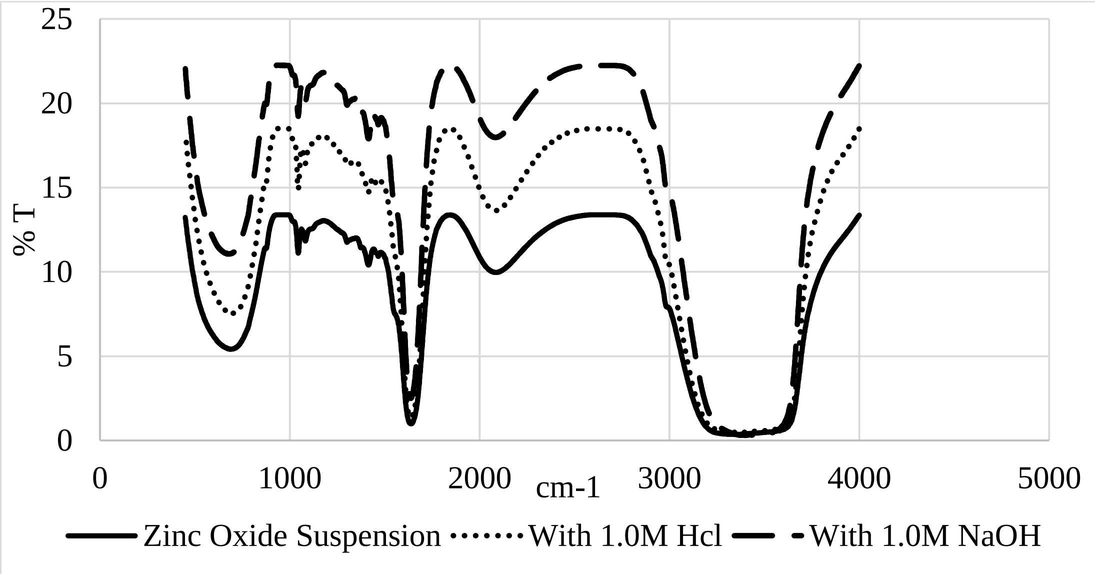


Figure 9: Spectra of zinc oxide suspension and with 1.0M of Hcl and NaOH

Figure 8 and 9 above show the resulting peaks after approximately 2 mL of 1.0M of hydrochloric acid and sodium hydroxide to alumna and zinc oxide suspensions. The spectra are comparatively the same with no new emergence of new peaks. Thus, no new species is formed after adding the acid and base.

Therefore, hydrochloric acid and sodium hydroxide with 1.0M or below can be used for the pH adjustment without forming any side products. In this experiment, 0.01M and 0.1 M of hydrochloric acid and sodium hydroxide are used to adjust the pH.

4.2 Effect of pH on Mixture of Ethanol – Water concentrations

Figure 10 illustrate that after adding zinc oxide, the pH of the suspension shifted to lower values from that of the base fluids. This indicate that the surface of the zinc oxide particles are acid terminated. The pH comparison can be clearly seen as in the graph below.

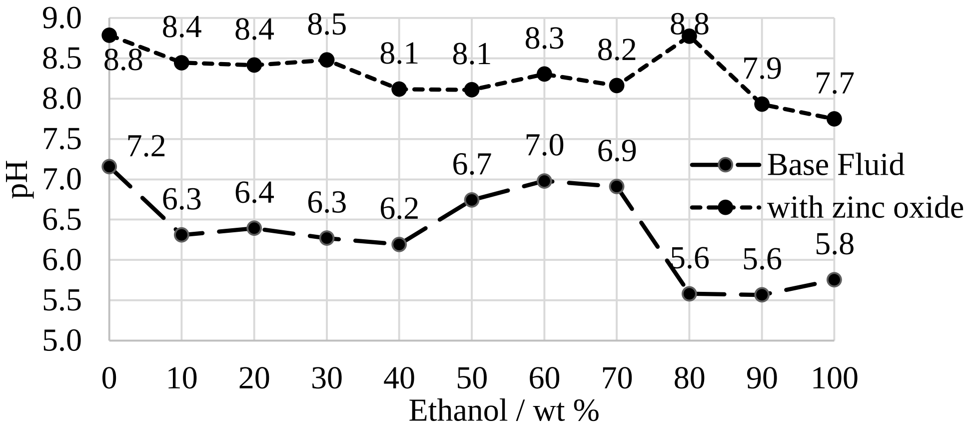


Figure 10: pH of natural base fluids and with zinc oxide

However, after adding alumina particles to the base fluid, the pH changes are in irregular pattern. For 0% to 70% ethanol with alumina particles, the pH shifted to lower values from that of the base fluids indicating that the surface of alumina particles are acid-terminated.

As for 70%-100% ethanol, the pH of the suspension shifted to higher values which indicate that the surface of alumina particles are base-terminated. The comparison can be seen as in figure 11 below

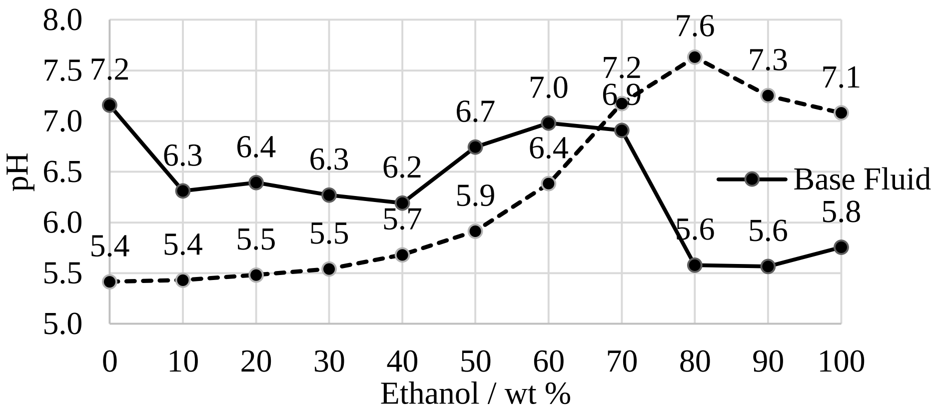


Figure 11: pH of base fluids and with alumina

4.3 Sediment Analysis

4.3.1 Alumina Suspension

Natural alumina suspension with 0% to 100% composition of ethanol are prepared and the pH are left as natural values. The sediment heights are measured at suitable time intervals. Then the sediment ratio, which is the ratio of sediment height to total suspension height is plotted against suitable intervals.

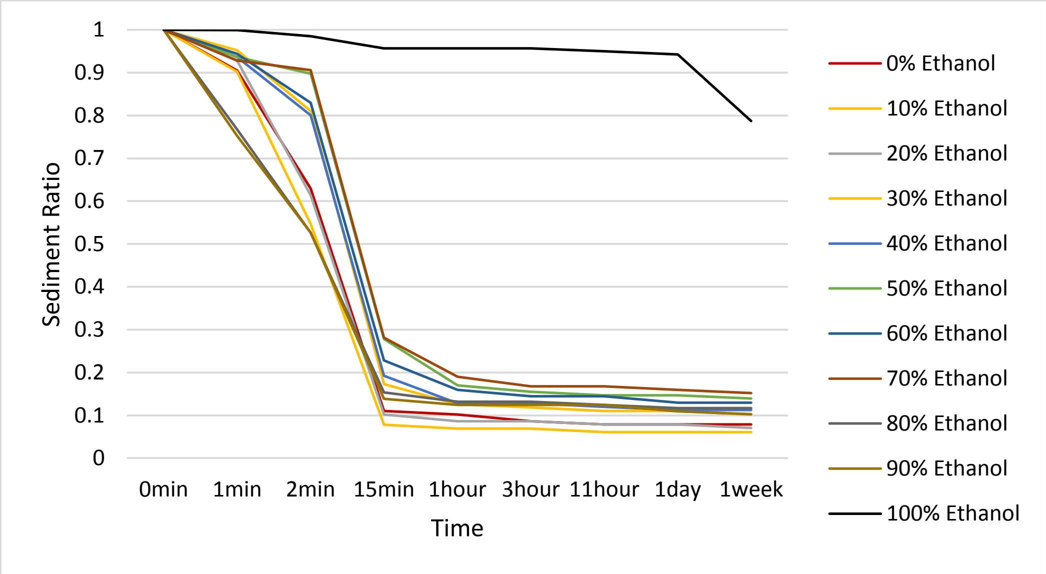


Figure 12: Graph of sediment ratio against time for natural alumina suspension

Figure 12 shows that the proportion of binary mixture of ethanol and water influence the sedimentation ratio. At 100% concentration of ethanol, the sediment ratio is the highest as compared to other concentrations and therefore is the most stable.

In the other concentrations, the sediment ratios fall less than 0.3 in 15 minutes. The reason may be due to the viscosity and interactions with nanoparticles can change with proportions of ethanol-water mixture.

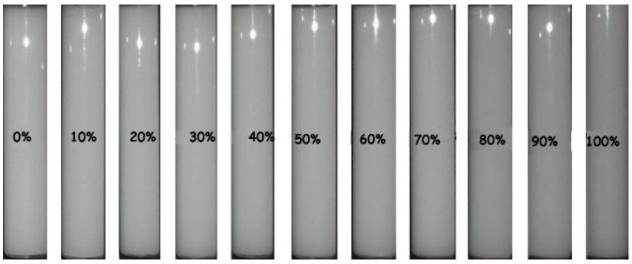


Figure 13: Sediment height for natural alumina suspension at t = 0

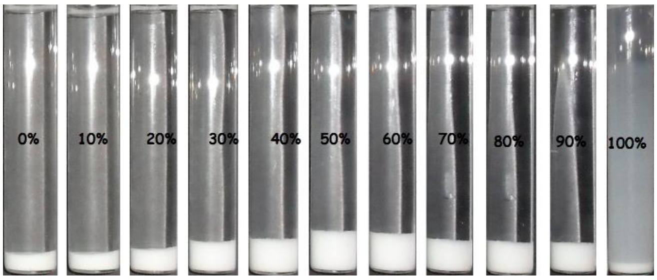


Figure 14: Sediment Height for natural alumina suspension at t = 1 Week

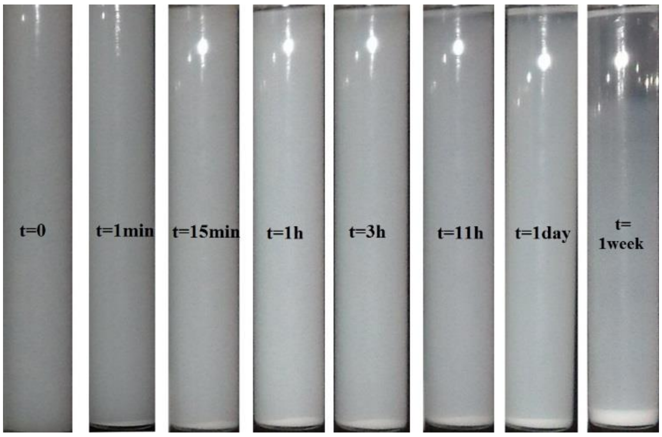


Figure 15: Sedimentation of alumina in 100% ethanol composition over time

The pH of the alumina suspensions are then adjusted to be around 2, 4, 8.5 and 10.5 to investigate the effects of pH on the sedimentation behavior. The pH of the suspensions are measured three times to take the average reading. The purpose is to obtain accurate and precise pH measurement.

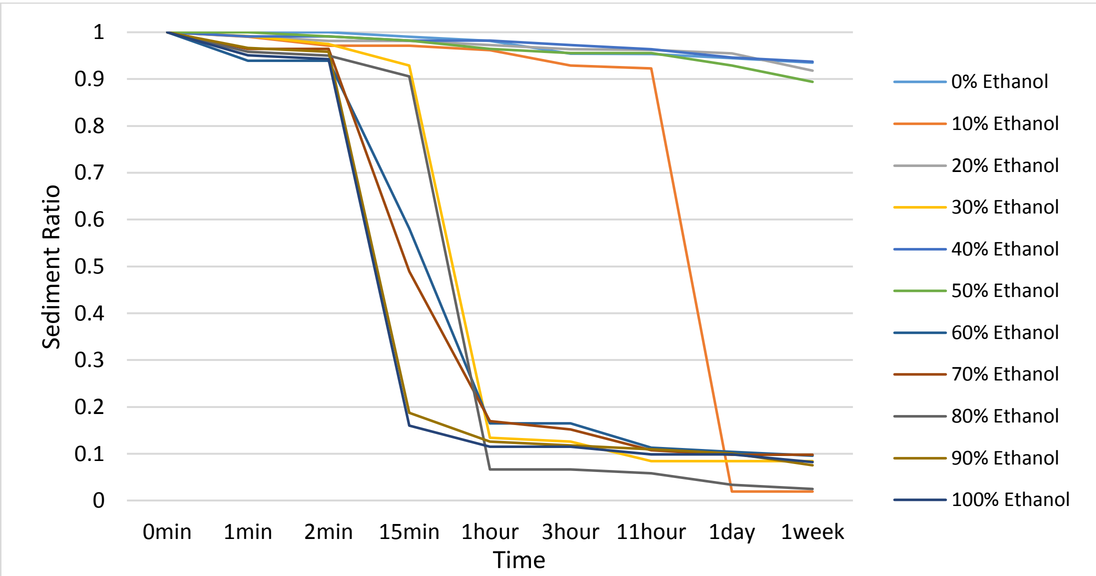


Figure 16: Graph of sediment ratio against time for alumina suspension at pH 2.5

Alumina Suspension in 0%, 10%, 40% and 50% of Ethanol. Figure 16 shows that the suspensions in 0%, 40% and 50% of ethanol are very stable compared to others as they able to maintain high sediment ratios approximately at 0.9 over 1 week. Whereas for the suspension in 10% of ethanol, it was stable over 11 hours but after one day, it became unstable and the sediment ratio fell below 0.1. The suspension are more stable compared to that of natural suspension as illustrated in the figure 18 and 19 below.

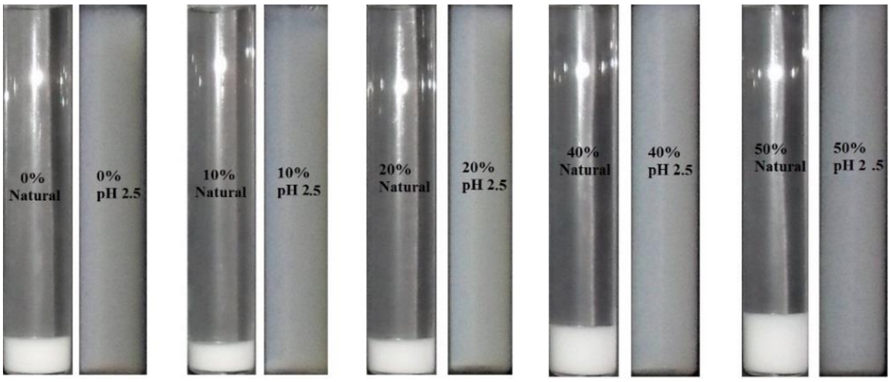


Figure 17: Comparison between sedimentation of natural alumina suspension and at pH 2.5 after 11 hours

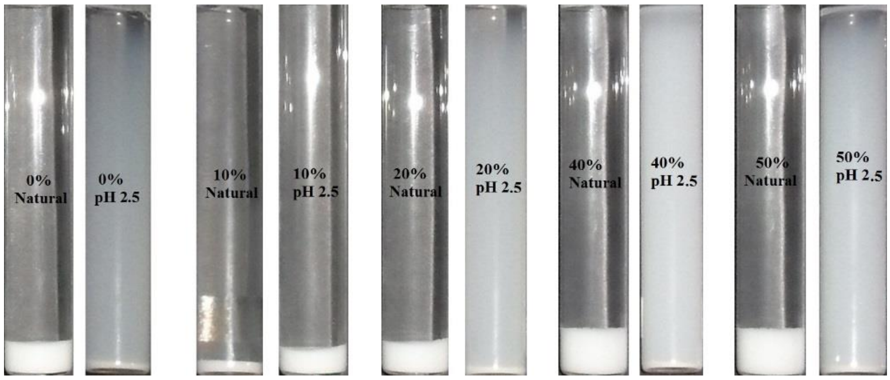


Figure 18: Comparison between sedimentation of natural alumina suspension at pH 2.5 after 1 week

Alumina Suspension in 0%, 30%, 60%, 70%, 80% and 90% of Ethanol. It is observed that pH has no significance effect on the alumina suspensions. Thus, it can be concluded that, pH 2.5 can only stabilized certain alumina suspensions only.

Alumina Suspension in 100% Ethanol. The suspension become less stable as compared to that of natural suspension. In natural condition, the sedimentation was far slower and the sediment ratio was high even after 1 week. Adjusting the pH to 2.5 tend to make the sedimentation faster and lower the sediment ratio to 0.2 after 15 minutes. The same behavior was observed at acidic and basic pH as illustrate in the figure below.

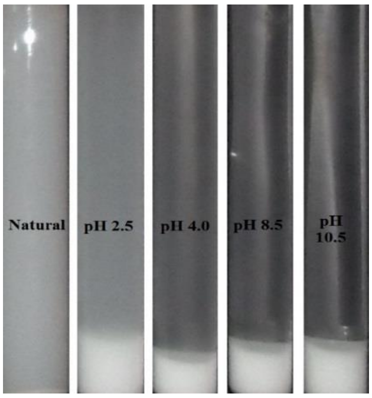


Figure 19: Comparison between the alumina suspensions in 100% ethanol at different pH after 15 minutes

Alumina Suspension at pH 4.0, 8.5 and 10.5. As the pH increased from 2, the suspension become less stable and the sediment ratios become lower. Figure 20 shows that, at pH 4.0 certain suspensions such as in 0% and 10% ethanol have better sediment ratio over time as compared to that of natural suspensions whereas other concentrations were not. The alumina suspensions were observed to be unstable at pH 8.5 and 10.5 as shown in figure 21 and 22.

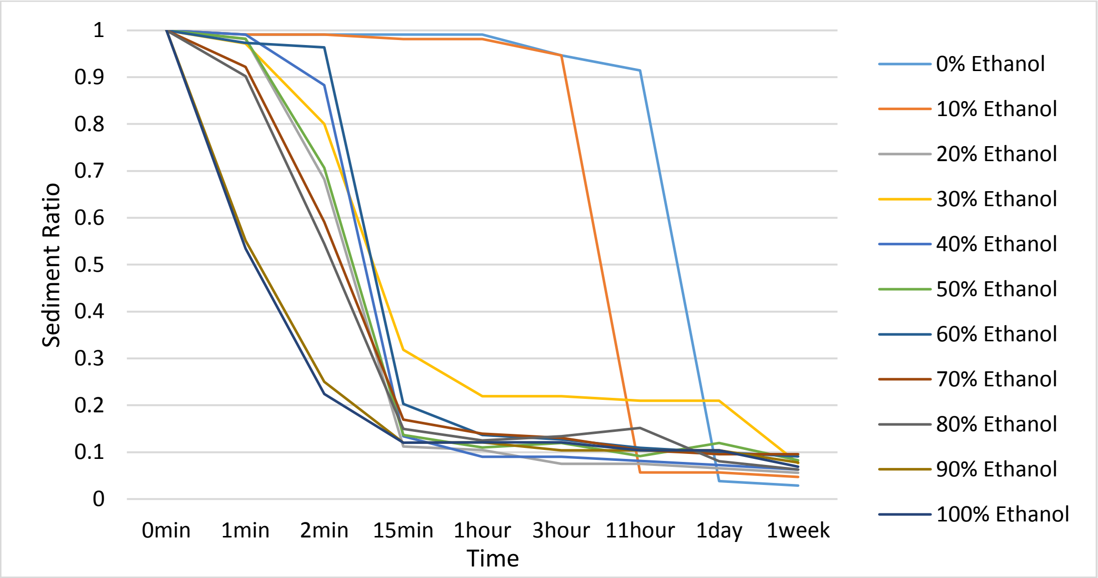


Figure 20 Graph of sediment ratio against time for alumina suspension at pH 4.0

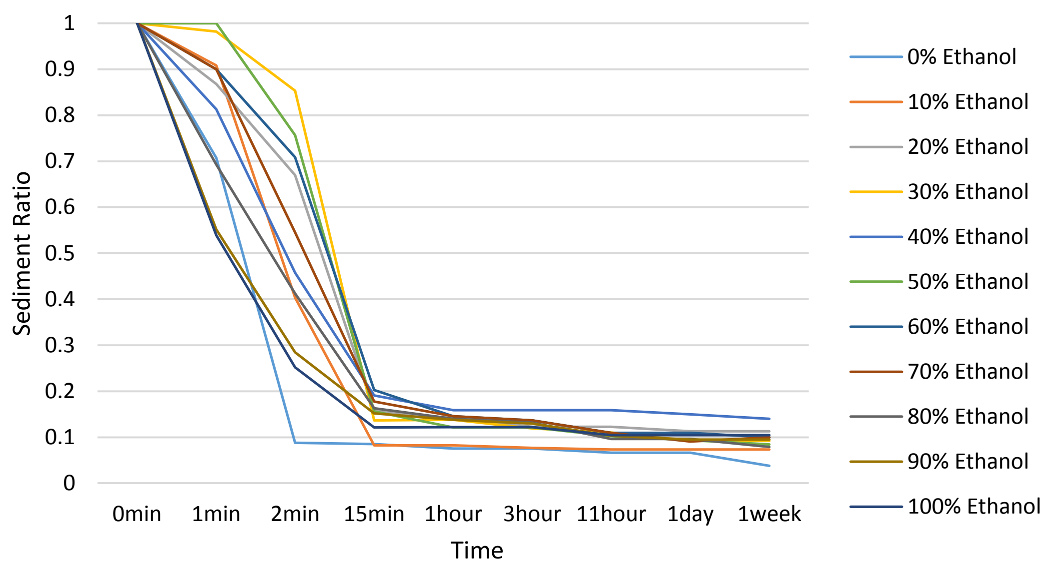


Figure 21 Graph of sediment ratio against time for alumina suspension at pH 8.5

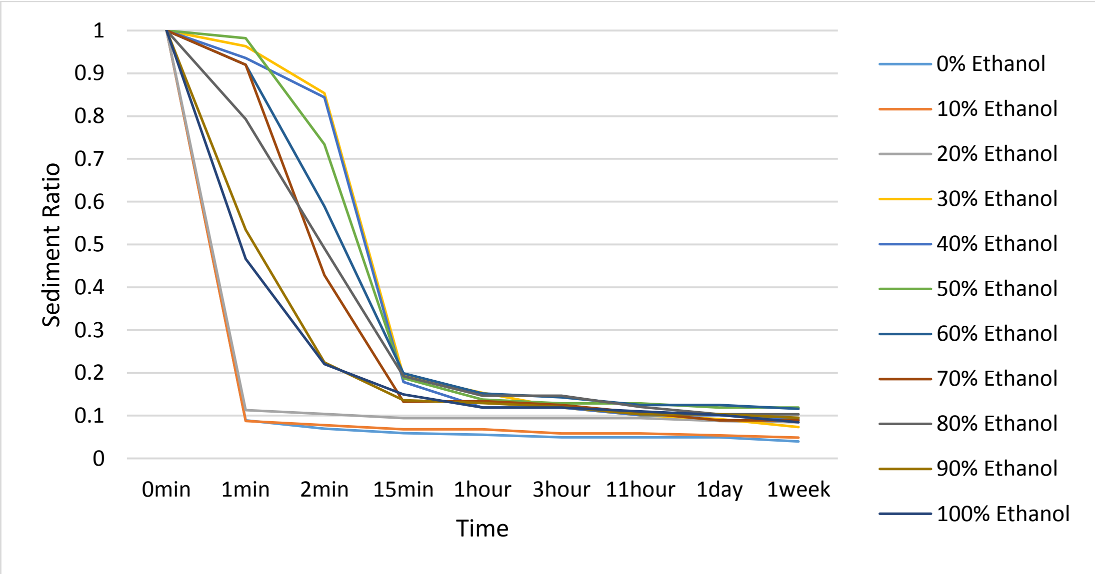


Figure 22 Graph of sediment ratio against time for alumina suspension at pH 10.5

4.3.2 Zinc Oxide Suspensions

The same procedure of sediment analysis for alumina was repeated for zinc oxide suspensions. Based on the sediment analysis it was found out that pH has insignificance effect on the settling behavior of the suspensions. The particles formed distinguishable sediments at the bottom after 2 minutes for each of pH values as shown in figure 23. Unlike alumina suspensions, an optimum pH at which a good sediment height can be maintained was not found in sediment analysis of zinc oxide suspensions. The suspensions are unstable at different pH values.

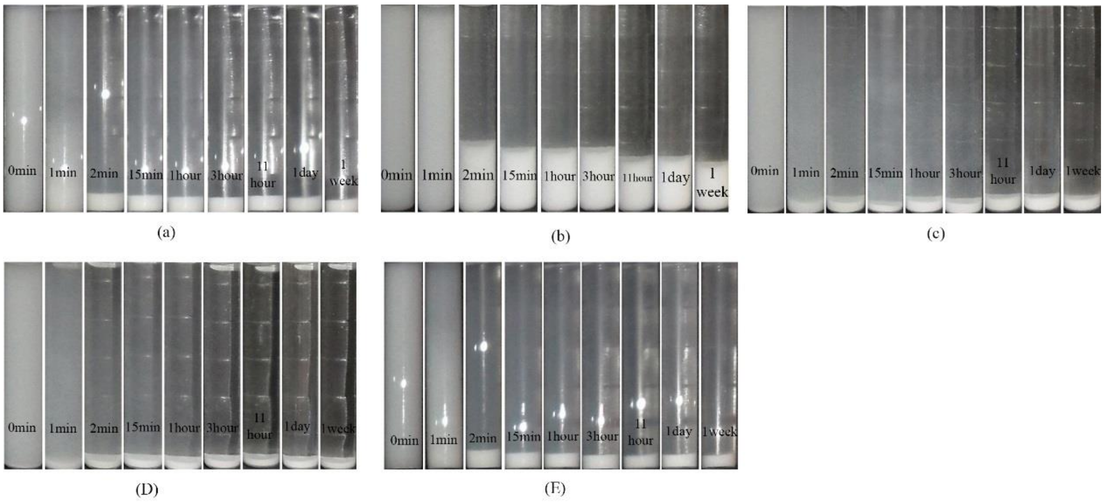


Figure 23: Sediment analysis of zinc oxide in 50 % ethanol at (a) natural pH (b) pH 2.5 (c) pH 4.0 (d) pH 8.5 (e) pH 10.5

4.4 Particle Size Distribution Analysis

To explain the settling behaviors of alumina and zinc oxide in sediment analysis, particle size distribution analysis was carried out. Particle size analysis is a characterization analysis by using particle size analyzer. A stable suspension has small particle size and vice versa. Large particle sizes are caused by agglomeration of particle.

4.4.1 Alumina Suspension

Figure 24 shows the smallest alumina particle size is at pH 2.5 with 600 d.nm. pH 3 gives 840.6 d.nm particle size and at other pH values, the particle sizes are far larger. The small particle size at pH 2.5 is due to minimum agglomeration. High agglomeration of particles result in large particles sized as illustrated at other pH values.

Therefore, pH 2.5 is the optimum pH for alumina suspensions in 50% ethanol concentration. Small size particles result in slow sedimentation compared to large particles. This explain the behavior of the suspension in sediment analysis in which high sediment ration was maintained over one by alumina suspension in 50% ethanol concentration at pH 2.5

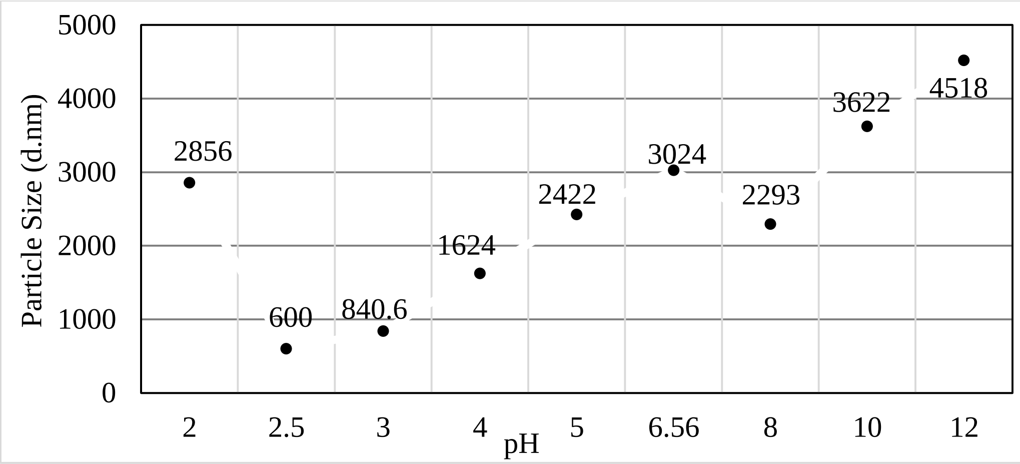


Figure 24: Size of alumina particles at different pH values

Table 3: Data of particle size analyzer for alumina suspension at pH 2.5 aind natural ph

pH	Z-Ave	PdI	Pk 1 Mean Int	Pk 2 Mean Int	Pk 3 Mean Int	Pk 1 Area Int	Pk 2 Area Int	Pk 3 Area Int	Scattering Angle
NS	3024	0.586	848.5	1848	50.63	93.5	4.4	2.1	173
2.5	600	0.156	610.8	0	0	100	0	0	173

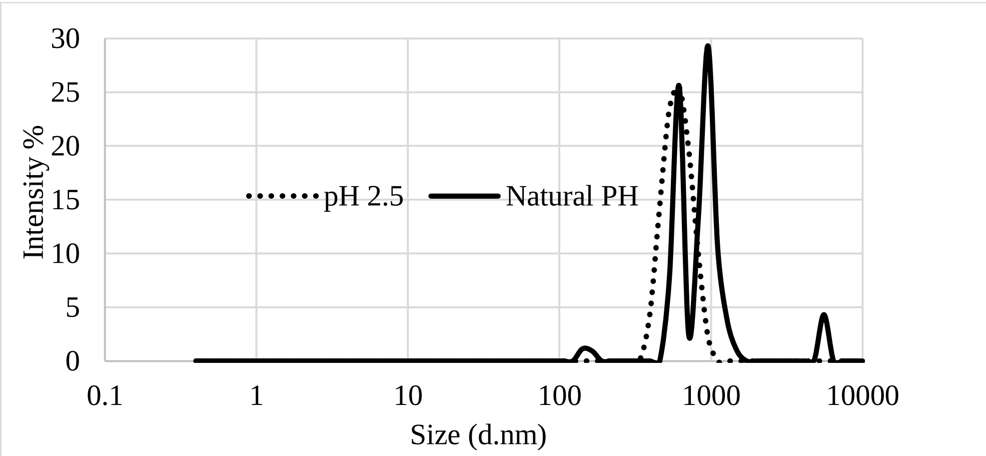


Figure 25: Particle size distribution for alumina suspension at pH 2.5 and natural pH

Table 3 and figure 25 are to compare the size of alumina at natural pH value and at pH 2.5. It show that pH can change the size of alumina suspension from 3024 d.nm in natural condition to 600 d.nm in pH 2.5. The reason for the small size is closely related to the high zeta potential at pH 2.5. High zeta potential result in small particle size due to high electrostatic repulsion force between the particles. The force prevents particles from attract each other to agglomerate and form sediments due to gravity.

In conclusion of particle size distribution for alumina suspension in 50% ethanol concentration, it was found out that pH 2.5 is the optimum pH value. The suspension is most stable at pH 2.5. This result matches with sediment analysis.

4.4.2 Zinc Oxide Suspension

Figure 26, 27 and table 4 show that the particle sizes of zinc oxide suspension in 50% ethanol concentration are large and comparatively the same with each other at different pH values. The particle size is the smallest at natural pH value (7.37). This indicate that the change in pH could not change the particle size to be smaller than that of natural pH condition.

The reason for the big particle sizes are due to high agglomeration. The particles tend to join together to form agglomerates which result in large particle size. Large particles are hard to disperse and form sediments at the bottom due to gravity. Therefore, large particles result in an unstable system.

In conclusion of the particle size analysis for the zinc oxide suspensions, it was found out that pH has no significant effect on the particle size. Therefore, the suspensions would be unstable regardless of pH change. This result confirms the validity of the sediment analysis which found out that zinc oxide suspensions were unstable at the adjusted pH values.

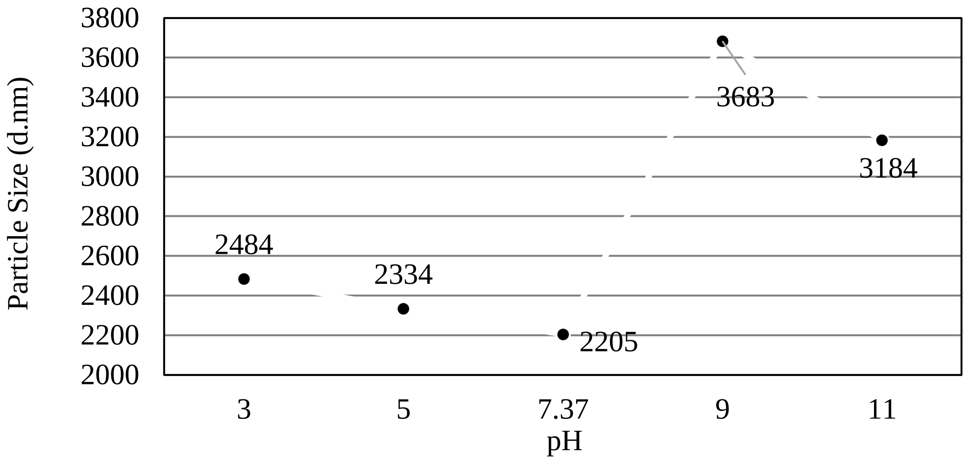


Figure 26: Particle size for zinc oxide suspension at different pH

Table 4: Data of particle size analyzer for zinc oxide suspensions at different pH

pH	Z-Ave	PdI	Pk 1 Mean Int	Pk 2 Mean Int	Pk 3 Mean Int	Pk 1 Area Int	Pk 2 Area Int	Pk 3 Area Int	Scattering Angle
Natural (7.37)	2702	0.276	1505	0	0	100	0	0	173
3.0	2484	0.65	828.4	0	0	100	0	0	173
5.0	2334	1	164.7	0	0	100	0	0	173
9	3184	0.491	2624	1775	0	82.2	17.8	0	173
11	3184	0.491	2624	1775	0	82.2	17.8	0	173

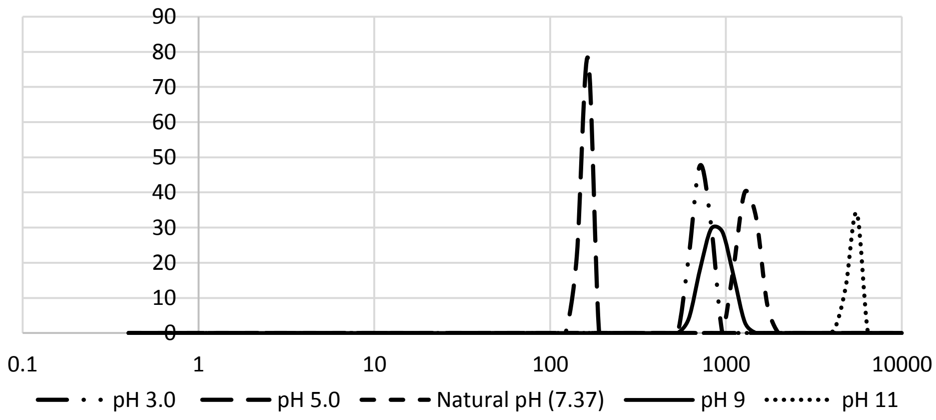


Figure 27: Particle size distribution for zinc oxide suspension at different pH values

4.5 Zeta Potential Analysis

Zeta potential analysis was carried out to explain the settling behavior and particle sizes of alumina and zinc oxide suspensions. The zeta potential values were measured using particle size analyzer on alumina and zinc oxide suspensions in 50% ethanol concentration at different pH values. Zeta potential has a close relationship with the seetling behavior and the particle size of suspensions. Suspension with high zeta potential value would has slow sedimentation and small particle size and therefore would be stable.

4.5.1 Alumina suspensions

Based on the figure 28, the zeta potential for the alumina suspension is the highest at pH 2.5 which indicates the alumina suspension is electrically most stable at pH 2.5. Hence, the electrostatic repulsion force between the particles is sufficient to overcome attraction and collision between particles caused by Brownian motion.

The probability of particle coagulation and settling are reduced as greater electrostatic force provide more free particles by increasing particle-particle distance. Hence, the stability of nanoparticles are improved Therefore, the degree of repulsion between the particles is the highest and less agglomeration is formed which explains the smallest particle size at pH 2.5.

At other pH values, the absolute values of zeta potential are at the minimum. Hence, the electrostatic repulsion force between particles is not sufficient to prevent the attraction force of the particles. Thus, the nanofluids have poor stability.

Figure 29 and 30 show the apparent zeta potential for the alumina suspension at pH 2.5 is far greater than that of natural pH. The maximum highest absolute value at pH 2.5 is 140 mV. The total counts against apparent of zeta potential at pH 2.5 register high zeta potential distribution as compared to that of natural pH. In comparison of the apparent zeta potential, alumina suspension in 50% ethanol is more stable at pH 2.5. This prove that, pH has significant effect on the stability of alumina suspension as the zeta potential can be increased at pH 2.5 to be greater than that of natural pH.

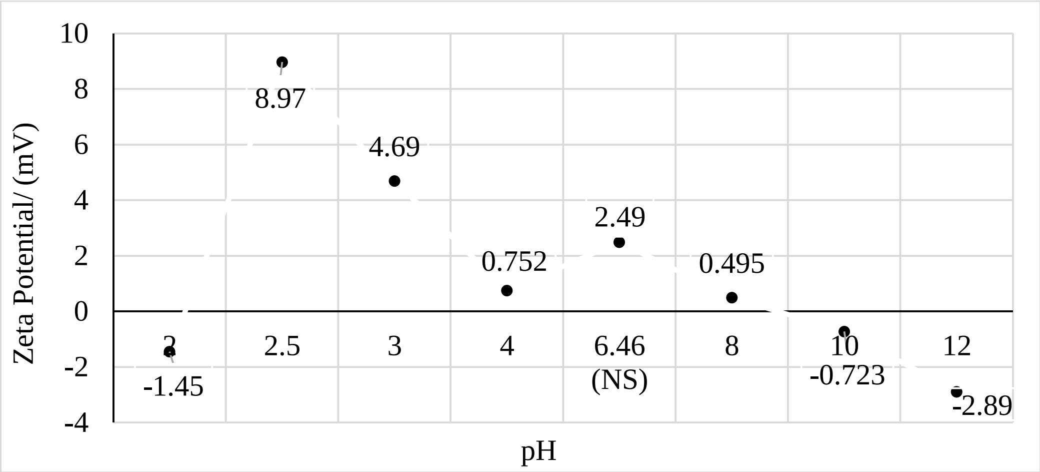


Figure 28: Zeta potential of alumina suspension in 50% ethanol concentration

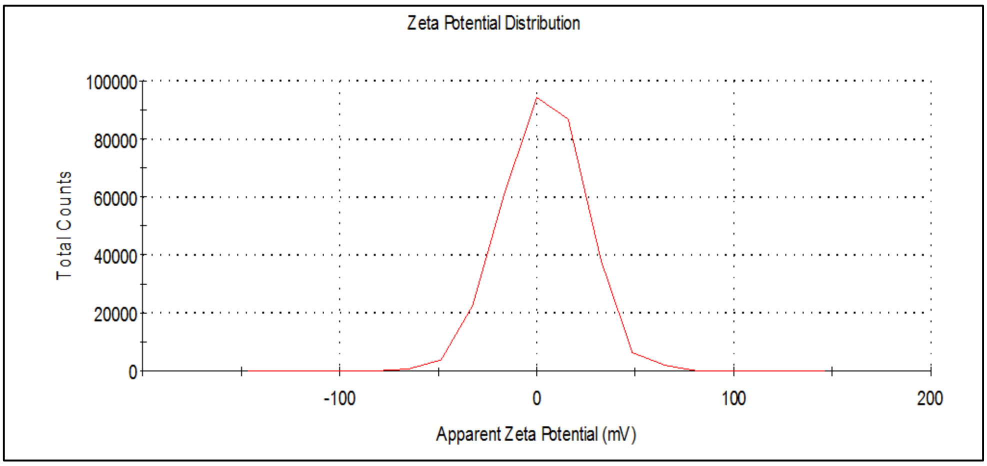


Figure 29: Zeta potential distribution of alumina suspension in 50% ethanol at natural pH

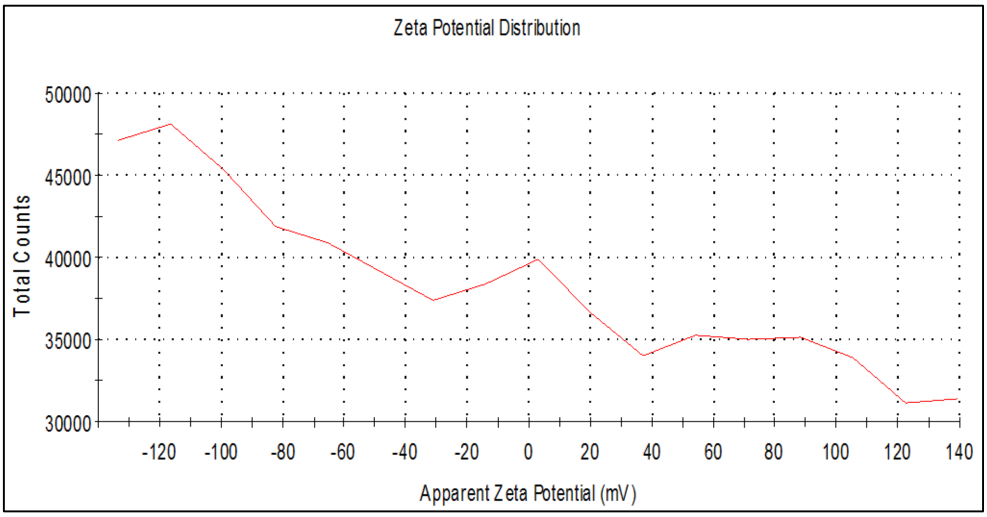


Figure 30: Zeta potential distribution of alumina suspension in 50% ethanol at pH 2.5

4.5.2 Zinc oxide suspensions

Figure 31 below illustrates that the minimum values of zeta potential of zinc oxide suspension in 50% ethanol are comparatively low at different pH. In fact, the zeta potential is the highest at natural pH (7.38). Figure 31 illustrate the zeta potential distributions of the zinc oxide suspensions at different pH values. It shows that the maximum apparent values of zeta potential at each pH values are comparatively the same.

This indicates pH has insignificant effect on the zeta potential of zinc oxide suspensions. Therefore, the degree of repulsion cannot be increased by changing the pH and this explain fast sedimentation of zinc oxide suspensions. The low values of zeta potential cause the particles to attract each other in Brownian motion. The repulsion forces are lower and therefore the particles join each other to form clumps and sediments.

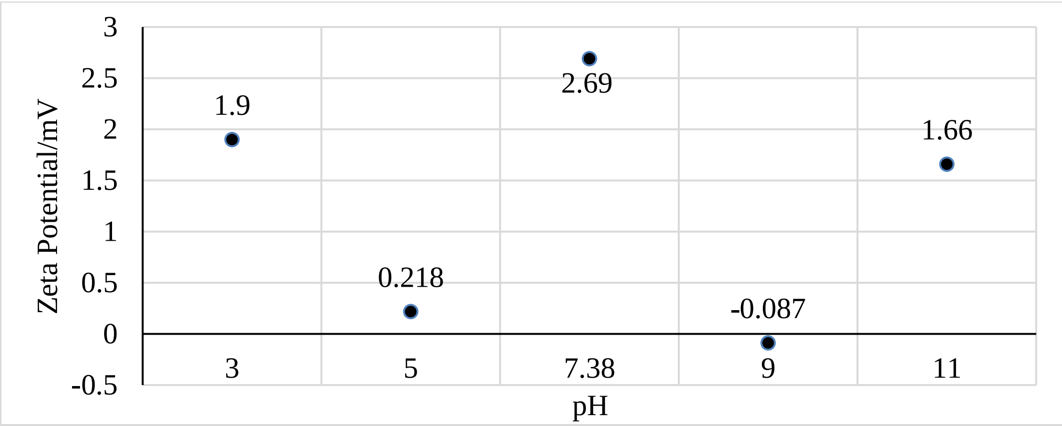


Figure 31: Zeta potential of zinc oxide suspension in 50% ethanol concentration

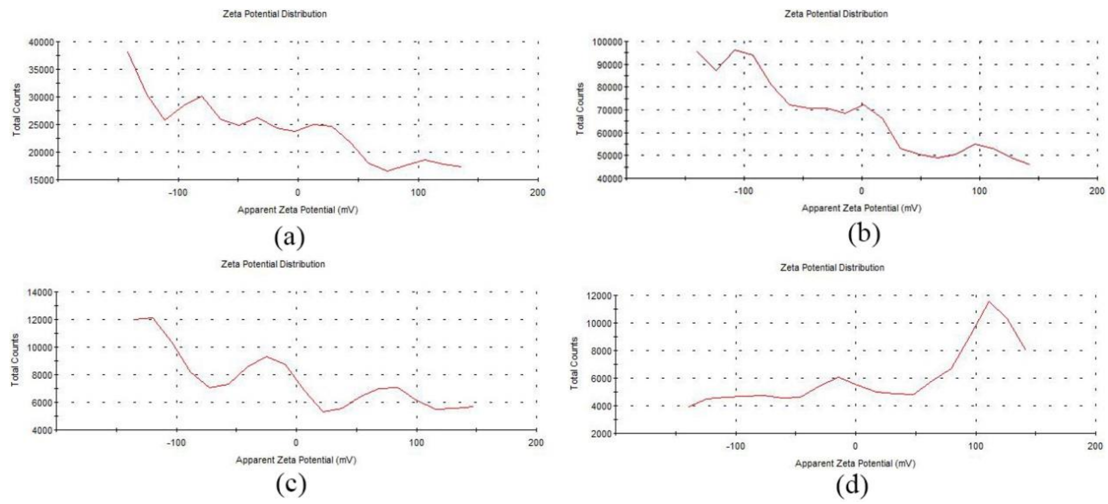
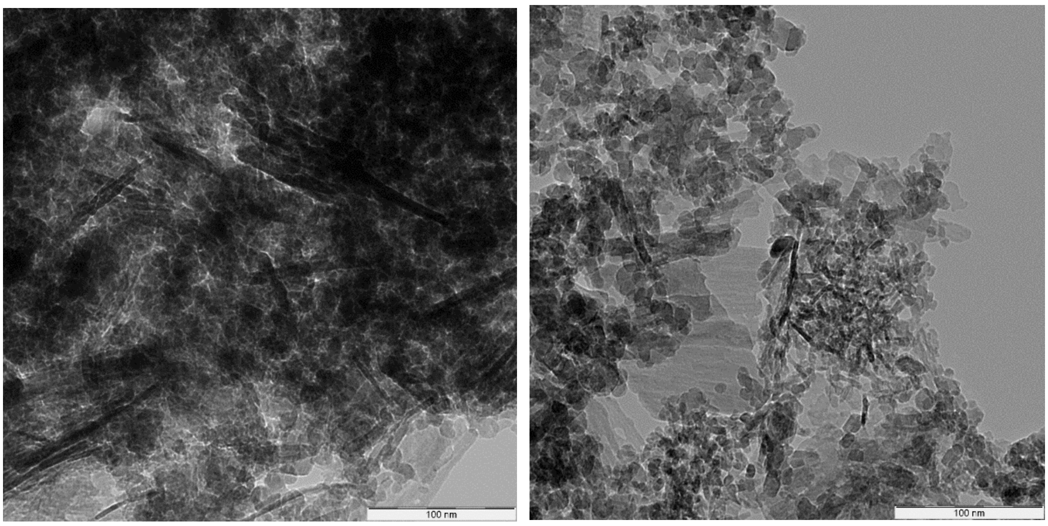


Figure 32: Zeta potential distribution of zinc oxide suspension in 50% ethanol at (a) natural pH (b) pH 3.0 (c) pH 5 (d) pH 9

4.6 Results of Transmission Electron Microscopic (TEM)

TEM analysis was performed to see particle size of alumina at natural pH value and at the optimum pH value, 2.5. Figure 33 shows that the suspension is less agglomerate at pH 2.5 as compared to that of natural pH condition. The reason for the less agglomeration is due to high electrostatic repulsion force between the particles. Less agglomerated suspension is more stable as the particles well-dispersed and undergo slow sedimentation. The TEM results confirm pH 2.5 is the optimal pH for the alumina suspension in 50% ethanol concentration.



(a) *(b)*

Figure 33: Photographs of TEM for alumina suspension at (a) natural pH (b) pH 2.5

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Addition of alumina and zinc oxide particles can change the pH of binary water-ethanol mixture. The surface of zinc oxide is acid-terminated as the pH was shifted to lower values. Same behavior was observed for alumina but not for the suspension in 80% to 100% of ethanol as the pH are shifted to higher values.

Alumina and zinc oxide particles have no side reaction with the base fluid as confirmed via FTIR analysis. The FTIR analysis also confirmed that no side products are formed after adding 1.0M of hydrochloric acid and sodium hydroxide for the pH adjustment.

In this study it was revealed that behaviour of alumina suspensions was effected by pH and the effects varied according to ethanol-water compositions. The optimum pH for alumina suspension in 50% ethanol-water is 2.5 as the particle size is the smallest and the zeta potential is the highest. The agglomeration is lesser at pH 2.5 as compared to that of natural pH. The highest high zeta potential, smallest particle size and less agglomeration at pH 2.5 is due to strong electrostatic repulsion force between the particles.

In this experiment, it is found that pH has no significant effect on zinc oxide suspensions. This was proved by the measurement of zeta potential and particle size. The zeta potential values and particle sizes were comparatively the same at different pH, indicate that pH variation cannot increase the electrostatic repulsion force between the zinc oxide particles. However this claim is subjected to the controlled variable in this experiment. Thus, the controlled variables such as type of sonicator and sonication time should be adjusted for future works to identify the optimum pH for zinc oxide suspension

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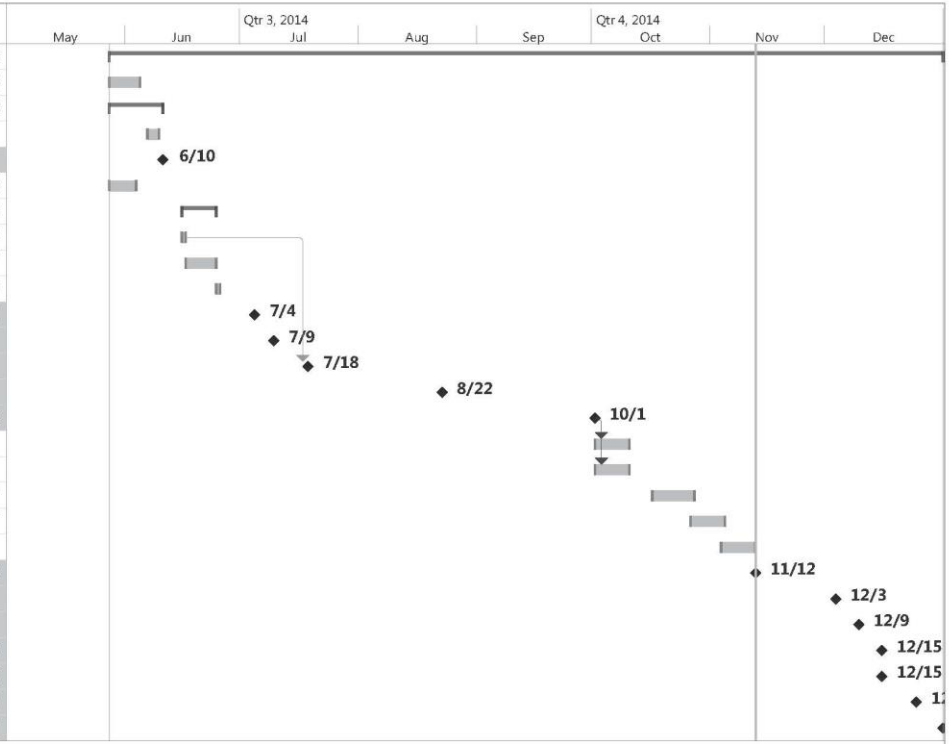
Appendix 1 – Project Gantt Chart

ID	Task Name	Duration	Start
1	**Overall Schedule**	**156 days**	**May 28**
2	Briefing & Kick Off Meeting	6 days	May 28
3	Literature Review	**10 days**	**May 28**
4	Literature Analysis	2 days	Jun 7
5	**Develop Problem Statements From the Literature**	1 day	Jun 10
6	Draft, Update & Finalize Literature Review	5 days	May 28
7	Methodology	**7 days**	**Jun 16**
8	Identify the required chemicals, Instruments and available equipmets	1 day	Jun 16
9	Develop methodology from literature & confirm the validity	6 days	Jun 17
10	E-Resource & End-Note Briefing	1 day	Jun 25
11	**Comletetion and Submmision of Extended Proposal**	**11 days**	**Jun 21**
12	**Proposal Defense Week**	**4 days**	**Jul 5**
13	**Approval for Purchase and Usage of Resources and Services**	**5 days**	**Jul 14**
14	**Interim Report Completion & Submission**	**16 days**	**Aug 1**
15	FTIR Analysis	**7 days**	**Sep 23**
16	Sedimentation Analysis for Alumina Natural Suspension	**7 days**	**Oct 2**
17	Sedimentation Analysis for Alumina Suspension at Different PH	**7 days**	**Oct 2**
18	Sedimentation Analysis for Zinc Oxide Natural Suspension	**7 days**	**Oct 17**
19	Sedimentaton Analysis for Zinc Oxide at Different pH	**7 days**	**Oct 27**
20	ZETA Sizer and TEM Analysis	**7 days**	**Nov 4**
21	Submission of Progress Report	**1 day**	**Nov 12**
22	Pre-EDX	**1 day**	**Dec 3**
23	Submission of Draft Report	**1 day**	**Dec 9**
24	Submission of Dissertation (Softcopy)	**1 day**	**Dec 15**
25	Submission of Technical Report	**1 day**	**Dec 15**
26	Oral Presentation	**3 days**	**Dec 22**
27	Submission of Dissertation (Hardcopy)	**1 day**	**Dec 31**



Milestone