KINETIC AGGREGATION AND SETTLING PROPERTIES OF SILICON DIOXIDE NANOPARTICLES IN CHEMICAL MECHANICAL POLISHING SYNTHETIC WASTEWATER

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SCHOOL OF CIVIL ENGINEERING
UNIVERSITI SAINS MALAYSIA
2022

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By

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This dissertation is submitted to

UNIVERSITI SAINS MALAYSIA

As partial fulfilment of requirement for the degree of

BACHELOR OF ENGINEERING (HONS.)
(CIVIL ENGINEERING)

School of Civil Engineering
Universiti Sains Malaysia

August 2022

Appendix A8

UNIVERSITI SAINS MALAYSIA

SCHOOL OF CIVIL ENGINEERING
ACADEMIC SESSION 2021/2022

FINAL YEAR PROJECT EAA492/6
DISSERTATION ENDORSEMENT FORM

Title: Kinetic Aggregation and Settling Properties of Silicon Dioxide Nanoparticles in Chemical Mechanical Polishing Synthetic Wastewater

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ACKNOWLEDGEMENT

Alhamdulillah, all praise to Allah S.W.T. for HIS blessing and granting a smooth sailing process for this research study to be conducted without major obstacles in the way. With HIS permission, all resources were easily attainable, ideas kept flowing, and the environment of writing this till its completion was eased throughout the entire journey. This final year research study successfully materialized with the invaluable support, guidance, assistance, and aspiration extended by many individuals. For this, I would like to express my sincere thanks to everyone involved.

First and foremost, I would like to dedicate all my hard work and achievements including the completion of my research work to my beloved family for their undivided love and support that has pushed me this far in my studies. To my parents, En. Azman Dahamat and Puan Norkiah Ahmad, thank you, Ayah and Ibu for loving me unconditionally, for all your sacrifices and for always being there for me whenever I needed you. I would not be where I am without your endless encouragement and continuous words of wisdom. I may not be able to return all that you have given me, but you are forever in my precious du'a. May Allah Taala always bestow HIS barakah upon you, grant you the highest place amongst the piety and protect you from all harm in this world and hereafter. To my siblings, thank you for always being my source of inspiration and backing me up when I was down. You will always be the jewels in my heart.

To my respected supervisor, Ts Dr Fatehah Mohd Omar, I would genuinely like to express my deepest appreciation for her dedication, time, and supervision throughout the execution of my final year research. Her confidence in me to carry out this study is of utmost value. Her consistent guidance, expertly advice and motivation not only aided me to perform my experimental work, but imposed a clear vision on the research background, data interpretation, and write-up of my data analysis.

Thank you to my kind and devoted mentor, Puan Noor Aina Mohamad Zuki for her absolute commitment to guiding me in the theoretical and research conduct of this study. At each stage of the research study, she demonstrated in detail the apparatus, methodology, and valuable information I necessarily needed. Her instantaneous inspiration and clear explanation of directions have enabled me to reach this stage with ease.

Not to forget the important people who facilitated my work in the laboratory with great significance. My heartfelt thanks to all the laboratory technicians in Environmental Laboratory 1, Puan Shamsiah Mohamed Ali, En. Muhammad Zaini Mohd Zuki and En. Ahmad Faris Ihsan, for assisting me in obtaining the materials and laboratory apparatus to prepare the samples for research purposes. A big thanks also to the En. Mohammed Nizam Mohd Kamal, the laboratory technician in Environmental Laboratory 2 has helped me analyse all samples in this study.

Finally, a big shout out to all my friends, colleagues, and roommates who made my life at USM a memorable one. Thank you for all the memories and the good times that we have shared. I never felt alone with your endless support, the good spirit in sharing knowledge and being there willing to help me completer my thesis. I wish all of my friends the best and success in their endeavours. Thank you for the grant support.

ABSTRAK

Industri semikonduktor adalah salah satu industri yang paling dipelopori di seluruh dunia kerana permintaan terhadap penegeluaran barangan semikonduktor seperti mikrocip, barangan elektronik, telefon, televisyen, dan sengkatan dengannya terus meningkat dari tahu ke tahun. Fenomena ini akan menyebabkan lebih banyak zarah-zarah halus yang terdapat dalam sisa buangan semikonduktor yang mudah melepasi proses penapisan. Pelepasan zarah-zarah halus ini akan memasuki tadahan air dan mempengaruhi keadaan persekitaran. Oleh itu, pemahaman terhadap ciri-ciri bahan pencemar terutamanya zarah halus dalam air sisa buangan semikonduktor perlu dianggap sebagai langkah pertama yang dilaksanakan sebelum merawat sisa buangan tersebut. Dalam kajian ini, nanozarah silikon dioksida (SiO_2) sintetik bersaiz 0.1mm telah digunakan. Tiga larutan berkepekatan berbeza iaitu 25, 50 dan 100 mg/L telah disediakan bagi tujuan mejalankan analisis terhadap kestabilan pH, potensi zeta dan saiz zarah pada larutan pH yang berbeza. Daripada analisis yang telah dijalankan, ia menujukkan bahawa potensi zeta dan saiz zarah akan berkadar secara langsung dari julat pH 2 hingga pH 12. Larutan SiO_2 berkepekatan 100 mg/L merekodkan potensi zeta yang tertinggi dan menghampiri titik sifar cas iaitu -2.98 mV dengan saiz zarah 277.6 d.nm pada pH 2.47. Kajian diteruskan lagi bagi mejalankan analisis terhadap 100 mg/L SiO_2 dengan larutan tambahan 10^{-3} M NaCl dan 0.15 M NaCl. Kedua-dua larutan NaCl ini digunakan bagi mengkaji ciri-ciri zarah halus SiO_2 di dalam simulasi air sungai dan air laut. Larutan NaCl yang ditambah dicampur dengan larutan SiO_2 mempengaruhi nilai potensi zeta dan saiz zarah SiO_2. Potensi zeta meningkat kepada nilai positif dan meningkatkan saiz zarah iaitu +0.6 mV dengan saiz zarah 766.1 d.nm untuk SiO_2 + 10^{-3} M NaCl, dan +0.037 mV dengan 1198 d.nm untuk SiO_2 + 0.15 M NaCl.

ABSTRACT

The semiconductor industry is one of the most favoured industries around the world as the demands for manufacturing the semiconductor product, microchips, as well as electronic devices such as telephones, television, etc. keep increasing year by year. Due to this scenario, numerous nanoparticles were present in the CMP wastewater that easily suspended and surpass the filtration process. The disposal of nanoparticles can enter the water bodies and affect the environment. Thus, an understanding of the characteristics of pollutants especially nanoparticles in the CMP wastewater needs to be taken as an important part before treating the waste. The synthetic nanopowder silicon dioxide (SiO_2) has been used in this study with the size of 0.1 mm. The SiO_2 NP solution was prepared for different suspensions (25, 50 and 100 mg/L) for the characterization of SiO_2 in terms of stability of pH, zeta potential and z-average hydrodynamic diameter at various pH. From this analysis, I can conclude that the zeta potential and the particle size of SiO_2 are relatively directly proportional to the pH range from pH 2 to pH 12. The SiO_2 suspension of 100 mg/L was found to have a close to the zero-negative charge of -2.98 mV with particle size 277.6 d.nm at pH 2.47. Then it was analysed in function of time to evaluate the stability of the particle at various pH. Next, the experiment was continued to analyse the characteristic behaviour of 100 mg/L of SiO_2 nanoparticles suspension with the presence of 10^{-3} M NaCl and 0.15 M NaCl. These two ionic strengths were used for the simulation of river and seawater to study the behaviour of the nanoparticles when they are being released into the environment. Consequently, the addition of NaCl affects the zeta potential and z-average hydrodynamic diameter of the SiO_2 nanoparticles. The zeta potential increase to positive values as well as increases the particle size of the nanoparticles which is +0.6 mV with 766.1 d.nm for $SiO_2 + 10^{-3}$ M NaCl, and +0.037 mV with 1198 d.nm for SiO_2 + 0.15 M NaCl.

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LIST OF ABBREVIATIONS

SiO_2	Silicon Dioxide
NPs	Nanoparticles
CMP	Chemical Mechanical Polishing
PZC	Point of Zero Charge
DLS	Dynamic Light Scattering
IEP	Isoelectric Point
NaCl	Sodium Chloride

CHAPTER ONE

INTRODUCTION

1.1 Semiconductor Industry

Semiconductors have particular electrical characteristics that supply operations like processing and display, power management, and light-to-electrical energy conversion. Semiconductors are materials with characteristics that fall halfway between those of metals and semiconductors. To create the final result, semiconductor manufacturing procedures use approximately one hundred different solutions and two hundred generic materials (Gilles & Loehr, 1994); Hitachi High-Tech Corporation, 2022).

The semiconductor industry creates and produces semiconductors, which are tiny electrical devices made of silicon, germanium, or gallium arsenide. Smaller, quicker, and cheaper products are essential for success in the industry of semiconductor. The smaller the chip is more beneficial as more power can be crammed onto one piece of chip. The greater the number of transistors on a piece of chip, the faster the performance and better its functionality (Semiconductor, 2022). Semiconductor manufacturing involves many complex and delicate processes, including silicon growth, oxidation, doping, photolithography, etching, stripping, dicing, metallization, planarization, cleaning, etc (Lin & Yang, 2004a).

Industries that make semiconductor integrated circuits employ high-tech processes such as wafer back grinding, die attachment, wire bonding, sawing, electroplating, trimming, shaping, encapsulating, and labelling in sequential order. Ultrapure water (UPW) is used extensively during the assembly of semiconductors, and the wastewater produced is also significant. Up to 40% of UPW is utilised in companies' typical semiconductor processes, mostly for cleaning and washing purposes (Teow et al., 2022).

Manufactures utilise about 200 organic and inorganic compounds as well as enormous volumes of water to create semiconductor chips. As a by-product, the wastewater generated from semiconductor manufacturing often holds a wide range of pollutants such as acids, alkalis, metals for example copper, lead, arsenic and antimony, ammonium, and nano oxide particles and other organic and inorganic chemicals. As every wastewater has its characteristics for its industry and application, thus for each wastewater treatment system must be matched and suitable for the application (Semiconductor Manufacturing: Achieving Water Authority Compliance – News, 2020). Aoudj and Khelifa (2017) stated that the effluent of the semiconductor industry that treating single stage is frequently inadequate. However, creating a procedure to decrease the level of pollutants in complex wastewater efficiently and cost-effectively is a challenging task to be done. This might be accomplished by selecting appropriate approaches and a strategy that will improve the overall performance of the treatment system.

1.2 Problem Statement

The high need for water cleanliness necessitates the use of enormous volumes of ultrapure water in the washing of silicon wafers during the manufacturing process. Because of the massive amounts of water required and the treatment of the wastewater from the semiconductor industry has become one of the primary issues (Omar et al., 2007). Thus, to comply with national and international environmental standards, the wastewater generated from CMP processes in the nanoelectronics industry must be handled appropriately (Zuki et al., 2019). However, it is needed to get know first the characteristics of the behaviour of the contaminants that presence in the waste generated to ensure the treatment applied is efficiently removes the pollutants. There is various treatment that has been analysed and published by researchers to treat the waste that is suitable for its constituents.

The nanoscale colloids in the chemical mechanical polishing (CMP) wastewater have a strong tendency to float and thus resulting in the high value of turbidity as well as chemical oxygen demand (COD). Regardless of the treatment procedures used, these nanoparticles will remain scattered in tiny clusters as they transit during the treatment process. These nanoparticles are easily suspended and unsettled, and thus will easily pass through the filtration process even after the advanced treatment. They have the potential to enter the municipal waste and water bodies. The disposal of these nanoparticles in the water bodies might affect the ecosystem as well as human health. Thus, observation is done to study the mechanism of aggregation and settling behaviour of the particles in terms of zeta potential and particle size.

1.3 Objectives

The objectives of this research study are:

1. To evaluate the characteristics and behaviour of silicon dioxide nanoparticles based on the kinetic aggregation and settling properties in synthetic suspension.
2. To investigate the kinetic aggregation behaviour of silicon dioxide nanoparticles in a systematic manner based on the ionic strengths.

1.4 Scope of the study

In this study, the synthetic wastewater of SiO_2 suspension was used as the sample to conduct the laboratory work analysis. Synthetic SiO_2 nanoparticles were used instead of the actual CMP wastewater in order to conduct the analysis in a controlled environment, which only analysed the SiO_2 nanoparticles and a single type of ionic strength. So, in this controlled environment, the analysis was limited only to 60 minutes to observe the aggregation rate. Within this duration, we will see how long the nanoparticles will remain aggregated and at which point they will start to disintegrate or be dispersed. A monovalent solution of NaCl was used as it is a common monovalent salt in the environment. The purpose of doing the simulation on the river and marine is to understand the behaviour of the SiO_2 nanoparticles when they are being released into the environment either river or seawater.

1.5 Significance of the study

This study evaluates the aggregation and settling behaviour of the SiO_2 nanoparticles that are present in the CMP wastewater that is disposed from the semiconductor industry to get a better understanding of the mechanism and behaviour of the nanoparticles when it is released into the environment. As there is growing demand for the semiconductor products such as electronic devices, thus it will increase the amount of waste produced by the semiconductor industry. An efficient treatment method needs to adopt to treat the wastewater before being discharged into the water bodies. Understanding the behaviour of the nanoparticles is needed to see in what condition the nanoparticles will efficiently be removed from the CMP wastewater. From this study, the behaviour of the SiO_2 nanoparticles in the simulation of river and marine were observed. This study is expected to provide insight and information regarding the mechanism of nanoparticles in the environment.

1.6 Thesis outline

This research study contains five chapters. Chapter 1 explain the introduction to this study that includes the background of the study, problem statements, objectives, scope of study and the significance of the study.

Chapter 2 provides the relevant literature review from the previous study on the semiconductor industry, waste generated from the semiconductor manufacturing process which is SiO_2 nanoparticles that are present in the CMP wastewater and the polluting issues. Moreover, this chapter also reviews the aggregation and settling behaviour of the silica nanoparticles. In addition, the zeta potential and particle size were also discussed as these two parameters will be analysed in this study.

Chapter 3 explains and describes the methodology of this research. This chapter also includes the laboratory equipment and materials as well as the experimental procedures that were conducted for this study.

Chapter 4 represents the results and discussion of the research study. The finding from the conducted experiments were discussed in this chapter. The charge of particles and size of the particles obtained from the experimental lab represents in the figure graphs and are being discussed for their aggregation and settling behaviour.

Last but not least is Chapter 5 which summarize and concludes the research of the study. This chapter highlights the significant findings of the study. The recommendations are also included in this chapter for future research exploration that correlated to the results of this study.

CHAPTER TWO

LITERATURE REVIEW

In many nations throughout the world during the past few decades, the electronic industry has seen rapid economic growth. It is anticipated that this industry will continue to develop quickly in the near future. In reality, the electronic industry comprises the production of a variety of products, one of which is a semiconductor. Semiconductors are used in a variety of products including computers and their compartments, communication tools, electronic control systems, and test equipment for research purposes and medicine. The numerous uses have made semiconductors one of the most important electrical items. The semiconductor industry has been expanding quickly at a double-digit rate recently due to the rising demand for this product (Lin & Yang, 2004b).

Silica is the chosen slurry for many CMP applications. As a result, chemistry plays a significant role in eliminating silica particles from various surfaces. In order to remove these silica particles, there are various techniques have been developed that can be applied. Surfactants one of the methods have been discovered to be highly beneficial in changing or altering the character of particles such that they can be readily removed from surfaces. To remove the particles during the process of semiconductor cleaning, an appropriate surfactant is added to the formulation (Yerriboina et al., 2022).

2.1 Chemical Mechanical Polishing (CMP) Wastewater

2.2.2 Characteristics of CMP Wastewater

The chemical mechanical polishing (CMP) technique is a common planarization technology used in the fabrication of microchips for producing integrated circuits (IC) and it was the first used to create ultra-smooth surfaces for the precision of optical instrument lenses (Hu et al., 2005; Zhao et al., 2020). In addition, this sector of semiconductors has grown into one of the most significant industries in Malaysia and elsewhere. According to the Malaysian Investment Development Authority's (MIDA) 20212 Investment Report, the semiconductor industry has become one of the top eight innovative and developing various technologies in the manufacturing industry. Recently, with the advancement of IC technology, particularly after entering the sub-micron process, the minimization of main dimensions, and the realisation of the high-density devices, the process of flatness and smoothness between the IC material layers is becoming increasingly crucial. The washing and cleaning stage in the process of CMP uses up to 40% of ultrapure water that is used in the manufacturing of semiconductors and consequently generates a significant amount of effluent. Nanosized or also called nanoparticle SiO_2, dissolved silicon, surfactants, oxidising agents, and heavy metals ion are the primary pollutants in CMP wastewater (Hu et al., 2005; Zhao et al., 2020). Table 2.1 represents the characteristics of the CMP wastewater (Kuan & Hu, 2009).

Table 2. 1 Characteristics of CMP wastewater (Kuan & Hu, 2009).

pH	8.54
Turbidity (NTU)	315.5
Conductivity (μs/cm)	247
Total solid (g/L)	3.836
Total Si (mg/L)	1580
Zeta potential (mV)	-41.6
Specific surface area of solids (m^2/g)	63
Minimum particle size (nm)	42

Chemical Mechanical Polishing (CMP) process is an important method in manufacturing semiconductors due to its ability to achieve and obtain local as well as global planarization in the fabrication of highly integrated devices. In another word, the CMP technology is the planarization of a surface in which a wafer is spun against a polishing pad while applying pressure in the presence of a silica-based alkaline slurry (Rahul et al., 1994). In the CMP process, there are two methods involved at the same time which are chemical reaction and mechanical polishing (Lee et al., 2016).

CMP removes materials by combining mechanical forces with chemical processes. Although CMP employs particles that might result in fatal flaws like a scratch, it has the longest planarization duration compared to other planarization techniques, making it crucial for device production. The fundamental working principle of the CMP procedure is the mechanical removal of the surface of the chemically softened material. A schematic of the CMP processes and material removal mechanism is shown in Figure 1.2. The polishing pad is connected to the platen, and the wafer is linked to the bottom carrier. The polishing pad is supplied with a slurry that contains abrasive particles and chemicals. The wafer is pressed onto the pad's surface by the polishing head. The slurry penetrates the interface between the wafer and polishing pad as a result of the counterclockwise rotation of both components. A diamond disk is used for pad conditioning in order to regulate and clean the pad surface (Lee et al., 2022).

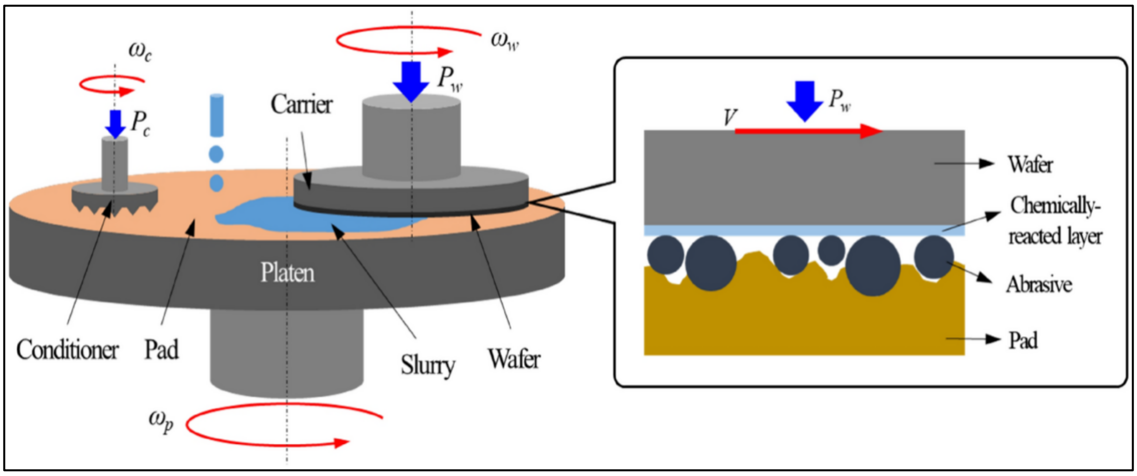

Figure 2. 1 Overview of CMP process (Lee et al., 2022).

2.1.2 Pollutants content in CMP Wastewater

The semiconductor sector generates a large amount of wastewater. If these wastewaters are released into the environment without being treated, they may be dangerous. Additionally, they contain recyclable and recoverable silicon residues (Teow et al., 2022). For typical CMP, a spinning wafer is pressed against a revolving polishing pad with the presence of the slurry which is in the aqueous solution of colloidal abrasive particles with varying chemical characteristics according to the application. The slurry has abrasive particles and is associated with chemical additives and the polishing of pads and machines are the three main factors involved in the CMP process (Zhao et al., 2020; Qin et al., 2004). According to Lin & Jiang (2003), the production of semiconductors has involved many complicated and complex processes such as the growth of silicon, oxidation process, planarization and polishing, cleaning and so on. In reality, the manufacturing industry makes up approximately 200 high purities of organic and inorganic substances either proprietary or generic. Furthermore, an enormous amount of ultrapure water is used in different washing and cleaning phases of semiconductor manufacturing. As a result, many forms of effluent are produced such as solvents, acids, bases, salts, fine oxide particles and other constituents matters that are found in the wastewater of semiconductors that are difficult to be treated (Lin & Yang, 2004b).

Presently, the manufacturing of semiconductors employs a variety of harmful chemicals as well as enormous amounts of water, resulting in highly toxic effluent. This industry needs a considerable amount of deionized water. Recycling process water is discouraged since it must be extremely clean, thus resulting in a large volume of wastewater (Gad, 2014). Semiconductors are made using a very complex process that involves depositing numerous layers on silicon wafers, patterning the layers with photolithography, and adding dopants to the conductivity. As a result of the process, poisonous organics, pH variations, fluoride, and arsenic are among the many varied and harmful components that are produced as gaseous, liquid, and solid waste streams (Vagliasindi and Poulsom, 1994).

The effluent or wastewater from semiconductors is very turbid, alkaline, and contains a high concentration of the total solids. It is also characterized by its strong black colour, high turbidity, high chemical oxygen demand (COD), low biodegradability and the presence of various solvents, acids, bases, fine oxide particles, as well as organic and inorganic pollutants, which will increase the concentration of bacteria and microorganism in the wastewater (Omar et al., 2013; Chou et al., 2010). The slurry produced by CMP is the primary source of inorganic and organic pollutants that are present in CMP wastewater. Depending on the nature of the CMP application, the inorganic impurities may involve suspended, nanoparticle solids formed by the abrasive slurry particles of SiO_2, Al_2O_3, or CeO_2. The quantity of oxygen utilised in the chemical oxidation of inorganic and organic materials in the wastewater is measured as COD (Chou et al., 2010).

2.1.3 Treatments Applied by Manufactures

Chemical coagulation/flocculation, electrocoagulation/flotation, and membrane filtration are all feasible treatment techniques that can be used to treat the wastewater CMP process. To increase settling and fulfil discharge limits, the treatment of wastewater often uses high doses of coagulants to expand and enlarge the nanoscale particles 100-fold during the chemical coagulation/flocculation process. This technique not only raises the expense of chemical consumption but also generates a considerable volume of sludge. On the other hand, the efficiency of electrocoagulation/flotation process treatment can be reduced as a result of electrode passivation and the addition of surfactants to the aqueous solutions. Hence, in order to overcome this matter, the membrane separation method has been used to treat the effluent of CMP by utilising either a single unit or a post separator (Juang et al., 2008).

2.2 Silicon Dioxide (SiO_2) Nanoparticles

2.2.1 Characteristics of SiO_2 Nanoparticles

Nanoparticles have several industrial, biotechnological, and biomedical or pharmaceutical uses due to their characteristics in structure, size, biocompatibility, large surface area and adaptable functionalization, which has resulted in their widespread use in a variety of fields. Although science and technology have altered our lifestyle and health care from medical to agriculture, there also have some adverse consequences and negative impacts of this innovation in contrast to the advantages. Nanotechnology has been one of the steppingstones responsible for this transformation, which has helped to mitigate some of the negative consequences. Among the different forms of nanoparticles, silica nanoparticles (SiO_2 NPs) have gained popularity for nanostructuring, drug delivery, and optical imaging agents as the Si NPs are stable and less toxic (Jeelani et al., 2019).

Mesoporous silica materials with pore diameters ranging between 2 to 50 nm have caught the interest of researchers due to their highly attractive physiochemical features, tuneable macroscopic shape, chemical activity, and mesoporous structure. In addition, they are particularly important for usage in a variety of sectors including adsorption, catalyst, and medicine. For example, silica also has been used for environmental pollution remediation, such as increased oil recovery to limit the liberation of brine, heavy metals, and radioactive chemicals into the water, removal of metal and non-metals, radioactive elements, and water purification (Jeelani et al., 2019; Kankala et al., 2020).

2.2.2 Effect of SiO_2 Nanoparticles on Health

Silica is non-toxic when it is used orally. Despite their inherent stable siliceous frameworks, outstanding mechanical strength and ideal morphological properties, pure mesoporous Si NPs have low drug loading efficiency, as well as compatibility and degradability concerns for therapeutic, diagnostic, and tissue engineering reasons. In 2008, a study was conducted that discovered that the higher the quantities of silica in water, the lower the chances of dementia. As the risk of dementia reduced, the amount of silica in the drinking water was raised to 10 mg/day. However, inhaling the finely split crystalline silica dust can lead to bronchitis, lung cancer, or silicosis due to the dust trapped in the lungs and constantly irritating the tissue and thus decreasing the lung capacity. Fine silica particles breathed insufficient numbers increase the incidence of rheumatoid arthritis and lupus (Admin, 2019; Kankala et al., 2020). Reijnders (2006) clarified in his study that the risk of nanoparticles is still limited compared to their plentiful applications. Indeed, Moore (2006) states the extremely huge surface area of the microscopic particles might result in the direct creation of damaging oxyradicals, which can cause cell damage. Theoretically, considerations show that the particles will be more poisonous if the particles have a smaller average diameter. This is because the particles with a larger specific surface area tend to have more bioactivity and bioavailability, as well as the capacity to generate reactive radicals (Yang et al., 2014).

2.2.3 Challenges while Handling SiO_2 Nanoparticles

Because of their inexpensive cost for production and surface modification, silica nanoparticles are widely adopted. However, controlling the stability of nanoparticle dispersion is critical in reservoirs with high salinity and temperatures. The transportation of nanoparticles to specific zones in the reservoir is critical to attaining the aim of increased recovery. As a result, transport parameters such as nanoparticle mobility and dispersion rheology are critical. These characteristics are affected by a variety of factor, including the size of particles and concentration (Metin et al., 2014). In an ionic solution, nanoparticles with a net charge will have a layer of ions with opposing charges tightly bonded to their surface, which is known as the Stern layer. A second diffuse outer layer is made up of ions that are only weakly connected. These two layers are referred to as the electrical double layer. As the particle travels owing to Brownian diffusion or applied force, the separation between ions in the diffuse layer that moves with the nanoparticles and ions that remain with the bulk dispersant is formed. The zeta potential is the electrostatic potential at this "slipping plane" border, and it is connected to the surface charge of the nanoparticles (Clogston and Patri, 2010).

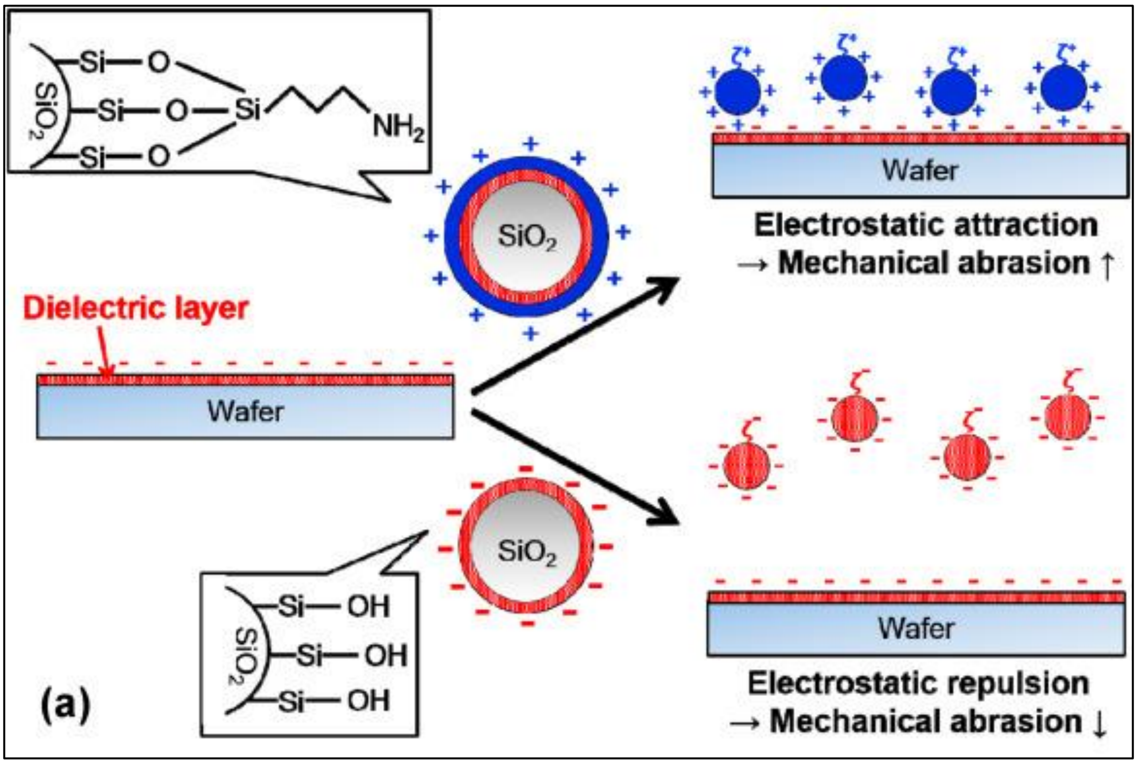

Figure 2. 2 The charge on the surface of colloidal silica with and without (3-Aminopropyl) triethoxtsilane (Hong et al., 2021).

Hong et al., (2021) said due to the same chemical structures, such as the Si-O-H and Si-OH moieties, the surfaces of both colloidal silica nanoparticles and the silica oxide dielectric layer were negatively charged. As a result, the adsorption of colloidal silica nanoparticles on the surface of the wafer dielectric layer was inhibited by the electrostatic repulsion induced by the same negative charge between the dielectric layer and colloidal silica nanoparticles. As illustrated in Figure 2.1, the electrostatic attraction between both the dielectric layer and colloidal silica nanoparticles was caused by the positively charged state of the colloidal silica surfaces after being treated with an amino silane. Therefore, for surface treatment, the material removal rate of the dielectric layer increased due to the amino-functionalized moieties on the surface of colloidal silica nanoparticles. Due to the better compatibility of colloidal silica with the dielectric layer, the insertion of amino moieties into colloidal silica surfaces will increase the material removal rate of the dielectric layer for the same concentration of colloidal silica nanoparticles. For the material removal rate augmentation, it is crucial to customize the surface charge of abrasives and patterned wafers.

2.3 Zeta Potential and Particle Size

The electrical potential created at the solid-liquid interface as a result of the relative mobility of solid particles and liquid is referred to as the zeta potential. According to reports, pH levels should be kept away from the iso-electric point (IEP) in order to create stable nanofluids. At this stage, the zero-potential is discovered at a precise pH value where particle attraction is maximised. Changing the pH or coagulant concentration will change the electrical charge density on the surface of the nanoparticles, promoting repulsive interactions between them (Cacua et al., 2019). Suspensions or dispersions of droplets in a liquid condition are encountered in many industries and used in a wide range of applications. To be functional, a suspension must be capable of suspending the dispersed phase for the duration of the product's lifetime and/or be quickly dispersed if sedimentation occurs. A variety of variables, both thermodynamic and kinetic, contribute to scattered phase stability. Steric and electrostatic stabilisation is an example of the former, which induce stability by particle repulsion, whereas kinetic stability may be produced by increasing the viscosity of the suspending medium, which slows particle aggregation and sedimentation (Larsson et al., 2012).

According to Larsson (2012), it is essential to establish some sort of barrier to prevent particles from aggregating and it can be accomplished by steric or electrostatic ways, such as adsorbing polymers or imparting a charge onto the surface of particles by altering the pH value. As illustrated in Figure 2.2, the Derhaguin-Landau-Verwey-

Overbeek (DLVO) theory attempt to explain such a force balance for an electrically charged suspension, where the combined or total energy (VT) is the sum of attractive (VA) and repulsive (VR) contributions. According to this hypothesis, an energy barrier caused by repulsive force prohibits two particles from approaching and sticking together unless the particles have enough thermal energy to overcome the barrier. The amplitude of zeta potential, which is the potential at the sliding plane between the particle and associated double layer with the surrounding solvent, might reflect the size of this potential barrier.

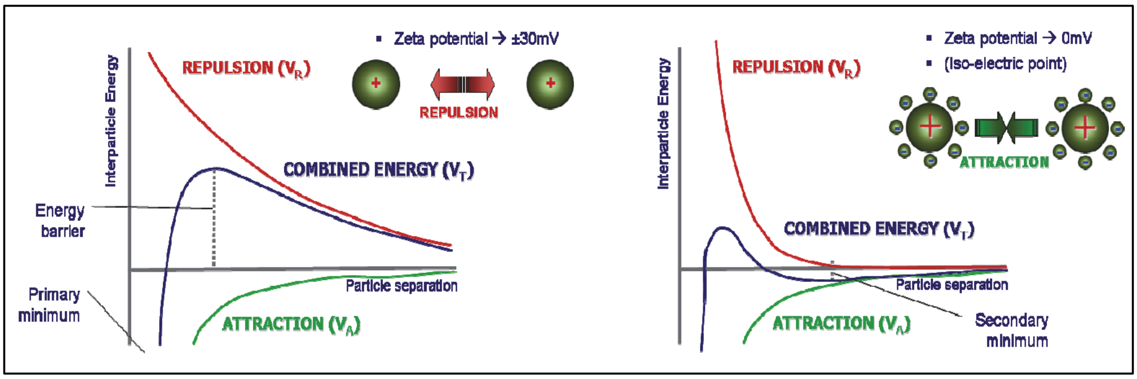

Figure 2. 3 Schematic diagram of variation free energy with particle separation for a suspension with (a) high zeta potential and (b) low zeta potential (Larsson et al., 2012).

From another study, it is stated that the stability and particle surface morphology of a colloidal system are two significant aspects that are highly controlled by the particle surface charge. Hence, zeta potential is used to measure the surface of the particles. Although zeta potential has been used in numerous colloidal systems, its theoretical underpinning and applicability in non-aqueous suspension, particularly in the absence of an extra electrolyte, remain highly restricted (Xu et al., 2006). As stated before, zeta potential will measure the charge on the surface of the particle. The zeta potential of dispersion is influenced by variations of pH, salt, and surfactant content. The IEP is a condition where the pH value at which the zeta potential will be zero, meaning that there is no electric charge on the surface of the particle. IEP of dispersion can assist forecast stability or instability and identify the main chemical species on the surface of an engineered particle (Isoelectric Point (IEP), 2022).

2.4 Kinetic Aggregation of Nanoparticles

2.4.1 Fractal Geometry

The particles in nanosuspensions move in a Brownian motion and move closer to the random particles in their surroundings. When the particles bind together due to their strong attraction forces, a cluster formation known as aggregation develops (Ilyas et al., 2014). Fractal dimension, stability ratio theories, and population balance are models that are commonly used to predict the aggregation kinetics of colloidal particles. The essential parameter that must be determined in these approaches is the aggregation rate. The absolute rates of rapid and slow aggregation regimes can be estimated experimentally using turbidity or size measurements, or numerically using the stability ratio technique (Metin et al., 2014).

The fractal dimension is determined by the rate of aggregation. For example, the lower the aggregation rate, the more time particle have time to arrange themselves into a more compact and dense structure, and the higher the fractal dimension. As a result, the term fractal dimension is adopted to characterize the structure of aggregates either dendritic or compact. Under controlled laboratory conditions, homo-aggregation produces aggregates with predictable fractal dimensions, whereas hetero-aggregation typically produces natural fractals (statistically self-similar over a limited range of length scales, making the aggregation state more difficult to describe and predict. The comparison of monodisperse, dendritic, and compact aggregated NPs clusters is shown in the figure below. The reactive surface area, reactivity, bioavailability, and toxicity can all be influenced by the physical dimensions and density of aggregates generated. When analysing data on density, transport, and toxicity, it is necessary to determine and analyse the structure of aggregates (Zhang, 2014a).

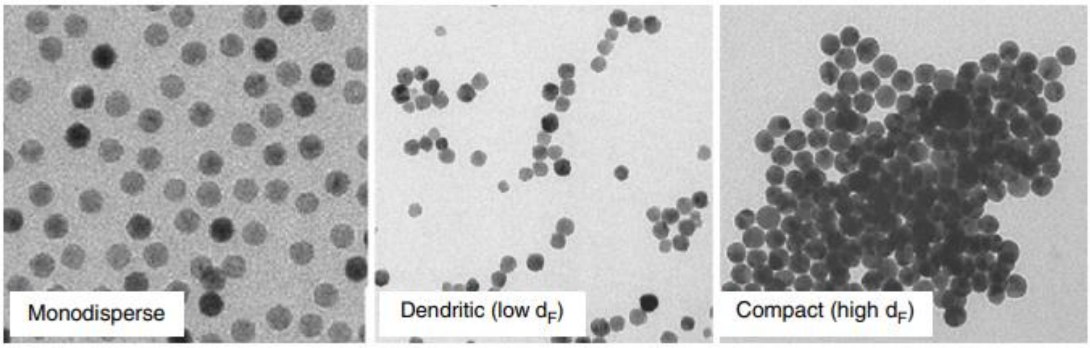

Figure 2. 4 Different aggregation states (Zhang, 2014b).

2.4.2 Fractal Growth of Aggregates

Zhang (2014) also stated that the formation and growth of clusters of nanoparticles (NPs) in aqueous dispersions are influenced by both interfacial chemical processes and particle transport mechanisms. Many toxicological tests have found it challenging to keep genuine nano-sized materials in the media, since NPs in the aqueous phase can aggregate slowly or quickly depending on solution chemistries and particle properties. NPs can aggregate into clusters as large as several microns in size, removing them from the nanometer range. The ability of NPs to aggregate in aquatic environments affects their mobility, fate, and other environmental interactions. Colloidal particle aggregation occurs when physical processes bring particle surfaces in contact with one another, and short-range thermodynamic interactions allow particle-particle attachment. The aggregation processes mostly are fractal where the mass of fractal aggregate, m(R) is proportional to the hydrodynamic radius, a_h, to a power d_F, the fractal dimension.

Colloid science is described as a field of chemistry concerned with colloids, where a heterogeneous systems is composed of a mechanical combination of dispersant and dispersion. In a continuous medium, the particles have a size range between 1 nm and 1 μm when being distributed. Particles size larger than this begins to settle out of suspension. The colloidal particles will aggregate when physical processes bring the surface of the particle in contact with one another, and short-range thermodynamic interaction will allow the particle-particle attachment to occur. Brownian diffusion will govern the long-range forces between individual nanoparticles for the particles with a size lower than 100 nm, thus resulting in the collision of particles (Hotze et al., 2010).

Metin et al., (2014) state that the SiO_2 nanoparticles will form fractal aggregates due to the collapse of the electrical double layer at high salt concentration and reducing the stabilizing repulsive force as a result. At concentrations higher than the critical salt concentration (CSC), the influence of NaCl concentration on the kinetic aggregation of silica nanoparticles is shown in Figure 2.4. The results showed an S-shaped curve on a semi-logarithmic time scale. The maximal effective diameter of the aggregate and the rate of silica nanoparticles aggregation both are grows as the concentration of NaCl rises.

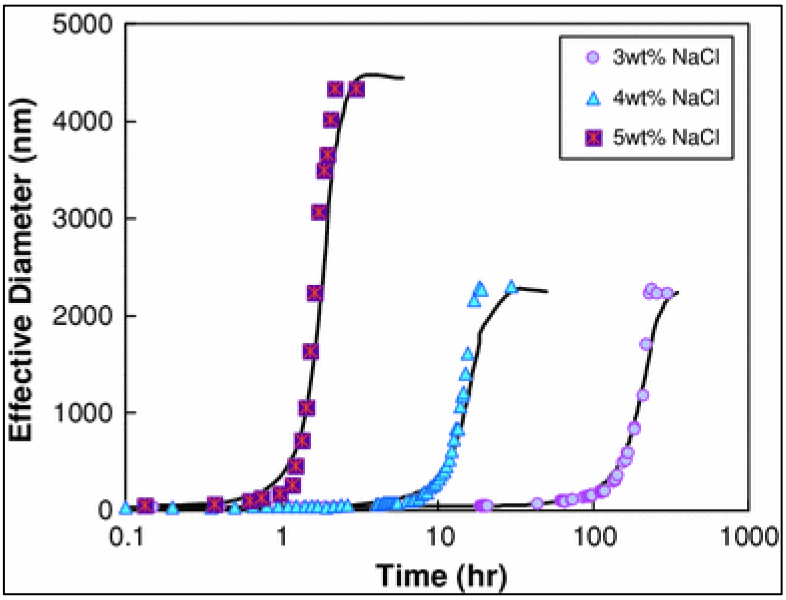

Figure 2. 5 Effect of NaCl concentration on the rate of aggregation expressed as measured by DLS (Metin et al., 2014).

The influence of NaCl on this aggregation behaviour could be explained by examining the interaction potential between two charged spherical nanoparticles as defined by

DLVO theory (Derjaguin and Landau 1941; Verwey and Overbeck 1948). The repulsive energy, which is a function of electrical double layer thickness, κ^{-1}, (m), decreases as the electrolyte concentration increases. As a result, the total interaction energy varies as a function of electrolyte concentration (Metin et al., 2014).

2.5 Settling Properties of Nanoparticles

2.5.1 Settling Suspension

A settling suspension of solid-liquid is a heterogenous combination of solid particles in a liquid, and it is a type of multiphase flow. When discussing solid-liquid settling suspensions, different particles size ranging from micro to millimeters with varying densities might be considered. Settling suspension is when a suspension that contains medium or coarser material whose density is greater than the liquid, will tend to settle and gather at the bottom of a vessel or any container (Silva et al., 2015).

Due to their remarkable magnetic, optical, thermal, and transport capabilities, nanoparticles have captured the attention of several scientific groups. One of these is thermal conductivity, which has undergone substantial research and discussion over the past 20 years (Liyanage et al., 2016). Nanotechnology advancements have resulted in the development of nanosized silica, SiO_2, which is commonly employed as filler in engineering composites. Metal contaminants in silica particles derived from natural resources make them unsuitable for sophisticated scientific and industrial uses. Thus, attention is focused on synthetic silica (colloidal silica, silica gels, pyrogenic silica, and precipitated silica), which is pure and mostly generated in amorphous powder forms as opposed to natural mineral silica (quartz, tridymite, and cristobalite), which is in crystalline forms (Rahman & Padavettan, 2012).

2.5.2 Factors Influencing Settling Suspension

Multiple factors influence the particle's terminal settling velocity in a fluid body, including fluid density and particle density, particle size and shape, concentration, degree of turbulence, and temperature of the solution. The Stokes law settling was first formulated for tiny, mm or µm of spherical size particles with low Reynold Numbers. There are two components for the drag force of a creeping flow over the rigid sphere which pressure drag $\left(F_p = \pi\mu dU\right)$ and the shear stress drag $(F = 2\pi\mu dU)$. A nanoparticle, on the other hand, will almost never meet the Stokes criteria due to its greater surface area-to-volume ratio. Surface forces trump gravitational forces in these instances. Furthermore, the intermolecular forces (Van der Waal's, iron-iron contacts, interactions of dipole-dipole, dispersion forces, and overlap repulsion), thermal vibrations (Brownian motion), and diffusivity will replace the Newtonian forces for a nanoparticle distributed in a liquid. As a result, the gravitational force will no longer dominate the settling velocity (Liyanage et al., 2016).

The main reason nanofluids are unstable is that nanoparticles settle down due to gravity, which is made worse by agglomeration. The proportion of Van der Waals forces due to the other forces is higher for nanoparticles than for microparticles. Van der Waals forces get weaker as the distance between two particles gets bigger. When particles stick together, the overall effective thermal conductivity of nanosuspensions goes down, which can lead to clogging (Ilyas et al., 2014).

2.6 Summary of Literature Review

In general, the waste produced by the semiconductor industry is increasing year by year as the demand for semiconductor products are keep rising. Semiconductor products have been widely used over the world in producing electronic devices such as television, telephones, computers, and others, as well as in producing microchips that are made of silicon, germanium, or gallium arsenide. The process of this producing semiconductors by CMP process led to a large amount of CMP wastewater. The wastewater produced must undergo a treatment process before being discharged into the environment. Although various treatment has been applied to treat the semiconductor wastewater, there are still problems that need to be faced as the nanoparticles are present in the CMP wastewater due to the slurry used. The nanoparticles are difficult to handle as there are very small in size and able to surpass the filtration process. Efficient treatment is needed depending on the characteristics of the waste disposal. Different characteristics of the waste will have different conditions of treatment that need to be considered. There is still a lack of information regarding the behaviour of nanoparticles in different conditions. Thus, this study was conducted to understand the behaviour of the nanoparticles in various pH and ionic strengths. CMP wastewater containing silica nanoparticles that are not fully treated might be entered into the environment such as rivers and the ocean. Thus, monovalent NaCl solution was used as the ionic strength which is 10^{-3} M and 0.15 M NaCl for the simulation of river water and seawater, respectively to see the behaviour of the silica nanoparticles when they were being released into the environment.

CHAPTER 3

METHODOLOGY

For this study, laboratory works were conducted in order to evaluate the characteristics of SiO_2 based on aggregation and disaggregation of the particles in terms of pH, zeta potential and z-average hydrodynamic diameter. pH will be monitored throughout the experiments to evaluate the behaviour of the SiO_2 NP for various pH to determine its charge and size of particles. Xu et al., 2005 clarified from their research that at pH below 4 ($pH < 4$), the zeta potential was in the vicinity of zero, while around pH 2 to pH 3 it reached the isoelectric point. The isoelectric point is the point on the surface of silica particles having the same positive and negative charges generated by the silanol groups. At this stage, the silanol group with the Si-OH structures are stable. While, based on Liu et al., 2019, have proved that silica nanoparticles with pH below 4 will become slightly positively charged, and in the alkaline state the silica tends to have highly negative charges.

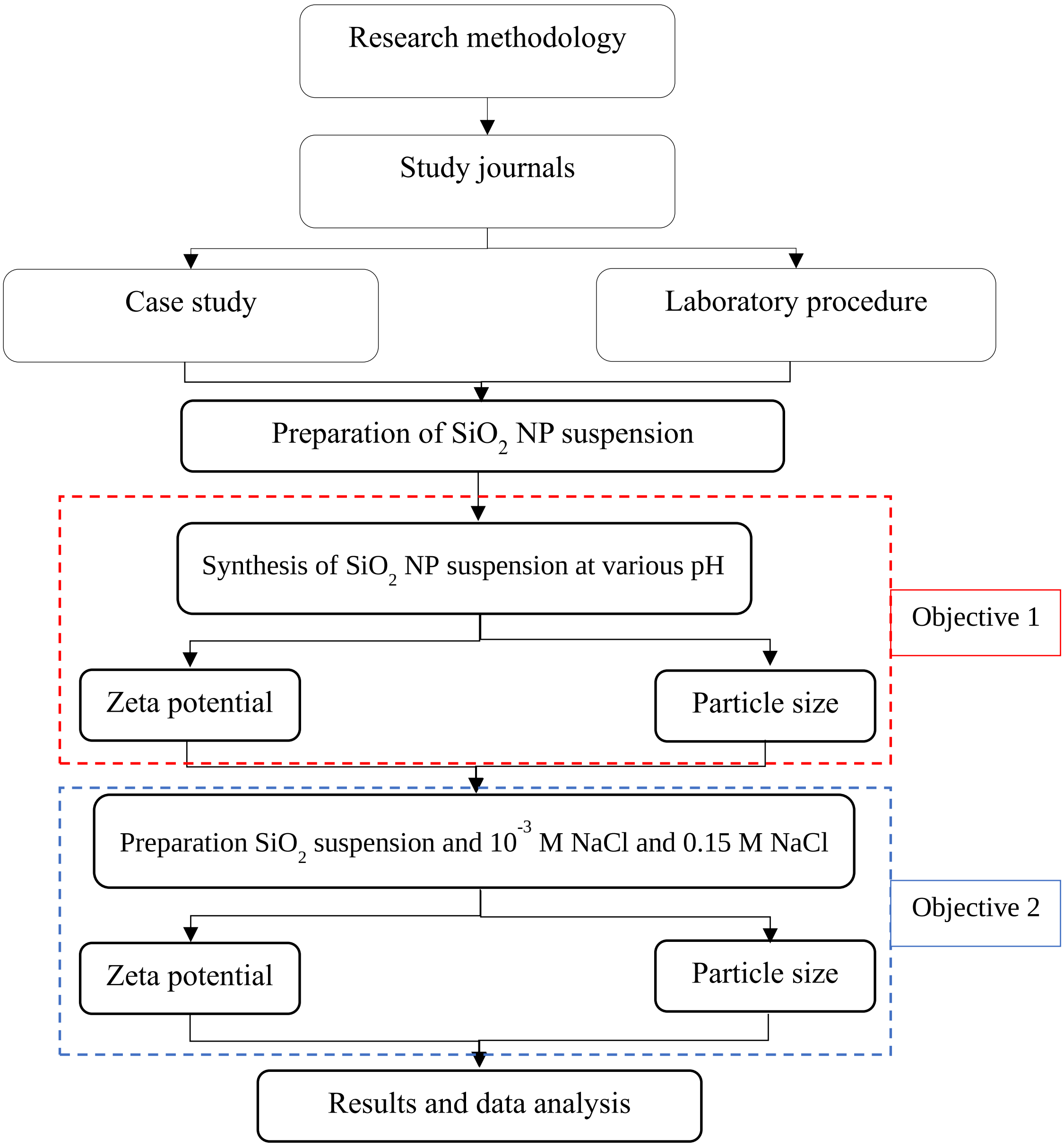

Figure 3. 1 Flow chart of methodology.

3.1 Preparation of SiO_2 Nanoparticles Suspensions

SiO_2 nanopowder with 99.0% purity and a nominal size of 0.1 mm was used in this work and was purchased from R & M Chemicals (Refer Appendix A). The stock suspension of SiO_2 (25, 50 and 100 mg/L) was prepared freshly before each experiment by directly adding the weighed of SiO_2 nanopowder into deionized water in the 100 mL of volumetric flask and was then dispersed by ultrasonication using an ultrasonicator for a minute. The solution was continued mixed with a magnetic stirrer for about 20 – 30 minutes to ensure the solution mixed well. In order to define the SiO_2 pH characteristics, the suspension was adjusted to various pH values in a range between pH 2 and 11 using diluted analytical grades 0.025 M NaOH and 0.025 M HCl. The pH was monitored with a pH meter (Mettler-Toledo, Switzerland) and the initial pH of the stock solutions were 6.19 (25mg/L), 6.48 (50 mg/L) and 5.75 (100 mg/L). Dynamic light scattering (DLS) measurements were conducted to analyse both the zeta potential and z-average hydrodynamic diameter with a Zetasizer Nano ZS (Malvern, UK) at 25℃.

3.2 Synthesis of SiO_2 in various pH

100 mg/L of SiO_2 solution was prepared before the experiment and was undergo ultrasonication for 1 minute. The solution was then continued being stirred for about 20 to 30 minutes to ensure the solution was mixed well and getting a homogeneous solution. The pH was monitored with a pH meter probe (Mettler-Toledo, Switzerland) and its initial pH was recorded at pH 5.34. The solution was then extracted every 10 minutes until the time reached 60 minutes (0, 10, 20, 30, 40, 50 and 60 minutes) to analyse the zeta potential and particle size of the SiO_2 nanoparticles in the sample. Noted also on pH of the solution for every extraction of the solution for the analysis of pH stabilization. The test was repeated for the various pH from pH 2 to pH 11. All the results were then tabulated and illustrated in the graph figure for the analysis.

3.3 Dynamic Light Scattering

The size of nanoparticles was measured using the Dynamic Light Scattering (DLS) method, and the zeta potential of SiO_2 nanoparticles was computed using the Smoluchowski equation at 25℃ using Zetasizer Nano ZS. The basic idea behind this art technology is to analyse the Brownian motion of the nanoparticles in the aqueous solutions. When an electrical field (E) is provided to the zeta capillary cell, the electrophoretic mobility of the sample is immediately measured. The sample's suspended charged nanoparticles are drawn to the electrode with the opposite charge. The velocity