AGGREGATION AND SEDIMENTATION OF ELECTROSTERICALLY STABILIZED IRON OXIDE NANOPARTICLE

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by

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LIST OF SYMBOL

	Symbol	Unit
U_E	Electrophoretic Mobility	mV
ξ	Zeta Potential	mV
ε	Dielectric Constant	-
ŋ	Viscosity	mPa.s
κ	Debye Length	-
Br	Remanent Magnetic Flux Density	T

LIST OF ABBREVIATIONS

CCC	Critical Concentration Coagulation
DLS	Dynamic Light Scattering
DLVO	Derjaguin-Landau-Verwey-Overbeak
Fg	Gravitational Force
HCl	Hydrochloric Acid
MIOPs	Magnetic Iron Oxide Nanoparticles
Fmag	Magnetophoresis Force
NdFeb	Neodymium Iron Boron
PSS	Poly(Sodium(4)Styrenesulfonate)
PZC	Point Of Zero Charge
Rpm	Rotation Per Minute

PENGAGREGATAN DAN PEMENDAPAN KESTABILAN ELECTROSTERIK ZARAH-ZARAH NANO IRON OKSIDA

ABSTRAK

Magnetik zarah-zarah nano iron oksida (MZIO) dan magnetik zarah-zarah nano iron oksida bersalut Poly(sodium(4)styrenesulfonate) (PSS) telah disediakan untuk mengkaji mengenai kestabilan koloid dan kinetik pemendapan zarah- zarah nano. MZIO bersalut PSS lebih stabil daripada MZIO yang tidak bersalut kerana tolakan elektrosterik antara zarah-zarah yang menahan daripada pengagregatan dan pemendapan berlaku. Potensi Zeta untuk MZIO bersalut PSS ialah -34.03 mV. Nilai potensi Zeta yang besar daripada 30 mV menunjukkan sampel mempunyai kestabilan koloid yang bagus. Lima kepekatan yang berbeza (10 ppm – 500 ppm) MZIO yang bersalut PSS dan tidak bersalut telah disediakan. MZIO yang tidak bersalut lebih pantas agregat dan mendap berbanding MZIO yang bersalut PSS. Pengagregatan dan pemendapan berlaku dengan lebih cepat apabila sumber magnet luar digunakan terhadap sampel kerana mengalami daya magnetophoresis. Kepekatan yang paling tinggi iaitu 500 ppm yang pertama selesai kerana MZIO yang lebih pekat mempunyai kekerapan pelanggaran yang lebih tinggi dan menyebabkan ia agregat dan mendap lebih cepat. Daya graviti bergantung kepada saiz zarah-zarah dan agregat di mana saiz yang besar lebih responsif terhadap magnet. MZIO yang bersalut PSS hanya mempunyai sedikit mendapan di bawah sampel.Saiz hidrodinamik sampel diukur menggunakan penyerakan cahaya dinamik (PCD). Dari ukuran PCD, MZIO bersalut PSS mempunyai saiz hidrodinamik lebih kecil daripada MIOP yag tidak bersalut untuk semua kepekatan. Saiz hidrodinamik MZIO bersalut PSS hampir sama manakala saiz hidrodinamik MZIO yang tidak bersalut berubah-ubah sepanjang masa pengukuran untuk semua kepekatan disebabkan oleh pembentukan agregat besar dan agregat kecil.

AGGREGATION AND SEDIMENTATION OF ELECTROSTERICALY STABILIZED IRON OXIDE NANOPARTICLE

ABSTRACT

The bare magnetic iron oxide nanoparticles (MIOPs) and Poly(sodium(4)styrenesulfonate) PSS-coated-MIOPs are prepared in order to study the colloidal stability and the sedimentation kinetic of the nanoparticles. The PSS-coated-MIOPs are more stable than the bare MIOPs due to electrosteric repulsion between particles that resist the aggregation and sedimentation. The zeta potential of MIOPs after coated with PSS is -34.03 mV. The value of zeta potential larger than 30 mV indicates that the samples have good colloidal stability. The bare MIOPs and PSS-coated-MIOPs are diluted into five different concentrations (10 ppm - 500 ppm). The bare MIOPs are aggregated and sediment faster than PSS-coated-MIOPs. The aggregation and sedimentation is enhanced when the external magnetic source exerted on bare MIOPs and PSS-coated-MIOPs because it experienced magnetophoresis force. The highest concentration of bare MIOPs which is 500 ppm settle first because more concentrated MIOPs have higher collision frequency thus it aggregated and sediment faster. The gravitational force is depends on the size of particles and the large aggregates more responsive towards the magnet. The PSS-coated-MIOPs only has little sediment at the bottom of the sample. The hydrodynamic sizes of samples are measured using dynamic light scattering (DLS). From DLS measurement, PSS-coated-MIOPs have smaller hydrodynamic size than bare MIOPs for all range of concentrations. The hydrodynamic size of PSS-coated-MIOPs is almost constant whereas the hydrodynamic size of bare MIOPs is fluctuated throughout the measurement time for all range of concentration due to formation of large aggregates and small aggregates.

CHAPTER ONE : INTRODUCTION

1.1.1 Research Background

Magnetic nanoparticles (MNP) are consisting of magnetic elements (such as iron, cobalt, nickel and their compounds). The magnetic nanoparticles have been used in many applications such as in biomedical application, industrial application and environmental application. However, magnetic nanoparticles are widely used in environmental application for removal of contaminants in wastewater.

Among all the magnetic nanoparticles that have been introduced, the most popular are nanoscale zero-valent iron (nZVI), magnetic iron oxide nanoparticles (MIOPs) Fe_3O_4 and γ-Fe_2O_3. Among them, MIOPs and also known as magnetite (Fe_3O_4), which is a ferromagnetic black color iron oxide of both Fe (II) and Fe (III), have received great interest for the researchers in their studies of treatment of polluted water due to its effectiveness. Due to the presence of the Fe^{2+}state, MIOPs is the preferred type that has the potential of acting as an electron donor (Mohammed et al., 2017).

The MIOPs are extremely small particle size and high surface area to volume ratio that causes the MIOPs have large removal capacity, fast kinetics and high reactivity for removal of contaminants in wastewater. The most important property of MIOPs is their magnetism that is very useful in the waste water treatment system (Tang and Lo, 2013).

1.2 Problem Statement

MIOPs have gained significant attention due to its uses in many applications especially in wastewater treatment plant. This is because of its ability to rapidly reduced contaminants in the water. However, MIOPs are rapidly aggregate due to van der Waals attraction and magnetic dipole-dipole attraction between particles that result in the settling of particles. Therefore, the surface of MIOPs must be modified in order to reduce the aggregation and sedimentation of the particles.

The surface of MIOPs are modified by coated it with the polyelectrolyte where the polyelectrolyte modified MIOPs are electrosterically stabilized. It has the ability to resist aggregation and sedimentation of particles. In this study, poly(sodium(4)styrenesulfonate)
PSS 70K is used as the polyelectrolyte to coat the MIOPs.

1.3 Objectives

The main objectives of this study are:

i. To study the effect of electrosteric stabilization on the hydrodynamic size and sedimentation kinetic of coated iron oxide nanoparticles
ii. To compare the colloidal stability and sedimentation kinetic of iron oxide nanoparticles between bare iron oxide nanoparticles and coated iron oxide nanoparticles

1.4 Scope of study

In this work, the magnetic iron oxide nanoparticles powder was utilized to prepare bare MIOPs and PSS-coated-MIOPs. The preparation of bare MIOPs and PSS-coated-MIOPs were done by physical method where both the samples were sonicated to ensure the suspension had good dispersity. For PSS-coated-MIOPs were rotated end over end for 24 hours using tube rotator to allow polymer to adsorb then the samples were washed to remove the free polymer from solution.

The sedimentation and aggregation kinetics were observed for bare MIOPs and PSS-coated-MIOPs under the presence and absence of external magnetic field. The sedimentation and aggregation also were analyzed by measuring the hydrodynamic size (diameter) by DLS for both MIOPs and PSS-coated-MIOPs. It was being observed over a certain time range. The magnetophoretic force and gravitational force for both samples were compared.

1.5 Organization of thesis

The following are the contents for each chapter in this study:

Chapter 1 introduces the magnetic nanoparticles, problem statement, research objectives and organization of thesis.

Chapter 2 discuss the literature review of this study which includes the application of MIOPs, the colloidal stability, DLVO and extended DLVO theory, factor affecting the colloidal stability and aggregation and sedimentation.

Chapter 3 covers the materials and details of methodology. It discusses on the description of equipment and materials used and experimental procedure.

Chapter 4 refers to the experimental results and discussions of the data obtained. Further elaboration on the sedimentation and aggregation kinetics and the hydrodynamic size measurements of bare MIOPs and PSS-coated-MIOPs under the conditions with magnetic field and without magnetic field are provided in this chapter.

Chapter 5 concludes all the findings obtained in this study. Recommendations are also included as well.

CHAPTER TWO : LITERATURE REVIEW

2.1 Magnetic Nanoparticles

MNPs are commonly composed of magnetic elements such as iron, nickel, cobalt and their oxides like magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), hematite (α-Fe_2O_3), cobalt ferrite (Fe_2CoO_4), chromium di-oxide (CrO_2). Magnetic Iron Oxide Nanoparticles (MIOPs) have got great interest among the researchers in their studies due to it uses in many applications such as in biomedical application, industrial application and environmental application. (Teja and Koh, 2009, Indira and Lakshmi, 2010).

2.1.1 Application of MIOP

In environmental application, the MIOPs act as an environmental remediation agent especially in wastewater treatment plant. The role of MIOPs in water treatment is as adsorbents that applied external magnetic field in order to separate and remove the contaminants in water (Carlos et al., 2013). The MIOPs have an ability to rapidly dechlorinate chlorinated organic to less harmful substances and immobilize heavy metals found in the contaminated groundwater. As adsorbents, the MIOPs also can remove arsenic from water (Hong et al., 2009). Figure 2.1 has shown the various applications of iron nanoparticle for in site groundwater remediation.

Besides that, the MIOPs have been widely used as photocatalyts where it used to degrade and reduce the toxicity of organic pollutants in order to enhanced photocatalysis effect. Photocatalysis is an advanced technology in photodegradation of organic pollutants. The catalytic properties of MIOPs for photocatalysis can cause safe and effective wastewater treatment nanotechnology is introduced (Xu et al., 2012).

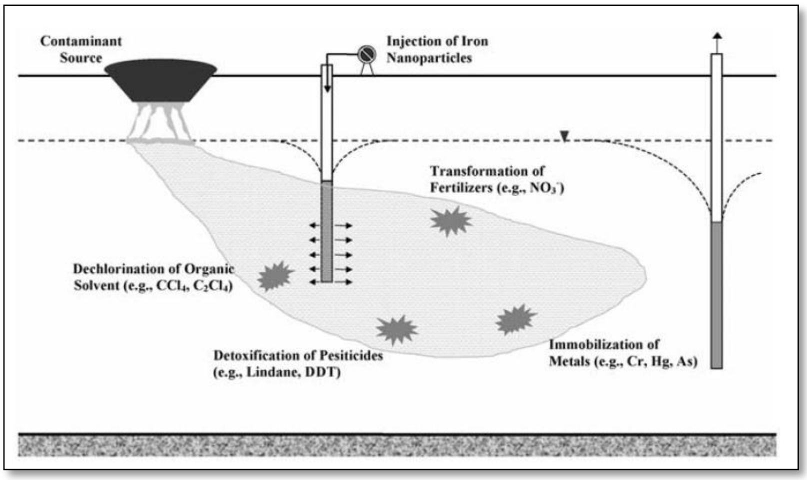


Figure 2.1 : Magnetic Iron Oxide Nanoparticles for in situ remediation (Zhang, 2003)

2.2 Colloidal Stability

Colloidal stability is defined as the ability of colloid dispersion to avoid aggregation for a specified time. If the particles have sufficiently high repulsion, the dispersion will resist aggregation and the colloidal system will be stable. But if there are no repulsion, then the particle will aggregate and sediment as shown in the Figure 2.2. The colloidal stability requires an energy barrier in the interparticle interaction potential (Phenrat et al., 2007).

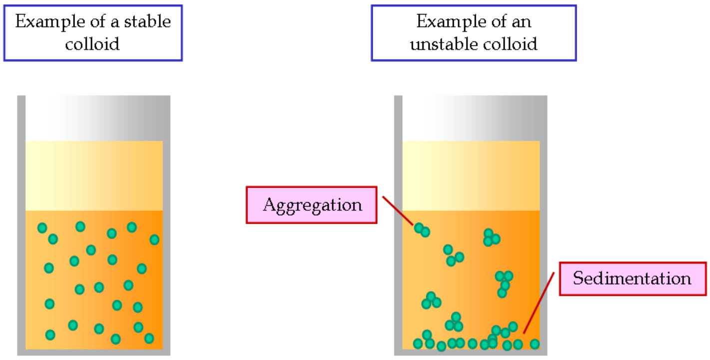


Figure 2.2 : Colloid Stability

The DLVO (Derjaguin-Landau-Verwey-Overbeak) theory is theory that explained on the stability of colloidal system that consists of charged particle (Ohshima, 2012). The extended DLVO theory is introduced due to nanoparticle coatings.

2.2.1 DLVO Theory of Colloid Stability

According to DLVO (Derjaguin-Landau-Verwey-Overbeak) theory of aggregation, the net interaction energy between particles is sum of the van der Waals attraction (V_A) and electrostatic double layer repulsive (V_R). This energy exists as the particles approach to each other due to the Brownian motion as shown in Figure 2.3.

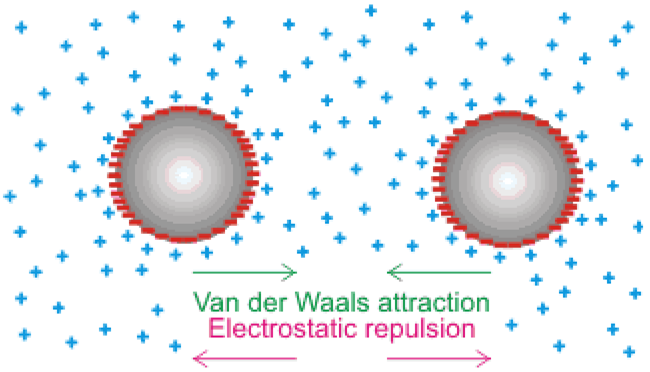


Figure 2.3 : Schematic Diagram with the Forces on the Particles

The van der Waals attraction (V_A) depends on chemical nature and size of particles while the electrostatic double layer repulsion (V_R) depends on density, surface charge and thickness of double layer. From DLVO theory, the repulsive forces results the energy barrier that prevent the two particles approaching one another and attaching together. The attractive force will attach the particles together when the particles collide with sufficient energy to overcome the energy barrier. If the particles have high repulsive forces, the particles will resist the aggregation and sedimentation. Therefore, the colloidal system will be stable. However, if there is low repulsive forces between particles, the particles tend to aggregate and sediment.

2.2.2 Extended DLVO Theory of Colloid Stability

The extended DLVO theory is used to explain the influence of polyelectrolyte on the surface of MIOPs. The extended DLVO theory includes both magnetic attraction and steric repulsions in addition to the usual van der Waals and electrostatic double layer forces where the magnetic properties have an important role in the stability and the transport of magnetic nanoparticles. (Hong et al., 2009, Phenrat et al., 2008). The magnetic attraction is existed among MIOPs due to the intrinsic permanent magnetic dipole moment (Yeap et al., 2012). As the distance between the particles decrease the magnetic dipole-dipole attraction become stronger (Ghosh et al., 2011).

There are three type stabilization mechanisms of particles, which are electrostatic stabilization, steric stabilization and electrosteric stabilization. The electrostatic stabilization occur when the particle interact due to the distribution of charge species in the system where it create an electrical double layer around the particle. The strong repulsion is occurred when two particles with the extended double layers approached to each other and double layer start to overlap. This will overcome the van der Waals attraction. The steric stabilization involved the polymer where the polymer is added to the system that adsorbed onto the particle surface that prevents the particle surface attracted to each other. If enough polymers are adsorbed, the adsorbed layer thickness is sufficient to keep particles separated by steric repulsion between the polymers layers (Ohshima, 2012). Figure 2.4 showed the electrostatic and steric stabilization of particles.

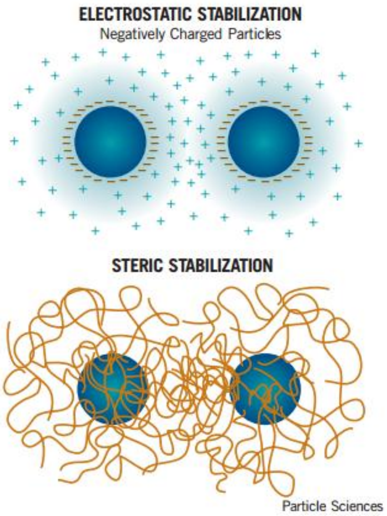


Figure 2.4 : Electrostatic and Steric Stabilization (ENERGY, 2009)

The electrosteric stabilization is the combination of steric stabilization and electrostatic stabilization where it is created by polyelectrolyte that coated to the particle. Between a pair of particles, there is steric repulsion that consists two additional terms which are osmotic repulsion (V_{osm}) and elastic steric repulsion (V_{elas}) as shown in Figure 2.5 (Phenrat et al., 2008, Fritz et al., 2002).

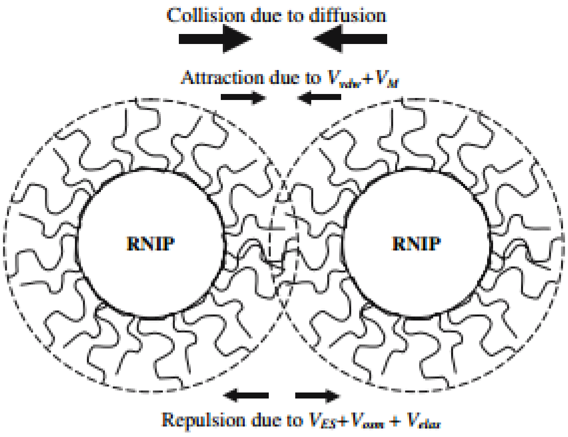


Figure 2.5 : Schematic representation of the forces acting on electrosterically stabilized polyelectrolyte-modified RNIP (Phenrat et al., 2008)

2.2.3 Factor affecting the Colloidal Stability

The surface modification of MIOPs with the polyelectrolyte increased the stability of the particle compare to the bare MIOPs. This is because the adsorbed polyelectrolyte layers can provide electrosteric repulsion that enhance the stability of the particle and resist the aggregation and sedimentation. For the bare MIOPs, the particle rapidly flocculates and sediment in solution due to strong van der Waals interaction and magnetic forces (Saleh et al., 2005, Phenrat et al., 2008).

The polyelectrolyte adsorption is confirmed by increase in the electrophoretic mobility (Kim et al., 2009). The electrophoretic mobility is the velocity of a particle in a unit of electric field. Zeta potential is related to the electrophoretic mobility by Henry equation (Swan and Furst, 2012);

$$U_E = \frac{2\varepsilon\xi f(\kappa a)}{3\text{ŋ}} \qquad (2.1)$$

Where,

U_E = Electrophoretic mobility (mV)

ξ = Zeta Potential (mV)

ε = Dielectric Constant

ŋ = Viscosity (mPa.s)

$f(\kappa a)$= Henry’s function

For Henry’s function, the κ is the Debye Length and the reciprocal of Debye Length, κ^{-1} indicates the thickness of the electrical double layer that related with the electrostatic interaction around the particle. The parameter ‘a’ refers to the radius of the particle (Swan and Furst, 2012). Particle with high zeta potential have lower aggregation rate compare with the particle of low zeta potential. The zeta potential value is measured using the dynamic light scattering (DLS). The value of zeta potential larger than 30mV indicates the good colloidal stability (Kim et al., 2009, Yeap et al., 2012, Hotze et al., 2010).

Several important factors affect the value of the zeta potential such as pH and ionic strength. Most of the nanoparticles have surface functional group that able to titrate by H^+ and OH^-. If alkali (high pH) is added then the particle tends to yields more negative charge whereas if acid (low pH) is added then the charge will be positively charge particle surface. Then, the zeta potential will be positive at low pH and negative at high pH. It will pass through the point of zero charge (pzc) that also known as the isoelectric point. The isoelectric point is the point when the zeta potential has no charge where particle remain stationary since there is no repulsion or attraction forces. The colloidal system at this point is least stable. As pH close to this point, the electrostatic double layer repulsion is decreased and the aggregation is occurred due to van der Waals attraction. The pH that far from the pzc is more stable (high zeta potential) because the particles tend to repel to each other (Hotze et al., 2010). Figure 2.6 showed the plot of zeta potential against pH that includes the position of isoelectric point.

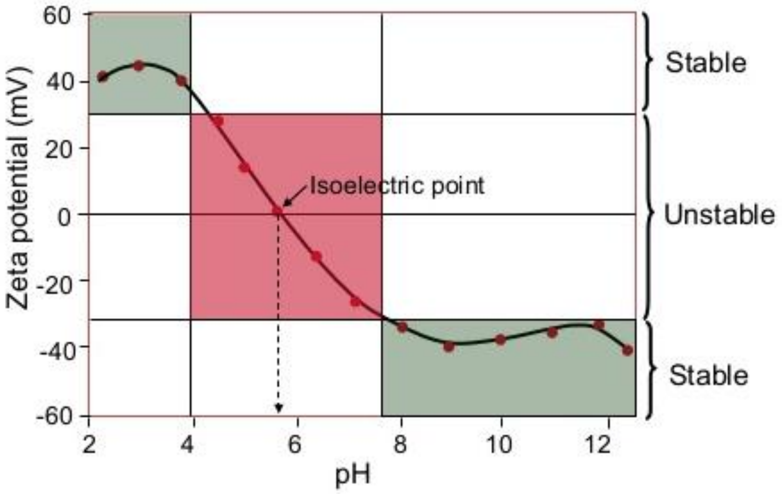


Figure 2.6 : Plot of Zeta potential versus pH showing the position of isoelectric point

As for the ionic strength effect, high concentration of ions will decrease the Debye length (κ^{-1}) that will compressed the electrostatic double layer. The ionic/salt concentration is related with the two regimes where the first regime is the fast or diffusion controlled aggregation that occurred for high salt concentration and the second regime is the slow or reaction controlled aggregation that occurred at low salt concentration. The aggregation rate is constant at high salt concentration because the aggregation is in the fast regime as shown in Figure 2.7. The aggregation rate is decreased rapidly because the energy barrier develops due to double layer interaction when the salt concentration is decreased. The transition between the slow and fast regime is referred as the critical coagulation concentration (CCC). The CCC is the minimum concentration of coagulant that causes rapid coagulation (Szilagyi et al., 2014, Hu et al., 2010, Hotze et al., 2010, Trefalt and Borkovec, 2014).

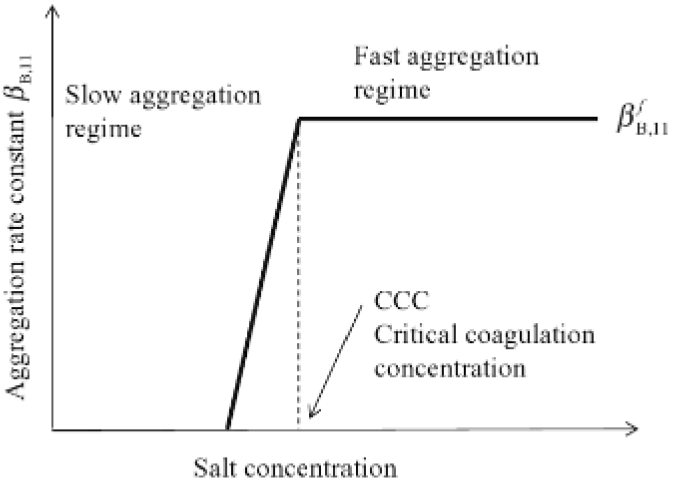


Figure 2.7 : Schematic representation on the aggregation rate constant as function of salt concentration (Ohshima, 2012)

2.3 Aggregation and Sedimentation

The flocculation for bare MIOPs occurs rapidly then it turns to micrometer-sized aggregates (gelation). It wills sediment from suspension. For bare MIOPs and modified MIOPs the sedimentation profile consists of 3 parts which are aggregation I, sedimentation I and sedimentation II as shown in figure 2.7. The sedimentation rate is low during the aggregation I. During this phase, the nanoparticle is aggregated but it still remains suspended since the bare MIOPs have not yet reached the critical size needed to sediment. During sedimentation I, the aggregates are reached a critical size and begin to sediment rapidly at time t_{crit}. t_{crit} is the time when the aggregates reached the critical size due to gravitational sedimentation that related with the formation of micrometer-sized aggregates from the nanoparticles and from the micrometer-sized aggregates to fractal clusters. (Phenrat et al., 2007, Phenrat et al., 2008, Kim et al., 2009)

The rate of aggregation and sedimentation is decreased for the modified MIOPs with the polyelectrolyte. The modified MIOPs do not formed the critical sized aggregates and remain suspended. The size of settling aggregates formed in the modified MIOPs is smaller than formed by bare MIOPs. The time for the modified MIOPs to aggregate to large gelled aggregates is longer than the bare MIOPs (Kim et al., 2009, Phenrat et al., 2008, Phenrat et al., 2007).

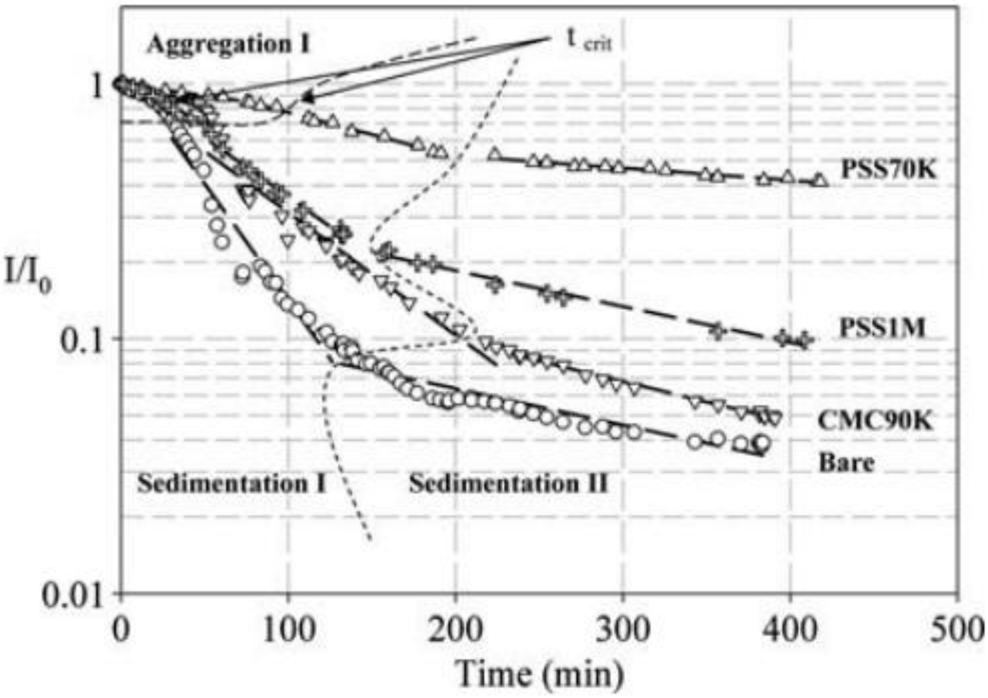


Figure 2.8 : Sedimentation curve for bare and surface modified MIOPs

CHAPTER THREE : MATERIALS AND METHODS

3.1 Materials

Table 3.1 : List of Materials

Materials	**Supplier**	**Usage**
• Magnetic Iron Oxide Nanoparticles(MIOPs)	Nanostructured & Amorphous Materials (NanoAmor)	Main Sample
• Poly(sodium(4)styrenesulfonate) (PSS)	Sigma Aldrich	Polyelectrolyte for coating MIOP
• Hydrochloric Acid (HCl)	Fisher Scientific	As a reagent

Table 3.2 : Properties of MIOPs

Properties	**Magnetic Iron Oxide Nanoparticles**
Other name	Magnetite
Molecular formula	Fe_3O_4
Molecular weight (g/mol)	231.53
Density, g/cm3	4.8-5.1
Boiling point	Not Available
Melting point	Not Available

Table 3.3: Properties of PSS 70k

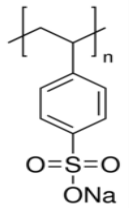
Properties	**Poly(sodium(4)styrenesulfonate)**
Other name	Poly(4-styrenesulfonic acid) sodium salt (PSS 70k)
Molecular formula	$(C_8H_7NaO_3S)_n$
Molecular weight (g/mol)	70 000
Density, g/cm3	0.801
Boiling point	Not Available
Melting point	Not Available
Chemical structure	

Table 3.4 : Properties of HCl

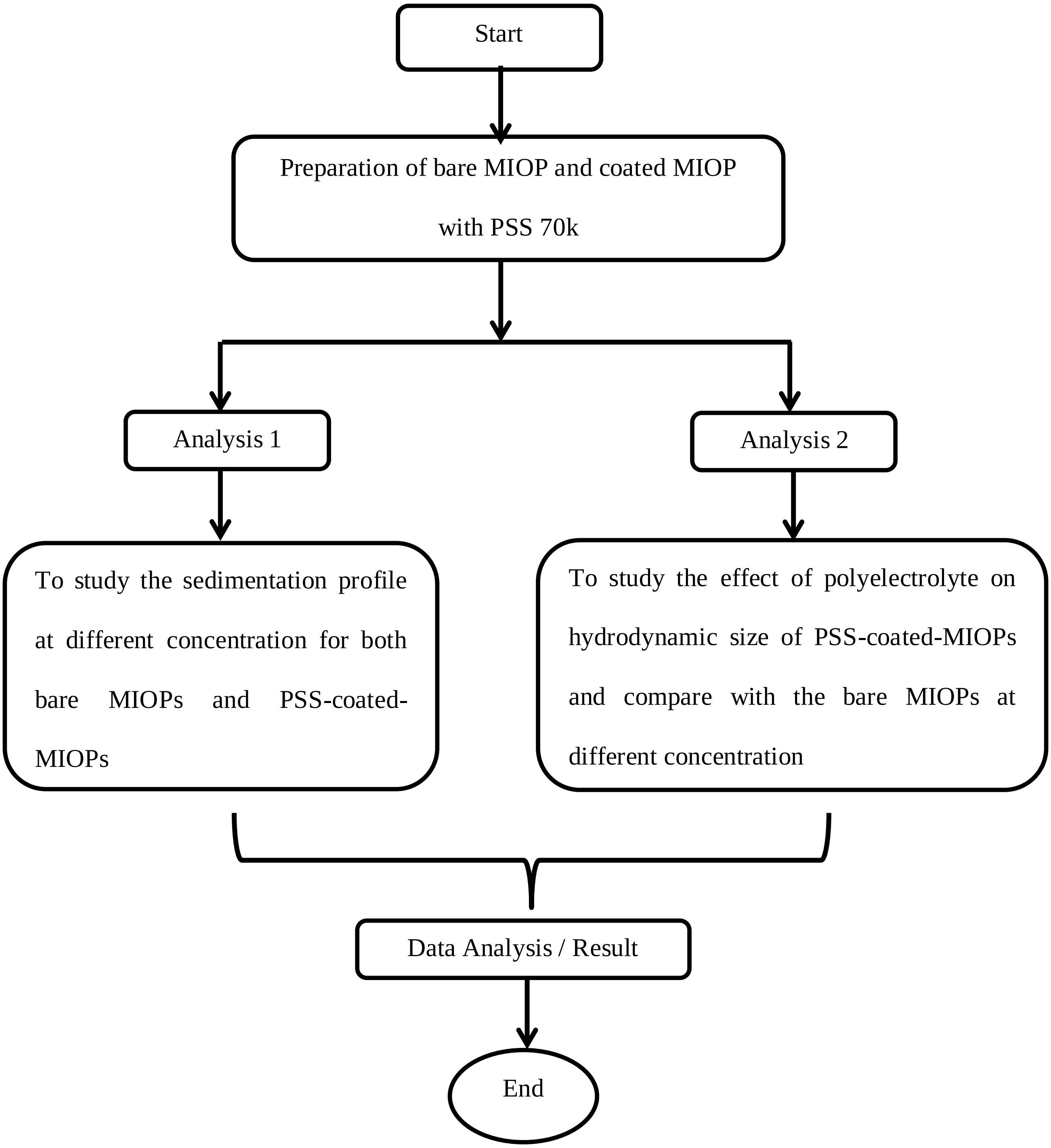
Properties	**Hydrochloric Acid**
Molecular formula	HCl
Molecular weight (g/mol)	36.45
Density, g/cm3	1.18
Boiling point	Not Available
Melting point	Not Available

3.2 Equipment

Table 3.5: List of Equipment

Equipment	**Model/Brand**	**Usage**
Sonicator	Elmasonic S10 H	To sonicate the sample
pH meter	Eutech pH 5+	To measure the pH value
Tube Rotator	Stuart	Bare and coated MIOPs formation
Centrifuge	Thermo Scientific Heraeus Megafuge 40	To separate liquid from solid
Dynamic Light Scattering	Malvern Instrument , UK	Analysis

3.3 Overall Flow of Research



3.4 Method of Preparation of MIOPs

3.4.1 Preparation of Bare MIOPs

A 5000mg/l of MIOPs (Fe_3O_4) suspension in deionized water was prepared in the glass scintillation vial then dispersed it by ultrasonification for at least 60 minutes using sonicator (Elmasonic S10 H) to ensure that this suspension had a good dispersity. Then, these bare MIOPs were used for the experiments.

3.4.2 Preparation of PSS-Coated-MIOPs

A 2500mg/l of MIOPs (Fe_3O_4) suspension in deionized water was prepared in the glass scintillation vial then dispersed it by ultrasonification for at least 60 minutes using sonicator (Elmasonic S10 H). Using the same steps, 5000mg/l of PSS 70k was prepared and sonicated it for 60 minutes. The pH of MIOPs suspension and PSS solution was adjusted to 3.5 by adding 0.1M HCl or 1.0M HCl. The pH adjustment was important to ensure that the charged for MIOPs and PSS was opposite to each other so that the physisorption of PSS and MIOPs via electrostatic attraction was occurred. The MIOPs suspension and PSS solution was mixed into the centrifuge tube. Then, the samples were rotated end over end for 24 hours using tube rotator (Stuart) at 40 rpm rotation speed to allow the polymer to adsorb. The samples were centrifuged at 5000 rpm for 20 minutes using the centrifuge (Thermo Scientific Heraeus Megafuge 40). After that, the samples were washed to remove the free polymer from solution. This process was repeated three times followed by ultrasonification for 10 minutes. Then, the PSS-coated-MIOPs were used for the experiments.

3.5 Zeta Potential Measurements

In this section, the bare MIOPs and PSS-coated-MIOPs were diluted with deionized water to a concentration of 10 ppm into glass scintillation vial. Then, the zeta potential of the bare MIOPs and PSS-coated-MIOPs were measured using DLS. Next, 1 ml of bare MIOPs were taken from the glass scintillation vial and transferred it into universal zeta clip cell. It is important to rinse the cuvette with deionized water and dry it before transferring the solution. Apart from that, it is also essential to make sure there is no air bubbles in within the solution before subjected to DLS measurement. Then, put the cell into DLS to determine zeta potential. All measurements were conducted at temperature of 25^{o}C. The steps above were repeated for PSS-coated-MIOPs.

3.5 Sedimentation Kinetic of MIOPs

For this part, the sedimentation kinetics of bare MIOPs and PSS-coated-MIOPs were studied under the presence and absence of external magnetic field. Under the absence of magnetic field, there no external magnetic source was used. First, the bare MIOPs were prepared by methodology mentioned in Section 3.4.1. Next, the bare MIOPs were diluted into a few different concentrations such as 10 ppm, 50 ppm, 100 ppm, 250 ppm, and 500 ppm into 100 ml measuring cylinder. Then, make sure all the samples were well dispersed in the measuring cylinder by stirred it with spatula. At the same time, took photo of all the samples every 1 minute for 5 hours in order to observe the sedimentation of bare MIOPs at different concentration.

Next, the PSS-coated-MIOPs were prepared by methodology mentioned in Section 3.4.2. Then, the steps above were repeated to observe the sedimentation of PSS-coated-MIOPs at different concentration. Then, the sedimentation of bare MIOPs and PSS-coated-MIOPs were compared and analyzed.

Under the present of magnetic field, grade N50 NdFeB cylindrical permanent magnet was used. The magnet was placed at bottom of the measuring cylinder.The bare MIOPs were prepared by methodology mentioned in Section 3.4.1. Next, the bare MIOPs were diluted into a few different concentrations such as 10 ppm, 50 ppm, 100 ppm, 250 ppm, and 500 ppm into 100 ml measuring cylinder. Then, make sure all the samples were well dispersed in the measuring cylinder by stirred it with spatula. At the same time, took photo of all the samples every 1 minute for 1 hour in order to observe the sedimentation of bare MIOPs at different concentration.

Next, the PSS-coated-MIOPs were prepared by methodology mentioned in Section 3.4.2. Then, the steps above were repeated to observe the sedimentation of PSS-coated-MIOPs at different concentration. Then, the sedimentation of bare MIOPs and PSS-coated-MIOPs were compared and analyzed.

3.6 Effect of Electrosteric Stabilization on Hydrodynamic Size

In this section, the hydrodynamic size of bare MIOPs and PSS-coated-MIOPs were studied under the presence and absence of external magnetic field. . Under the absence of magnetic field, there no external magnetic source was used. First, bare MIOPs and PSS-coated-MIOPs were prepared by methodology mentioned in Section 3.4.1 and Section 3.4.2. Then, both samples were diluted to a concentration of 10 ppm into 100 ml measuring cylinder. Next, the hydrodynamic sizes of the bare and PSS-coated-MIOPs were measured using DLS as shown in Figure 3.1. In this regard, 1ml of bare MIOPs was taken from the top of the measuring cylinder that containing 10 ppm bare MIOPs and transferred it into the DLS disposable cuvette. It is important to rinse the cuvette with deionized water and dry it before transferring the solution. Apart from that, it is also essential to make sure there is no air bubbles in within the solution before subjected to DLS measurement. Then, put the cuvette into DLS to monitor the hydrodynamic sizes of the samples. All measurements were conducted at temperature of 25°C. The hydrodynamic sizes of the samples were recorded every 15 minutes for first hours and every 30 minutes for next 5 hours using the DLS.

Next, the same procedure was used for 10 ppm PSS-coated-MIOPs. Then, the steps above were repeated for 50 ppm, 100 ppm, 250 ppm and 500 ppm of bare MIOPs and PSS-coated-MIOPs. Under the present of magnetic field, grade N50 Neodymium Iron Boron (NdFeB) cylindrical permanent magnet was used. The magnet was placed at bottom of the measuring cylinder. Then, the steps above were repeated for bare MIOPs and PSS-coated-MIOPs. However, under present of magnetic field, the samples was taken from the center of the measuring cylinder and the hydrodynamic size of the samples were recorded every 2 minutes for 1 hour for bare MIOPs while for PSS-coated-MIOPs the samples were recorded for 2 hours.

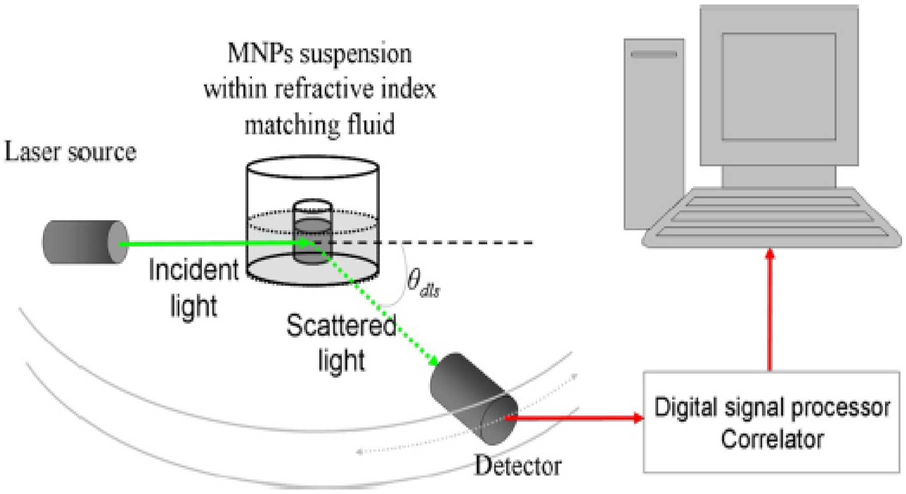


Figure 3.1 : Working Principle of DLS measurements (Lim et al., 2013)

3.7 Comparison of magnetophoresis force and gravitational force

In this section, the magnetophoretic force and gravitational force for bare MIOPs and PSS-coated-MIOPs for all range of concentration were calculated and compared. The magnetophoresis force can be determined by using following equation:

$$F_{mag} = \mu \nabla B = Ms.V.\nabla B \tag{3.1}$$

Where, F_{mag} = Magnetophoresis force ($\mathrm{kgms^{-2}}$)

μ = Magnetic dipole moment (emu)

M_S = Saturation magnetization per unit mass (emu/g)

V = Volume of particles ($\mathrm{m^3}$)

∇B = Magnetic flux density gradient (T/m)

The magnetic flux density gradient can be calculated by using:

$$\nabla B = \frac{B_r r^2}{2}\left[\frac{1}{[(y+h)^2]^{\frac{3}{2}}} - \frac{1}{[y^2+r^2]^{\frac{3}{2}}}\right] \tag{3.2}$$

Where, B_r = Remanent magnetic flux density (T)

r = Radius of cylindrical magnet (m)

h = Height of cylindrical magnet (m)

y = Vertical distance from magnet (m)