

**CLUSTERING OF POLYELECTROLYTE COATED MAGNETIC
NANOPARTICLES UNDER REPETITIVE CYCLE OF MAGNETIZATION**

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by

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LIST OF SYMBOLS

	Symbol	Unit
N^*	Aggregation parameter	-
U_{DD}	Dipole-dipole interaction energy	J
μ_E	Electrophoretic mobility	$\mu\text{m.cm/V.s}$
μ	Magnetic permeability	N/A^2
B	Magnetic induction	T
D_f	Diffusion coefficient	m^2/s
H	External magnetic field	A/m
k_B	Boltzmann constant	$\text{m}^2.\text{kg/s}^2.\text{K}$
M	Degree of magnetization	A/m
pH	Potential of hydrogen	-
R_H	Hydrodynamic radius	nm
Γ	Magnetic coupling parameter	-
χ	Magnetic susceptibility	-
ζ	Zeta potential	mV

LIST OF ABBREVIATIONS

DLS	Dynamic Light Scattering
EDL	Electrical Double Layer
HGMS	High Gradient Magnetic Separator
IEP	Isoelectric Point
IONPs	Iron Oxide Nanoparticles
MNPs	Magnetic Nanoparticles
NdFeB	Neodymium Iron Boron
PDDA	Poly (diallyldimethylammonium chloride)
PZC	Point of Zero Charge
SF-IONPs	Surface-Functionalized Iron Oxide Nanoparticles

PERGUMPALAN ZARAH-ZARAH MAGNETIK BERSALUT POLIELEKTROLIT
DI BAWAH PENGARUH KITARAN MAGNETISASI BERULANG

ABSTRAK

Sampel zarah-zarah iron oksida (ZIO) terdedah telah disediakan dan telah difungsikan dengan menggunakan elektrolit poli(diallyldimethylammonium chloride) (PDDA) sebagai agen pelapisan untuk meningkatkan kestabilan koloid ZIO dalam penggantungan. Kehadiran PDDA sebagai lapisan yang terserap pada ZIO mewujudkan penstabilan elektrosterik terhadap zarah-zarah dalam penggantungan, dengan itu menghalang tarikan van der Waals dan daya interaksi dipole-dipole magnet antara zarah-zarah yang mengurangkan agregasi zarah. Pencirian ZIO terdedah dan ZIO yang telah difungsikan dilakukan dengan menggunakan pengetatan cahaya dinamik (PCD) untuk pengukuran saiz zarah dan potensi zeta. Pencirian tersebut untuk memastikan ZIO berjaya dilapisi oleh makromolekul PDDA. Sampel ZIO disediakan dalam 3 kepekatan yang berlainan (50, 100 dan 500 ppm) untuk menjalankan kajian mengenai kesan pendedahan berulang sampel ZIO terhadap medan magnet. Fokus utama adalah kesan ke atas saiz gumpalan yang terbentuk dan kestabilan koloid selepas terdedah kepada magnetisasi berulang. Kitaran magnetisasi sampel ZIO bermula dari 1 kitaran diikuti dengan 3 dan 5 kitaran magnetisasi. Untuk saiz kluster yang terbentuk, tidak banyak perbezaan yang dapat dilihat dari ukuran saiz zarah oleh PCD untuk semua kepekatan hasil peningkatan kitaran magnetisasi. Hal yang sama berlaku kepada kajian terhadap kestabilan koloid yang telah dilakukan melalui kajian kinetik oleh UV-Vis spektrofotometer, melalui pengukuran penyerapan oleh sampel ZIO. Kadar peluruhan untuk penyerapan yang dinormalisasi hampir sama bagi semua kitaran magnetisasi dan kepekatan yang membuktikan bahawa magnetisasi berulang mempunyai kesan yang kurang penting ke atas kestabilan zarah dalam penggantungan.

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ABSTRACT

The sample of naked iron oxide nanoparticles (IONPs) was prepared and been functionalized by using poly (diallyldimethylammonium chloride) (PDDA) electrolyte as a coating agent in order to improve the colloidal stability of the IONPs in the suspension. The presence of PDDA as an adlayer adsorbed on IONPs introduced electrosteric stabilization towards particles in suspension, thus suppressed the van der Waals attraction and magnetic dipole-dipole interaction force between particles reducing particles aggregation. Characterization of naked IONPs and functionalized IONPs been conducted by using dynamic light scattering (DLS) for particles size and zeta potential measurement. The characterization to ensure the successful coating of IONPs with PDDA macromolecules. The IONPs samples are prepared into 3 different concentration (50, 100 and 500 ppm) to conduct the study on effect of repetitive exposure of IONPs sample towards magnetic field. The major focuses would be the effect on the cluster size formed and colloidal stability of particles suspension after been subjected to repetitive magnetization. The magnetization cycle of IONPs samples was started from 1 cycle followed by 3 and 5 magnetization cycles. For cluster size formed, as going up the magnetization cycle there was not much different can be seen from the particles size measurement by DLS for all concentrations. The same thing goes to study on colloidal stability of particles been conducted through kinetic study by UV-Vis spectrophotometer, measuring the absorbance of IONPs sample. The decay rate for normalized absorbance was almost the same for all magnetization cycles and concentrations that proving the repetitive magnetization has relatively insignificant effect towards particles stability in suspension.

CHAPTER 1 - INTRODUCTION

1.1 Research Background

1.1.1 Magnetic Nanoparticles (MNPs)

Much research in recent years showed the importance of magnetic nanoparticles (MNPs) and its considerable promise in many applications. Crucial efforts are spent on this research area to study the current development of MNPs, their characterizations and behaviours. At the same time, the research providing some techniques in improving and enhancing their applicability in broad range of applications such as pollutant removal from wastewater (Mohammed et al., 2017, Gautam et al., 2016), nanomagnetic materials for targeted drug delivery (Mehta, 2017), act as cancer targeting dual magnetic resonance imaging probe (Yang et al., 2017) and more.

MNP is a nanoscale magnetic material with the size approximately within 1-100 nm that had been proved to have a very unique properties as which different from their bulk counterpart (Booker and Boysen, 2005). This unique feature of magnetic nanoparticles is highly dependent on its size. The size of MNPs play the major role in characterizing the nanoparticles as some of its chemical and physical properties are greatly dependent on the nanoparticle diameter itself (Lim et al., 2013). The size of MNPs is too small that the particles exhibit some characteristics that not possible to be observed in larger particles such as having high surface to volume ratio which make it available for applications such as high metal removal or drug delivery (Lim et al., 2013).



Figure 1.1 Magnetic Nanoparticles (MNPs) suspension in aqueous medium.

1.1.2 Surface Functionalization of MNPs

The high surface energy properties of MNPs in the suspension will lead to agglomeration that increase the particles size over time. In order to reduce those surface energy, MNPs such as magnetite (Fe_3O_4) nanoparticles in many cases are coated with either surfactants or polymers (Ditsch et al., 2005). Such surface functionalization introduce electrostatic and steric stabilization of particles in suspension to limit the occurrence of particles agglomeration while synthesizing the stable and desired size of clusters for any particular applications (Yeap et al., 2014). Colloidal stability of the particles in suspension can be achieved as electrostatic repulsion between particles introduced will overcome the van der Waals attractive force and magnetic dipole-dipole interaction force.

Electrostatic stabilization is a process at which the dissociation of ionic structures on the particle surface and selective ion adsorption cause the dispersed particles in a suspension to carry electric charge (Instruments, 2017a). In the case the particles having the same charges, they will tend to repel each other. For this process to occur, electric double layer (EDL) fundamental plays a major role, which is the layer that surrounds the particles in suspension including the absorbing ions on the surface of the particles and a film of counter-charged suspension medium. In other words, EDL actually is electrically neutral and can be divide into 3 parts, which are surface charge, stern and diffuse layer. Surface charge also known as charged ions that primarily dissociated from the particle surface. For stern layer, it is counter ion layer, which opposite to the surface charge that attracted to particle surface and attached together by electrostatic force. Diffuse layer is a film of the suspension medium adjacent to the particles that contains free ions. As the particles move in suspension medium, the layer will remain attached to the particle and the boundary of this layer is known as slipping plane. The electrical potential measured

on this boundary is known as zeta potential, which is important in indicating the stability of colloidal suspensions (Kopeliovich, 2013).

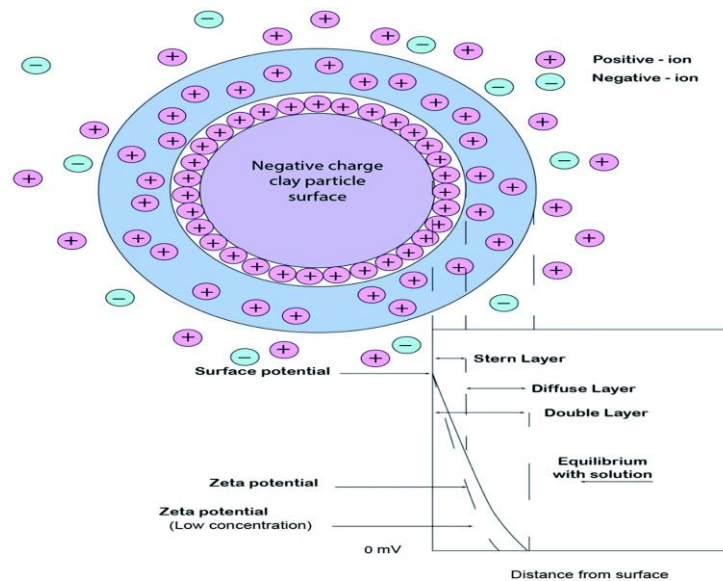


Figure 1.2 Electrical Double Layer (EDL) illustration on particles

(Jafarbeglou et al., 2016).

Steric stabilization is a phenomenon at which the repulsion potential is created by the presence of polymeric coating on the particles to prevent particles agglomeration. As the coated particles approach, the particles will overlap and penetrate the polymer envelopes of each other. The overlapping cause the polymer concentration to increase as well as osmotic pressure. This will lead the suspension medium (solvent) to move to this area thus repelling away the particles. Besides, each polymer chain generates huge amount of entropy due to its sorts of different conformations in suspension medium. However, the overlapping polymer envelopes cause the reduction in amount of polymer conformation thus reducing the entropy, affecting the Gibbs energy that might be unfavourable. Thus, it leads to repulsion in order to maintain the stability of particles in suspension (Instruments, 2017b).

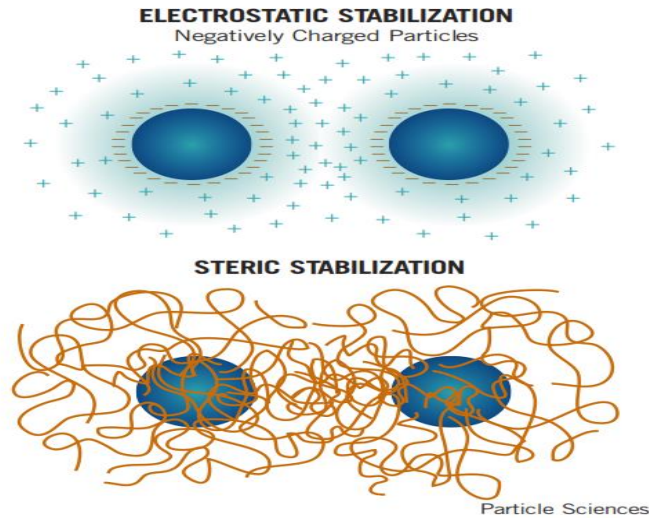


Figure 1.3 Illustrations of Electrostatic and Steric Stabilization

(Sciences, 2009).

1.1.3 Magnetization of MNPs

Magnetization of MNPs is a situation at which those nanoparticles been magnetized when exposed towards a magnetic field. Magnetization is an important parameter been used in characterizing the properties of nanomaterials. The behaviour of nanoparticles under influence of an external magnetic field depending on two main factors, which are magnetic susceptibility and permeability. Magnetic susceptibility (χ) describes degree of magnetization (M) under the influence of an external magnetic field (H). For magnetic permeability (μ), it indicates the change of magnetic induction (B) induced by an external magnetic field (H) (Yadollahpour and Rashidi, 2015).

$$M = \chi H \quad (1.1)$$

$$B = \mu H \quad (1.2)$$

This matter relates to saturation magnetization of MNPs that describing the state at which an increase in applied magnetic field cannot further increase the magnetization of the particles. In several applications, nanoparticles with higher saturation magnetization are preferred due to its higher sensitivity and efficiency (Colombo et al., 2012). Previous researches have proved that saturation magnetization increases linearly

with size until reaching its bulk value (Lin et al., 2006). Another peculiar behaviour of MNPs at zero magnetization in absence of applied magnetic field, such MNPs known as superparamagnetic. In presence of external magnetic field, the particles will acquired magnetic dipoles. The interaction energy of two magnetic dipoles with dipole moments m_1 and m_2 can be expressed as (Ku et al., 2016);

$$E_{m_1 m_2} = \frac{1}{4\pi\mu} \left[\frac{m_1 m_2 - 3(m_1 \cdot e_r)(m_2 \cdot e_r)}{|l|^3} \right] \quad (1.3)$$

Where μ is the medium permeability, l is the distance between two magnetic dipoles and e_r is the unit vector of the centerline of the two magnetic dipoles. If the case where the magnetic moments for both magnetic dipoles are the same (magnitude and direction), Equation 1.3 can be simplified as followed (Ku et al., 2016);

$$E_{mm} = \frac{|m|^2(1 - 3\cos^2\theta)}{4\pi\mu|l|^3} \quad (1.4)$$

Where m is magnetic dipole moment which $m = 4\pi\mu\beta R^3 H$ and θ is the angle between the direction of external magnetic field and the centreline of two magnetic dipoles.

$$\beta = \frac{\mu_k - \mu_r}{\mu_k + 2\mu_r} \quad (1.5)$$

Where μ_k and μ_r are the relative permeability of magnetic nanoparticles and the medium respectively, R is radius of magnetic dipole and H is the intensity of magnetic field, kA/m.

As been introduced towards magnetic field, the motion of MNPs in magnetic gradient is called magnetophoresis (Faraudo et al., 2013). Superparamagnetic property offer better control in many applications such as drug delivery as they provide strong magnetic response towards external applied magnetic field (Kolhatkar et al., 2013).

1.2 Problem Statement

Recently, development of MNPs been well established and shows a significant role in diverse areas of science and technology. However, MNPs seems to rapidly aggregate due to presence of van der Waals attraction and magnetic dipole-dipole force between particles, thus cause the particles instability throughout the suspension. Therefore, surface functionalization been introduced providing electrosteric stabilization towards particles in suspension and prevent aggregation.

Under the influence of external magnetic field, the particles would move toward the region with the highest field gradient lead to particles separation from aqueous media or can be known as magnetophoresis. The highly stabilized particles should possess longer separation time. In this work, the repetitive exposure of MNPs towards external magnetic field have been conducted to study its effect towards colloidal stability of particles in the suspension and its cluster size formed throughout magnetization. Poly (diallyldimethylammonium chloride) (PDDA) is used as polyelectrolyte to coat iron oxide MNPs and permanent magnet (NdFeB) been used to provide external magnetic field applied on the particles suspension.

1.3 Research Objectives

The objectives of conducting this study will be:

1. To illustrate the influences of repetitive exposure of magnetic nanoparticles to magnetic field.
2. To investigate the role of repetitive magnetization on cluster size formed.
3. To record the colloidal stability profile of magnetic nanoparticles after subjected to repetitive magnetization.

1.4 Scope of Study

Through this research, iron oxide nanoparticles (IONPs) have been used for preparation of naked IONPs suspension and been functionalized with poly (diallyldimethylammonium chloride) (PDDA) for preparation of PDDA-coated IONPs suspension. To ensure the good dispersion of both naked and surface functionalized IONPs in aqueous suspension medium, the samples were sonicated for a certain time. The characterization of any samples were done by using Malvern Zetasizer dynamic light scattering (DLS) equipment in order to determine the particles' size and zeta potential. Through those parameters, the success of particles coating can be ensured.

The colloidal stability profile of IONPs samples were recorded by using UV-Vis Spectrophotometer equipment with the presence of external magnetic field induced by permanent magnet neodymium iron boron (NdFeB). Magnetization of IONPs samples were for several times to study the effect of repetitive magnetic field exposure towards functionalized IONPs stability in the suspension. For each magnetization cycle, the size of particles in IONPs suspension are measured by using DLS equipment to study the effect of repetitive magnetic field on clusters size formed.

1.5 Organization of the Thesis

This thesis consists of five main chapters which can be describe as follows:

- **Chapter 1**

Provides brief introduction towards magnetic nanoparticles and overview on how important it is towards current development of science and technology. Problem statement, research objectives, scope of study and organization of this thesis also been included in this chapter.

- **Chapter 2**

Provides a literature review that related to this research work that includes the related theory of MNPs research, previous study on colloidal stability of MNPs in suspension by researchers and working principle of DLS measurement in characterization step.

- **Chapter 3**

Provides the details on materials, chemicals and research methodologies involved in experimental work. The overview of overall experimental works been illustrated in this chapter through flowchart for a better understanding in research flow.

- **Chapter 4**

Provides the detail discussions on the results obtained from experimental works. The results such as size and zeta potential of both naked and functionalized IONPs, colloidal stability profile from repetitive magnetization of IONPs and cluster size measurement on samples from magnetization cycle are provided in this chapter.

- **Chapter 5**

Provides the summary and conclusion of all results obtained through this research works. This chapter also concludes the overall research work and provides some recommendations that require improvement for future studies that related to this research field.

CHAPTER 2 - LITERATURE REVIEW

2.1 DLVO Theory

DLVO theory named from Derjaguin, Landau, Verwey and Overbeek is a theory that provides a description on colloidal stability of the suspension. Based on this theory, the stability of the colloidal system is highly dependent on balance between electrostatic repulsive force and van der Waals attractive forces (Hwang, 2011).

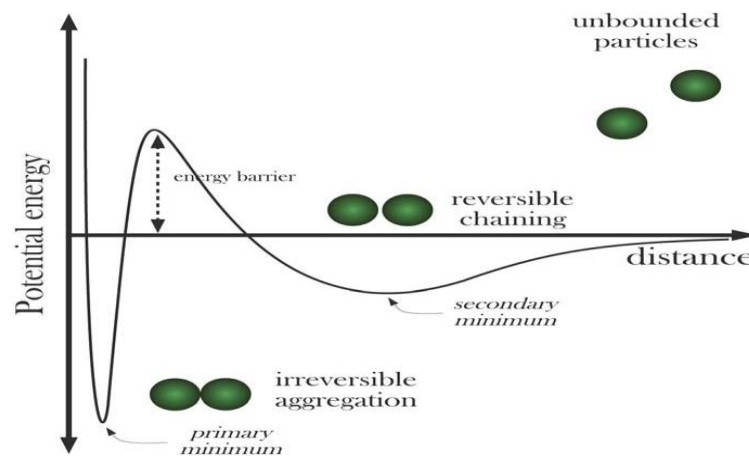


Figure 2.1 Energy profile of interaction between two MNPs (Faraudo et al., 2013).

As shown in **Figure 2.1** above, DLVO theory explains the tendency of colloids to agglomerate or separate by combining 2 curves of electrostatic repulsion and van der Waals attractive forces. Secondary minimum is the condition at which the particles having a great distance but still cause aggregation to occur. However, reversible aggregation of the particles can be easily redispersed due to its weak attraction between the particles. Primary minimum is a state where the attraction force overpower the repulsive force at short distance between the particles, cause particles agglomeration and the state is irreversible. However, a very high energy barrier need to be overcome to achieve primary minimum, cause the particle to stay at secondary minimum where the process only involve weak attraction and reversible aggregation (Faraudo et al., 2013). At maximum energy barrier, which can be known as primary maximum, the repulsion is

much greater than attraction force causes the particles to rebound when collide to each other and remain disperse in the suspension (Inc., 2016). The energy barrier must be higher than thermal energy, otherwise will lead to particles aggregation.

2.2 Chain Formation and Aggregation Theory

Superparamagnetic particles acquire induced magnetic dipoles and dipole-dipole interaction as been exposed towards an external magnetic field. The dipole-dipole interaction energy between two superparamagnetic nanoparticles can be written as:

$$U_{DD} = \frac{\mu_0 m^2}{4\pi r^3} (1 - 3 \cos^2 \theta) \quad (2.1)$$

Where m is magnetic dipole moment, r is separation distance between particles, μ_0 is magnetic permeability of free space and θ is the angle between direction of external magnetic field and the line joining the both centers of particles. The relevance of particle-particle magnetic interaction of particles dispersed in a liquid much depends on how strong it is as been compared to thermal energy. The ratio of both energies can be defined as a magnetic coupling parameter that can be written as (Jordi et al., 2011):

$$\Gamma = \frac{|U_{DD}^{max}|}{k_B T} = \frac{\mu_0 m_s^2}{2\pi\sigma^3 k_B T} \quad (2.2)$$

Physically, $\Gamma \gg 1$ indicates the scenario at which dominated by magnetic interaction, thus favouring aggregation while for $\Gamma \ll 1$ as an indicative for the situation that dominated by thermal agitation that favouring dissociation. However, the possibility of chain formation not only depending magnetic coupling parameter as mentioned before. The main results in analysing the behaviour of the system is controlled by the aggregation parameter N^* as (Faraudo et al., 2013):

$$N^* = \sqrt{\phi_0 e^{\Gamma-1}} \quad (2.3)$$

For $N^* \leq 1$, the system does not involve any chain formation while for $N^* > 1$ will involve the chain formation in fluid. Thus, as the large values of Γ involved, very large values of N^* will be obtained. Large values of N^* will lead the system to non-equilibrium state at which the average chain size grows continuously with time (Faraudo et al., 2013).

2.3 Colloidal Stability of MNPs

Through surface functionalization of MNPs with polyelectrolyte, the stability of the MNPs in the suspension medium can be enhanced due to presence of both electrostatic and steric stabilization as been discussed previously. At the same time, functionalization can provide protection on the particles from oxidation (Wu et al., 2008). From previous study, it is proven that the naked MNPs without any functionalization are extremely unstable even at low ionic strength and concentration with the particles tend to aggregate to larger clusters in a short time (Yeap et al., 2012). The collision and interaction between MNPs in suspension are practically unavoidable without surface functionalization.

Ditsch and co-workers (2005) previously have studied the clustering and the stability of functionalized MNPs with polymer. They focused on exploring the suitable method that the clusters of controlled size can be produce and the stability of MNPs suspension can be enhanced. By using different molecular weight of polymers, they studied how good the functionalization of MNPs can be done and how its affect the colloidal stability. The optimal molecular weight has been found that providing maximum stability for MNPs suspension, however the clusters formed too small for efficient high gradient magnetic separation (HGMS) recovery process.

Li and co-workers (2017) conducted a study of finding a way to moderate the wild electrostatic force of attractions between MNPs and polymers in order to generate the

aggregates with controlled shape and morphology, which at the same time provides better colloidal stability and avoid early phase separation. The study focused on moderating the interaction by reacting MNPs and polymers at critical value of ionic strength (I_s^c) of aqueous suspension medium. Through their findings, above I_s^c will result the screening of those electrostatic interactions while for below than I_s^c , instantaneous phase separation took place due to formation of large aggregates lead by very strong electrostatic interactions.

There are still several factors that might affect the colloidal stability of MNPs suspension in aqueous medium that been discovered in previous study done by researchers. MNPs size also play major role as for general, smaller particles are more likely to enter aggregation state compared to larger ones due to higher energy barrier is expected as the particle size increases. The impact of shape and crystal structure of particles on colloidal stability are still unknown due lack of study (Gambinossi et al., 2014). For surface chemistry factors, the colloidal stability is better in high ionic strength media because of steric and hydration repulsions existence (Grasso et al., 2002).

For solution condition, an increase in ions concentrations in solutions provide indirect effect on colloidal stability by increasing the electrostatic interactions (Gambinossi et al., 2014). The decrease of particles surface charge resulting from adsorption of ions on MNPs and as the surface charge approaching the isoelectric point (IEP) will favour the aggregation state of particles (Zhang and Buffle, 1995). Isoelectric point is a pH value at which the particle does not carries net electrical charge or in order words, the amount of both negative and positive charges on the particles surface are the same. The term IEP is interchangeably with point of zero charge (PZC) term (Cleaves, 2011).

Hotze and co-workers (2010) discussed the effect of pH on colloidal stability. As pH moves towards PZC (zero zeta potential), the EDL repulsion will be reduced and the aggregation will be triggered by van der Waals attraction force. To ensure stability of colloidal suspension, the absolute value of zeta potential should be larger than 30 mV (Yeap et al., 2012). The colloidal stability of particles can be illustrated as shown in graph of zeta potential dependence on pH below.

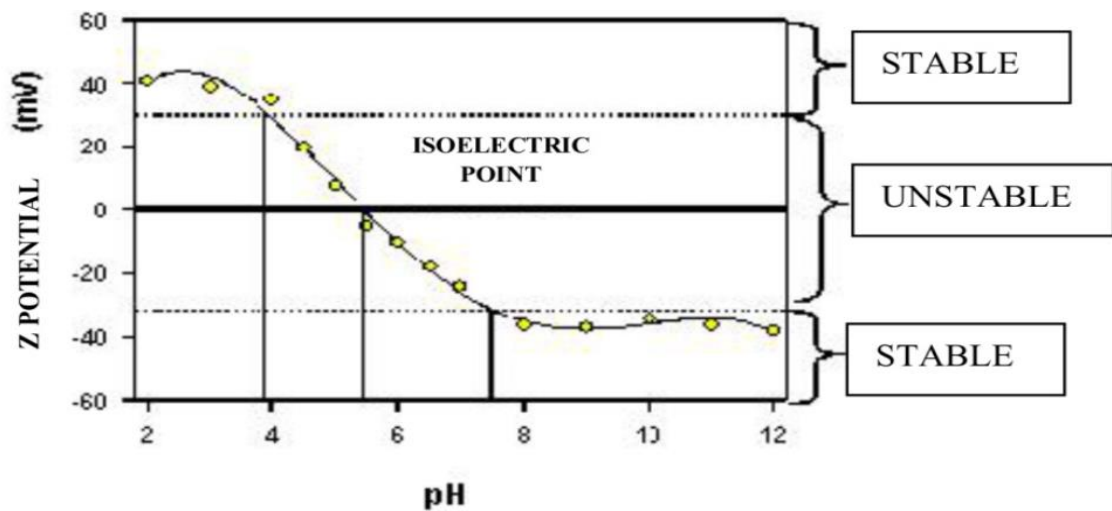


Figure 2.2 Graph of zeta potential against pH value (Talero et al., 2013).

2.4 DLS Measurement for MNPs Characterization

Dynamic Light Scattering (DLS) also known as Photon Correlation Spectroscopy or Quasi-Elastic Light Scattering that becoming one of popular method in characterizing the MNPs. One of the purposes utilizing DLS is to determine size of the MNPs. The DLS works by exposing the MNPs suspension with a light beam that strikes on MNPs surface cause the incident light to scatter. Due to the MNPs undergo random motions in the suspension, the scattered light undergoes Doppler shift, which means the change in scattered light frequency or wavelength during the scattering effect. As for large particles, it move slowly in suspension thus small Doppler shift generated while for small particles that move faster provide large Doppler shift.

The detector detect the scattered light and measures the fluctuations in light intensity results from Doppler shift for a period. The data been analyzed by autocorrelation function (correlator) and autocorrelation function as a function of delay time is extracted.

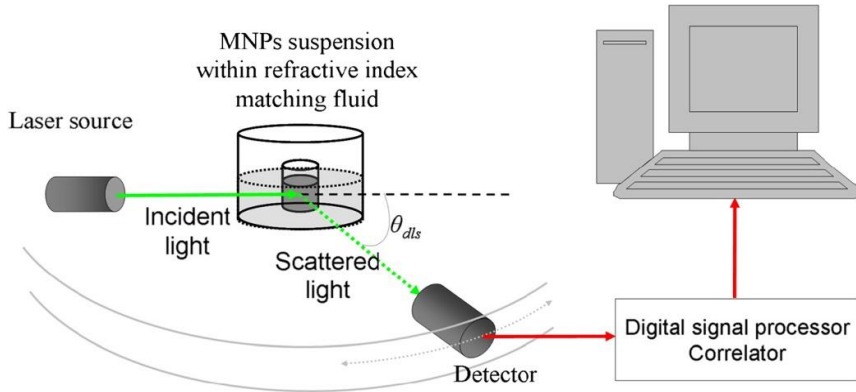


Figure 2.3 Typical experimental setup for DLS measurement (Lim et al., 2013).

As show in **Figure 2.4**, decay of this function is used to extract the particles size. The faster decay of this function results from smaller particles. The decay rate, Γ is derived from experimental data by a curve fit.

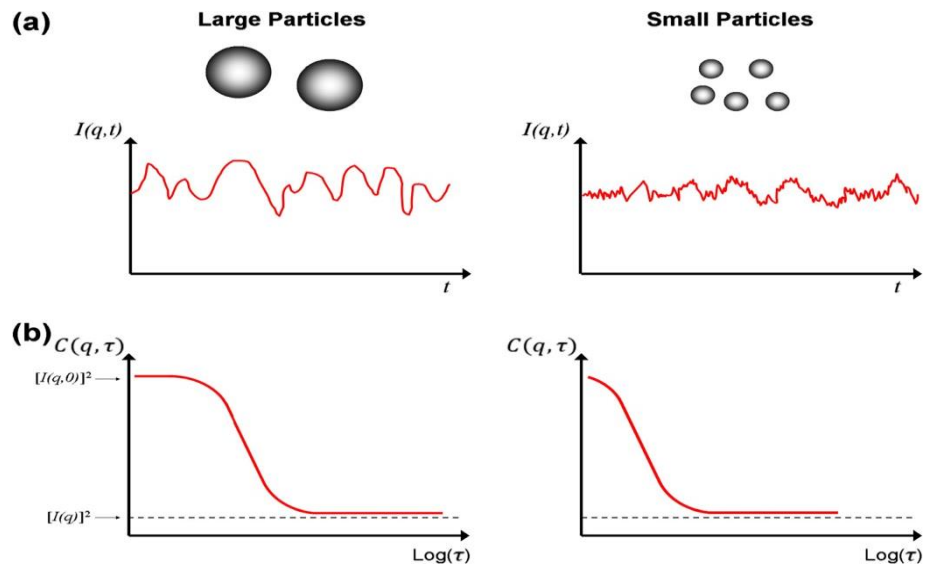


Figure 2.4 Illustration of typical (a) intensity measurement of scattered light with time and (b) autocorrelation function in DLS with delay time (Lim et al., 2013).

Thus, diffusion coefficient, D_f can be obtained from:

$$\Gamma = D_f q^2 \quad (2.4)$$

$$q = (4\pi n/\lambda)\sin(\theta_{DLS}/2) \quad (2.5)$$

where n is the refractive index of the solution, λ is the wavelength of incident light in vacuum and θ_{dis} is the scattering angle. After obtaining the D_f value, hydrodynamic size R_H of the MNPs suspension can be calculated from Stokes-Einstein equation ($D_f = k_B T / 6\pi\eta R_H$), where k_B is Boltzmann constant, T is temperature of suspension and η is viscosity of surrounding media.

For several types of DLS equipment such as Zetasizer, the measurement of zeta potential of the MNPs also available. However, the measurement of zeta potential cannot be done directly as it must be deduced from electrophoretic mobility of charged MNPs under applied electric field. Electrophoretic mobility is the velocity of the particles moving under the influence of applied electric field. The electrophoretic mobility μ_E of particles firstly calculated as $\mu_E = V/E$, where V is the particles velocity and E is the electric field strength. After obtaining μ_E value, the zeta potential, ζ was calculated by using Henry's equation (Bhattacharjee, 2016):

$$\mu_E = \frac{2\varepsilon_r \varepsilon_0 \zeta f(Ka)}{3\eta} \quad (2.6)$$

Where ε_r is relative permittivity, ε_0 permittivity of vacuum, $f(Ka)$ is Henry's function and η is viscosity at experimental temperature.

CHAPTER 3 - MATERIALS AND METHODS

3.1 Experimental Flowchart

The flowchart of the overall experimental works conducted is showed as in **Figure 3.1** below.

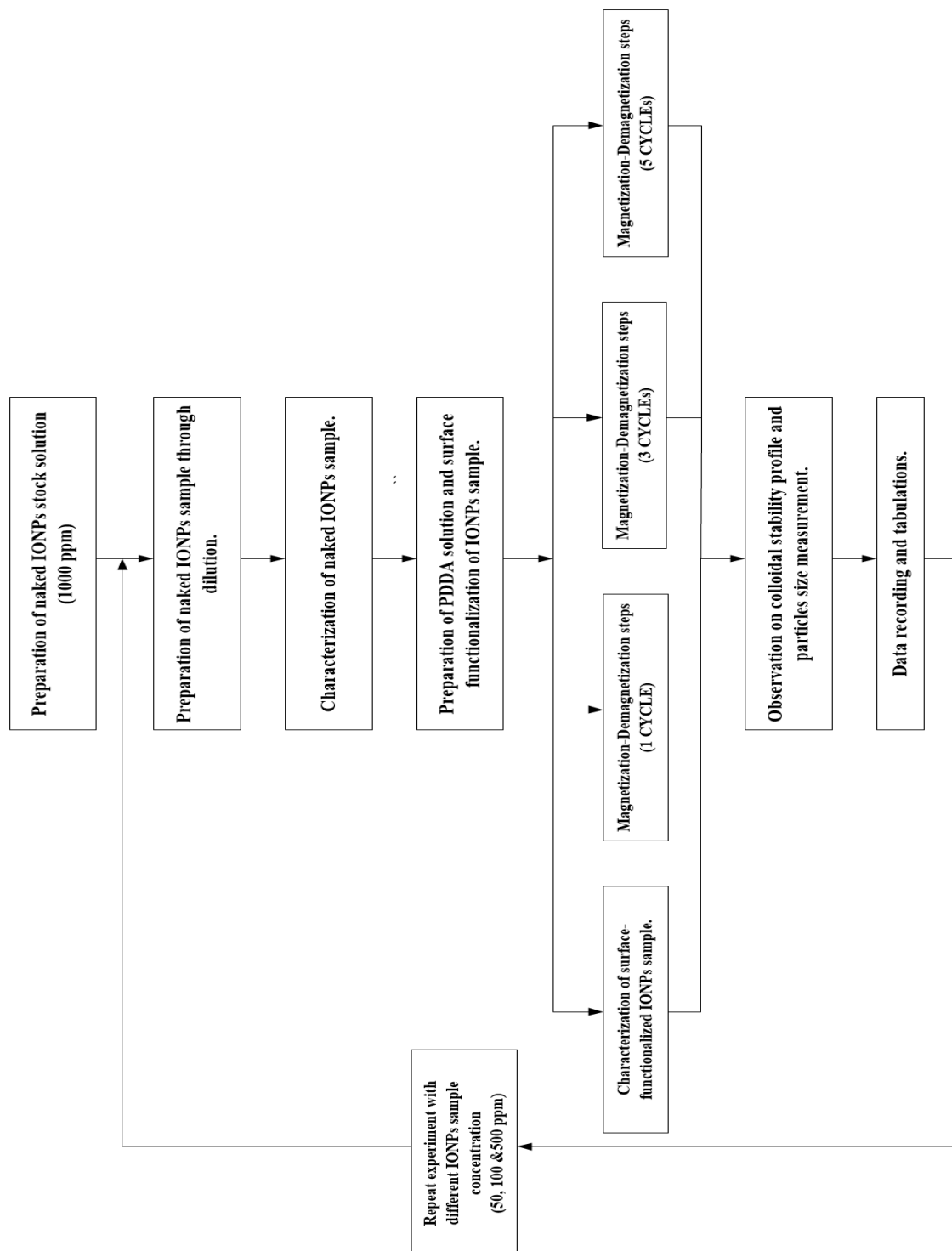


Figure 3.1 Overall Experimental Flowchart

3.2 Chemicals and Materials

Iron (II, III) oxide nanoparticle (IONPs) powders, Fe_3O_4 (APS, 98+% purity, 20-30 nm, MW: 231.53) were obtained from Nanostructured and Amorphous Materials supplier. For functionalization of nanoparticles purposes, low molecular weight (MW: 100,000-200,000) Poly (diallyldimethylammonium chloride) (PDDA) electrolyte were purchased from Sigma-Aldrich (Aldrich Chemistry) supplier. For dissolution, dilution and suspension medium of nanoparticle, deionized water produced from Milli-Q ultra water purification system with 18.2 M Ω cm of resistivity been used throughout the experimental work. Cylindrical permanent magnet which made of neodymium iron boron (NdFeB grade N50) obtained from Ningbo YuXiang E&M Int'l Co been used for magnetization purposes in this experiment.

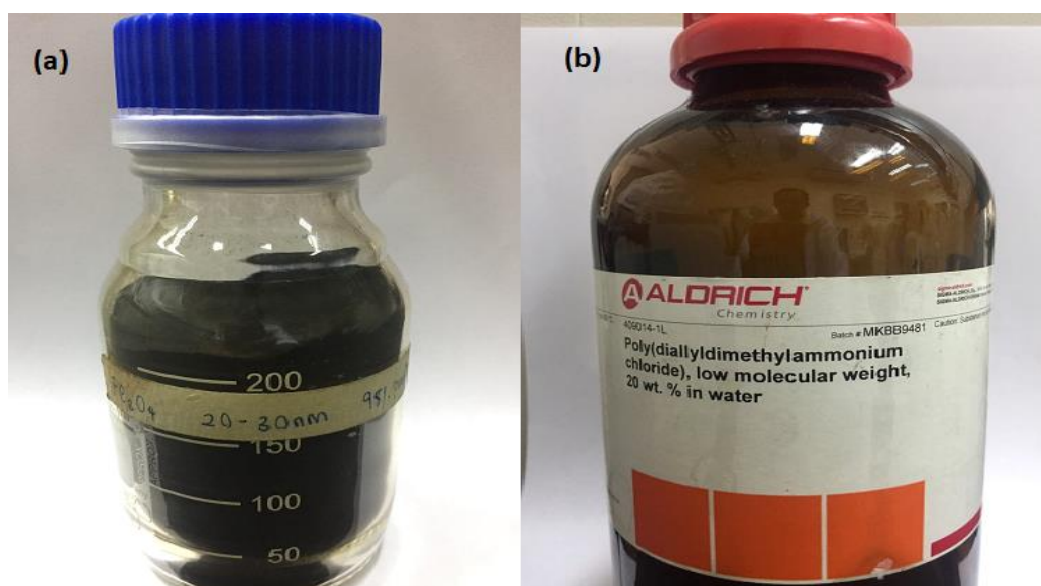


Figure 3.2 Chemicals used (a) Iron Oxide nanoparticles (IONPs) powders and (b) Poly (diallyldimethylammonium chloride) (PDDA) electrolyte.

3.3 Equipment

To complete the experimental work, there were several equipment been used throughout the study. **Table 3.1** below lists all the equipment been used and the purpose of utilizing those equipment.

Table 3.1 List of equipment

Equipment	Brand /Model/Supplier	Function
Water bath sonicator	Fisherbrand (FB 15050)	Sonicate nanoparticles sample and promote dissolution.
Electronic balance	A&D Company Limited (HR-250AZ)	Weighing the nanoparticle powders.
End-to-end rotating mixer	Stuart (SB3)	Promote mixing process.
Centrifuge	Thermo Scientific (Heraeus Megafuge 40)	Separate the nanoparticles from liquid medium.
UV-Vis Spectrophotometer	Agilent Technologies (Cary 60)	Measuring absorbance of the sample.
Zetasizer – Dynamic Light Scattering (DLS)	Malvern Instruments Zetasizer Nano ZS	Measuring zeta potential and hydrodynamic size.
Universal oven	Memmert Model 100-800	Drying up the apparatus.

3.4 Experimental Procedures

3.4.1 Characterization of Naked IONPs

Firstly, 10 mg of IONPs are dissolved into 10 mL of deionized water to produce a stock solution with concentration of 1000 ppm, been sonicated for an hour to ensure a nicely dispersed IONPs suspension throughout the medium. From the stock solution, 40 mL of 100 ppm IONPs solution is prepared as a sample through dilution with deionized water and been sonicated for 10 minutes. From that sample, 10 mL of 10 ppm IONPs solution is prepared through dilution for characterization process of naked IONPs solution. This been done in order to avoid multiple scattering effects and particle interactions. Characterization process was done by Malvern Zetasizer-Dynamic Light Scattering (DLS) equipment to determine the hydrodynamic size, polydispersity index and zeta potential of the naked IONPs sample prepared as showed in **Figure 2.3** from Chapter 2.

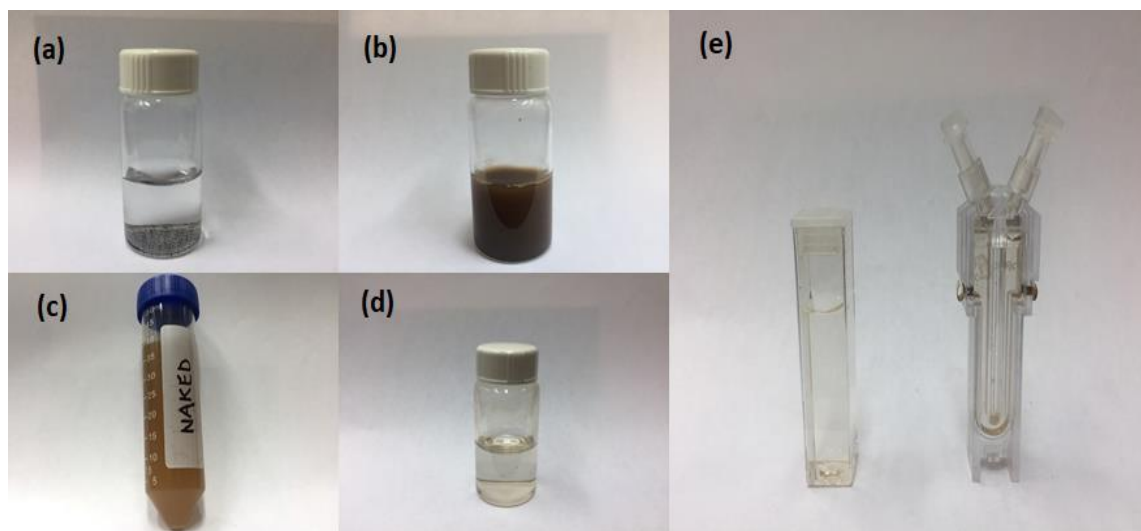


Figure 3.3 Preparation steps of naked IONPs solution (a) stock solution (before sonication), (b) stock solution (after sonication), (c) naked IONPs sample solution, (d) diluted 10 ppm IONPs sample for characterization and (e) sample cuvette (from left to right: hydrodynamic size and zeta potential) for DLS measurement.

3.4.2 Surface Functionalization of IONPs

IONPs are been functionalized by using low molecular weight PDDA electrolytes. Surface functionalization of IONPs purposely to impart electrostatic and extra steric stabilization on IONPs to help limiting the occurrence of particle agglomeration, which at the same time enhances the stability of colloidal suspension. PDDA solution is prepared by adding 5 mL PDDA stock into 30 mL of deionized water, further mixed by using end-to-end rotating mixer at speed of 40 rpm for an hour to ensure complete dissolution of PDDA. Then, 10 mL of 100 ppm IONPs solution from previous naked sample is been added into the PDDA solution prepared and once again been mixed by using end-to-end rotating mixer at speed of 40 rpm for 2 hours to allow complete functionalization of IONPs by PDDA. Later, the complete surface-functionalized IONPs (SF-IONPs) are collected and excess PDDA been discarded. The collected SF-IONPs are redispersed in deionized water and been subjected to centrifugation for 20 minutes at speed of 9900 times gravity. This washing steps been conducted for at least 2 times to ensure a complete removal of all excess PDDA. After finished the washing steps, the SF-IONPs collected been redispersed in 10 mL of deionized to form a final SF-IONPs suspension with concentration of 100 ppm. Repeat the surface functionalization process to form final 30 mL of SF-IONPs sample solution.

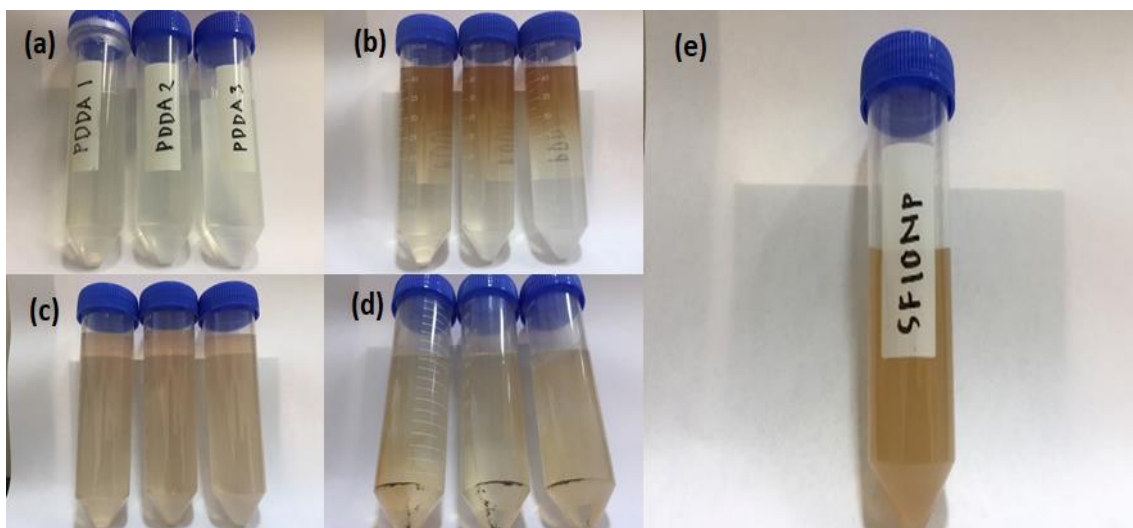


Figure 3.4 Preparation steps of SF-IONPs solution (a) Preparation of PDDA solution, (b) Mixture of naked IONPs sample and PDDA solution (before rotation), (c) Mixture of naked IONPs sample and PDDA solution (after rotation), (d) IONPs sample after washing steps and (e) final 30 mL of SF-IONPs sample solution.



Figure 3.5 Preparation steps of SF-IONPs solution (a) Sonication of IONPs sample by water bath sonicator, (b) Rotation of IONPs sample by end-to-end rotating mixer and (c) Washing steps of IONPs by centrifuge machine.

3.4.3 Characterization of Surface-Functionalized IONPs

From 100 ppm SF-IONPs sample solution, 10 mL of 10 ppm SF-IONPs solution is prepared through dilution for characterization process of SF-IONPs solution. Characterization process was done by Malvern Zetasizer-Dynamic Light Scattering (DLS) equipment to determine the hydrodynamic size, polydispersity index and zeta potential of the SF-IONPs sample prepared as showed in **Figure 2.3** from Chapter 2. This characterization step is to ensure the successful coating of IONPs with PDDA solution.

3.4.4 Repetitive Cycle of Magnetization Step

Next, 3 mL of SF-IONPs suspension was filled in a standard 1x1x4 cm disposable cuvette for magnetization step. The kinetic behaviour of the dispersed particle under magnetization step been recorded by measuring the absorbance to observe the colloidal stability profile of the suspension for 10 minutes using UV-Vis spectrophotometer (Cary 60) at wavelength of 532 nm. Due to this magnetization step, modification has been done on UV-Vis unit by inserting NdFeB permanent magnet and customized magnet holder, as setup shown in **Figure 3.6**. After completing the magnetization process, the magnetic field is removed from the sample which resulting demagnetization of SF-IONPs sample. The sample is been put under sonication again for 10 minutes to redisperse the particles throughout the suspension medium. Then, 10 mL of 10 ppm SF-IONPs is prepared from previous magnetized sample to measure the cluster size formed due to magnetization. The magnetization-demagnetization steps are repeated for at least 5 times to observe the effect of repetitive magnetization on clustering of IONPs and its colloidal stability in suspension. The data collected from this experiment been presented as an average from three independent samples.

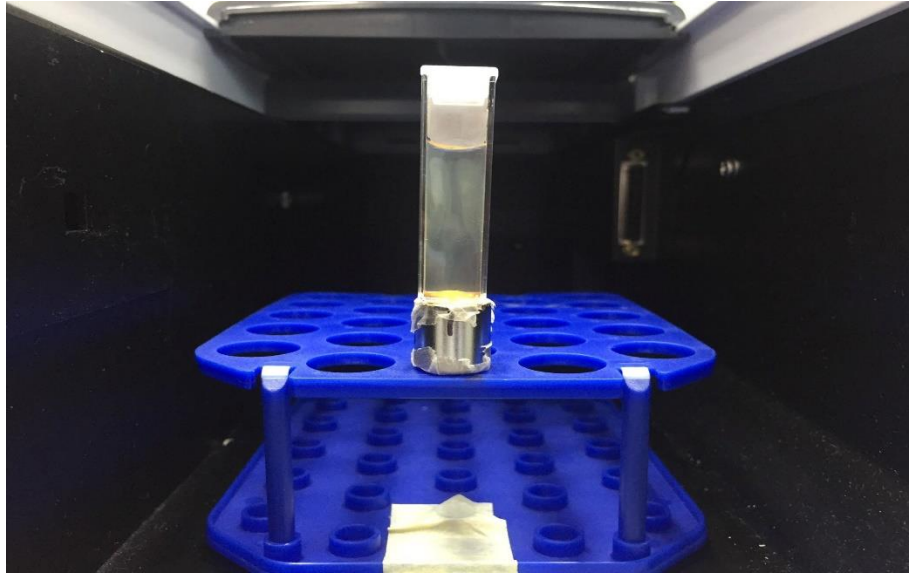


Figure 3.6 Magnetization cycle experimental setup with custom magnet holder.

CHAPTER 4 – RESULTS AND DISCUSSION

4.1 Characterization of Naked IONPs and Surface-Functionalized IONPs

Malvern Zetasizer-DLS equipment been employed to determine the particles size in suspension as well as the zeta potential of the IONPs sample before (naked IONPs) and after the functionalization step (SF-IONPs). The measurement done before and after the functionalization step in order to confirm the successful coating of IONPs particle by PDDA. All characterization steps are conducted by using the samples that been diluted to 10 ppm to avoid multiple scattering effects and particle interactions. As shown in **Figure 4.1** which giving the size distribution for three sets of DLS measurement, it can be observed that the average particle size of naked IONPs was a bit larger compared to SF-IONPs, with 462 nm and 310.87 nm respectively. This happened due to unstable condition of naked IONPs in the suspension that cause the particles to aggregate faster forming the larger particles due to high surface energy properties of IONPs (Ditsch et al., 2005).

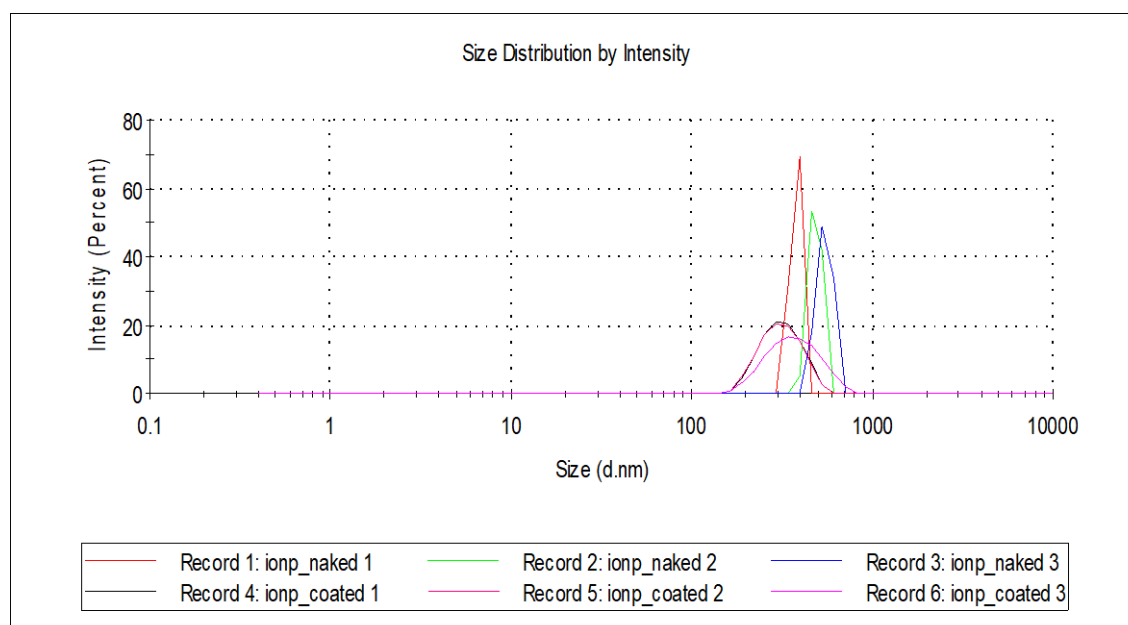


Figure 4.1 DLS size distribution of naked IONPs and SF-IONPs suspension.