INFLUENCES OF FREELY SUSPENDED POLYELECTROLYTE ON AGGREGATION KINETICS OF MAGNETIC NANOPARTICLES

By

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LIST OF ABBREVIATION

Abbreviation	Description
DLVO	Derjaguin-Landau-Verwey-Overbeek
DLCA	Diffusion Limited Cluster Aggregation
RLCA	Reaction Limited Cluster Aggregation
DOM	Dissolved Organic Matter
CCC	Critical Coagulation Concentration
PSS	Poly(sodium-4-styrenesulfonate)
PDDA/PDADMAC	Poly(diallyldimethylammonium chloride)
IONPs	Iron Oxide Nanoparticles
PSS-IONPs	PSS coated iron oxide nanoparticles
PDDA-IONPs	PDDA coated iron oxide nanoparticles
Naked-IONPs	Bare iron oxide nanoparticles
DLS	Dynamic Light Scattering

PENGARUH POLIELEKTROLIT YANG BEBAS TERAMPAI TERHADAP KINETIK PENGGELOMPOKAN NANOPARTIKAL MAGNETIK

ABSTRAK

Kajian ini dilakukan untuk mengkaji pengaruh polielektrolit yang terampai secara bebas terhadap kinetik penggelompokan nanopartikel magnetik bersalut. Nanopartikel pada awalnya dilapisi dengan polimer iaitu poli(sodium-4-styrenesulfonate) (PSS) dan poli(diallyldimethylammonium chloride) (PDDA). Telah dihipotesiskan bahawa interaksi antara daya penipisan and penyambungan elecktrosterik akan memainkan peranan dominan dalam mempengaruhi kestabilan kolloid nanopartikal magnetik bersalut. Kesan daripada polielektrolit yang terampai secara bebas dalam ampaian dikaji pada kepekatan yang berbeza menggunakan spektrofotometer UV-vis dan secara kualitatif melalui perubahan warna ampaian dari masa ke masa.

Melalui kajian ini, diperhatikan bahawa kadar penggelompokan dan kelajuan pemendapan IONP tidak bersalut adalah yang tertinggi pada nilai masing-masing 0.006/min dan 0.0372mm/min. Sementara PSS-IONPs dan PDDA-IONPs mempunyai kadar penggelompokan yang jauh lebih rendah dengan nilai masing-masing 0.0021/min dan 0.0027/min.

Kehadiran polielektrolit bercas sama dalam ampaian nanopartikel bersalut akan menyebabkan kadar penggelompokan yang lebih tinggi dan diperhatikan paling tinggi untuk ampaian 100 ppm PSS-IONPs dalam larutan PSS 100 ppm dan 100 ppm PDDA-IONPs dalam larutan PDDA 150 ppm dengan kadar masing-masing 0.0031/min dan 0.055/min. Selain itu, peningkatan kepekatan polielektrolit dalam ampaian menyebabkan kadar pemendapan kelompok nanopartikel berkurang dan kadar pemendapan terendah yang diperhatikan adalah untuk ampaian 100 ppm PSS-IONPs dalam larutan PSS 100 ppm dan ampaian 100 ppm

PDDA-IONPs dalam larutan 100 ppm PDDA dengan kelajuan pemendapan masing-masing 0.00495mm/min dan 0.0057mm/min. Melalui kajian pengimejan, pada kepekatan polielektrolit yang lebih tinggi, kluster dengan saiz yang dapat dilihat muncul lebih awal sementara kadar pemendapan lebih perlahan.

INFLUENCES OF FREELY SUSPENDED POLYELECTROLYTE ON AGGREGATION KINETICS OF MAGNETIC NANOPARTICLES

ABSTRACT

This study was carried out to find the influences of freely suspended polyelectrolyte on the aggregation kinetic of coated magnetic nanoparticles. The nanoparticles was first coated with a polymer which is poly(sodium-4-styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDDA). It is hypothesized that the interplay between the depletion and electrosteric bridging effects would play a dominance role on influencing the colloidal stability of the coated magnetic nanoparticles. Such effect of having freely suspended polyelectrolyte in the suspension was studied at different concentration using UV-vis-spectrophotometer and qualitatively through colour change of the suspension over time.

Through this study, it was observed that the aggregation rate and settling velocity of the naked IONPs suspension calculated was the highest at the values of 0.006/min and 0.0372mm/min, respectively. While PSS-IONPs and PDDA-IONPs has considerably lower aggregation rate which was 0.0021/min and 0.0027/min, respectively.

The presence of the same charged polyelectrolyte in the suspension of coated nanoparticles will cause higher aggregation rate which was observed highest for the suspension of 100 ppm PSS-IONPs in 100 ppm PSS solution and 100 ppm PDDA-IONPs in 150 ppm PDDA solution with the rate of 0.0031/min and 0.055/min, respectively. Apart from that, the increase of concentration of polyelectrolyte in the suspension causes the sedimentation rate of nanoparticle clusters to decrease and lowest sedimentation rate observed was for suspension of 100 ppm PSS-IONPs in 100 ppm PSS solution and 100 ppm PDDA-IONPs in 100 ppm PDDA solution with the settling velocity of 0.00495mm/min and 0.0057mm/min, respectively. From

imaging study, at higher concentration of polyelectrolyte an observable cluster size appeared earlier while the sedimentation rate slower.

CHAPTER 1 INTRODUCTION

The focus on magnetic nanoparticles nowadays have been increasing due to the possibilities of various uses and applications especially in environmental and biological fields. However, it was reported that magnetic nanoparticles will aggregates in aqueous solution just like other colloid suspensions experience as stated by theory of colloids stability Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. DLVO theory stated that colloids in suspension will undergo agglomeration/aggregation due to Van der Waals forces which is the force that attracts the colloids particles to clump together and steric or electrostatic force repulsion if the surface of the particles are charged or contains polymer sticking out. Furthermore, magnetic nanoparticles are attracted to each other with additional attraction force which is the magnetic force between the particles. Thus, various studies on stabilization of magnetic nanoparticles using polymers was done to increases the possibilities of its usage in everyday life. The colloidal stability of nanoparticles can be increased by adsorbing of surface modifying process of nanoparticles by using electrolyte or charged molecules. This is due to the existence of steric or electrostatic barrier on the surface of the particles which will provide extra repulsion force between the nanoparticles as shown in Figure 1. 1
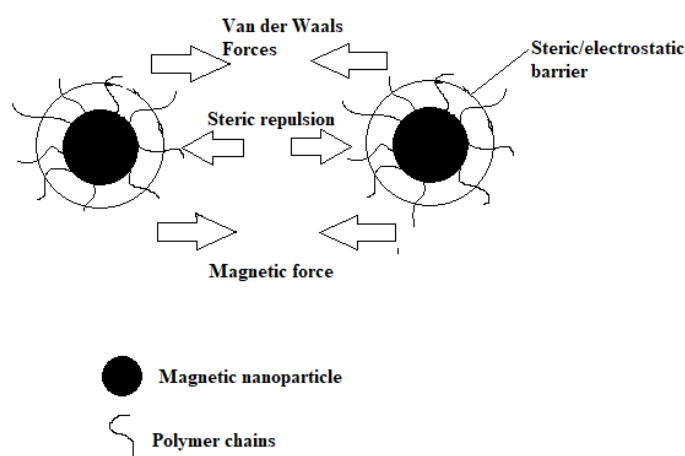
Figure 1. 1 Interaction of stabilised nanoparticles in a suspension

The issues of using polymers or polyelectrolytes to impart electrosteric stabilized properties on the magnetic nanoparticles was identified to cause complexation between the coated nanoparticles and other polyelectrolytes as it can forms bridging flocculation, depletion flocculation or neutralization of surface charge affecting the stabilization of the nanoparticles(Li et al., 2017; Seebergh & Berg, 1996; Tombácz et al., 2016; Yeap & Tia, 2019). This project is carried out to study the effect of polyelectrolytes on the colloidal stability of the magnetic nanoparticles to gain insights of the probable mechanism of aggregation of coated magnetic nanoparticles with polyelectrolytes.

1.1   Background Study

Utilization of magnetic nanoparticles such as ferrites and metal oxides are the most common since they can exhibit superparamagnetic properties in which the magnetization can randomly flips direction under the influence of temperature which is important for their dispersion in aqueous solution (Enriquez-Navas & Garcia-Martin, 2012). Magnetic nanoparticles specifically magnetite have been widely used in biological and environmental fields for the removal of pollutants or heavy metals such as uranium in aqueous solution (Zhu et al., 2018), drug delivery vehicle for brain tumours (Chertok et al., 2008), magnetic resonance imaging (MRI) contrast agents for detection of lymph node (Masoudi et al., 2012), and protein detection (Zhang et al., 2017). However, the application of using magnetic nanoparticles faced challenges due to the nanoparticles undergoing aggregation and sedimentation in suspension due to low colloidal stability.

Aggregation of nanoparticles in aqueous is a commonly found problems since magnetic nanoparticles are readily aggregates in aqueous solution. It is due to the attraction forces which are Lifschitz-van der Waals forces and magnetic forces (Karvelas et al., 2021; Quik et al., 2014) that attracts the nanoparticles together. The categories of fate affecting magnetic nanoparticle

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in environment are 1) transformation which are surface modification, homoaggregation, heteroaggregation and dissolution, and 2) transport processes which are advection and sedimentation. The aggregation of nanoparticles can be classified into two which are homoaggregation and heteroaggregation (Quik et al., 2014). Homoaggregation is the aggregation of nanoparticles with other nanoparticles while heteroaggregation is the aggregation between nanoparticles with natural colloids or other molecules. Mechanism of aggregation of magnetic nanoparticles can be further classified into diffusion limited cluster aggregation (DLCA) and reaction limited cluster aggregation (RLCA). DLCA happens when there are no net repulsive forces acting upon the nanoparticles during aggregation and RLCA happens when there are extra repulsive forces acting on the particles which prevent the nanoparticles from readily aggregates (Vikesland et al., 2016). This phenomena causes issues for further uses of the nanoparticles in other fields due to the unwanted aggregation and sedimentation of nanoparticles in environmental water or biological ecosystem.

Thus, several methods of stabilizing magnetic nanoparticles were carried out to improve the dispersion and stability of magnetic nanoparticle in aqueous solution such as through immobilization or coating of polyelectrolyte onto the surface of the nanoparticles. This method can induce an electrosteric hindrance properties on the nanoparticle surfaces which will prevent the aggregation and sedimentation of the nanoparticle due to the additional repulsive forces acted on the nanoparticles. However, after the surface modification process, the coated nanoparticles are needed to be washed several times to remove polyelectrolyte residues in the suspension(Meng et al., 2013). This is because some recent studies found that the presence of polyelectrolyte in the suspension can induce nanoparticles to undergo depletion flocculation or bridging flocculation which reduces the stability of the nanoparticles (Yeap & Tia, 2019) or having some complexation between nanoparticles and polyelectrolytes(Yan et al., 2014). However, there are not many studies that stress on the influence of remained residue

polyelectrolyte causing the aggregation and sedimentation of magnetic nanoparticle in polyelectrolyte and most of the theories are related to the neutralization of oppositely charged magnetic nanoparticles with polyelectrolyte causing a double layer coating on the surface(Tombácz et al., 2016).

Dispersion flocculation happens when there are too many molecules of polyelectrolyte in the solution that is not adsorbed onto the surface of the nanoparticles and float around freely inside the solution. This phenomena causes the solvent to move from lower concentration zone to higher concentration zone creating a depletion zone between the nanoparticles that draws them together (Abbott, 2017; Jenkins & Snowden, 1996). Bridging flocculation happens when the polyelectrolyte is adsorbed onto the surface of the nanoparticles and a part of the molecules such as the tails are left dangling in the solution causing the tails to form bridges with another nanoparticle (Lu et al., 2005) as shown in Figure 1. 2. Thus, this project is carried out to show the influences of free polyelectrolyte on the aggregation and sedimentation kinetics of the magnetic nanoparticles and compare and discuss the stability of different viscoelastic properties magnetic nanoparticles in the polyelectrolyte.

Bridging Flocculation

Depletion zone

● Nanoparticles

⌒ Polymer Chain/polyelectrolyte
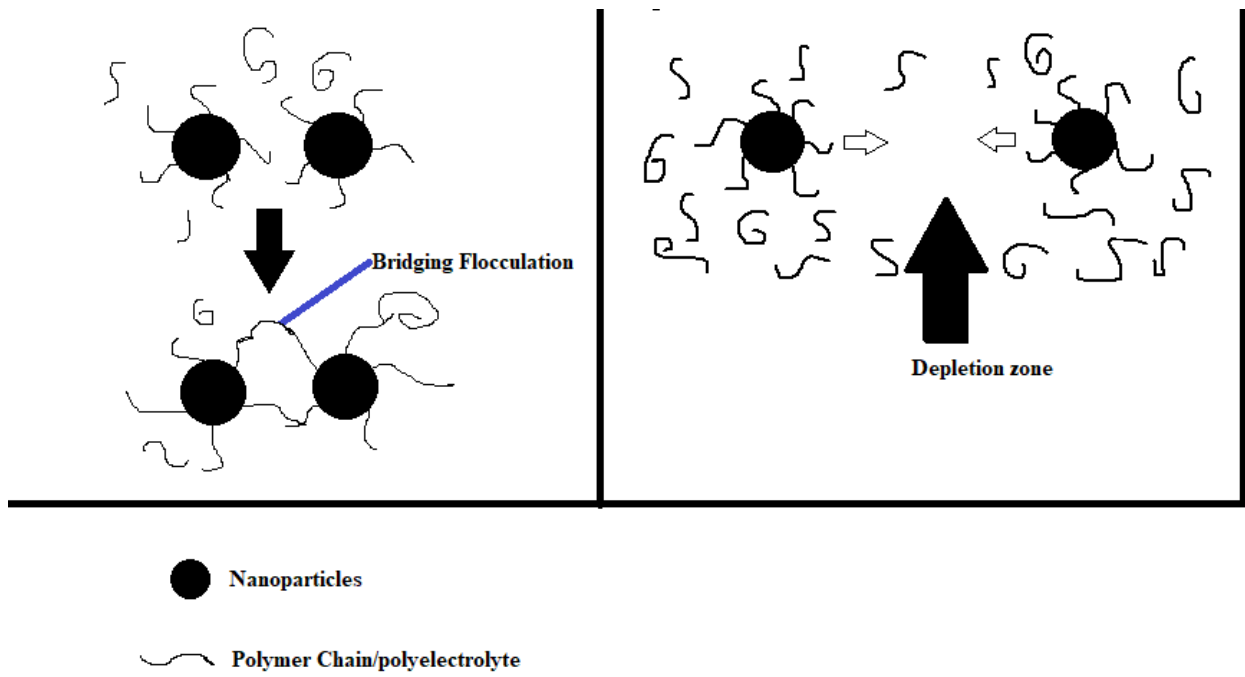
Figure 1. 2 Bridging and Depletion flocculation of nanoparticles

1.2   Problem Statement

Colloidal stability of nanomaterials is crucial for various engineering application. For environmental engineering application is concern, one of the popular strategies is to impart colloidal stability to the nanomaterials by immobilization of anionic polyelectrolyte to the particle's surface. The adsorbed layers of polyelectrolyte introduce electrosteric hindrance to prevent aggregation. However, after the surface modification process the particle suspension need to go through few cycles of washing to remove residue polyelectrolyte, which if remained in the solution, will cause depletion attraction or bridging flocculation between the particles. Here, we would be investigating the influences of free polyelectrolyte on the aggregation/sedimentation kinetics of the magnetic nanoparticles.

1.3   Objectives

1.   To record the kinetic profile of natural sedimentation process of magnetic nanoparticles coated with polyelectrolyte.

2.   To deconvolute the time dependency of aggregation and sedimentation process during magnetic nanoparticle settlement.

CHAPTER 2 LITERATURE REVIEW

Studies of colloid stability of magnetic nanoparticles have been widely carried out through the decades due to the importance of application of this nanoparticles in the future. Colloids suspension theory by Derjaguin-Landau-Verwey-Overbeek found that the suspension of colloids have the ability to agglomerates due to Van-der Waals forces that attracts the particles together(Abbott, 2017). Magnetic nanoparticles also aggregates due to the attraction of magnetic forces between the nanoparticles(Tombácz et al., 2016). Derjaguin and Landau also studied that colloids with polymer coating or ionic coating have electrostatic or steric repulsion force in which can increase the stability of colloids suspension(Churaev, 1999).

Quik et al. (2014) studied the colloidal stability of magnetic nanoparticles in environment water through numerical methods. The authors stated that sedimentation by homoaggregation is observed to be negligible at low concentration of magnetic nanoparticles and homoaggregation of ENPs in environment does not play in the environment due to stabilising effect of DOM. Increasing the concentration of DOM(dissolved organic matter) can cause the decrease in sedimentation rate thus proving that the heteroaggregation of magnetic nanoparticles with the DOM plays a significant role in the sedimentation of the magnetic nanoparticles.

Thus, stabilisation of magnetic nanoparticles through surface modification was carried out. Hajdú et al. (2009) studied the effect of stabilising the magnetic nanoparticles using humic acid and citric acid. The critical coagulation concentration which is the minimum concentration for aggregation of magnetic nanoparticles in solution containing NaCl was recorded. The results are shown in Figure 2. 1.

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Stabilizer	Amount added (mmol/g)	Electrophoretic mobility ($\times 10^{-8}$ m²/V s)	CCC (mM)
Magnetite pH ~6	–	2.65	25
Citrate pH ~6	0.65	−2.61	40
			60
	1.5	−2.85	80
	4.5		90
Humic acid pH ~4	0.08	0.833	7
	0.16	−1.795	20
	1.64	−2.669	220

Figure 2. 1 Critical coagulation concentration of the coated nanoparticles for each polymer as specified (Hajdú et al., 2009).

The results showed that humic acid have higher CCC in NaCl solution which showed that the stability of the humic acid coated magnetic nanoparticles are higher due to the steric or electrostatic repulsion by the coating.

A study by Vikesland *et al.* (2016) on the aggregation and sedimentation of TMAOH and NaOH coated magnetite in presence of electrolyte at different salt concentration showed the aggregation of magnetic nanoparticles in low salt concentration is slower compared to high salt concentration. Vikesland *et al.* (2016) stated that at high salt concentration, the aggregation is limited by diffusion limited cluster aggregation due to the effect of diminished electrostatic repulsive barrier.

2.1 Interaction Of Coated Magnetic Nanoparticles Suspension With Polyelectrolyte

The study of interaction of magnetic nanoparticles in polymer or polyelectrolyte is important to understand the effect of polyelectrolyte to the colloidal stability of magnetic nanoparticle suspension. Li et al. (2017) studied the interaction of poly(acrylic acid) coated maghemite with cationic homopolyelectrolyte such as poly(diallyldimethylammonium chloride) (PDADMAC) and poly(ethyleneimine) (PEI) in the suspension by direct mixing the stock solution with the nanoparticle suspension and the result was observed under TEM and

DLS equipment. It was reported that by direct mixing the oppositely charged coated nanoparticles and homopolyelectrolyte, the suspension immediately undergo dispersion due to electrostatic repulsion, after a certain amount of time, the particles form large aggregates due to complexation which forms salt bridges with the polyelectrolyte. Further increase of concentration of polyelectrolyte causes the nanoparticles to form larger aggregates and forms coral like structure, while in the presence of external magnetic field, the aggregates form a cylindrical structure.

Apart from that, Yan et al. (2014) also studied the same concept by direct mixing of poly(trimethylammonium ethyl acrylate)-b-poly(acrylamide) copolymer with poly (acrylic acid) coated magnetic nanoparticles. The authors reported that the aggregation undergo slow aggregation or complexation, and the hydrodynamic size of the aggregates experience a sharp maximum at isoelectric point. The authors suggested that adding polyion causes neutralization on the surface of nanoparticles which showed increase of hydrodynamic size and the size experience maximum when the overall charge of polyion and magnetic nanoparticle is equal, the excess polyion is then adsorbed onto the surface of magnetic nanoparticle which gives charges to the nanoparticles and reduced the size of aggregates and restabilized the suspension due to the presence of electrostatic repulsion.

Golas et al. (2010) studied the stabilisation of magnetic nanoparticles using polymer stabilizers and then redispersing the coated nanoparticles with the excess of polymer on the surface of nanoparticles. The authors first synthesized the coated nanoparticles through ATRP method, the adsorption of the polymer onto the magnetic nanoparticles surface are then calculated and the excess of polymer was determined. During the absorption process of polymer onto nanoparticles, the authors reported that a rapid sedimentation of the nanoparticles was observed. The authors suggested that this is due to the depletion attraction by unadsorbed polyelectrolytes in the solution.

Safi et al. (2010) studied the interaction of citrate coated nanoparticles with 3T3 fibroblast cell medium, it was reported that the authors observed a steep increase of hydrodynamic size of the coated nanoparticles in the medium, this is due to the destabilisation of the coated nanoparticles by the cell medium.

Furthermore, Demirelli et al. (2021) studied the effect of influence of polycation competition on the aggregation threshold of the coated magnetic nanoparticles. The magnetic nanoparticles was coated with poly (acrylic acid) and then added with polycation solution. The authors observed that in salt free aqueous solution, the coated nanoparticles, the aggregate size increased until at isoelectric point which is $Z=1$ and hydrodynamic size is lower at other point due to the dispersion of magnetic nanoparticles.

Other than that, Dong & Lo. (2013) studied the effect of humic acid on the stabilised magnetic nanoparticles, the humic acid interaction showed different results with different types of coating. Starch coated nanoparticles in humic acid containing water shows an increase of hydrodynamic size of aggregates which showed the humic acid either adsorbed to the magnetic nanoparticle surface or the humic acid forms bridges between the coated nanoparticles which causes the increase of aggregates size. While PAA modified nanoparticles and Tween modified nanoparticles showed a lower degree of aggregation due to the stabilisation because of the electrostatic force.

2.2   Sedimentation Profiles Of Coated Magnetic Nanoparticles In Polyelectrolyte Containing Solution.

The sedimentation of coated magnetic nanoparticles in polymer or polyelectrolyte have been studied by many researchers to study the influence of polyelectrolyte on the sedimentation of magnetic nanoparticles. Among studies that have been carried out is the study of the sedimentation of coated magnetic nanoparticles in the presence of polyelectrolyte by Yeap &

Tia (2019). The authors studied the sedimentation of poly (sodium-4-styrenesulfonate) coated magnetite in the suspension with presence of poly(diallyldimethylamonium chloride) (PDDA) and another suspension containing surfactant poly (sodium-4-styrenesulfonate) (PSS). The sedimentation profile of the coated magnetic nanoparticles in the solutions are as shown in Figure 2. 2 and Figure 2. 3.
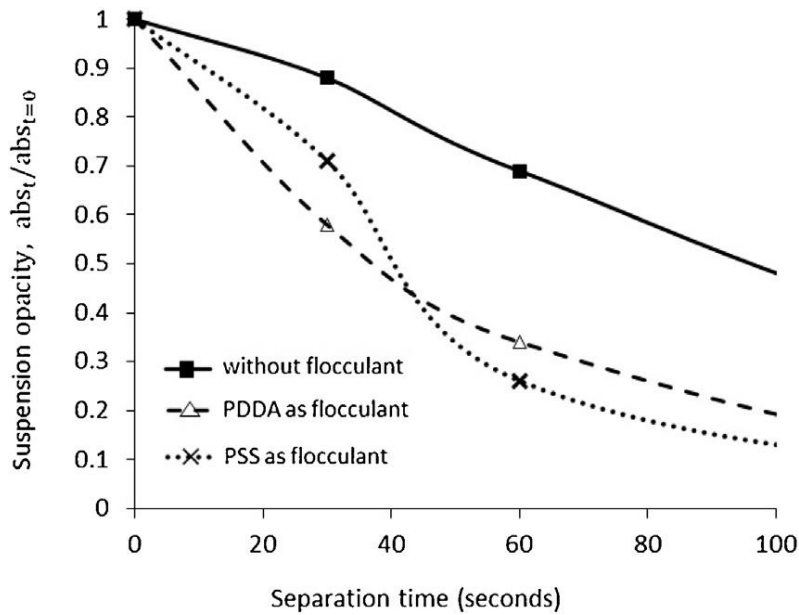

Figure 2. 2 The sedimentation profile of PSS coated magnetite in flocculant at 100 s of time as specified (Yeap & Tia, 2019)
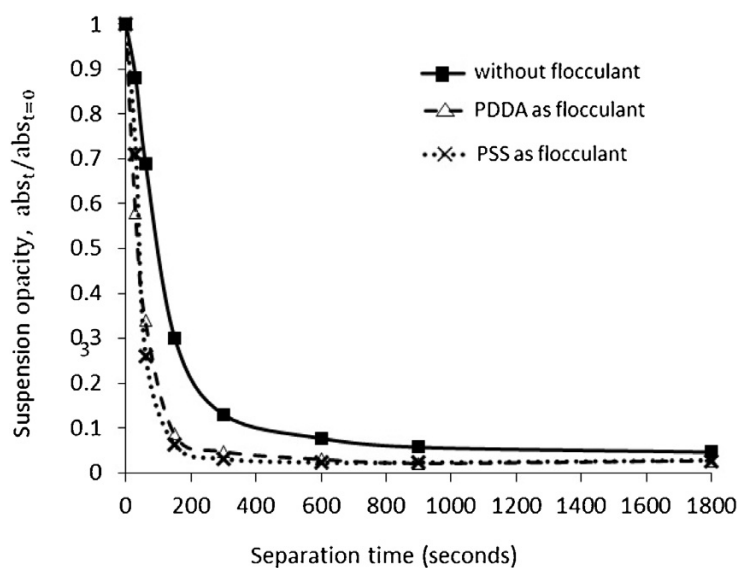

Figure 2. 3 The sedimentation profile of coated magnetite in polyelectrolyte as specified in(Yeap & Tia, 2019)

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From the sedimentation profile of the coated magnetite in polyelectrolytes, it was observed that the sedimentation of PSS-NP is the slowest when there are no flocculant added and the sedimentation of the nanoparticles in the flocculant is significantly faster. For PDDA flocculant, PDDA flocculant has oppositely charged polyelectrolyte which can cause ionic bridging flocculation to occur between the nanoparticles and causes the hydrodynamic size of the aggregates to be bigger compared to other suspension. The resuspension of the aggregates showed that the aggregate of PDDA flocculant added suspension is irreversible due to the ionic bridging between the nanoparticles. While PSS flocculant showed slower sedimentation compared to PDDA flocculant but faster compared to when there are no flocculant added to the suspension. The authors stated that it was due to the depletion flocculation occurred during the sedimentation of magnetic nanoparticle which causes the depletion force to cause the aggregation of magnetic nanoparticles happened faster.

Another study of the sedimentation of coated magnetic nanoparticles in polymer which is mineral oil was carried out by Du et al. (2020). The magnetic nanoparticle was first coated with carbon layer and then the sedimentation of the coated magnetic nanoparticles in mineral oil was studied by the authors. The sedimentation profile of the process is shown in Figure 2. 4.
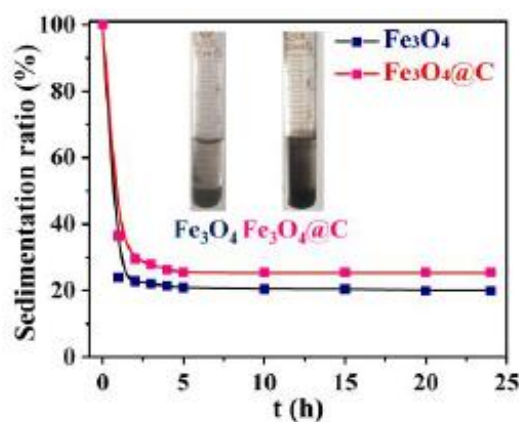

Figure 2. 4 The sedimentation profile of coated and uncoated magnetic nanoparticles in mineral oil as (Du et al., 2020).

From the graph of sedimentation of carbon coated magnetic nanoparticle in mineral oil, the sedimentation ratio of coated magnetic nanoparticles showed lower sedimentation ratio compared to uncoated magnetite. This is due to the density mismatch of the magnetic nanoparticle and mineral oil and due to the wettability of the coated magnetic nanoparticles due to the porosity of the nanoparticle which increases the permeability of the particles.

CHAPTER 3 METHODOLOGY

This chapter encloses the methods used in this study of the effects of freely suspended polyelectrolytes on the aggregation kinetics of coated magnetic nanoparticles.

3.1   Overview of Research Methodology

This final year project focuses on the effect of freely suspended polyelectrolyte on the aggregation kinetics of the natural sedimentation of coated magnetic nanoparticle of the same polyelectrolyte. The experiment was designed to study the aggregation and sedimentation kinetic of coated magnetic nanoparticles with freely suspended polyelectrolyte using UV-vis-spectrophotometer and through recording of sedimentation of the said suspension by qualitatively observe the color change of the suspension. The effect of polyelectrolyte to the formation of aggregation, aggregation and sedimentation rate and settling velocity was calculated and discussed. The progress throughout the research is shown in the Figure 3. 1.
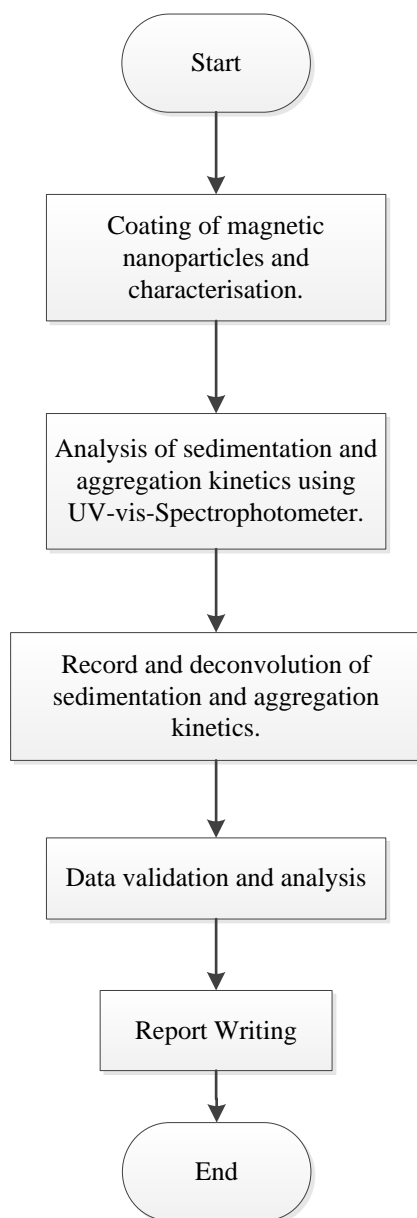
```mermaid
flowchart TD
    Start --> Coating
    Coating --> Analysis
    Analysis --> Record
    Record --> Data
    Data --> Report
    Report --> End
```

Start

Coating of magnetic nanoparticles and characterisation.

Analysis of sedimentation and aggregation kinetics using UV-vis-Spectrophotometer.

Record and deconvolution of sedimentation and aggregation kinetics.

Data validation and analysis

Report Writing

End

Figure 3. 1 Flow diagram throughout the research of the final year project.

3.2   Coating of Magnetic Nanoparticles and Characterization

The magnetic nanoparticles was coated with two types of polymer which are poly(sodium-4-styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDDA). Firstly, bare magnetic nanoparticles was obtained from Sigma Aldrich Malaysia. Then, 100 ppm of 50 ml magnetic nanoparticles was sonicated for 30 min to get a well dispersed suspension. Meanwhile, a solution of PSS was prepared by dispersing 0.548 g of PSS into 50 ml of deionised water while sonicating until homogenous. Then, the solution is let sonicated for 30 mins. Meanwhile, the pH of the bare nanoparticle suspension was adjusted to pH of 3.52. Then, the bare magnetic nanoparticle suspension was added to the PSS solution in a dropwise manner while sonicating. Then, the resulting suspension was rotate overnight. After rotating overnight, the resulting suspension (PSS-IONPs) was washed three times by centrifuging the solution at 10000x for 20 mins, then pouring supernatant, readding deionised water and sonicating for 10 min and repeating for three times. The resulting coated nanoparticles (PSS-IONPs) is then redispersed into 50 ml of deionised water. The same step was repeated for PDDA while using 0.641 g of PDDA and pH of the bare magnetic nanoparticles was adjusted to pH of 10.

The naked and coated magnetic nanoparticles was characterized using Malvern-Zetasizer dynamic light scattering (DLS) machine. The table below shows the characteristics of the nanoparticles.

Table 3. 1 Hydrodynamic sizes and zeta potential obtained from DLS-Malvern Zetasizer

Nanoparticle Type	Hydrodynamic Size (nm)	Zetapotential (mV)
Naked-IONPs	1276.33	-33.83
PSS-IONPs	1526.65	-55.26
PDDA-IONPs	1520.73	+62.47

3.3   Kinetic Study of the Magnetic Nanoparticles Suspension with Polyelectrolyte

The kinetic study of the sedimentation and aggregation of magnetic nanoparticles was carried out by using UV-vis-spectrophotometer. Briefly, 3 ml of 100 ppm naked-IONPs was prepared and inserted into a cuvette and sonicated for 2 min. Then, the cuvette is inserted into a space in UV-vis-spectrophotometer and the kinetic study of the absorbance over time of the suspension was recorded over 300 min of time span. The same step was repeated for 100 ppm PSS-IONPs and 100 ppm PDDA-IONPs. To study the effect of polyelectrolyte on the kinetics of the magnetic nanoparticles, 1.5 ml of 200 ppm PSS-IONPs was added to a 1.5 ml of 100 ppm, 200 ppm and 300 ppm of PSS solution to obtain a suspension of 100 ppm PSS-IONPs 50 ppm, 100 ppm PSS-IONPs 100 ppm, 100 ppm PSS-IONPs 150 ppm PSS solution. The sample is then inserted into a cuvette and the same step as the naked-IONPs was repeated. The same was repeated for PDDA-IONPs while adding it into PDDA solution.

From the data obtained, the graph can be divided into three section which are aggregation, sedimentation 1 and sedimentation 2 as was done by Ng et al (2020). From the slope of the graph of each section, the rate of each phase can be obtained. The settling velocity of the suspension clusters can be calculated by multiplying the sedimentation length with the slope which in this case the sedimentation length is the relevant length scale of the spectrophotometer beam which is 1.5 mm(Agilent Technologies Inc, 2019).

3.4   Deconvolution of Sedimentation and Aggregation Kinetics of Magnetic Nanoparticles.

Samples as the same section above was prepared in a 3 ml cuvette. Then, the suspension was sonicated for 2 min. The suspension was then located under a bright place and recording of the sedimentation of the suspension was obtained for a time span of 2 hours. The change of color of the suspension was observed and discussed.

CHAPTER 4 RESULTS AND DISCUSSIONS

4.1   Kinetic Profile of Natural Sedimentation of Magnetic Nanoparticles

Kinetic profile of natural sedimentation of magnetic nanoparticles was recorded using UV-vis spectrophotometer.

4.1.1   Role of Coating on the Kinetic Study of Magnetic Nanoparticles

The experiment was carried out by first coating the magnetic nanoparticles with two types of polymer which are poly(sodium-4-styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDDA). The PSS coated magnetic nanoparticles will be referred as PSS-IONPs while PDDA coated magnetic nanoparticles will be referred as PDDA-IONPs from this point on. Then, the PSS-IONPs, PDDA-IONPs and Naked magnetic nanoparticles(Naked IONPs) was dispersed in deionised water at room temperature at pH 7 in a cuvette. The suspensions are then sonicated for 2 minutes and then the kinetic studies are observed through UV-vis-spectrophotometer and the data was recorded. The results are as shown below in Figure 4.1. 1.
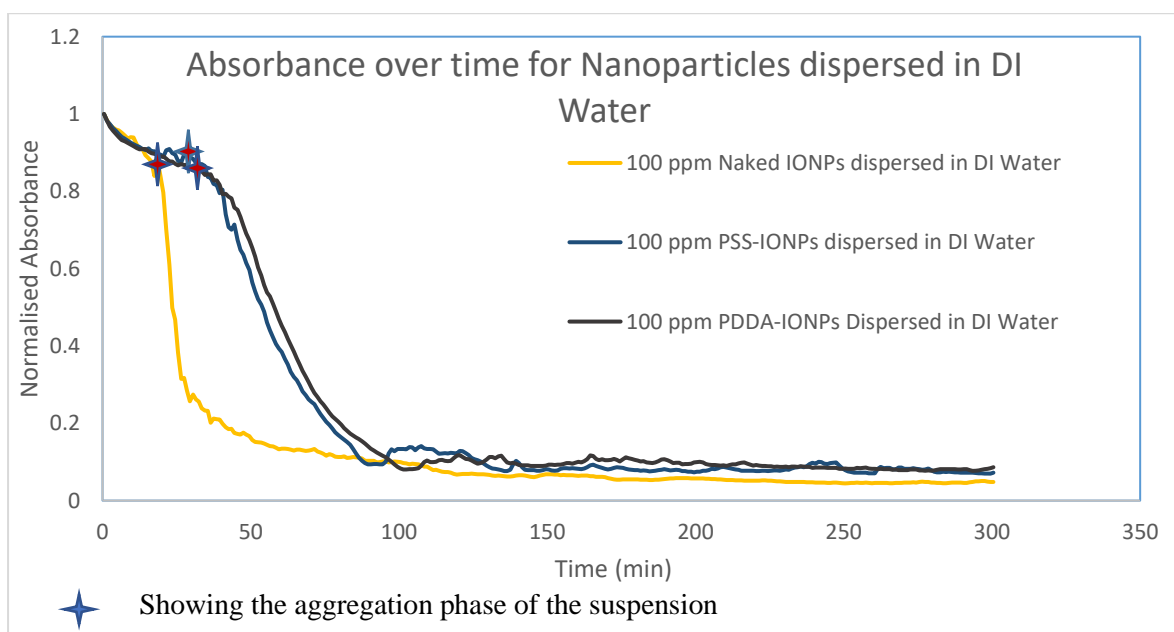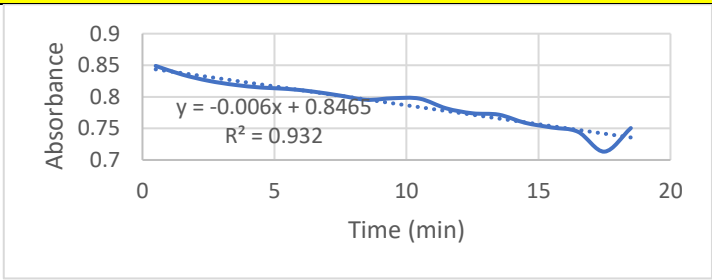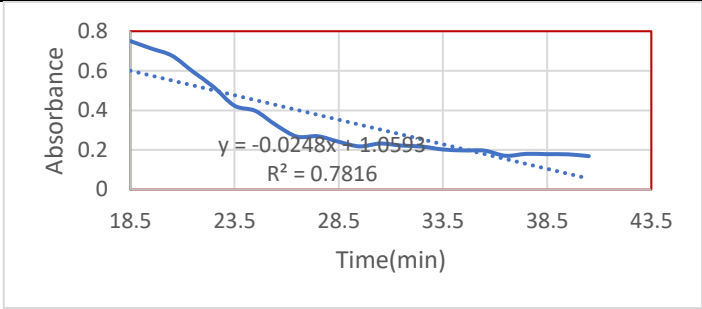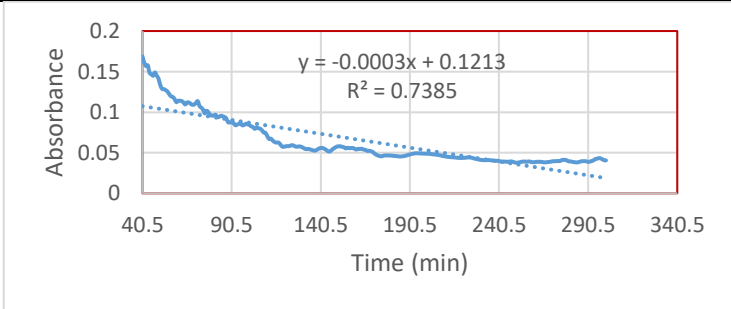

Figure 4.1. 1 The kinetic study of various nanoparticle suspension dispersed in DI water

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The kinetic study gives a graph of change of absorbance of the suspension with time. From the graph, we can obtain the rate of aggregation and sedimentation also the velocity which can be calculated by multiplying the slope of the section and the length scale (Ng et al., 2020), l_B which in this case is the relevant length scale of the spectrophotometer beam which is 1.5 mm(Agilent Technologies Inc, 2019). The graphs can be further divided into three stages, aggregation, sedimentation 1 and sedimentation 2 as tabulated below.

Table 4.1. 1 Sections of the graphs for each suspension and calculated values of settling velocity

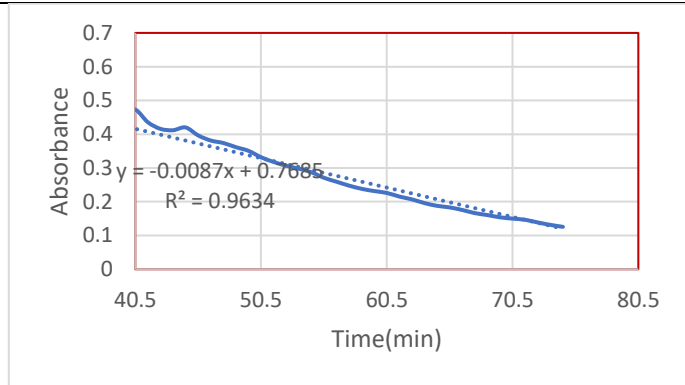| 100 ppm Naked IONPs in DI Water	
Aggregation	 Slope : 0.006/min
Sedimentation 1	 Slope : 0.0248/min Settling Velocity : 0.0372 mm/min
Sedimentation 2	 Slope : 0.0003/min Settling Velocity : 0.00045mm/min
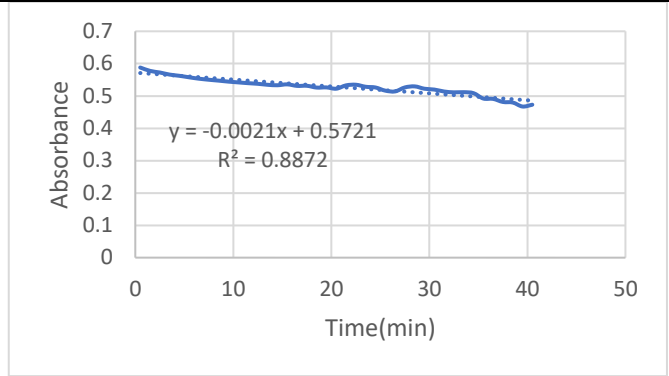
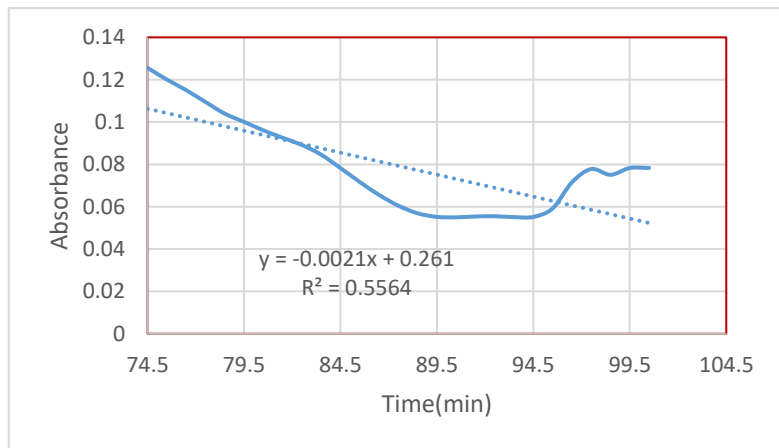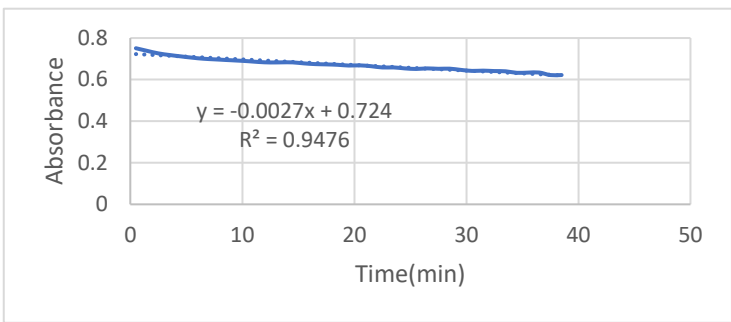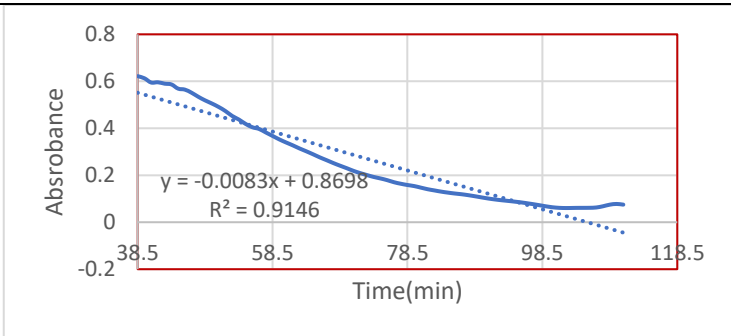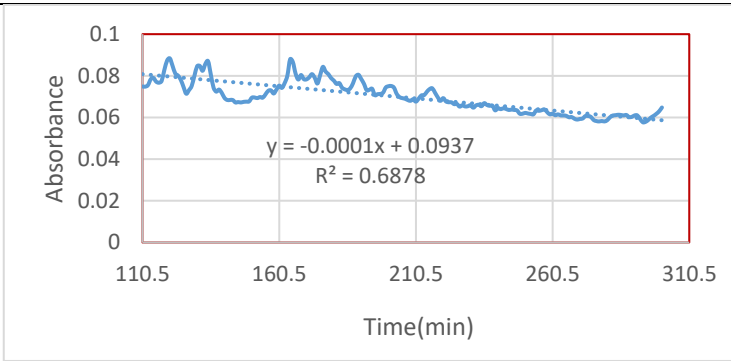| 100 ppm PSS-IONPs in DI Water	
Aggregation	Slope : 0.0021/min
Sedimentation 1	Slope : 0.0087/min Settling Velocity : 0.01305mm/min
Sedimentation 2	Slope : 0.0021/min Settling velocity : 0.00315mm/min

100 ppm PDDA-IONPs in DI Water	
Aggregation	 Slope : 0.0027/min
Sedimentation 1	 Slope : 0.0083/min Settling Velocity : 0.01245mm/min
Sedimentation 2	 Slope : 0.0001/min Settling Velocity : 0.00015 mm/min

From Table 4.1. 1 it was observed that naked IONPs suspension have highest aggregation rate and sedimentation rate which with values of 0.006/min and 0.0248/min. The settling velocity of the naked IONPs suspension calculated was the highest 0.0372mm/min. Compared to naked IONPs, PSS-IONPs and PDDA-IONPs has considerably lower aggregation rate which was 0.0021/min and 0.0027/min, respectively. This is due to coating of

nanoparticles provides charges on the surface of the nanoparticles which provide electrosteric repulsive forces between each of the coated nanoparticles. Electrosteric repulsive forces provides a forces which repulse the attractive forces of the nanoparticles which are magnetic dipole-dipole forces and Van der Waals forces thus causing lesser and smaller aggregates formed (Marimón-Bolívar & González, 2018; Yeap et al., 2012). Apart from that, the sedimentation rate settling velocity of the coated nanoparticles are lower compared to the naked IONPs, due to lesser and smaller aggregates formed, the energy needed to settle to the bottom is higher. Marimón-Bolívar (2018) studied the effect of coating Fe nanoparticles with glutathione and observed that its stability in water medium is higher compared to naked Fe nanoparticles is due to the steric repulsions of the carboxyl, amine and thiol groups on the surface of the material.

From the table above, it was observed that the aggregation rate and sedimentation rate of the PSS-IONPs suspension is lower compared to PDDA-IONPs suspension even though PDDA-IONPs have smaller hydrodynamic size and higher ionic strength and PSS have bigger molecular weight compared to PDDA. This results showed opposite of the results obtained by Yeap (2012) which the aggregation rate of 1000k PSS compared to 70k PSS was observed to be lower due to the polymers with higher molecular weight have longer chain thus causing an increase in the particles collision and improved the occurrence of bridging between the coated nanoparticles.

4.1.2   Effect of Freely Suspended Polyelectrolyte on the Aggregation Kinetics of the Coated Nanoparticles.

The Experiment for this section of the result was carried out in the same manner as the above section by solution of suspension with PSS solution with different concentration (50 ppm, 100 ppm and 150 ppm) for PSS-IONPs suspension while PDDA-IONPs suspensions was

carried out with solutions of PDDA polymer with concentration of 50 ppm, 100 ppm and 150 ppm. The results obtained are recorded and plotted as shown below.
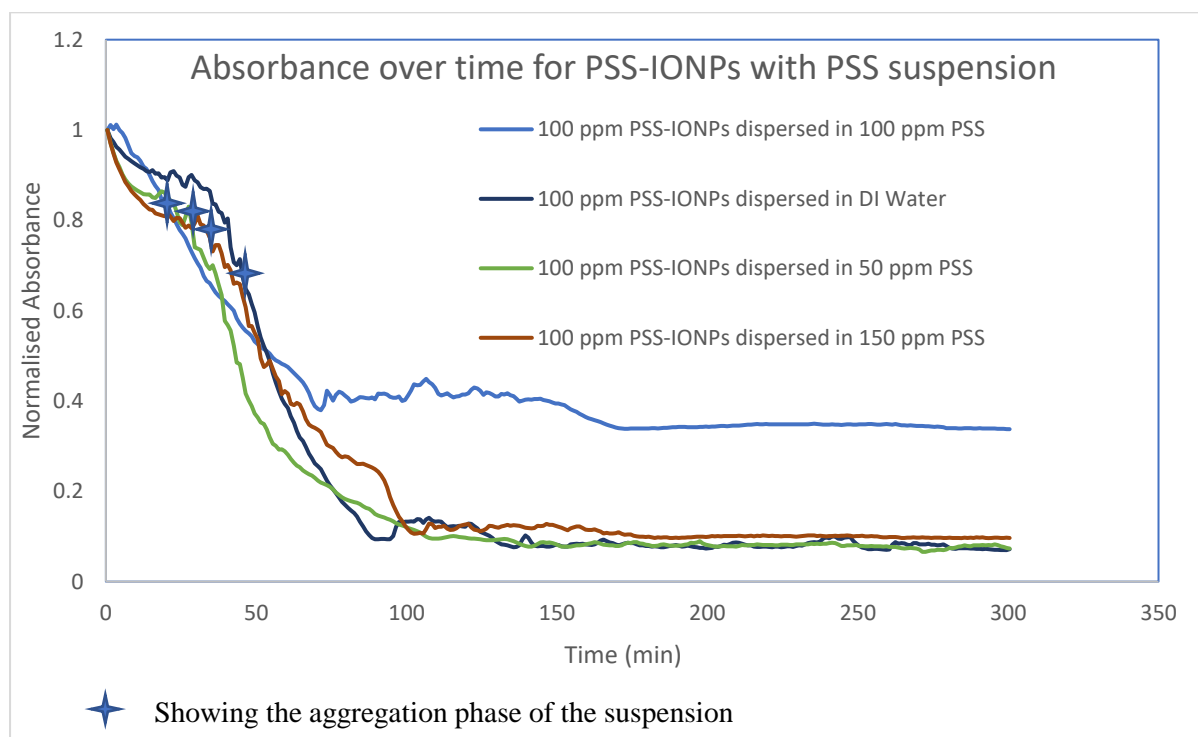

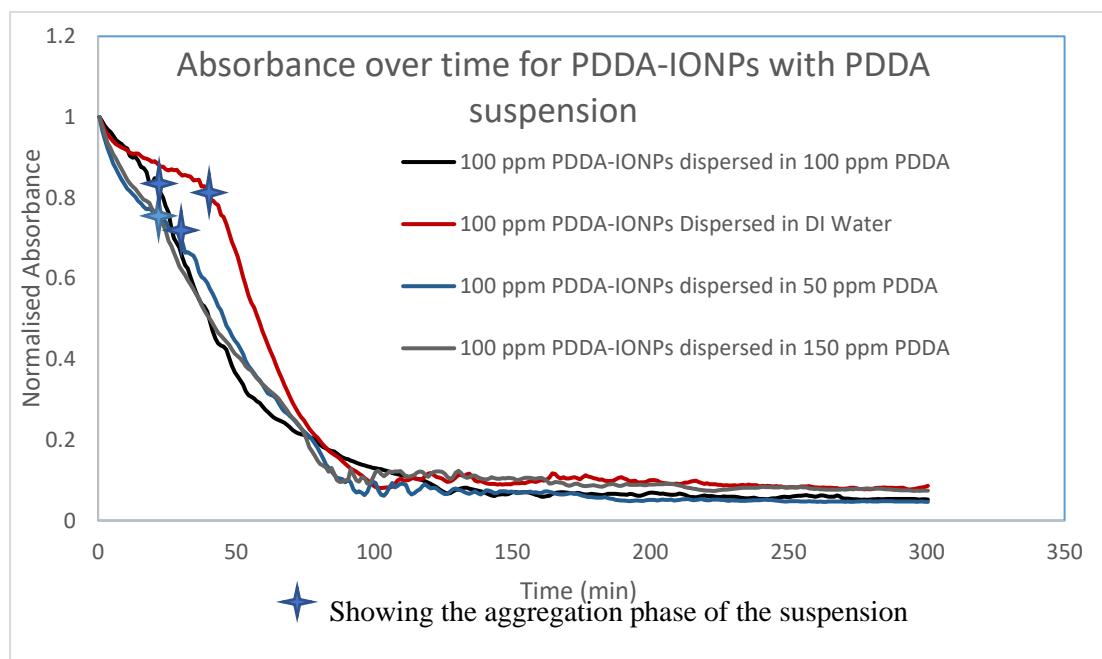Figure 4.1. 2 Kinetic Study of the PSS-IONPs in PSS suspension with varying concentrations

Figure 4.1. 3 Kinetic Study of the PDDA-IONPs in PDDA suspension with varying concentrations

The stages of each graph are tabulated as shown below.

Table 4.1. 2 Sections of the graphs for each suspension of PSS-IONPs in PSS solution with various concentration

100 ppm PSS-IONPs in DI Water	
Aggregation	$y = -0.0021x + 0.5721$ $R^2 = 0.8872$
Sedimentation 1	$y = -0.0087x + 0.7685$ $R^2 = 0.9634$
Sedimentation 2	$y = -0.0021x + 0.261$ $R^2 = 0.5564$

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