MAGNETOPHORESIS INDUCED HYDRODYNAMIC FLOW OF NON-NEWTONIAN FLUID

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MAGNETOPHORESIS INDUCED HYDRODYNAMIC FLOW OF NON-NEWTONIAN FLUID

by

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LIST OF ABBREVIATIONS

MNPs	Magnetic Nanoparticles
HGMS	High-Gradient Magnetic Separation
LGMS	Low-Gradient Magnetic Separation
DLVO	Derjaguin–Landau–Verwey–Overbeek Theory
PEG	Polyethylene Glycol
PVP	Polyvinylpyrrolidone
PEO	Polyethylene Oxide
PAA	Polyacrylamide
MB	Methylene Blue
NdFeB	N-50-Graded Neodymium Boron Ferrite Permanent Magnet
DLS	Dynamic Light Scattering
RPM	Rotation Per Minute
PDI	Polydispersity Index

LIST OF SYMBOLS

Symbol	Description	Unit
B	Magnetic flux density	T
B_r	Remanent magnetic flux density	T
c	MNPs concentration	kg/m^3
D	Diffusivity of MNPs	m^2/s
f_m	Volumetric magnetic force on MNPs solution	N/m^3
g	Acceleration due to gravity	m/s^2
h	Height of cylindrical magnet	m
η	Dynamic viscosity of fluid	N.s/m^2
J	MNPs outlet flux	m^{-2} s^{-1}
k	Rate constant of separation kinetic profile	min^{-1}
k_B	Boltzmann's constant	J/K
Lc	Characteristic length	m
M	Volumetric magnetization of MNPs solution	A/m
m	Molarity of solution	moles/L

p	Pressure	N/m^2
N	Number of MNPs	-
N*	Aggregation parameter	-
ρ	Density of MNPs solution	kg/m^3
R_h	MNPs hydrodynamic radius	m
r	Radius of cylindrical magnet	m
T	Temperature	K
u	Magnetophoretic velocity of MNPs	m/s
V	Volume of solution	m^3
V_s	Volume of MNPs solution	m^3
v	Kinematic viscosity of fluid	m^2/s

Magnetophoresis Menyebabkan Kesan Hidrodinamik dalam Bendalir Bukan Newtonian

ABSTRAK

Terdapat beberapa teknik pemisahan bagi campuran heterogen boleh digunakan untuk memisahkan campuran kepada komponen individu. Sebagai contoh, pengemparan, penapisan dan juga penjerapan. Penjerapan adalah kaedah yang lebih berkesan dan kos efektif berbanding dengan teknik pemisahan yang lain. Pemisahan magnetik dengan menggunakan nanopartikel magnetik adalah satu daripada kaedah penjerapan dan semakin popular berbanding teknik penjerapan yang lain. Walau bagaimanapun, apabila saiz bahan yang terlibat dikurangkan kepada saiz nano, tingkah laku zarah dari segi aliran, pencampuran dan fenomena lain akan berbeza dengan bahan makroskopik. Ini membawa kepada sebab untuk menganalisis dan menyiasat kelakuan nanopartikel dan interaksi yang terlibat apabila nanopartikel berada di dalam medium cecair. Pemisahan magnet dengan medan magnet yang kecerunan rendah telah digunakan untuk mengkaji aliran hidrodinamik zarah apabila parameter pengagregatan ditetapkan pada bawah perpaduan. Fokus utama dalam kajian ini adalah kesan hidrodinamik dalam cecair bukan Newtonian. Nombor Grashof magnet yang telah dikira untuk larutan nanopartikel magnet dalam cecair Newtonian adalah lebih besar daripada dalam cecair bukan Newtonian. Ini menunjukkan bahawa keapungan magnet dan juga perolakan bendalir dalam cecair Newtonian lebih ketara berbanding dengan yang dalam cecair bukan Newtonian.

MAGNETOPHORESIS INDUCED HYDRODYNAMIC FLOW OF NON-NEWTONIAN FLUID

ABSTRACT

For heterogeneous mixture, there are some separation techniques can be used to separate the mixture into individual component. For example, centrifugation, filtration and also adsorption. Adsorption is the most efficient and cost effective methods compared to other separation techniques. Magnetic separation by using magnetic nanoparticles is one of the adsorption methods and is gaining more popularity among other techniques. However, when the size of the materials involved are reduced to nano size, the particles behavior in terms of flow, mixing and other phenomena will be different with macroscopic materials. This makes the reason to analyze and investigate the nanoparticles behavior and the interaction involved when the nanoparticles are inside the fluid medium. Low gradient magnetic separation is used to investigate the hydrodynamic flow of the particles when the aggregation parameter is fixed at below unity. The main focus in this research is the hydrodynamic effect in non-Newtonian. The magnetic Grashof number calculated for MNPs solution in Newtonian fluid is greater than in non-Newtonian fluid. This indicates that the magnetic buoyancy and also the fluid convection in Newtonian fluid significant is more significant than that in non- Newtonian fluid.

CHAPTER 1: INTRODUCTION

1.1 Introduction

The magnetic nanoparticles (MNPs) are often used to separate targeting compounds in the presence of externally applied magnetic field. The process where motion of MNPs relative to the surrounding fluid is controlled by the magnetic field is known as magnetophoresis (Pshenichnikov and Ivanov, 2012). Due to the importance and the vast application of the MNPs, the understanding of transport behavior of MNPs in the solution is crucial to enhance the use of MNPs. Magnetic cooperation effect and hydrodynamic effect are the 2 factors that will affect the separation rate by using MNPs. In this project, the main interest here is the hydrodynamic effect of MNPs in Non-Newtonian fluid, so that comparison can be made with the finding about this effect in Newtonian fluid.

1.2 Problem Statement

It is an indisputable fact that handling nanomaterial is a challenging yet difficult task. Therefore, nanomaterial often used with a fluid medium, either is air or aqueous medium. When the nanomaterial is present in a surrounding fluid, there are theory lies behind the interaction between the nanoparticles and also between the nanoparticles and medium. The effect that present between the nanoparticles and aqueous medium are the hydrodynamic effect in which the interaction between the nanoparticles is not significant. Since the size of the nanomaterial is in nano scale, the slight movement of the fluid or the nanoparticles inside the fluid will have major influence on the flow of the nanoparticles. As the important hydrodynamic effect is not yet well-establish and often being neglected, it could be tough to understand the detailed theory lies behind and thus the prediction of the flow of nanoparticles in fluid medium may often deviate from the actual observation. Leong has managed to prove the hydrodynamic effect when the magnetic nanoparticles in the water medium (Leong et al., 2015). For current study is to address the difference when the nanoparticles is in a non-Newtonian fluid medium instead of water.

1.3 Objectives

a) To demonstrate the generation of hydrodynamic flow in non-Newtonian fluid.
b) To confirm the particle concentration effect on initiating convective current in non-Newtonian fluid.
c) To probe the kinetic of convective current generated by magnetophoresis.

1.4 Hypothesis

The viscosity of the fluid around the magnetic nanoparticles will slow down the particles movement and the fluid convection of the particles. This will eventually slow down the homogeneity of the dye throughout the MNPs solution. The higher the particle concentration, the more magnetic nanoparticles will be attracted to the magnet, the faster the convective current present in the fluid.

CHAPTER 2: LITERATURE REVIEW

Magnetic separation can be divided into two types, which is high-gradient magnetic separation (HGMS) and low-gradient magnetic separation (LGMS). HGMS is a conventional magnetophoresis driven technology for removing the magnetic particles by attaining a large magnetophoretic force on the particles to overcome the randomization energy and opposing force(s). Conventionally, a packed bed of magnetically susceptible wires with diameter of about 50 µm in an electromagnet is usually used in creating the high magnetic field gradient required (Moeser et al., 2004). The same gradient magnetic separation could also be achieved from the distortion of the magnetic field generated by the magnetizable packing materials in a packed bed column. The generated magnetic field gradient by the methods mentioned is very intense and localized (Leong et al., 2017). However, these HGMS methods could be inappropriate in applying MNPs in some field such as biomedical applications. This is because the human body will not be able to sustain the heat dissipated due to the Joule effect during the use of high gradient magnetic field (Mariani et al., 2010).

LGMS is a recent found separation method by Yavuz et al (2006) where a permanent magnet with a magnetic flux density gradient of $\bigtriangledown B < 100\ Tm^{-1}$ is used to generate a low gradient magnetic field and collect superparamagnetic magnetite nanocrystal of 4 nm. The particle motion is controlled by an external applied magnetic field which is created by the placement of a permanent magnet outside the MNPs solution (Yavuz et al., 2006).

For LGMS, Vincent Schaller et al (2008) has proven that in order to accelerate the MNPs particle separation in LGMS, the magnetic cooperative effect or so-called reversible aggregation (De Las Cuevas et al., 2008) and hydrodynamic effect (Leong et al., 2015) are two important enhancement factors (Schaller et al., 2008). The magnetic cooperative effect will happen when the particle concentration is high enough and interparticle magnetic dipole-dipole interaction of close distance contact is greater than the thermal energy based on the dipole coupling constant, λ (Andreu et al., 2011, Schaller et al., 2008). This effect will then cause formation of chainlike particle aggregates aligned with the externally applied magnetic field (Schaller et al., 2008). Then, the aggregates of different sizes will follow a deterministic drift of different speed in the direction of the magnetic gradient. During the magnetic separation, aggregates will collide each other and eventually making longer and thicker aggregates (Faraudo and Camacho, 2010).

Since the typical colloidal superparamagnetic particles used in magnetophoresis applications are microspheres stabilized electrostatically, so Faraudo and Camacho (2010) introduce magnetic interaction into classical Derjaguin–Landau–Verwey–Overbeek (DVLO) theory (Fendler, 1996) to study the interaction between the particles (Faraudo and Camacho, 2010). In DLVO theory, the colloidal stability is determined by the balance between Van der Waals attraction and double-layer repulsion which increase exponentially with decreasing distance. Hamaker constant can be used to estimate the attraction force.

On the other hand, hydrodynamic effect is the interaction between MNPs and surrounding fluid due to momentum transfer through the collision between MNPs and the fluid (Leong et al., 2015). Lesser number of discussion of hydrodynamic effect compared to magnetic cooperative effect has been done. However, the interaction between the particles and surrounding is indeed crucial since most of the application involve controlling the motion of magnetic particle in suspended fluid and has significant effect during the separation of magnetic particles suspended in the fluid. Therefore, the interest in this project are to study the interaction between particles in terms of hydrodynamic effect. In order to study the hydrodynamic effect only, aggregation parameter, N* should be smaller than unity, which represents negligible reversible aggregation and also the significant magnetic interaction between MNPs and fluid (Andreu et al., 2011).

The presence of low magnetic field from the external applied magnet will create fluid convection. The convective flow in the magnetophoresis of a MNPs solution occurs when the MNPs tend to be attracted towards the region with higher magnetic flux density. At the portion near to the magnet, the MNPs are being collected magnetically causing the concentration of the MNPs is temporary reduced. Thus the volumetric magnetization of that portion of the solution is relatively lower compared to that of the portion which is further away from the magnet. Then, the MNPs solution with greater volumetric magnetization is driven closer to the magnet due to the magnetic buoyancy force to replace the portion of MNPs solution with lower volumetric magnetization. The fluid convection is the contribution to mixing process and continuous homogenization of MNPs suspension. This convective current that is induced during magnetophoresis will improve the efficiency of low gradient magnetic separation (LGMS) (Leong et al., 2015).

Fluid convection also cause homogeneity throughout the MNPs solution or the instantaneous migration of dye inside MNPs solution. When MNPs are travelling in a surrounding fluid with a different viscosity compared to the MNPs, a velocity gradient is present in the solution, the hydrodynamic interaction between the MNPs and fluid will cause the non-magnetically responsive surrounding fluid to gain momentum from the magnetic force that is acting upon the MNPs suspended in the solution under an external magnetic field, then only the fluid convection under magnetophoresis will occur (Leong et al., 2015).

The concentration of MNPs and magnetic field gradient will influence the convective flow and eventually the time taken for the dye homogenization. The higher the concentration, the faster the homogenization rate. Besides, motion of the particles is due to the fluid convective motion when low magnetic gradient, mostly due to the effect of the direct magnetophoretic force causing greater the magnetic field gradient (Leong et al., 2017).

The magnetic buoyancy mentioned is the force exerted on an object that is immersed in a fluid which has higher volumetric magnetization compared to the object itself in the presence of magnetic field applied externally (Henjes, 1993). Magnetic buoyancy in magnetophoresis is similar with the natural convection in heat transfer. Therefore, Grashof number, Gr, which is a dimensionless number used to represent the ratio of the buoyancy force to viscous force in a natural convective flow system, is analogous to magnetic buoyancy number, Gr_m. Magnetic Grashof number is a ratio of magnetic buoyancy force to viscous force, and is shown in the following equation:

$$\mathrm{Gr_m} = \frac{\nabla B(\frac{\partial M}{\partial c})_H (c_s - c_\infty) L_c^3}{\rho v^2} \tag{2.1}$$

Where M is magnetization per unit mass of MNPs solution, c is concentration of MNPs solution, c_s is MNPs concentration of the surface adjacent to the magnet, c_∞ is bulk MNPs concentration, L_c is the characteristic length, ρ is density of MNPs solution and v is the kinematic viscosity of the fluid (Holman, 1986).

When Gr_m is greater than unity, the magnetophoresis induced convection is significant. However, if magnetic nanoparticles are applied in a non-Newtonian fluid medium, such as blood, the theory or observations might differ with the findings from the study done by Leong et als (2015) because the MNPs solution used is in a Newtonian fluid (Leong et al., 2015). A non-Newtonian fluid is a fluid, which the dynamic viscosity varies with the ratio of shear stress to rate of shear, at constant temperature and pressure. The hypothesis can be made is that magnetic Grashof number is smaller when the viscous force is greater. This means that the convective motion of the MNPs in more viscous polymer solution will be slower compared to in water (Newtonian fluid).

The reasons to investigate the hydrodynamic flow in non-Newtonian fluid is because MNPs is now evolving into various kind of field, especially biomedical field. There is a lot of fluids or mediums other than water are involved in biomedical application (Gupta and Gupta, 2005) (Pankhurst et al., 2003). The major interest are focus on the human blood medium. As discuss at the beginning of the literature review, magnetic nanoparticles are able to play an important role in treating chronic diseases in more effective manner compared to the latest medical technology available now. This fruitful achievements had been encouraging enough to merit further investigation in controlling the movement of MNPs in interested fluid medium. Investigation into manipulation of the magnetic nanoparticles are launched by the researchers actively in a bid to establish explicit theory behind the transport behavior of the magnetic nanoparticles. This will definitely help in better controlling the magnetic nanoparticles if used inside human body. Again, the hydrodynamic flow has always been overlooked but this profound effect is in fact worth to be further discussed.

Chapter 3: MATERIALS AND METHODOLOGY

3.1 Materials

The materials required for this project are mainly synthetic polymer, deionized water, MNPs solution, dye and a magnet. This project involve non-Newtonian fluid which can be made by synthetic polymer powder. The polymer should not have any charges to avoid any further interaction between the polymer particles with the magnetic nanoparticles that will alter the coating on the MNPs and also the hydrodynamic size of the MNPs. The synthetic polymer powders that can be used are polyethylene glycol (PEG), polyvinylpyrrolidone (PVP), polyethylene oxide (PEO) and polyacrylamide (PAA) solutions (Lu et al., 2017). Polyethylene glycol (PEG) is used in this project. As for the deionized water used is come from the Milli-Q ultra water purification system. This system has 18.2 MΩ of resistivity.

The concentrated MNPs solution can be bought from Ocean Nanotech, which consists of aqueous suspension of iron oxide nanoparticles coated with polyethylene glycol (PEG). The size of the MNPs bought is 30 nm and in the concentration of 1 g/L. Concentrated methylene blue (MB) of 3000 mg/L is used as the dye for visually tracing the fluid motion in the solution during magnetophoresis. The usage of any other chemical compounds with colour are definitely appropriate to be used as long as the zeta potential of the dye is considered during the interaction between the MNPs and the visual effect observed is clear and easy to be recorded. A syringe is used to insert the dye into the surface of the polymer solution containing desired amount of the magnetic nanoparticles.

A cylindrical N-50-graded neodymium boron ferrite (NdFeB) permanent magnet with remanent magnetization of 1.45T is also needed to induce active manipulation of the magnetic nanoparticle. The NdFeB magnet was obtained from Ningbo YuXiang E&M Int'l Co, Ltd. A low remanent magnetization magnet is used due to mentioned benefits in literature review section compared to the high gradient magnetic separation produced by high remanent magnetization magnet. The magnet with mentioned remanent magnetization is fixed in the project, to allow us compare the result fairly with the previous work done by Sim Seong Leong (Leong et al., 2015).

3.2 Equipment

A digital camera also prepared to capture the dye tracing throughout the experiment. Besides that, Brookfield DV-III Ultra Programmable Rheometer / Viscometer (LV Model) is needed for us to carry out the calibration of the viscosity of the polymer solution. The viscosity of a series of polymer solution are measured to identify and decide the appropriate viscosity of the polymer solution to be used throughout my experiment. Dynamic light scattering (DLS) (Malvern Instrument Zetasizer ZS) is also used to determine the hydrodynamic size of MNPs.

3.3 Experimental Procedure

3.3.1 Overall Procedure

The overall experimental procedure is shown in the figure below:

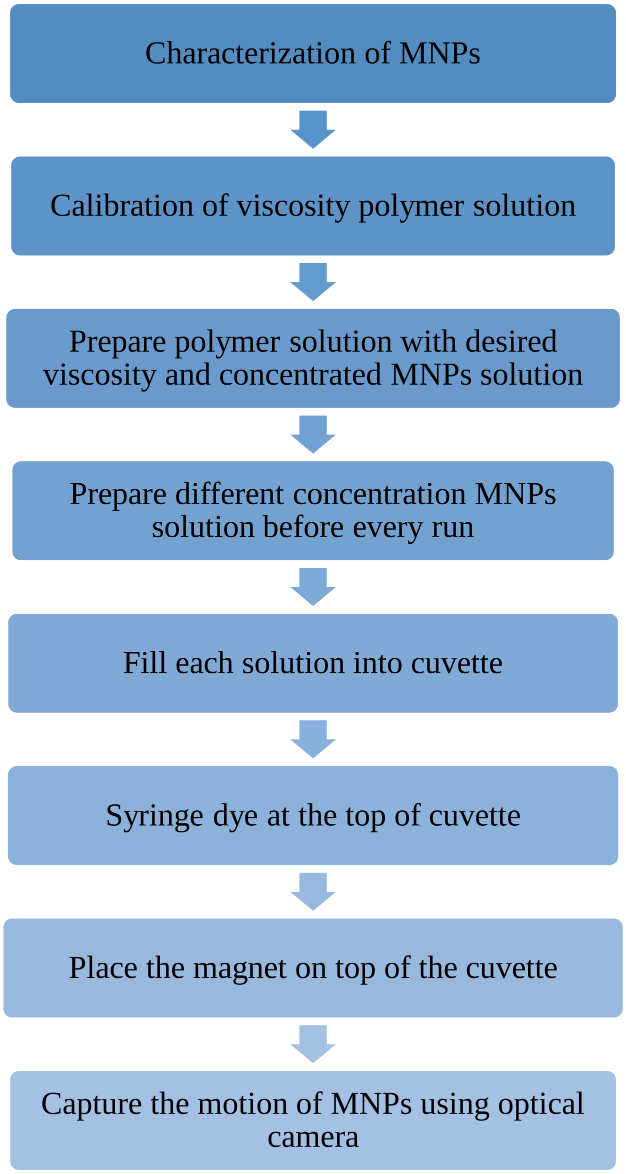


Figure 3.1 Schematic flow diagrams of overall experimental procedure

3.3.2 Characterization of MNPs

Hydrodynamic size of MNPs

MNPs solution was first diluted to 10 mg/L to reduce the effects of multiple scattering and particle interaction. Dynamic light scattering (DLS) (Malvern Instrument Zetasizer ZS) is also used to determine the hydrodynamic size of MNPs. The particles in the sample move randomly due to Brownian motion. When there is light beam passing through this sample, reflection, refraction and diffraction of light will happen. When the light is scattered around, a detector at an angle of 173˚ to the incident light will detect and measure the light intensity scattered. A graph of intensity of the scattered light detected vs time will be plotted and will be fitted into the correlation function. The correlation function is analyzed by using cumulants method to obtain the translational diffusivity, D of the MNPs suspended in a solution (Lim et al., 2013). After that, hydrodynamic size of the particles can be obtained from the Stokes-Einstein equation (Lim et al., 2010) after substituting the diffusive coefficient. MNPs by assuming all the MNPs are spherical in shape (Lim et al., 2013).

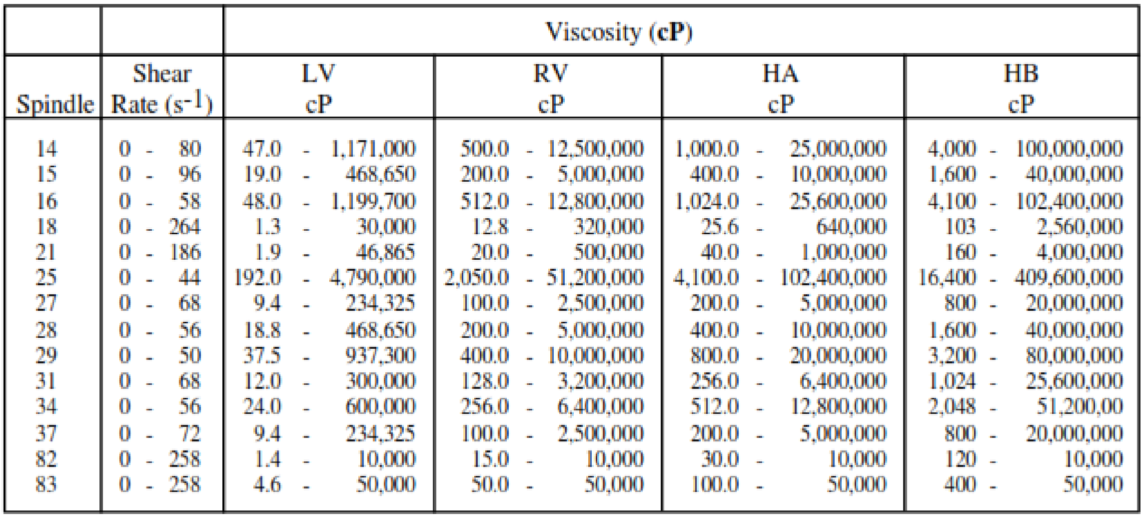
$$D = \frac{k_B T}{6\pi\eta R_h} \tag{3.1}$$

Where k_B is Boltzmann constant, T is absolute temperature, η is the dynamic viscosity of fluid and R_h is the hydrodynamic radius of the MNPs.

3.3.3 Calibration of the polymer solution

The polyethylene glycol (PEG) polymer powder with the molecular weight of 10000 g/gmol is used. If a lower molecular weight polymer is used, the amount needed to reach high desired concentration will be a lot more and it is not advisable. When producing high concentration polymer solution, the high quantity of polymer will be difficult to dissolve in the deionized water. After that, a 500,000 ppm of PEG polymer solution is prepared in a volumetric flask. About 15 mL of the solution is taken for the viscosity measurement. Spindle 21 and 70 rotation per minute (RPM) are the setting on the viscometer used to measure the viscosity. The choice of the RPM is because the spindle tend to shake when 80 and above RPM is applied, and in order to avoid any influence on the spindle rotation, the RPM between the ranges of 60 to 80 RPM should be chosen. For the model LV viscometer, the viscosity range for the series of the polymer involved is fall on the spindle 18 (AMETEK.Inc., 2017). However, due to lack of equipment, spindle 21 is chosen.

Table 1 Selection of spindle based on viscosity range (AMETEK.Inc., 2017)



		Viscosity (cP)			
Spindle	Shear Rate (s^{-1})	LV cP	RV cP	HA cP	HB cP
14	0 - 80	47.0 - 1,171,000	500.0 - 12,500,000	1,000.0 - 25,000,000	4,000 - 100,000,000
15	0 - 96	19.0 - 468,650	200.0 - 5,000,000	400.0 - 10,000,000	1,600 - 40,000,000
16	0 - 58	48.0 - 1,199,700	512.0 - 12,800,000	1,024.0 - 25,600,000	4,100 - 102,400,000
18	0 - 264	1.3 - 30,000	12.8 - 320,000	25.6 - 640,000	103 - 2,560,000
21	0 - 186	1.9 - 46,865	20.0 - 500,000	40.0 - 1,000,000	160 - 4,000,000
25	0 - 44	192.0 - 4,790,000	2,050.0 - 51,200,000	4,100.0 - 102,400,000	16,400 - 409,600,000
27	0 - 68	9.4 - 234,325	100.0 - 2,500,000	200.0 - 5,000,000	800 - 20,000,000
28	0 - 56	18.8 - 468,650	200.0 - 5,000,000	400.0 - 10,000,000	1,600 - 40,000,000
29	0 - 50	37.5 - 937,300	400.0 - 10,000,000	800.0 - 20,000,000	3,200 - 80,000,000
31	0 - 68	12.0 - 300,000	128.0 - 3,200,000	256.0 - 6,400,000	1,024 - 25,600,000
34	0 - 56	24.0 - 600,000	256.0 - 6,400,000	512.0 - 12,800,000	2,048 - 51,200,00
37	0 - 72	9.4 - 234,325	100.0 - 2,500,000	200.0 - 5,000,000	800 - 20,000,000
82	0 - 258	1.4 - 10,000	15.0 - 10,000	30.0 - 10,000	120 - 10,000
83	0 - 258	4.6 - 50,000	50.0 - 50,000	100.0 - 50,000	400 - 50,000

After setting up, the polymer solution taken is filled into the sample container of the viscometer until the solution cover the spindle. The parameters measured is then recorded.

The viscometer used is capable of measuring both viscosity and shear stress at fixed shear rate. The selected spindle will be hanged with the spindle body inside the sample container. Then, the sample solution is poured inside the container until the spindle is immersed entirely in the solution. The spindle is drove through a calibrated spring. By using the spring deflection which is measured with a rotary transducer, the viscous drag of the fluid against the spindle can be measured. Parameters such as the rotational speed of the spindle, the size and shape of the spindle and the full scale torque of the calibrated spring will affect the measuring range (AMETEK.Inc., 2017).

The next step is the dilution step. Once the desired molarity and the volume for the diluted solution is decided, the required volume of the concentrated solution can be calculated by using the equation:

$$m_1 V_1 = m_2 V_2, \tag{3.2}$$

Where m_1 is molarity of the concentrated solution, V_1 is volume of the concentrated solution, m_2 is the desired molarity of the dilute solution, and V2 is the desired volume of the dilute solution. (Quansys Biosciences, 2018)

After taking the required amount of the concentrated solution, deionized water is added to the desired volume of the dilute solution. The viscosity and the shear stress of the new concentration are measured by using the viscometer again. These steps are repeated for the other polymer concentration until reaches 1,000 ppm polymer solution.

3.3.4 Preparation of Polymer solution

10,000 ppm PEG molecular weight 10,000 g/gmol is chosen for this entire experiment. The required mass of the polymer powder can be calculated from the multiplication product of the desired concentration with the desired volume of this solution.

3.3.5 Preparation of MNPs solution

The concentrated MNPs solution from Ocean Nanotech is in the concentration of 1 g/L. Firstly, 2 mL of the concentrated MNPs solution is taken out to be diluted with 18 mL polymer solution made to produce a concentrated 100 ppm MNPs solution.

3.3.6 Preparation of Dye

0.03g of methylene blue powder is measured and transferred into a bottle. Then, 10 mL of deionized water is added to produce a 3 g/L methylene blue solution.

3.3.7 Dye-tracing experiment

A dye-tracing experiment need to be carried out to enable us to visually trace the fluid motion during magnetophoresis. First and foremost, polymer solution of different initial concentration of MNPs are prepared. The required amount of the concentrated MNPs solution to produce a desired MNPs concentration can also be calculated from the same formula used in dilution step. The initial concentration used will be 0 for blank solution, 5, 10, 20, 50, 100 mg/L. Then, 4.3 mL of each polymer solution with MNPs is filled into separate cuvettes. By using a syringe, the methylene blue is introduced at the top of each cuvette. The reason of injecting the dye at the top of the cuvette is the dye has a lower density than the polymer solution. This density problem has caused some difficulties when injecting the dye at the bottom of the cuvette as the dye will float to the surface of the polymer solution almost immediately and cause the whole polymer solution to be coloured even though the cuvette has yet to be placed on top of the magnet. Besides that, the polymer solution with MNPs is required to be filled until it reaches almost the top end of the cuvette so that the magnet is not too far away from the polymer solution for better observation. After that, the permanent magnet is placed on top of the cuvette. A digital camera used to capture the motion of MNPs during magnetophoresis started recording once the permanent magnet is placed on the cuvette with the MNPs solution and the dye (Leong et al., 2015).

Figure 3.2 Setup for the dye experiment

3.3.8 Simulation of kinetic of convective current

The simulation is done by using a software named COMSOL Multiphysics 5.3. This software enable us to stimulate the magnetophoresis happened in the experiment. During the stimulation, several physics theories can be added together. With the correct inputs of the parameters used in experiment, the results can be stimulated and even animations of the results can be performed (COMSOL, 2018).

In COMSOL Multiphysics version 5.3, the Computational Fluid Dynamics (CFD) and Chemical Reaction Engineering Modules were chosen in the numerical computational work to solve this hydrodynamically interacting model in two dimensional space. In the simulation, drift-diffusion equation, continuity equation and also the Navier-Stokes equation will be used.

Under the presence of external magnetic field, there are four forces acting on MNPs that govern the motion of MNPs in the MNPs solution. First is the magnetic force due to the response of magnetic dipole moment in MNPs to the externally applied magnetic field. Second is the viscous drag force due to the resistance contributed by the relative motion of MNPs in the solution. The other forces are the gravitational force and also the Brownian force. Brownian force is originated from thermal motion and this force induces the diffusion of MNPs along the MNPs concentration gradient. The transport behaviour of MNPs in the fluid throughout magnetophoresis, due to the combination of diffusion and fluid advection effects, is described by drift-diffusion equation (Furlani and Ng, 2008):

$$\frac{\partial c}{\partial t} = D\nabla^2 c - \nabla \cdot (\boldsymbol{u}c) \tag{3.3}$$

where c is concentration of MNPs solution, u is magnetophoretic velocity of MNPs and D is diffusivity of MNPs in the solution which can be calculated by using Einstein-Stokes equation (Lim et al., 2010) as mentioned in this paper under the section ‘Characterization of MNPs’. The drift-diffusion equation can be found in COMSOL Multiphysics under ‘Transport of Diluted Species’ physics.

The convective motion of the MNPs solution is computed by the Continuity and Navier-Stokes equations (Bird et al., 2006) which can be found in COMSOL Multiphysics under ‘Laminar Flow’ physics:

$$\nabla \cdot \boldsymbol{u} = 0 \tag{3.4}$$

$$\rho\left(\frac{\partial \boldsymbol{u}}{\partial t} + \boldsymbol{u}.\nabla \boldsymbol{u}\right) = -\nabla p + \eta \nabla^2 \boldsymbol{u} + \rho \boldsymbol{g} + \boldsymbol{f_m} \tag{3.5}$$

Where u is the velocity vector of the MNPs solution, ρ is density of MNPs solution, p is absolute pressure, g is the gravitational force and f_m is the magnetic force acting on unit volume of MNPs solution.

Navier-Stokes equation need to be included in the hydrodynamically interacting magnetophoresis model is because the momentum obtained by MNPs due to the response of magnetic dipoles to the externally applied magnetic field, is allowed to be transferred to the surrounding fluid as a consequence of the viscous property possessed by the fluid. Both the Continuity and Navier-Stokes equations govern the momentum transfer within the MNPs solution by connecting its spatial fluid flow profile to viscosity and external forces imposed onto it, specifically magnetic and gravitational forces (Leong et al., 2015).

CHAPTER 4: RESULT AND DISCUSSION

4.1 Characterization of MNPs

Figure 4.1 shown is the intensity distribution of particles sizes which is measured based on the scattering of light and this size distribution is the fundamental result from Dynamic Light Scattering (Malvern Instruments Worldwide, 2011). Two peaks are observed where the first peak falls at the hydrodynamic size of 91.35 nm with the intensity percentage of 93.7% whereas the second peak falls at the hydrodynamic size of 3149 nm with the intensity percentage of 6.3%. The larger size particles found could be caused by the formation of MNPs cluster or presence of relatively larger contaminants such as dust found in the solution.

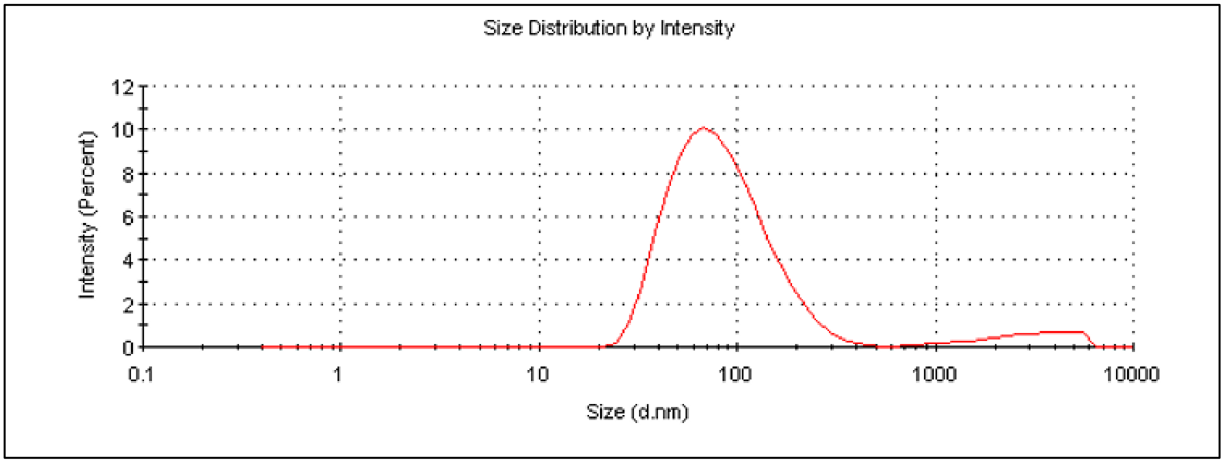


Figure 2.1 Size distribution of Fe_2O_3 MNPs by intensity

The formation of cluster is because some of the particles have insufficient thermal energy to overcome the dipole-dipole interaction (Schaller et al., 2008). Thus, the particles will attracted to each other and form aggregates. Another factor is the presence of relatively larger impurities, which might be caused by low quality of cleanliness of the environment or the water source. Both of the factors will lead to inaccuracy of the raw data. This is because the average of the distribution data will shift to the bigger size, although the number of the bigger size particles is far lesser than the remaining number of smaller nanoparticles.

From the Figure 4.2, volume distribution is measured based on the volume or mass, this distribution is directly generated from the intensity distribution by the conversion using Mie theory (Fu and Sun, 2001). Although the size distribution based on the quantitative amount of the particles, but the volume distribution will still different due to the different volume of the particles.

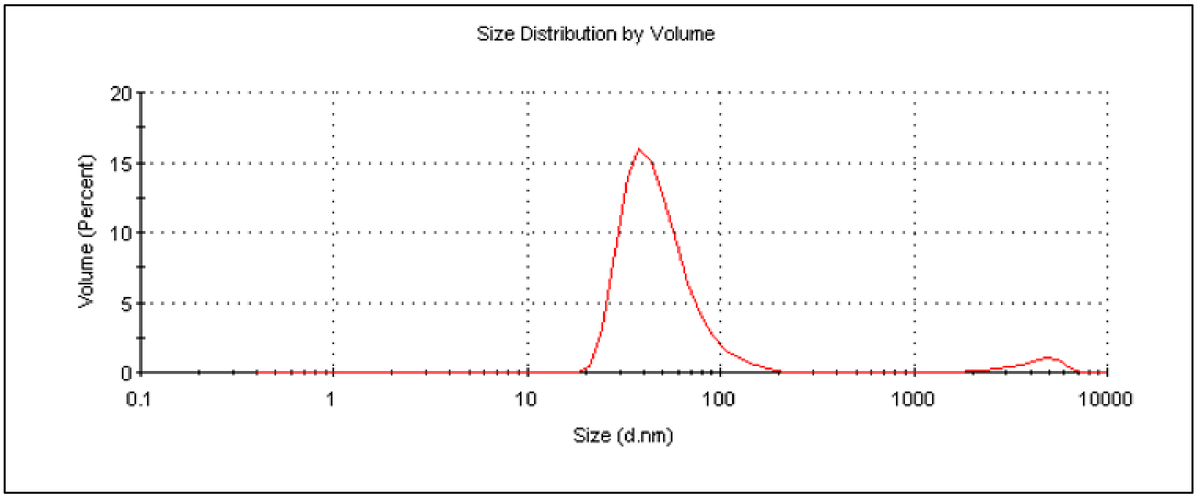


Figure 4.2 Size distribution of Fe_2O_3 MNPs by volume

During the conversion, a few of the assumptions should be made. The assumption includes all the particles are spherical and homogeneous, the optical properties of the particles are known and the intensity distribution has no any error (Malvern Instruments Worldwide, 2011). Similar to the intensity distribution, two peaks are observed where the first peak is falls at the hydrodynamic size of 49.33 nm with the intensity percentage of 95.5% whereas the second peak falls at the hydrodynamic size of 4310 nm with the intensity percentage of 4.5%. Besides, the polydispersity index (PDI) represent the dispersion of overall size distribution. The PDI for the MNPs solution in this case is 0.262. If PDI is less than 0.05, means highly monodispersed standards. If PDI is more than 0.7, means that the sample has wide distribution of size. Thus, the PDI obtained are considered as in the range of good quality (Malvern Instruments Worldwide, 2011).

4.2 Calibration of Polymer Solution

From the calibration curve shown in Figure 4.3, the concentration larger than 100,000 ppm have start to increase exponentially. This means that almost 2 times higher viscosity solution is obtained with the same increment in the concentration of the polymer. If polymer solution with much greater viscosity is chosen, the dye experiment might take very long time to complete due to much greater momentum transfer is required for the induced fluid convection to occur in more viscous fluid medium. Therefore, only 10,000 ppm polymer solution with 1.43 cP is chosen in order to reduce the required time for the MNPs solution to reach fully homogenization stage.

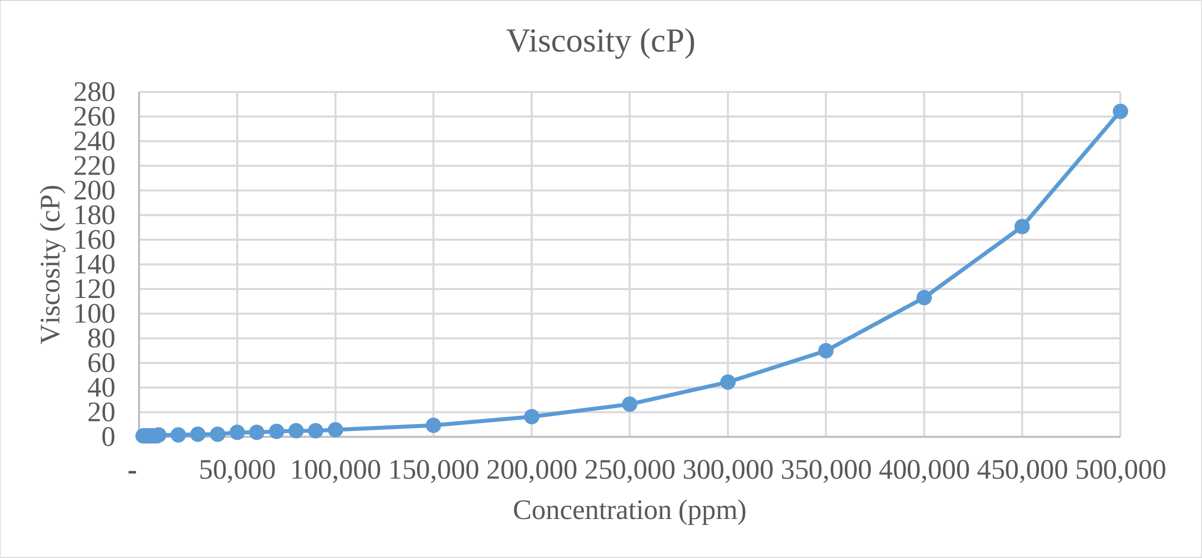


Figure 4.3 Calibration curve of PEG solution

4.3 Dye-Tracing Experiment

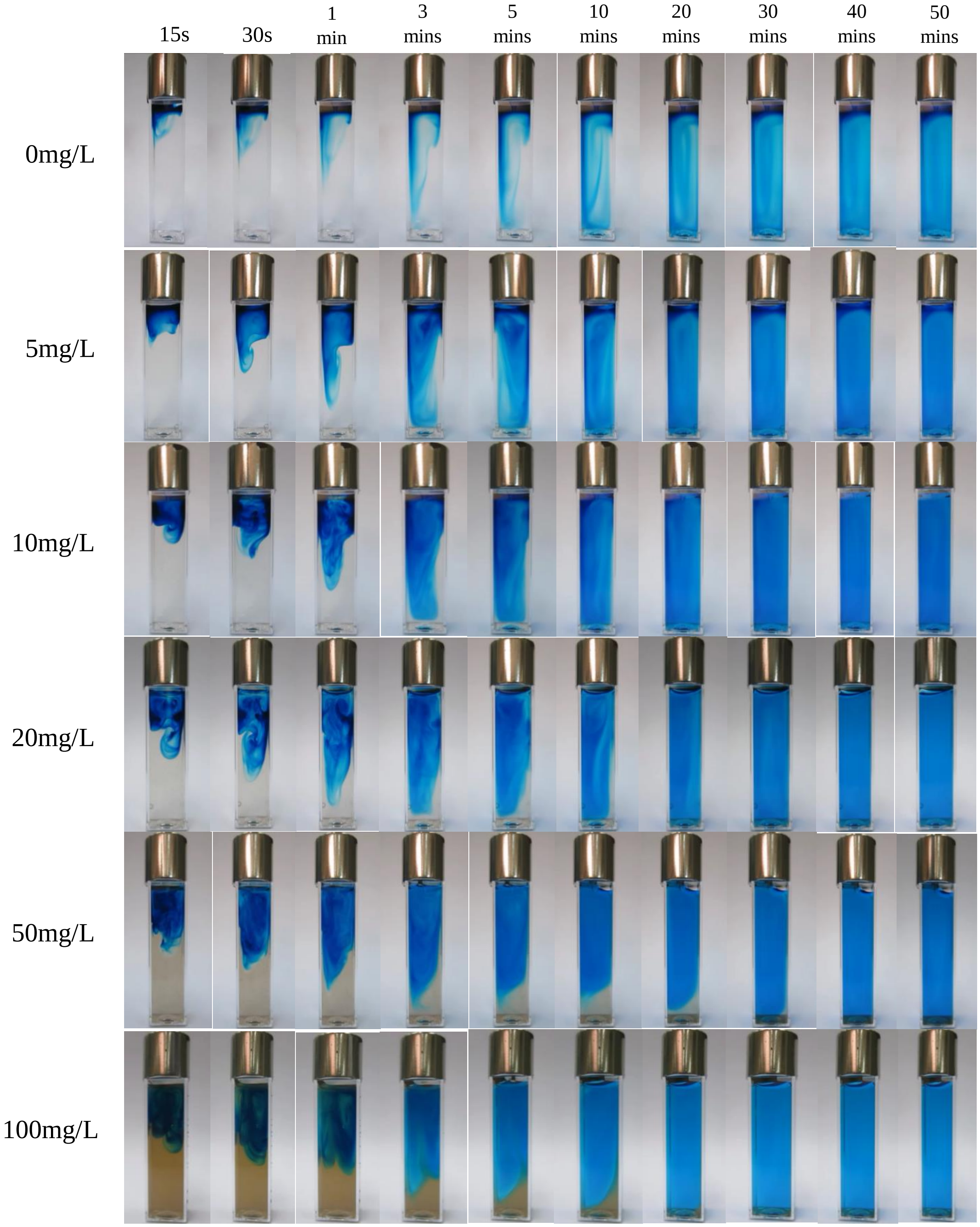


Figure 4.4 Time lapse images for different MNPs concentration in 1.43 cP PEG polymer solution

Figure 4.4 is the combination of the time lapse of different MNPs concentration throughout the experiment. The first row shown in the Figure 4.4 is the control experiment with the absence of any MNPs in the solution. By comparison, the higher the MNPs concentration, the faster the dye homogenized the whole solution completely during magnetophoresis. During magnetophoresis, higher MNPs concentration causes greater magnetic convective flux when large amount of MNPs gain momentum from the magnetic field applied. Then, fluid convection happened which can be observed by the dispersion of the dye in circular motion in the fluid medium. The hydrodynamic effect play a vital role here for the momentum to be able to transfer from MNPs to the surrounding fluid. Since the aggregation parameter, N* is smaller than 1, the interaction between the MNPs are negligible. Thus, the momentum is unlikely to transfer from the MNPs to the surrounding fluid.

However, the time taken is doubled when the surrounding fluid is 10,000 ppm PEG solution instead of water (Leong et al., 2015). The viscosity of the fluid medium act as the resistance to the MNPs' motion to travel in fluid convection. Therefore, the fluid convection in Newtonian fluid is more significant than non-Newtonian fluid. More inertial force as described in the magnetic Grashof number is needed in order to overcome the viscous force in the surrounding fluid. For instance, in order to allow the same amount of MNPs to travel with the same speed during the magnetophoresis in more viscous fluid medium, greater externally applied magnetic field is needed. This is to contribute more inertial force on the MNPs. Otherwise, higher concentration of the MNPs should be used.

4.4 Magnetic Buoyancy

In order to calculate the magnetic Grashof number , ▽B first need to be computed by using the equation below (Leong et al., 2015):

$$\nabla B \approx \frac{\partial B}{\partial y}\boldsymbol{e_y} = \frac{B_r r^2}{2}\left[\frac{1}{[(y+h)^2 + r^2]^{\frac{3}{2}}} - \frac{1}{[y^2 + r^2]^{\frac{3}{2}}}\right]\boldsymbol{e_y} \qquad (4.1)$$

Where B is magnetic flux density, y is vertical distance from magnet pole face, B_r is the remanent magnetic flux density, r and h is the radius and height of the magnet respectively and e_y is the unit vector pointing to the positive y-direction (Leong et al., 2015). Then, the value calculated is substituted into the magnetic Grashof number equation to obtain the graph as shown in Figure 4.5.

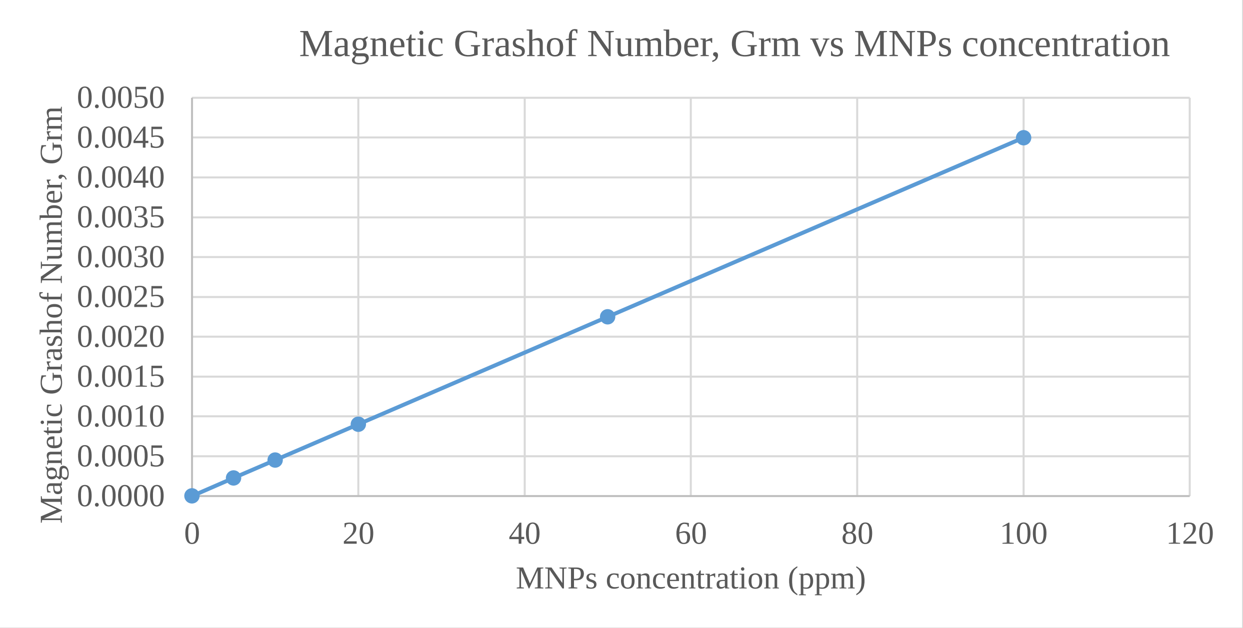


Figure 4.5 Magnetic Grashof Number of different MNPs concentrations in 1.43 cP PEG polymer solution

The result shown that the magnetic Grashof number is directly proportional to the MNPs concentration. This result conducted by Leong et als (2015) also yield a directly proportional graph, but the magnetic Grashof number for MNPs concentration in Newtonian fluid from 0 to 100 mg/L are in the range from 10 to 5000 (Leong et al., 2015). This means that the magnetic buoyancy force in Newtonian fluid is greater than in non-Newtonian fluid. The higher magnetic Grashof number in Newtonian fluid also indicates that the fluid convection in Newtonian fluid is more significant than that in non- Newtonian fluid.

4.5 Simulation of kinetic of convective current

4.5.1 Initial and Boundary Condition

First and foremost, the initial and boundary condition should be defined for the hydrodynamically interacting magnetophoresis model. A few assumptions have been made to simulate this model. At the beginning of magnetophoresis, the fluid is assumed to be stagnant (u = 0) and the MNPs concentration is assumed to be uniform throughout the whole solution. Since the MNPs solution is uniformly distributed and amount of MNPs in the solution, N is related to MNPs concentration by the equation (Leong et al., 2015):

$$N = cV_s \tag{4.2}$$

Where c is the concentration of the MNPs solution and V_s is the volume of MNPs solution. N follows the first order kinetic with exactly the same rate constant, k as that of c shown in the equation below (Leong et al., 2015):

$$N = c_0 V_s e^{-kt} \tag{4.3}$$