SYNTHESIS OF METAKAOLIN ACID-BASED GEOPOLYMERS FOR DYE REMOVAL

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Dissertation submitted in partial fulfilment of the requirement for

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CERTIFICATION OF APPROVAL

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own concept as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

SITI JARODAH MOHD AFFANDI

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ABSTRACT

Textile industry and dye-containing wastewater is worldwide pollution problems. The residual dyes contained organic pollutants to natural water resources or wastewater treatment systems. The discovery of geopolymers has been a breakthrough in the field due to its amorphous and porous structure. The objectives of this research are to synthesize and characterize metakaolin (MK) phosphorous acid-based geopolymers using different SiO_2/Al_2O_3 ratio.The optimum ratio of silica to alumina was furthered study by added different percentage of pore-forming agent. Raw material, kaolin was calcined to produce metakaolin which was then mixed with H_3PO_4, distilled water, alumina oxide/ silica oxide powder to produce slurry mixture. The mixture was then cured 80℃ for 24 hours. Different properties of geopolymers have been characterized for its particle size and porosity. The solubility test was conducted and the best geopolymer was chosen to be modified by pore-forming agent to increase the porosity. Adsorption experimental test on dye solution was conducted by varying the adsorbent dosage, pH and contact time. The optimum silica to alumina ratio of the geopolymer was the GP-R2.4 that gave the highest percent removal of 90%. Meanwhile, study on addition of pore-forming agent showed an optimum of 3% pore-forming agent in the geopolymer gave the highest percent removal of 100%. Meanwhile the optimum pH value for adsorption test is 10 and the increment in the adsorbent dosage usage increased the percentage of removal. The adsorption activities for both with and without pore-forming agent fitted the pseudo second order kinetic model. Besides, the adsorption study for both with and without pore-forming agent found to be fitted into the Langmuir Isotherm model.

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ABBREVIATION

GP	Geopolymer
MK	Metakaolin
NaOH	Sodium Hydoxide
HCl	Hydrochloric Acid
PAGP	Phosphoric Acid-based Geopolymer
PEG	Polyethylene Glycol

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

One of the main sources with severe pollution problems worldwide is the textile industry and its dye-containing wastewater. According to Baban et al., (2010) and Robinson et al. (2001), the worldwide annual production of 10, 000 different textile dyes are estimated to be $7x10^5$ metric tonnes. It is stated that about 10-25% of textile dyes are lost during the dyeing process while 2-20% is directly discharged as aqueous effluents in different environmental components. These residual dyes from different sources such as textile industries, bleaching industry, pharmaceutical and tannery are considered a wide variety of organic pollutants introduced into the natural water resources or wastewater treatment systems.

In particular, the discharge of dye-containing effluents into the water environment is undesirable, not only because of their colour, but also because many of dyes released and their breakdown products are toxic, carcinogenic or mutagenic to life forms mainly because of carcinogens, such as benzidine, naphthalene and other aromatic compounds (Zaharia et al., 2009). Without adequate treatment, these dyes can remain in the environment for a long period of time. For instance, the half-life of hydrolysed Reactive Blue 19 is about 46 years at pH 7 and 25˚C (Hao et al., 2000).

In Malaysia, according to Environmental Quality (Industrial Effluents) Regulation 2009, Fifth Schedule, the permissible concentration of Colour ADMI in wastewater are 100 mg/L and 200 mg/L for Standard A and Standard B, respectively. Meanwhile, the acceptable conditions for discharge of industrial effluent for textile industry containing Chemical Oxygen Demand (COD) are 80 mg/L and 250 mg/L for Standard A and Standard B, respectively.

Nowadays, there are many processes and techniques been used to remove dyes in wastewater, but somehow, there are still disadvantages or drawbacks (Refer Table 1.1 & Table 1.2) which motivate more research on relatively more sustainable and effective ways to treat the dyes contaminated wastewater. For instance, membrane separation process method that uses the membrane's micro-pores to filter and makes use of membrane selective permeability to separate certain substances in wastewater. The most often for dye wastewater treatment id mainly based on membrane pressure such as reverse osmosis, ultra-filtration, etc.. Even though membrane separation is new, high efficient, and low energy consumption technology, it is however not large-scale promoted due to its limitations especially in term of having high investment, membrane fouling, requiring special equipment and so on (Ranganathan et al., 2007).

Due to these drawbacks of membrane, adsorption becomes one of the options in treating dye in textile industry wastewater. The common adsorbents used in adsorption process in industry nowadays are activated carbon, zeolites and clay. Apart from raw natural resources, geopolymers were also being studied on their adsorption capabilities of dye due to the porous structure of geopolymers.

Table 1.1: Dyes Treatment Methods and Its Limitations(Carmen & Daniela, 2012).

Treatment Methodology	**Limitations**
Precipitation, coagulation-flocculation	-Agglomerates separation and treatment. -Selected operating conditions.
Electro-kinetic coagulation	-High sludge production.
Ozonation	-Not suitable for dispersal dyes. -Short half-life of ozone.
Oxidation with NaOCl	-Cost intensive.
Adsorption	-Regeneration is expensive and result in loss of adsorbent.

Table 1.2: Various Types of Agricultural Waste Adsorbents(Carmen & Daniela, 2012).

Adsorbents	Properties	Drawbacks
Activated carbon	-Specific surface area 500 – 1500 m^2/g -Pore volume of 0.3 cm^3/g -Bulk density of 300-550 g/L	-Very expensive. -Cost intensive regeneration process.
Coal ashes	-BET surface area ranging from 300 - 800 m^2/g -Pore volume of 0.18 – 0.41 microns	-Larger contact times and huge quantities are required. -Specific surface areas are lower than activated carbon.
Zeolite	-BET surface area ranging from 300 – 700 m^2/g	-Does not allow reasonable flow rate to be applied in industry.

1.1.1 Adsorption using Geopolymers

Adsorption is a mass transfer process whereby a substance is transferred from its original liquid phase to the adsorbent which is normally in solid phase. Though there are different types of modified materials being used as adsorbent for wastewater treatment application, there are still drawbacks, which then lead to motivating research and discovery of new adsorbent materials. For example, clinoptilolite, followed by mordenite, are the most studied natural zeolites for the removal of metal ions, ammonia and dyes.

However, the main disadvantages of zeolites is their extremely permeability in which zeolites do not allow reasonable flow rate to be applied in industry. Besides, according to Hernandez et al., (2008), chitosan a deacetylated derivative of chitin usually obtained by a reaction with NaOH reaction that consist of process removing the acetyl radical and leaving a free primary amino group. The presence of these amino sites increases the adsorption of dyes and the formation of chelates with metal ions in acidic conditions. This property makes chitosan an interesting low cost option for the adsorption of pollutants from wastewater. Unfortunately, the very change of structure that gives chitosan adsorbing capabilities also makes it easily soluble in weak, dilute acidic solutions.

In recent years, geopolymer adsorbents have become scientific interests due to the two major advantages which are low energy consumption and no CO_2 emission in the preparation process. At present, as cited by M. Wang et al., (2010) there are mainly three kinds of aluminosilicate sources for the preparation of geopolymer which are metakaolin (calcined kaolin), fly ash and chemically synthesize kaolin.

Other than that, there is another type of geopolymers which is phosphoric acid-based geopolymers, where it has been successfully synthesized and characterized byLe-Ping et al., (2010). Table 1.3 shows the summary of some literature studies on phosphoric acid-based geopolymer. However, existing literatures on acid-based geopolymer are scant. Thus, wastewater treatment using a geopolymer as an adsorbent should be merits further examination.

On the other hand, Li and Zhu (2011) has study the effect of polyethylene glycol (PEG) in enhancing the porosity of the structure of rice husk char. It is reported that increasing PEG amount could significantly enhance the surface area and the other textural properties. Besides, increasing the amount of PEG used could enhance the amount of PEG amount of composites. Hence, after calcinations, the composites prepared by using larger quantity of PEG would lose more PEG, making the corresponding porous silica have higher specific surface area (Li & Zhu, 2011).

Table 1.3: Literature Works on Phosphoric Acid-Based Geopolymers.

Year	Authors	Geopolymer Used	Parameter Tested
2008	Dan S. P., John V. H., Joel D., Mark G. B., Bruno A. L., Yosuke S., Eric R. V.	Phosphoric acid-bonded metakaolin (MKP), and metakaolin based-geopolymer (MKGP) Activator: Phosphoric acid	Solid/solid ratio, and solid liquid ratio
2010	Liu L., Cui X., Qiu S., Yu J., Zhang L.	Metakaolin Activator: Phosphoric acid	Solid/solid ratio, solid/liquid ratio, liquid/liquid ratio and curing temperature.
2013	Hanen D., Soumaya L., Samir B., Mourad A., Zouhir F.	Metakaolin Activator: Phosphoric acid	Solid/liquid ratio and frequency.

1.2 PROBLEM STATEMENT

Wastewater that is discharged by the dye manufacturing and textile finishing industries has become an environmental concern. The legal requirements concerning discharge of contaminated waste water are reinforced in many countries and the discharge fees are increasing. During the dyeing process, the dye is dissolved into the process water and it is still there when the process later is released as effluent. The effluent contains high content of dyestuff, surfactants, and other additives that are generally made up of organic compounds with a complex structure which have poor bio-degradability.

The removal of dyes from wastewater is essential to ensure the sustainability of balance ecosystem, clean environment and public health. However, existing methods of removing dyes such as membrane process, irradiation, chemical treatment, etc. have limitations which include low permeability rate, sludge formation, advanced technology and so on. Adsorption using geopolymer definitely has high potential to replace current ways of removing dyes due to its proven porosity, high compressive strength, low cost, thermally stable and corrosion resistant properties.

Even though there has been no report on the adsorption capabilities of phosphoric acid-based geopolymer on dyes, due to the similar properties with alkaline-based geopolymers and even superior performance, phosphoric acid-based geopolymer has great potential to provide better dyes removal efficiency. Thus, this study will focus on phosphoric acid –based geopolymers effectiveness in removing dyes from the textile wastewater industry. Understanding that different operating conditions bring different effects on the adsorption process, this research will examine the effects of alumina to silica ratio and amount of pore-forming agent on the modified acid-based geopolymer.

1.3 OBJECTIVES OF STUDY

The main objectives of the study are:

i. To synthesize, characterize and select the optimum silica to alumina ratio of PAGP.
ii. To modify and determine the effect of percentage of pore-forming agent to the optimum ratio of PAGP.
iii. To examine the effect of pH, adsorbent dosage, and contact time onto adsorption activities.
iv. To study the kinetic models and isotherm of adsorption exhibit by metakaolin phosphoric acid-based geopolymers with pore-forming agent.

1.4 SCOPES OF STUDY

The scope of studies is this research basically are divided into three parts which are designing, selection, and characterizations of geopolymers, adsorption capabilities of geopolymers, as well as the result analysis. The scope of the research will focus on the use of metakaolin (MK) phosphoric acid-based geopolymers as adsorbents in dyes removal. Different samples of MK phosphoric acid-based geopolymers will be synthesized by using different silica to aluminum ratio. The optimum ratio will be furthered study by adding different percentage of pore-forming agent amount. The samples were mixed at ambient temperature under specific ratio before the slurry mixture is left in the oven at temperature of 80 ° C for 24h. Characterization of the geopolymers will be done by using BET to determine the porosity of the geopolymer. The compositions of geopolymers will be determined using FTIR while the adsorption capabilities will be investigate using the UV-Vis Spectroscopy by measuring the composition or concentration of the dye solution. Apart from that, the adsorption capabilities of adsorbent will be tested using methylene blue while varying the pH of the solutions, adsorbent dosage and the contact time between the adsorbent and adsorbate.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

According to the Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulation in 1979, the industrial effluents quality can be divided into two standards. Standard A is applied to inland waters within catchment areas mentioned in Fourth Schedule in the same regulation, and Standard B is applied to other inland waters. From the Malaysia Environmental Quality, the Fifth and Seventh Schedule showed the acceptable conditions for discharge of industrial effluents with/ without containing COD (Refer Table 2.1 and Table 2.2):

Table 2.1: Acceptable Conditions for Discharge of Industrial Effluent

FIFTH SCHEDULE [Subregulation 11(1), 11(2), 11(3)] ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT OR MIXED EFFLUENT OF STANDARDS A AND B				
	Parameters	Unit	Standard	
			A	B
	(1)	(2)	(3)	(4)
(i)	Temperature	˚C	40	40
(ii)	pH value	-	6.0 – 9.0	5.5 – 9.0
(iii)	BOD, at 20˚C	mg/L	20	50
(iv)	Suspended solids	mg/L	50	100
(v)	Mercury	mg/L	0.005	0.05
(vi)	Cadmium	mg/L	0.01	0.02
(vii)	Chromium, hexavalent	mg/L	0.05	0.05
(viii)	Chromium, trivalent	mg/L	0.20	1.0
(ix)	Arsenic	mg/L	0.05	0.10
(x)	Cyanide	mg/L	0.05	0.10
(xi)	Lead	mg/L	0.10	0.5
(xii)	Copper	mg/L	0.20	1.0
(xiii)	Manganese	mg/L	0.20	1.0
(xiv)	Nickel	mg/L	0.20	1.0
(xv)	Tin	mg/L	0.20	1.0
(xvi)	Zinc	mg/L	2.0	2.0
(xvii)	Boron	mg/L	1.0	4.0
(xviii)	Iron (Fe)	mg/L	1.0	5.0

(xix)	Silver	mg/L	0.1	1.0
(xx)	Aluminium	mg/L	10	15
(xxi)	Selenium	mg/L	0.02	0.5
(xxii)	Barium	mg/L	1.0	2.0
(xxiii)	Fluoride	mg/L	2.0	5.0
(xxiv)	Formaldehyde	mg/L	1.0	2.0
(xxv)	Phenol	mg/L	0.001	1.0
(xxvi)	Free chlorine	mg/L	1.0	2.0
(xxvii)	Sulphide	mg/L	0.50	0.50
(xxviii)	Oil and grease	mg/L	1.0	10
(xxix)	Ammoniacal nitrogen	mg/L	10	20
(xxx)	Colour	ADMI*	100	200
*ADMI – American Dye Manufacturers Institute				

Table 2.2: Acceptable Conditions for Discharge of Industrial Effluent Containing COD for Specific Industry Sector.

SEVENTH SCHEDULE
(Regulation 12)
ACCEPTABLE FOR DISCHARGE OF INDUSTRIAL EFFLUENT CONTAINING CHEMICAL OXYGEN DEMAND (COD) FOR SPECIFIC TRADE OR INDUTRY SECTOR

	(1)	(2)	(3)	(4)
	Trade/Industry	Unit	Standard	
			A	B
(a)	**Pulp and paper industry**			
(i)	Pulp mill	mg/L	80	350
(ii)	Paper mill (recycled)	mg/L	80	250
(iii)	Pulp and paper mill	mg/L	80	300
(b)	**Textile industry**	mg/L	80	250
(c)	**Fermentation and distillery industry**	mg/L	400	400
(d)	**Other industries**	mg/L	80	200

Table 2.1 shows the limit of all the parameters limit for both Standard A and Standard B in Environmental Quality. It is very essential to keep the amount of these heavy metals way below the permissible concentration limit to avoid leakage of heavy metals to free water and poison the marine ecosystem. Meanwhile, Table 2.2 gives the overall concentration limit of different industries to discharge effluent to

the environment. From this table, the concentration limit for textile industry based on Standard A and Standard B are 80mg/L and 250mg/L respectively.

2.2 TEXTILE INDUSTRY

The word textile means to weave which was adopted from the Latin word ‘*texere*’. Textiles can be woven by both hand and machines. The raw materials for textiles are natural and synthetic fibres (Elliott, Hanby, & Malcolm, 1954). The sources of natural fibres are mineral, animals and plants. With the advancement of technology, fibres can now be extracted from chemicals. However, plant sources yield a large amount of fibres than those obtained from animal and mineral sources. Most of the textiles produced are as a result of spinning of fibres from the yarns(Kuusisto, 2010).

The textile industry is classified into three main categories: cellulose fibres (cotton, rayon, linen, hemp and lyocell), protein fibres (wool, angora, mohair, cashmere and silk), and synthetic fibres (polyester, nylon, spandex, acetate, acrylic, ingeo and polypropylene). The type of dyes and chemicals used in the textile industry are found to differ depending on the fabrics manufactured. Reactive dyes (remazol, procion MX and cibacron F), direct dyes (congo red, direct yellow 50, and direct brown 116) naphthol dyes (fast yellow GC, fast scarlet R and fast blue B) and indigo dyes (indogo white, tyrian purple and indigo carmine) are some of the dyes used to dye cellulose fibres (Lorimer, Mason, Plattes, Phull, & Walton, 2001). Protein fibres are dyed using acid dyes (azo dyes, triarylmethane dyes and anthraquinone dyes) and lannest dyes (Blue 5G and Bordeaux B) (Moody & Needles, 2004; Schmidt et al., 2003). Other dyes, like dispersed dyes (Disperse yellow 218 and disperse navy 35), basic dyes (basic orange 37and basic red 1) and direct dyes, are used to dye synthetic fibres (Burkinshaw, 1995).

It is well known that textile industries produce large amounts of liquid wastes that contain organic and inorganic compounds (Elliott et al., 1954). As cited by Ghaly et al., (2014) during the dye processes, not all dyes that are applied to the fabric are fixed on them and there is always a portion of these dyes that remains unfixed to the fabrics and gets washed out. These unfixed dyes are found to be in high concentrations in textile effluents. However, the amount of water consumed and released also varies depending on the type of fabrics produced. About 0.08-0.15 m^3 of water is used to produce 1 kg of fabrics, Pagga and Brown (1986) estimated that about 1,000-3,000 m^3 of water is let out after processing about 12-20 tonnes of textiles per day.

The characteristics of textile effluents vary and depend on the type of textile manufactured and the chemicals used. The textile wastewater effluent contains high amounts of agents causing damage to the environment and human health including suspended and dissolved solids, biological oxygen demand (BOD), chemical oxygen demand (COD), chemicals, odour and colour. Most of the BOD/COD ratios are found to be around 1:4, indicating the presence of non-biodegradable substances, as cited by Ghaly et al., (2014). Typical characteristics of textile effluents are shown in Table 2.4. Besides, Ghaly et al., (2014)mentioned that the textile effluents contain trace metals like Cr, As, Cu, and Zn, which are capable of harming the environment. Meanwhile, Table 2.3 shows the summary of sources of pollution in the textile industry which consists of several process flow. The most significant sources of pollution among various process stages are pre-treatment, dyeing, printing and finishing of textile materials.

Dyes in water give out a bad colour and can cause disease like haemorrhage, ulceration of skin, nausea, severe irritation of skin and dermatitis (Tufekci et al., 2007). They can block the penetration of sunlight from water surface preventing photosynthesis. Dyes also increase the biochemical oxygen demand of the receiving water and in turn reduce the reoxygenation process and hence hamper the growth of photoautotrophic organisms. The suspended solid concentrations in the effluents play an importance role in affecting the environment as they combine with oily scum and interfere with oxygen transfer mechanism in the air-water interface.

Inorganic substances in the textile effluents make the water unsustainable for use due to the presence of excess concentration of soluble salts. These substances even in a lower quantity are found to be toxic to aquatic life (Masupha, 2008). Some of the inorganic chemicals like hydrochloric acid, sodium hypochlorite, sodium hydroxide, sodium sulphide and reactive dyes are poisonous to marine life (Blomqvist, 1996; Masupha, 2008). The seriousness of water pollution depends on the quantity of water and chemicals used in the wet process. The average water consumption for various fabrics is tabulated in Table 2.5.

The dye concentration in a dye house range from 0.01 g/L to 0.25 g/L depending on type of the dye and the process carried out (Greijer et al., 2008). Textile dyestuffs are found to contain a large amount of organic substances which are difficult to degrade and are resistance to aerobic degradation. They are also found to reduce into carcinogenic agents under anaerobic conditions (Jain et al., 2003).

Table 2.3: Types of textile wastes produced (Ghaly, Ananthashankar, Alhattab, & Ramakrishnan, 2014).

Process	Emission	Wastewater	Solid wastes
Fibre preparation	Little or none	Little or none	Fibre waste and packaging waste
Yarn spinning	Little or none	Little or none	Packaging wastes, sized yarn, fibre waste, cleaning and processing waste
Slashing/sizing	VOCs	BOD, COD, metals, cleaning waste, size	Fibre lint, yarn waste, packaging waste, unused starch-based sizes
Weaving, knitting & tufting	Little or none	Little or none	Packaging waste yarn and fabric scraps, off-spec fabric, used oil
Desizing	VOCs from glycol esters	BOD from sizes lubricants, blocides, anti-static compounds	Packaging waste, fibre lint, yarn waste, cleaning and maintenance materials
Scouring	Little or none	Disinfectants, insecticide residues, NaOH, detergents oils, knitting lubricants, spin finishes, spent solvents	Little or none
Bleaching	VOCs from glycol ester and scouring solvents	H_2O_2, stabilizers, high pH	Little or none
Singeing	Small amount of exhaust gases from the burners exhausted with components	Little or none	Little or none
Mercerizing	Little or none	High pH, NaOH	Little or none
Heat settling	Volatilization of spin finish agents-synthetic fibre manufacture	Little or none	Little or none
Dyeing	VOCs	Metals, salt, surfactants, organic processing assistants, cationic materials, colour, BOD, COD, sulphide, acidity/alkalinity, spent solvents	Little or none
Printing	Solvents, acetic acid-drying and curing oven emission combustion gases	Suspended solids, urea, solvents, colour, metals, heat BOD, foam	Little or none
Finishing	VOCs, contaminants in purchased chemicals, formaldehyde vapours, combustion gases	COD, suspended solids, toxic materials, spent solvents	Fabric scraps and trimmings, packaging waste

Table 2.4: Characteristics of typical untreated textile wastewater (Ghaly et al., 2014).

Parameter	Range
pH	6-10
Temperature (˚C)	35-45
Total dissolved solid (mg/L)	8,000- 12,000
BOD (mg/L)	80-60,000
COD (mg/L)	150-12,000
Total suspended solids (mg/L)	15-8,000
Total dissolved solids (mg/L)	2,900-3,100
Chlorine (mg/L)	1,000-6,000
Free chlorine (mg/L)	<10
Sodium (mg/L)	70%
Trace elements (mg/L)	
Fe	<10
Zn	<10
Cu	<10
As	<10
Ni	<10
B	<10
F	<10
Mn	<10
Hg	<10
PO4	<10
Cn	<10
Oil & grease (mg/L)	10-30
TNK (mg/L)	10-30
NO2-N (mg/L)	<5
Free ammonia (mg/L)	<10
SO4 (mg/L)	600-1000
Silica (mg/L)	<15
Total Kjeldahl Nitrogen (mg/L)	70-80
Color (Pt-Co)	50-2,500

Table 2.5Average water consumption for various fabrics (Ghaly et al., 2014).

Processing subcategory	Water consumption (m^3/ton fibre material)		
	Minimum	Median	Maximum
Wool	111	285	659
Woven	5	114	508
Knit	2	84	377
Carpet	8.3	47	163
Stock/yarn	3.3	100	558
Nonwoven	2.5	40	83
Felted fabric finishing	33	213	933

2.3 ADSORPTION

2.3.1 Adsorption Theory

Adsorption is a separation process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid adsorbent, forming, a molecular or atomic film which are the adsorbate. It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. When the adsorbent become saturated with the adsorbate, the adsorbent will be generated by acid wash or water-wash. The mechanism of adsorption process can be explained in three steps which are diffusion, migration and adsorption process (Figure 2.1).

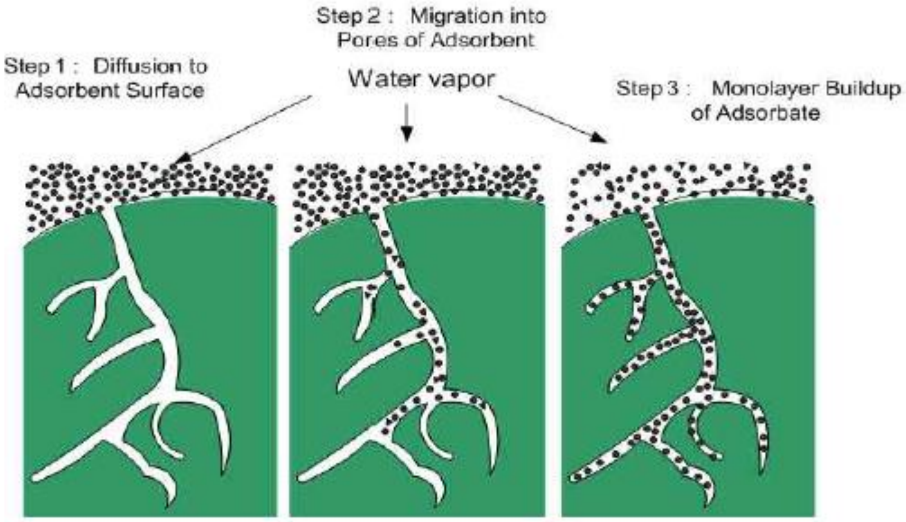

Figure 2.1 Mechanism of Adsorption (Kim & Chea, 2012).

2.3.2 Type of Adsorptions

Similar to the surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements such as ionic, covalent or metallic of the constituent atoms of the material are filled. But atoms on the clean surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorptions (Refer Table 2.6).

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals interaction, which are also responsible for the non-ideal behavior of real gases. Meanwhile, chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces. The differences between physisorption and chemisorption have been summarized in Table 2.6.

Table 2.6: Differences between Physisorption and Chemisorption (Jaafar & Nhatasha, 2006).

Physisorption	**Chemisorption**
Type of interaction. Intermolecular forces (Van der Waals).	Type of interaction: strong, covalent bond between adsorbate and adsorbent.
Low enthalpy: $\Delta H < 20$ kJ/mole	High enthalpy: $\Delta H \sim 400$ kJ/mole
Low temperature, always under the critical temperature of adsorbate.	High temperature.
Process is not specific.	Process is highly specific.
Adsorption takes place in multilayer.	Adsorption takes place only in monolayer.
Low activation energy.	High activation energy.
Reversible can be desorption.	Irreversible
Non-selective surface attachment.	Selective surface attachment.

2.3.3 **Types of Adsorbent**

The adsorbent is the separating agent used to express the difference between molecules in a mixture: adsorption equilibrium or kinetics. As adsorbent is a substance, usually porous in nature and with high surface area that can be adsorb substances onto its surface by intermolecular forces.

Many adsorbents have been tested on the possibility to lower dye concentrations from aqueous solutions, such as activated carbon, peat, chitin, and others (Tahir & Rauf, 2006). Commonly used adsorbents are activated carbon, silicon polymers and kaolin. Different adsorbents have selective adsorption of dyes. But, so far, activated carbon is still the best adsorbent of dye wastewater. Because activated carbon has selection to adsorb dyes, it can effectively remove the water-soluble dyes in wastewater, such as reactive dyes, basic dyes, and azo dyes, but it cannot adsorb the suspended solids and insoluble dyes. Moreover, the activated carbon cannot be directly used in the original textile dyeing wastewater treatment, while generally used in lower concentration of dye wastewater treatment or advanced treatment because of high cost regeneration (Wang et al., 2011).

Recent investigations have focused on the development of adsorbents by using various raw materials such as agricultural waste, industrial by-products, natural materials and modified biopolymers (Barakat, 2011). The development is due to the discovery of raw materials with lower cost yet higher adsorption capacities. Some of the adsorbents used for dye or methylene blue is tabulated below, (Refer Table 2.7).

Table 2.7: Types of Adsorbent used for Dye or Methylene Blue Removal

Year	Authors	Adsorbent	Adsorbate	Experimental Parameters
2004	V.K. Grag, Moirangthem A., Rakesh K., Renuka G.	Formaldehyde treated sawdust and phosphoric acid treated sawdust carbon of Indian Rosewood	Methylene blue	Adsorbent dosage, initial dye concentration, pH and contact time.
2006	Lin Li, Shaobin W. and Zhinghua Z.	Fly ash and natural zeolite Activator: NaOH	Methylene blue and crystal violet	NaOH: fly ash ratio, fusion temperature
2006	Sharifah Nhatasha Syed Jaafar	Natural clay	Methylene blue	Initial concentration of dye solution.
2009	W.T. Tsai,H.R Chen, K.C. Kuo, C.Y Lai, T.C Su, Y.M. Chang and J.M. Yang	Shell Powders	Methylene blue	Initial dye concentration
2010	Miodrag S., Dragan D., Mile N. and Mirjana M.	Ash	Textile vat dye	Adsorbent dosage, initial dye concentration, pH and agitation time.
2011	Dharmendra S. K., Surendra B., and Abishek G.	Azadirecta indica leaves (Neem)	Methylene blue	pH, adsorbent dosage, contact time and initial dye concentration.
2013	M. Abbas, Muaz Zakaria, S.H. M-Setapar, and M.A Che-Yunus	Sludge from palm oil effluent Activator: ZnCl2 and KOH	Methylene blue	Initial dye concentration
2014	Ould Brahim, M. Belmedani, A. Belgacem, H. Hodoun, Z. Sadaoui.	Activated carbon	Methylene blue	Contact time, pH, adsorbent dose and dye concentration.
2014	Y.C. Wong, K.N. Ranjini and W.A Wan-Nurdiyana	Activated carbon (orange peel and rice husk)	Congo red and acid yellow 36 dye	Adsorbent dosage

2.3.4 **Classification of Adsorbent**

The adsorption capacity of an adsorbent is a function of the surface area of the pores in its body. Generally the internal surface area of pores is several orders of magnitude larger than the outer surface of the adsorbents. Consequently the adsorbent can adsorb huge quantities of adsorptive. Traditionally adsorbent are classified according to the average diameter of their inner pores. The pore size determines the type of substance that can be adsorbed. Three classes are given below (Refer Table 2.5).

Table 2.8: Class of Adsorbent

Class of Adsorbent	**Average Diameter of Inner Pores**
Micro porous adsorbents	2 A^{o} to 20 A^{o}
Meso porous adsorbents	20 A^{o} to 500 A^{o}
Macro porous adsorbents	> 500 A^{o}

2.4 GEOPOLYMER

The term *geopolymer* was first used by J. Davidovits in the late 1970s and nowadays identifies a family of amorphous alkali or alkali-silicate activated aluminosilicate binders (Colangelo et al., 2013). Geopolymers are material which is made up of polymeric Si-O-Al functional group, creating a framework similar to zeolites, but more amorphous instead of crystalline. There are small aluminosilicate clusters with dispersed pores within a highly porous network (Huang & Han, 2011). Since the late seventies of the 20th century, geopolymers have been considered for replacing traditional structural materials by reason of their excellent properties and high performance (Davidovits, 1982). Geopolymers have been used in many applications and one of the major applications is in the construction industry. This is due to its quick curing time and high tensile strength. Other applications of the geopolymers include archaeology and heavy metal adsorption. Apart from that, geopolymers can be synthesized easily under normal ambient condition using different raw materials, for instance metakaolin and fly ash. Metakaolin is simply a heated kaolin which also known as china clay while fly ashes are waste from thermal power factories. Both raw materials have high aluminosilicate and highly favourable to synthesize geopolymers.

2.4.1 **Geopolymerization**

Geopolymerization is a geo-synthesis reaction involving silico-aluminitae sources. Source of alumina in and silica acts as a source of precursor that readily dissolved in the alkaline solution, and synthesized by alkaline and/or silicate activation which lends itself to the process of geopolymerization (Duxson et al., 2007; Heah et al., 2012). According to (Xu & Van Deventer, 2002), the basic step of geopolymerization is the dissolution of the solid aluminosilicate oxide in a acid or alkali solution to form SiO_4 and AlO_4 tetrahedral units. It is newly developing field of research which provides a mature and cost effective solution to many problems by utilizing solid wastes or byproducts where hazardous residue has to be stored under critical environmental conditions (Khale & Chaudhary, 2007).

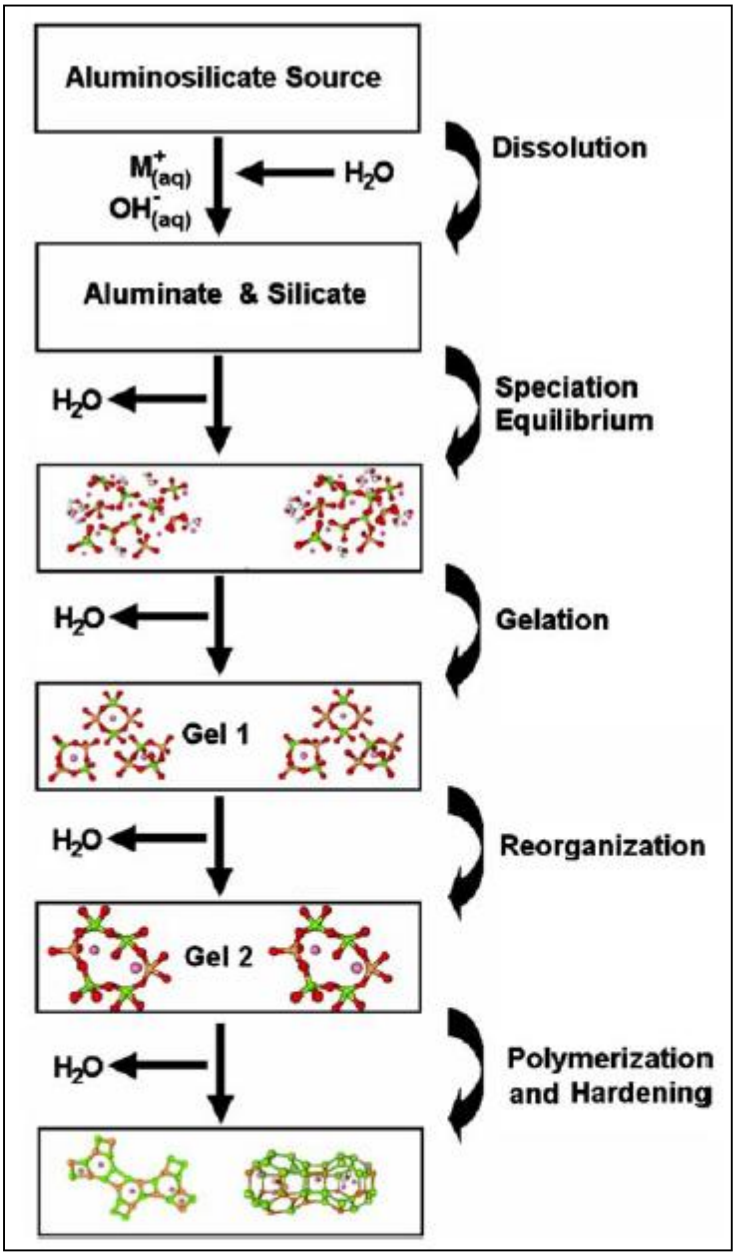

Figure 2.2 Conceptual Model for Geopolymerization (Peter Duxson et al., 2007).

In the 1950s, Glukhovasky proposed a general mechanism for the alkali activation of materials primarily comprising silica and reactive alumina (Refer Figure 2.2). The Glukhovsky model divides the process into three stages which are destruction-coagulation, coagulation-condensation, and condensation-crystallization (Duxson et al., 2007). Firstly, the dissolution of the solid aluminosilicate source by alkaline hydrolysis produces aluminate and silicate species. A complex mixture of silicate, aluminate and aluminosilicates is thereby formed once they species released by dissolution incorporated into the aqueous phase. The dissolution of amorphous aluminosilicates is rapid in high pH, which then quickly creates a supersaturated aluminosilicate solution. Concentrated solution due to condensation process will result in the formation of a gel, as the oligomers in the aqueous phase from large networks. After gelation, the system continues to rearrange and reorganize, as the connectivity of the gel network increases, resulting in three-dimensional aluminosilicate network commonly attributes to geopolymers.

2.4.1.1 Raw Material

The main sources of metakaolin are either kaolin or paper sludge after suitable treatment. Kaolin is one of the most widely used industrial minerals where its world’s total output exceeds 25 million tonnes (Nkoumbou et al., 2009). Under normal environmental conditions, kaolin is quite stable. However, when kaolin heated to temperature of 650 - 900℃, it loses 14% of its mass in bound hydroxylions (Rashad, 2013). This heat treatment, or calcination, breaks down the structure of kaolin such that the alumina and silica layers become puckered and lose their long-range order. Resulting from this dehyroxylation and disorder is metakaolin, a highly reactive transition phase (Barnes & Bensted, 2002), amorphous material with pozzolanic and latent hydraulic reactivity, suitable for use in cementing applications (Kostuch, Walters, & Jones, 2000).The exothermal dehydroxylation reaction is represented by Equation (1) (Palomo et al., 1999).

$$2Al_2Si_2O_5(OH)_4 \rightarrow 2Al_2Si_2O_7 + 4H_2O$$

2.4.1.2 Alkali/ Acid Activators

Alkali activators can be divided into two groups which are alkali hydroxide which meant for dissolution of raw materials, and sodium (or potassium) silicate solution which acting as a binder (Phair, Van Deventer, & Smith, 2004). As reported in the studies by (Khale & Chaudhary, 2007), strong alkalis are required to activate the silicon and aluminium present raw material. Alkali metal salts and/or hydroxide are necessary for the dissolution of silica and alumina as well as for the catalyst of the condensation reaction. The common activators are NaOH, Na_2SO_4, Na_2CO_3, K_2SO_4, KOH or a little amount of cement clinker.

Acid-based geopolymers are slightly different from other alkaline-based geopolymer (metakaolin-based). This is due to the addition of acid solution during the synthesize process, causing a different polymeric linkage being formed between silica, aluminum and phosphorus. The synthesis by using acidic medium yielding poly(silico-aluminates) – poly(sialate) type of geopolymers.Work done by Le-Ping et al., (2010) shows that phosphorous acid-based geopolymers formed are amorphous, porous and displayed excellent thermal stability. Even though there is no research being done on the application of phosphoric acid-based geopolymer, the proven porous properties have made them a potential adsorbent material.

2.4.2 Synthesis of Phosphorous Acid-based Geopolymers

The synthesis method of phosphoric acid-based geopolymer according to Le-Ping et al., (2010) can be done by adding phosphoric acid to the mixture of metakaolin and α-Al_2O_3 at ambient temperature. Metal powder such as Al and Fe can be added as a pore-forming agent. This work done have shown that the geopolymers formed will posses different properties as the component ratios are altered. For instance, the amount of pore-forming agent has an effect on the porosity and the compressive strength of the synthesized geopolymers. The higher the Al content, the higher the porosity of the sample and the lower the compressive strength. It is also reported that the lower water content will result in higher viscosity and smaller final pore size. Meanwhile, if the water content is too high, the viscosity will be quite low and lead to the disappearance of all pores.

2.4.3 Adsorption using Geopolymers

Geopolymer has been studied and exhibit the quality of effectiveness due to its porous structure. A lot of studies and research are still on going to examine the adsorption capabilities of geopolymers.

A comparison study between fly ash and zeolite has been studied for dye removal by Li et al., (2006). The experimental parameters of this study is to investigate the effect of contact time, pH of dye solution, fly ash to alkali activator ratio, and the effect of fusion temperature. It is reported that natural zeolite presents higher adsorption capacity than fly ash around $5x10^{-5}$ and $4x10^{-5}$ mol/g for methylene blue and crystal violet, respectively. Meanwhile, the geopolymers produces the highest adsorption capacity at $1.2x10^{-4}$ and $2.4x10^{-4}$ mol/g for methylene blue and crystal violet. Apart from that, low adsorption capacity was observed when the fly ash to NaOH ratio is low. The removal efficiency for crystal violet is higher than 90%, but for methylene blue, the removal efficiency is below 85%. Thus, it is found that geopolymers produced by conversion of fly ash generally exhibit higher capacity than fly ash itself and natural zeolite.

On the other hand, there is no study had been done by using metakaolin for dye removal by using acid-based geopolymers. Although phosphoric acid-based geopolymers exhibit qualities as adsorbent, the effects of acidic based on dye removal is yet to be investigated. Hence, the main focus in this research work will be on the dye removal efficiency of the new material, which is phosphoric acid-based geopolymer.

2.4.4 Equilibrium Relations for Adsorption

Adsorption is usually described through isotherm, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure for gas or concentration for liquid. One can find several models describing process of adsorption, namely Freundlich isotherm, Langmuir isotherm, BET isotherm, etc.

2.4.4.1 Linear Isotherm

For the linear isotherm, the relationship can be expressed using equation 2.1:

$$q = Kc \qquad \text{(Eq. 2.1)}$$

where,q = (kg adsorbate/kg adsorbent), c = kg adsorbate/ m^3 fluid, K = constant in m^3/kg adsorbent.

2.4.4.2 **Freundlich Isotherm**

The Freundlich isotherm is mostly applicable to physical adsorption and useful for liquid system. Equation 2.2 shows the correlation between q and c.

$$q = Kc^n \quad \text{(eq. 2.2)}$$

$$\log q = \log K + n \log c \quad \text{(Eq 2.3)}$$

By plotting the graph of log q against log c, the slope of the graph will be the value of n while the y-intercept will be the log K, according to Equation 2.3. as cited by Dada (2012), the constant K is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process. If n=1 then the partition between the two phases are independent of concentration. If value 1/n is below one, it indicates a normal adsorption. On the other hand, 1/n being above indicates cooperative adsorption. Thus, the smaller 1/n, the greater the expected heterogeneity.

2.4.4.3 **Langmuir Isotherm**

The Langmuir isotherm is the strongly favorable type of adsorbent for an adsorption process. It describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent. The Langmuir isotherm is valid for monolayer adsorption into a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based on the assumptions, Langmuir represented the following equation (Eq. 2.4):

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \quad \text{(Eq. 2.4)}$$

Q_o is expressed as kg adsorbate/ kg solid while K_L is kg/m^3. The equation is applied with assumption of monolayer adsorption, actives sites on adsorbent are fixed, adsorption reached equilibrium and adsorption process is reversible. The value of Q_o and K can be determined by plotting graph 1/q_e versus 1/C_e according to Equation 2.5.

$$\frac{1}{q_e} = \frac{1}{Q_o K_L C_e} + \frac{1}{Q_o} \qquad \text{(Eq. 2.5)}$$

2.4.4.4 Temkin Isotherm

This isotherm contains a factor that explicitly taking into account of adsorbent-adsorbate interactions. By ignoring extremely low and large value of concentrations, the model assumes that of all molecules in the layer would decrease linearly rather than logarithmic with coverage (Dada et al., 2012). The model is given by the following equation (Eq. 2.6 and Eq. 2.7):

$$q_e = \frac{RT}{b} \ln(A_r C_e) \qquad \text{(Eq. 2.6)}$$

$$q_e = \frac{RT}{b_r} \ln A_r + \left(\frac{RT}{b}\right) \ln C_e \qquad \text{(Eq. 2.7)}$$

As implied in the equation, its derivation is characterized by uniform distribution of binding energies was carried out by plotting the quantity sorbed q_e against *ln*C_e, and the constant were determined from the slope and intercept.

2.5 CHARACTERIZATION AND ANALYTICAL TECHNIQUES

There are various analytical techniques being adopted in this research. Several tests and analysis has been carried out on geopolymerS to determine the chemical compositions, surface structure, porosity and particle size using various tools.

2.5.1 Determination of Chemical Composition and Functional Group

Fourier Transform Infrared Spectrometry (FTIR) is an important tool to identify functional group of sample. In FTIR, infrared radiation is being emitted to the sample and similarly to other spectroscopy, part of the radiation will be absorbed by the sample while some passes through the sample. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint, no two unique molecular structures produce the same infrared spectrum.

Figure 2.6 and Figure 2.7 shows the FTIR result of a study conducted by Zhang et al., (2012) of metakaolin by reaction of alkali activator under a variety of conditions such as NaOH concentration, solid/liquid ratio, heat evolution rate, etc.

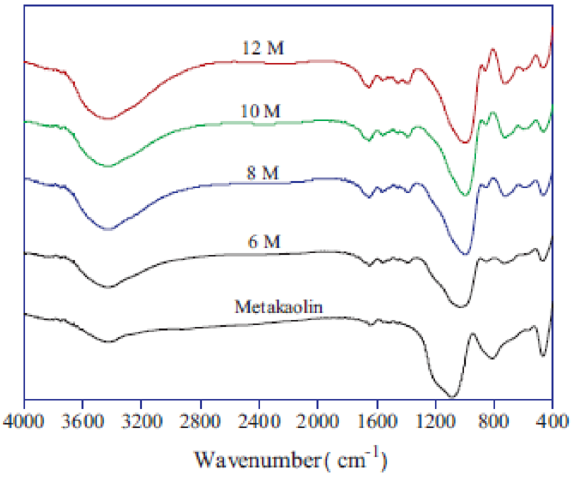

Figure 2.3: FTIR spectra of MK and the geopolymerization products after activation with NaOH solution at 30˚C for 72 h (Zhang et al., 2012).

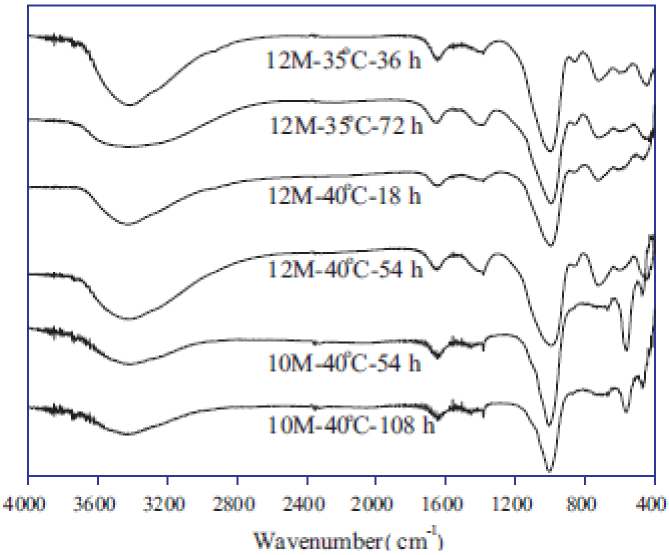

Figure 2.4: FTIR spectra of selected geopolymerization products of MK activated with NaOH solution at 30˚C and 40˚C for different periods (Zhang et al., 2012).

The most evident spectral different are found in the low-wavenumber region (400-800 cm^{-1}) and the middle-wavenumber region (800-125- cm^{-1}). As cited by (Zhang et al., 2012), in the low-wavenumber region, for the spectrum of MK, the bands around 465 cm^{-1} are assigned to T-O-T bending modes in TO_4 and the band at 800 cm^{-1} is assigned to the Al-O bending mode of AlO_6 octahedra. After geopolymerization, the intensities of these two bands both decrease, particularly at ~800 cm^{-1}, indicating the breakdown of the original octahedral structure of the residual kaolinite particles. The band at 710 cm^{-1} (Refer Figure 2.6) in the geopolymer spectra indicated the formation of Al^{IV} as the main environment in the polymer. The small band centered at ~600 cm^{-1} is probably caused by T-O vibration in double rings in zeolite precursors. Meanwhile, a more prominent band at 557 cm^{-1} (Refer Figure 2.7) appears only in the system of 10M-40˚C-54h and 10M-40˚C-108 h, this band is typically assigned to the external linkage vibration of the TO_4 tetrahedra in the double rings of zeolite.

2.5.2 **Analysis of Surface Structure.**

X-ray Diffraction (XRD) is used for a wide variety of material characterization studies. Primarily, the technique identifies crystalline species in material. In addition to compound identification, XRD can also be used to determine strain, preferred orientation, crystallographic structure, and grain size of crystalline materials. When x-ray diffraction is used in a glancing angle mode, crystalline structure as a function of depth can be obtained.

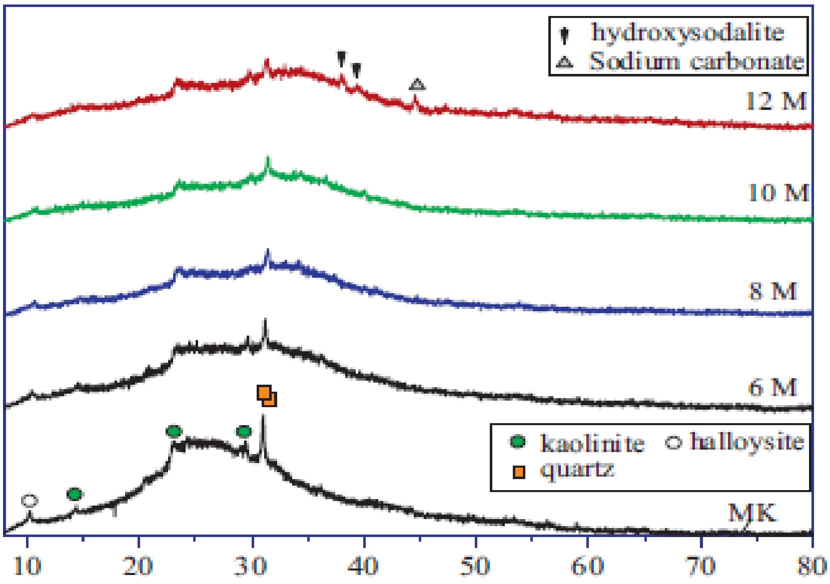

Figure 2.5: Co Kα radiation XRD patterns of MK and its geopolymerization products after activation with NaOH solution of 6-12 mol/L at 30˚C for 72 h (Zhang et al., 2012).

Figure 2.9 shows the XRD data for MK and the geopolymer samples obtained after 72 h of reaction at 30˚C. The MK used is largely amorphous, with a small quantity of quartz as an impurity phase, and minor kaolinite and halloysite. As reported by (Zhang et al., 2012), the broad peak observed from 15 to 35^o 2θ in MK has been broadened up to 40^o 2θ after reaction with NaOH solution, with the center gravity shifted to higher angle, as is well known to occur during geopolymer formation of metakaolin.

2.5.3 Determination of Pore Size Distribution and Porosity

Brunauer-emmet-Teller (BET) analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in m^2/g yielding important information in studying the effects of surface porosity and particle size in many applications.

The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Physical adsorption results from relatively weak forces (Van der Waals forces) between the adsorbate gas molecules and the adsorbent surface area of the test powder.

2.5.4 Determination of Dye Concentration

UV-Visible Spectrocopy is used in this research work to determine the concentration of dye or methylene blue in the solution. The concentration of the dye will be measured before and after adsorption test to investigate the adsorption capabilities of the geopolymers.

CHAPTER 3
METHODOLOGY

3.1 INTRODUCTION

The research work of this study is divided into four main stages, which are to synthesis and select the optimum silica to alumina ratio, to study the effect of percentage of pore-forming agent (poly ethylene glycol, 20,000) into the optimum ratio, to characterize the geopolymers and experimental testing of adsorption of methylene blue on geopolymers. The overview of this study can be seen in Figure 3.1.

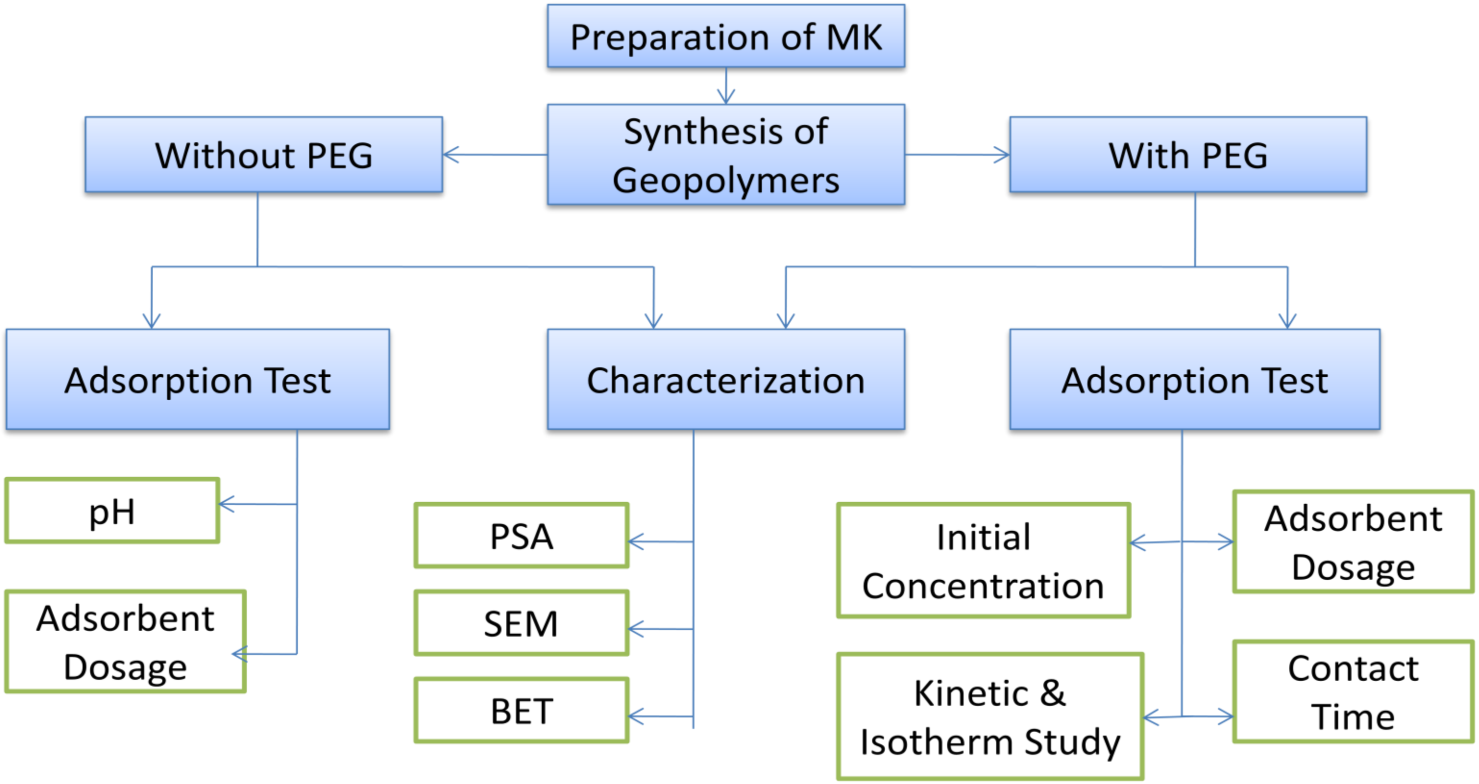

Figure 3.1: Overview of the Process Flow for Adsorption of Dye Removal.

3.2 MATERIALS

Phosphoric acid (85%, Merck), Kaolin (R&M chemicals) and poly ethylene glycol (MW 20000, Merck) were used in this study. De mineralized water was used to prepare geopolymer paste.

3.3 PREPARATION AND CHARACTERIZATION OF RAW MATERIAL

The raw material kaolin was calcined in the furnace for 600 ^{0}C for 4 hours before being used to synthesize MK phosphoric acid-based geopolymer (Refer Table 3.1).

Table 3.1: Preparation of Raw Material

Raw Material	Description
Metakaolin	• Used as Al_2O_3 source for the synthesis of geopolymers. • Metakaolin is produced by the calcinations process of the kaolinite at temperature of 750℃ for 5 hours in the furnace. • The high temperature metakaolin is cooled at room temperature for 24 hours.

3.4 SYNTHESIS OF PHOSPHORUS ACID-BASED GEOPOLYMERS

In this research, phosphoric acid-based geopolymers were synthesized by adopting a method reported by Le-Ping et al., (2010). Meanwhile, the experimental parameters for adsorption experiments were adopted from a research by (Hameed, 2009). Geopolymers were synthesized using different alumina to silica and phosphate to alumina ratios. Besides, the modification was made to the optimum ratio of geopolymer by adding different amount of pore-forming agent (polyethylene glycol). The sample preparation is summarized as below.

Metakaolin, aluminum oxide, PEG, phosphoric acid and distilled water were mixed in a mixer for 10 minutes to obtain an aqueous slurry having molar ratios SiO_2/ Al_2O_3=1, 2, 2.4, 3. Pore-forming agent, (PEG) was added at a mass fraction of 2%, 3%, 4% and 5% of the water used. Mixtures were stirred for 3 minutes before poured into cubic moulds, and then sealed to prevent water loss. The cubes were cured at 80˚ C for 24 hours. The dried materials were crushed and sieved to desired mesh size of 125µm. The prepared samples were stored in an airtight container for further use. Methylene blue solution (500ppm) was prepared from methylene blue powder (R&M chemicals) using de-mineralized water. This stock solution was used to prepared different solutions.

Table 3.2: Synthesis Parameters for Geopolymers With and Without PEG.

Sample	**Name**	**Silica to alumina ratio**	**Percentage of PEG (%)**	**Phosphoric acid to alumina ratio**	**Water to MK ratio**
Without PEG	GP-R1	1	None	1	1
	GP-R2	2			
	GP-R2.4	2.4			
	GP-R3	3			
With PEG	GP-PEG2	2.4	20	1	1
	GP-PEG3		30		
	GP-PEG4		40		
	GP-PEG5		50		

3.5 BATCH ADSORPTION MATERIALS AND METHODS

The adsorption experiment was conducted using geopolymers as adsorbents and methylene blue as adsorbate. Experimental setups focused on the adsorption capacity using geopolymer by examining the influence of pH, adsorbent dosage, initial adsorbate concentration and contact time as given in Table 3.2.

3.5.1 Effect of pH

In this study, the effect of solution pH on adsorption of dye (methylene blue) on phosphoric acid-based geopolymer was studied by adding 0.50g of geopolymer into 50mL of methylene blue having initial concentration 50ppm at different pH values at 25C. The pH was adjusted with 0.1 M of hydrochloric acid (HCl) or 0.1 M sodium hydroxide (NaOH) solutions and measured by using pH meter (Metler Toledo). The samples were agitated for 180 min at a constant agitation speed of 130 rpm. The dye concentrations were measured by a double beam UV-Vis spectrophotometer (lambda 1800, shimadzo, Japan) at 664 nm wavelength. Prior to the measurement, a calibration curve was obtained using standard methylene blue solutions with the known concentration.

3.5.2 Effect of Adsorbent Dosage

In this study, the effect of adsorbents dosage on adsorption of methylene blue was studied by adding different amount of adsorbents 0.5g and 1.0g into 50mL of 50ppm methylene blue solution as shown in Table 3.2. Agitation was made for 180 minutes at constant agitation speed of 130 rpm.

3.5.3 Effect of Contact Time

To study the effect of contact time on the methylene blue adsorption known amount of geopolymers were added into a number of 250mL stoppered glass (Erlenmeyer flasks) containing a definite volume (50mL in each flask) of fixed initial concentration (50mg/L) of the dye solution without changing the solution pH at 25 ℃. Flasks were placed in the thermo stated water bath shaker and agitation was provided at 130 rpm for allocated time to measure the dye concentrations at equilibrium.

3.5.4 Kinetic and Isotherm Study

Experimental data obtained from the contact time experiment will be used to determine which kinetic and isotherm model that the adsorption activities of phosphoric acid both with and without PEG fitted into. The calculation process was aided by using Microsoft Office Excel Spreadsheet.

Table 3.3: Experimental Design for Adsorption Test

Experimental Parameters/ Type of Adsorbent	Initial Dye Concentration (mg/L)	Temperature (˚C)	pH	Adsorbent Dosage (g)	Time (min)
Without PEG	50	25˚C	3 5 7 9 10	0.5 1.0	30 60 90 120 150 180
With PEG	50 100 200 500	25˚C	7	0.25 0.5 0.75 1.0	10 20 30 60 90 120 240

CHAPTER 4

RESULT AND DISCUSSION

4.1 PHYSICAL PROPERTIES

4.1.1 Particle Size Distribution Analysis of Geopolymers

During the experiment, the particle size to of each adsorbent has been determined using Particle Size Analyzer equipment and tabulated in Table 4.1. The particle size of these two types calcined and non-calcined do not differ much which is only about 13% and 5% deviation respectively.

Table 4.1: Particle Size of Adsorbents.

Without PEG	**d (0.5) microns**
GP-R1	3.921
GP-R2	3.532
GP-R2.4	3.307
GP-R3	3.351
With PEG	**d (0.5) microns**
GP-PEG2	6.041
GP-PEG3	6.169
GP-PEG4	6.272
GP-PEG5	6.981

Table 4.1 showed three types of the geopolymers, which are without PEG, with PEG without calcinations and also with PEG and calcined. From these three types, it can be seen that for each type, the deviation of the particle sizes are 16%, 13% and 6% respectively. Generally, the smaller the particle size, the higher the surface area. Thus, smaller surface area is expected to have higher capability in adsorption test. However, other characterizations analysis should be done to know about the porosity of the geopolymers.

4.2 INITIAL ADSORPTION EXPERIMENT RESULT WITHOUT THE PRESENCE OF PEG

Initial adsorption test had been carried out using methylene blue solution to determine the adsorption ability of GP-R1, GP-R2, GP-R2.4, and GP-R3. The effect of adsorbent dosage and pH has been carried out to observe the adsorption process by geopolymers. The aim of this experiment is to determine the best ratio of geopolymer to be furthered study by adding pore-forming agent.

4.2.1 Effect of Initial Adsorbent Dosage

The adsorption process has been carried out using 50mL of 50ppm methylene blue solution. Adsorbent dosage of 0.5g and 1.0g has been used to study the effect of initial dosage on adsorption capabilities of GP-R1, GP-R2, GP-R2.4, and GP-R3. Figure 4.1 and 4.2 are the results of experiment respectively.

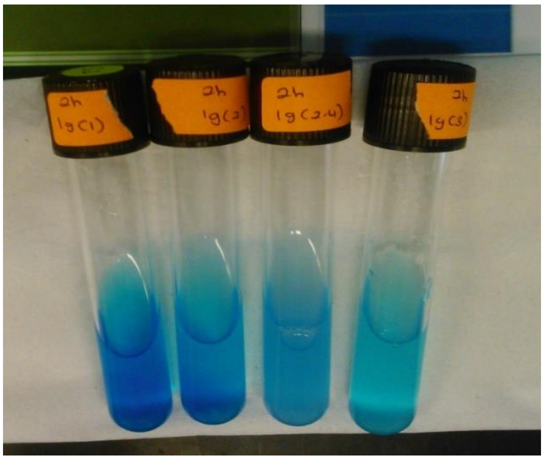

Figure 4.1: 0.5g of GP-R1, GP-R2, GP-R2.4, and GP-R3 in 50mL of 50ppm Methylene Blue after 3hours.

With UV-Vis Spectrometer used, the exact concentration of methylene blue can be obtained and a graph of percentage removal versus time for both 0.5g and 1.0g adsorbents dosage is plotted in Figure 4.2 to Figure 4.5. The removal percentage of methylene blue is calculated by using Equation 4.1.

$$Percent\ Removal, \% = \frac{c_o - c_e}{c_0} x100\% \qquad \text{Equation (4.1)}$$

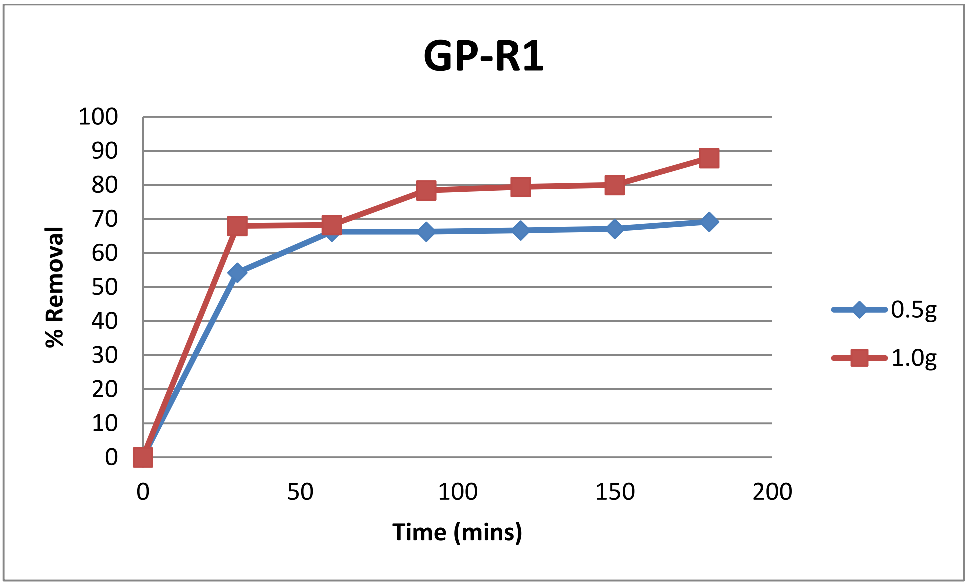

Figure 4.2: Graph of Percentage Removal vs Time of Adsorbents GP-R1 at Initial Concentration of 50ppm.

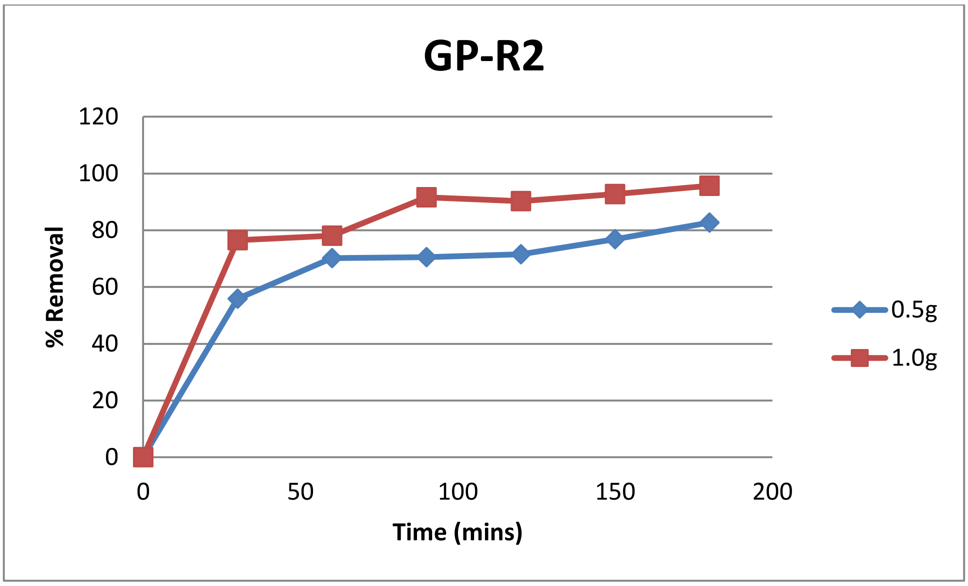

Figure 4.3: Graph of Percentage Removal vs Time of Adsorbents GP-R2 at Initial Concentration of 50ppm.

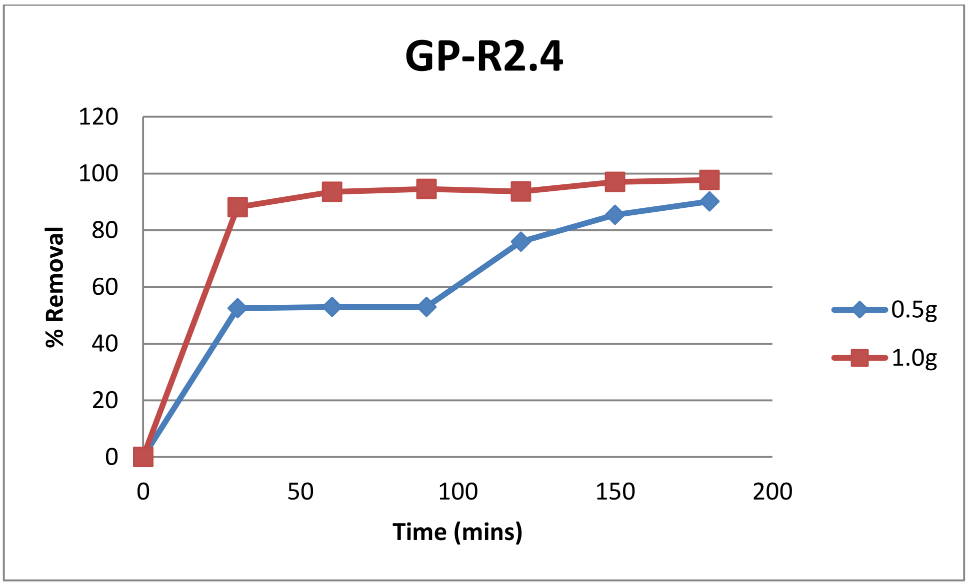

Figure 4.4: Graph of Percentage Removal vs Time of Adsorbents GP-R2.4 at Initial Concentration of 50ppm.

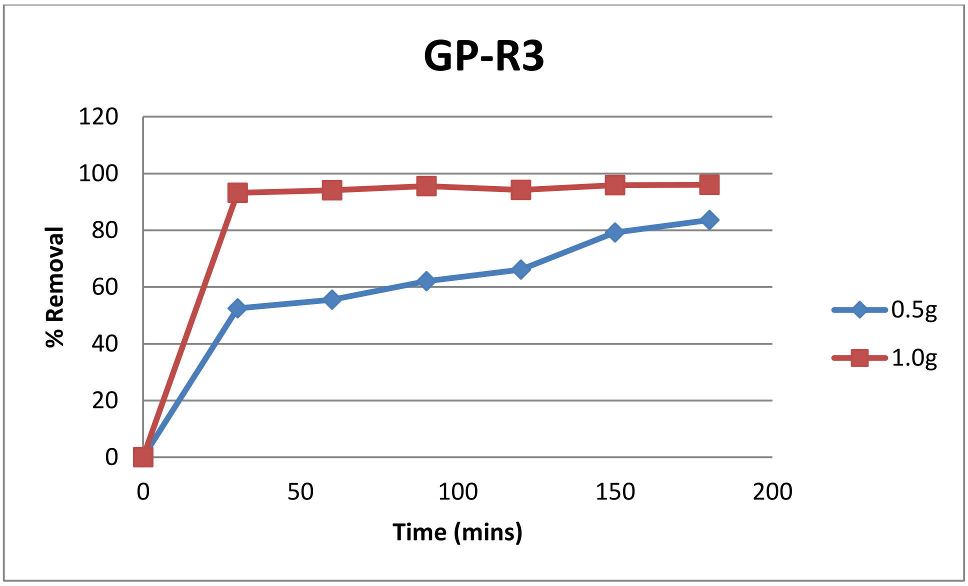

Figure 4.5: Graph of Percentage Removal vs Time of Adsorbents GP-R3 at Initial Concentration of 50ppm.

Form the Figure 4.2 to Figure 4.5 above, the adsorption activity of methylene blue is increase as the initial geopolymers dosage increase. From results shown, 1.0g of adsorbents are able to achieve up to 97% compared to 0.5g adsorbents which is only up to 90% adsorption capability. Besides, for both at adsorbent dosage of 0.5g and 1.0g, GP-R2.4 showed the highest percentage removal which is 90% and 98% respectively. Thus, it can be concluded that GP-R2.4 is more active compared to GP-R1, GP-R2, and GP-R3.

4.2.2 **Effect of pH**

From the effect of adsorbent dosage, adsorbent of GP-R2.4 is chosen as a sample in examining the effect of pH towards the adsorption activity by geopolymers. Five different pH values (3, 5, 7, 9, and 10) have been studied and the result is shown in Figure 4.4.

Figure 4.6: Effect of pH on Adsorption of Methylene Blue by Using GP-R2.4.

Figure 4.6 shows that the adsorption activities of geopolymers increase as the pH increase. The percentage removal of methylene blue is up to 99.8% as the pH is increases to 10 (Figure 4.7).

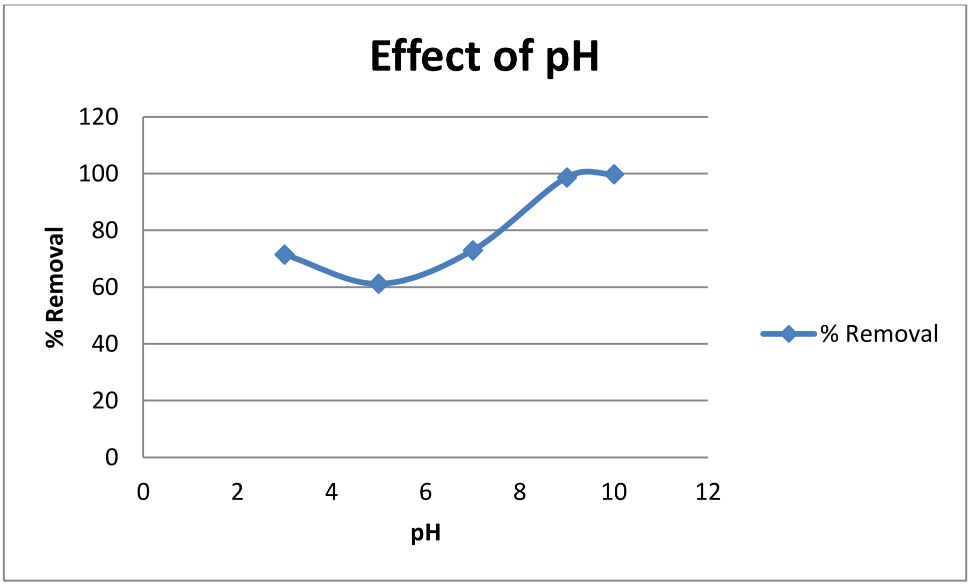

Figure 4.7: Graph of Percent Removal of Methylene Blue Based on the Effect of pH.

4.3 INITIAL ADSORPTION EXPERIMENT RESULT WITH THE PRESENCE OF PEG

From the first part, the adsorption test is done without adding polyethylene glycol (PEG) that acts as pore-forming agent. For this second part, the initial adsorption test had been carried out using methylene blue solution to determine the adsorption capability of GP-PEG2, GP-PEG3, GP-PEG4, and GP-PEG5. The effect of adsorbent dosage, initial concentration and contact time has been carried out to observe the adsorption process by geopolymers.

4.3.1 Effect of Initial Adsorbent Dosage

The adsorption process has been carried out using 50mL of 50ppm methylene blue solution. Adsorbent dosage of 0.25g, 0.5g, 0.75g and 1.0g has been used in order to study the effect of initial dosage on adsorption capabilities of GP-PEG2, GP-PEG3, GP-PEG4, and GP-PEG5. Figure 4.8 to Figure 4.11 are the results of this experiment respectively.

Figure 4.8: Effect Of Initial Adsorbent Dosage On Methylene Blue Adsorption Using GP-PEG2.

Figure 4.9: Effect of Initial Adsorbent Dosage on Methylene Blue Adsorption Using GP-PEG3.

Figure 4.10: Effect of Initial Adsorbent Dosage On Methylene Blue Adsorption Using GP-PEG4.

Figure 4.11: Effect Of Initial Adsorbent Dosage On Methylene Blue Adsorption Using GP-PEG5.

From Figure 4.8 to Figure 4.11, the adsorption activity of methylene blue increase as the initial geopolymers doasage increase. From the results shown, it can be observed that the adsorbent dosage reach optimum at 0.5g. Besides, the result showed that the adsorption activity of GP-PEG3 is more active as compared to GP-PEG3, GP-PEG4, GP-PEG5. This observation is expected due to the relatively higher porosity of GP-PEG3 compared to other geopolymers.

With UV-Vis Spectrometer used, the exact concentration of methylene blue can be obtained and a graph of percent removal of methylene blue versus adsorbent dosage is plotted in Figure 4.12 by using Equation 4.l.

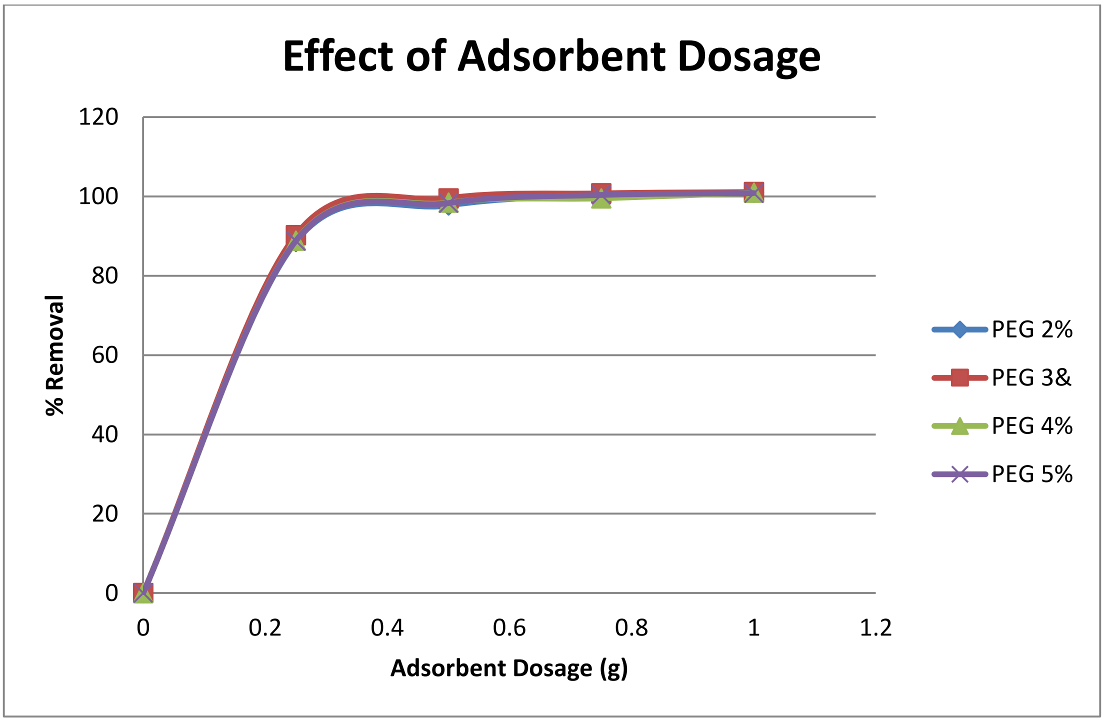

Figure 4.12: Effect of Initial Adsorbent Dosage on Methylene Blue Adsorption Using GP-PEG2, GP-PEG3, GP-PEG4, GP-PEG5

Figure 4.12 show that all the adsorbents have quite similar percentage removal. All of geopolymers clearly show the excellent removal capacity and able to achieve up to 100% removal when nearly around 0.4g of adsorbent dosage is used. From the data obtained GP-PEG3 has the highest percentage removal compared to others. At 0.25g, GP-PEG3 had percentage removal of 90.24% while GP-PEG2, GP-PEG4, GP-PE5 have percentage removal of 88.56%, 88.87% and 88.79% respectively.

4.3.2 **Effect of Contact Time**

The kinetic study of GP-PEG2, GP-PEG3, GP-PEG4, GP-PEG5 adsorption capabilities is observed by conducting the adsorption test using 50mL of 50ppm methylene blue solution. The sample extraction of 5mL is done at time of 0, 10, 20, 30, 60, 90, 120, and 240 minutes.

The concentration of methylene blue at each time for each geopolymers is determined and the graph of percent removal of methylene blue versus contact time is plotted using the data obtained (Figure 4.13 to Figure 4.15).

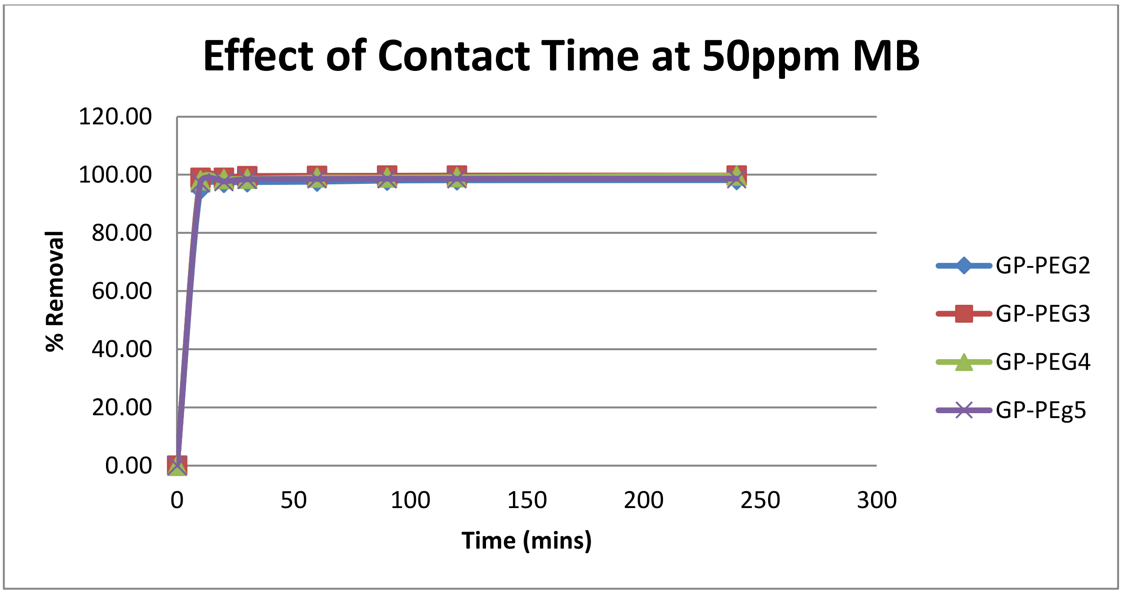

Figure 4.13: Effect of Contact Time at Initial Concentration of 50ppm.

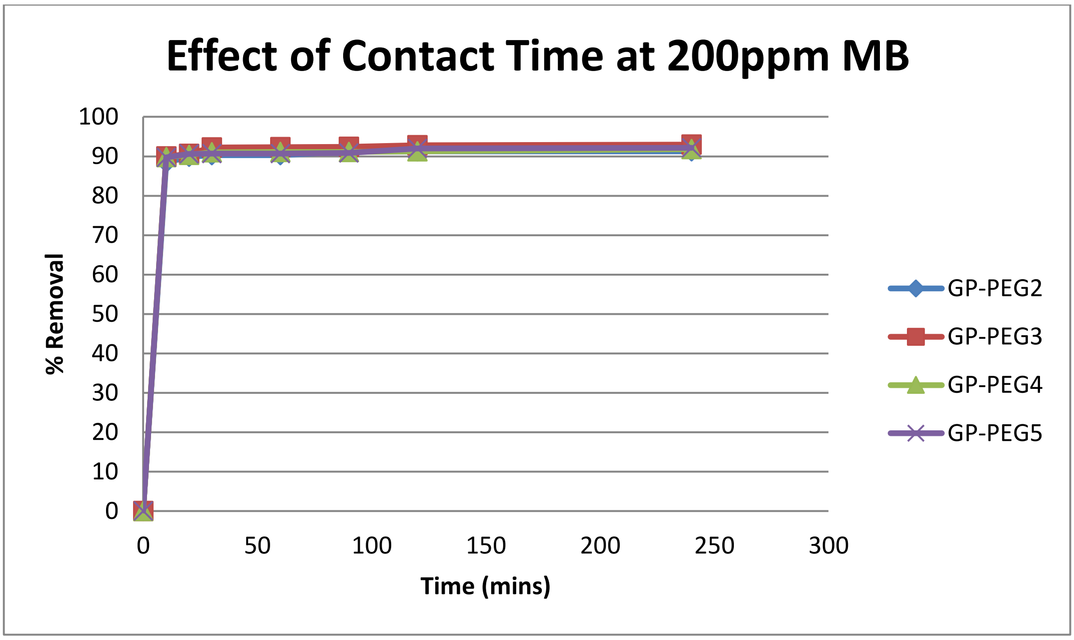

Figure 4.14: Effect of Contact Time at Initial Concentration of 200ppm.

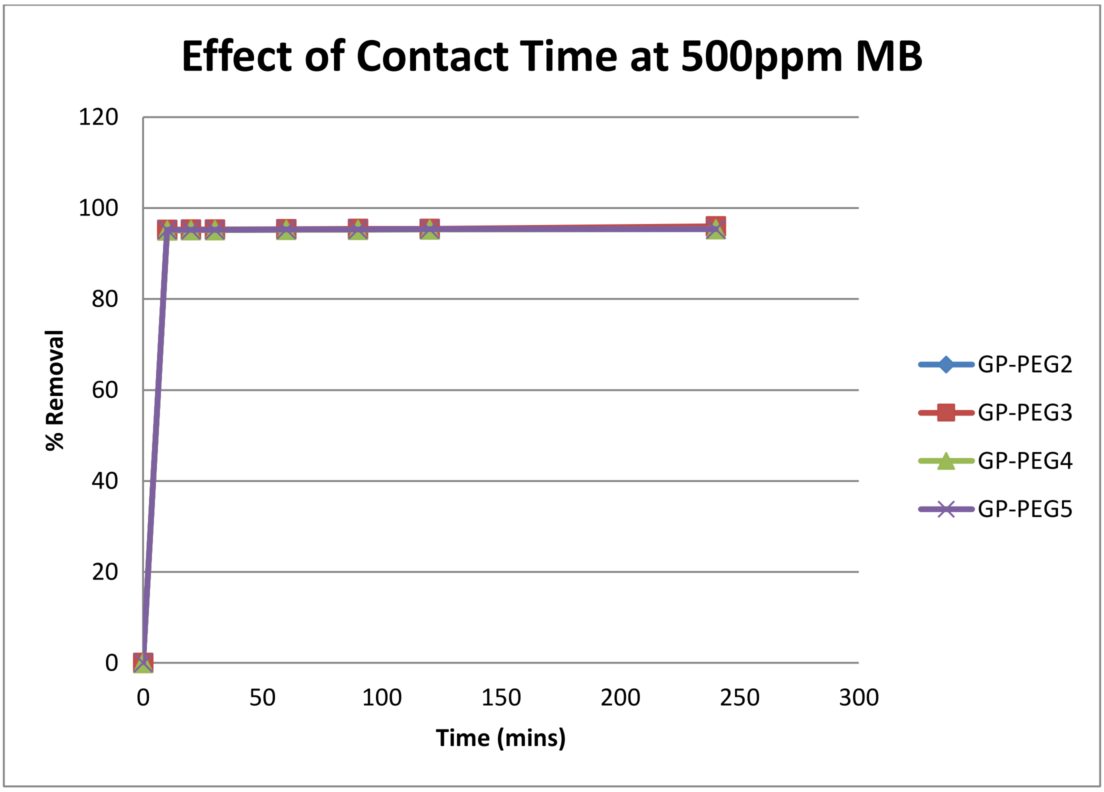

Figure 4.15: Effect of Contact Time at Initial Concentration of 500ppm.

From Figure 4.13 to Figure 4.15, the adsorbents showed great adsorption capabilities even at the higher initial concentration. However, the trending of the adsorption does not linear as the percentage removal at 500ppm is higher compared to the percentage removal at 200ppm. From these three figures, it can be concluded that the percentage removal of 50ppm can reach up to 99.75% while percentage at 200ppm and 500ppm can reach up to 93% and 96% respectively. Besides, from the data collected, the GP-PEG3 has the highest percentage removal at all initial concentrations.

4.3.3 **Kinetic Study**

The kinetic study of GP-PEG1, GP-PEG2, GP-PEG3 and GP-PEG5 adsorption capabilities was observed by conducting the adsorption test at 50ppm of initial concentration of methylene blue solution and a sample extraction at 10, 20, 30, 60, 90, 120 and 240 minutes. Experimental data was used to plot graph of Figure 4.5 and Figure 4.16 to study the kinetic model of adsorption activities by phosphoric acid-based geopolymers.

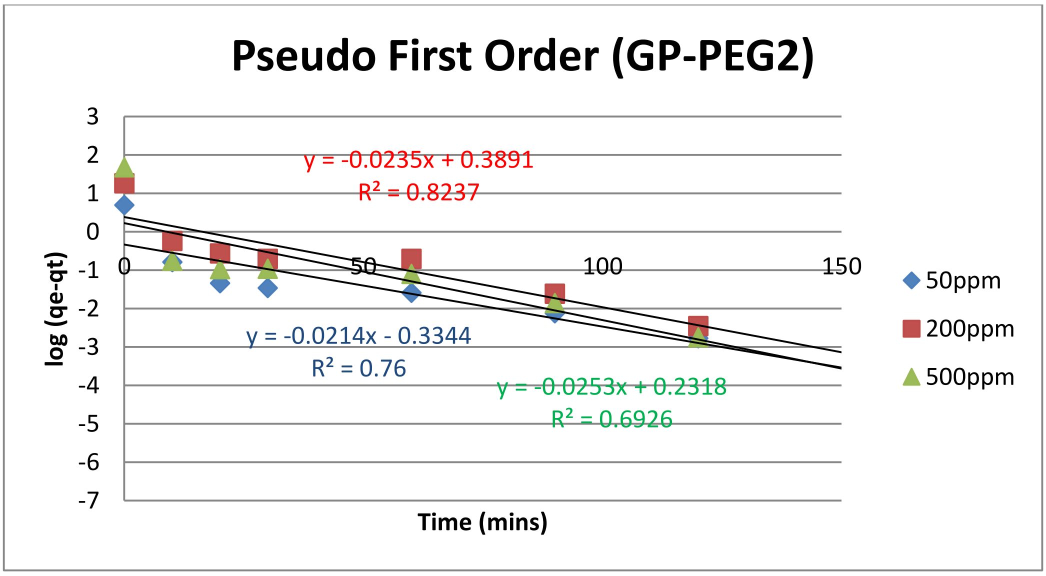

Figure 4.16: Pseudo First Order of GP-PEG2.

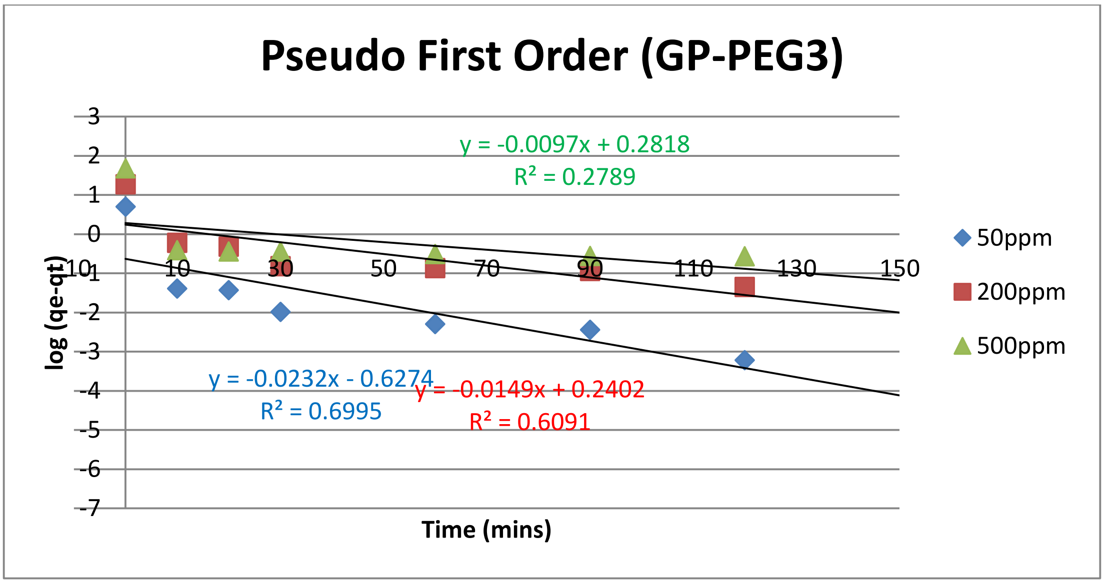

Figure 4.17: Pseudo First Order of GP-PEG3.

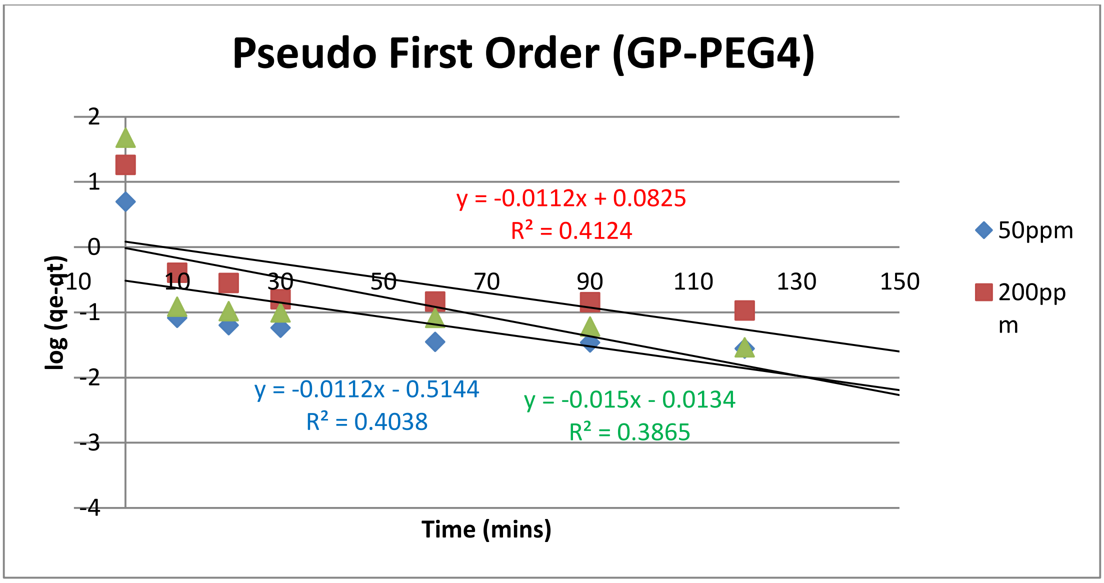

Figure 4.18: Pseudo First Order of GP-PEG4.

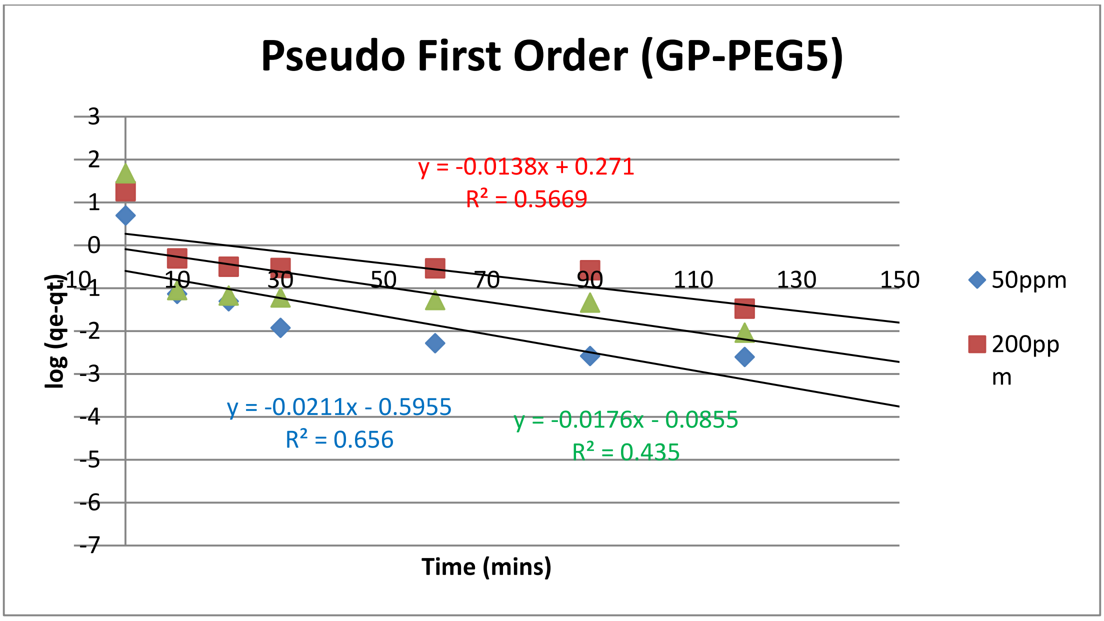

Figure 4.19: Pseudo First Order of GP-PEG5.

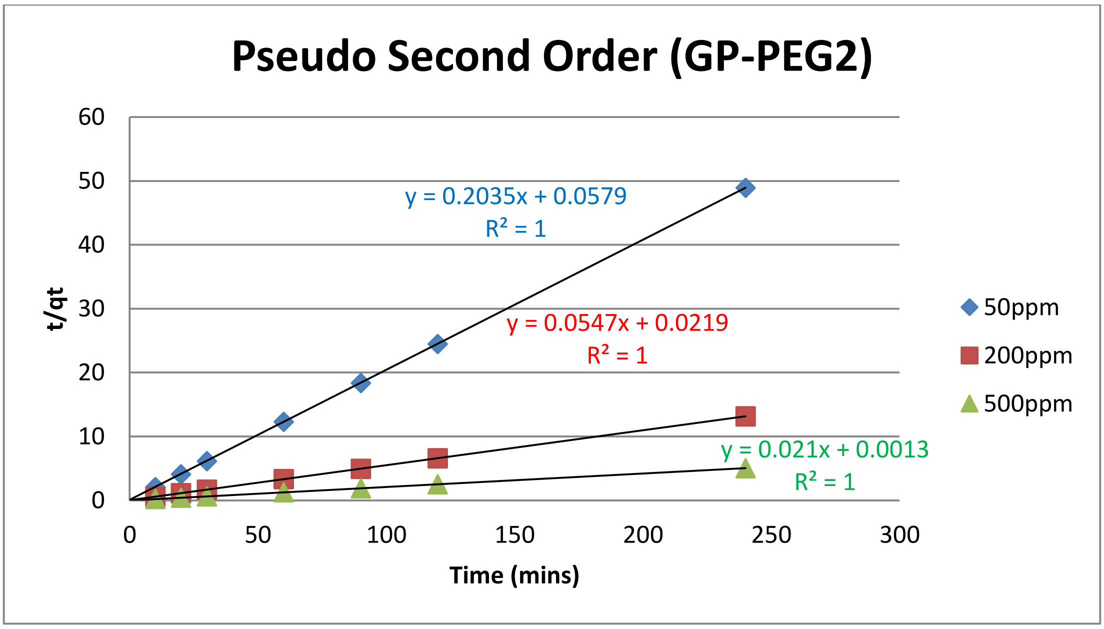

Figure 4.20: Pseudo Second Order of GP-PEG2.

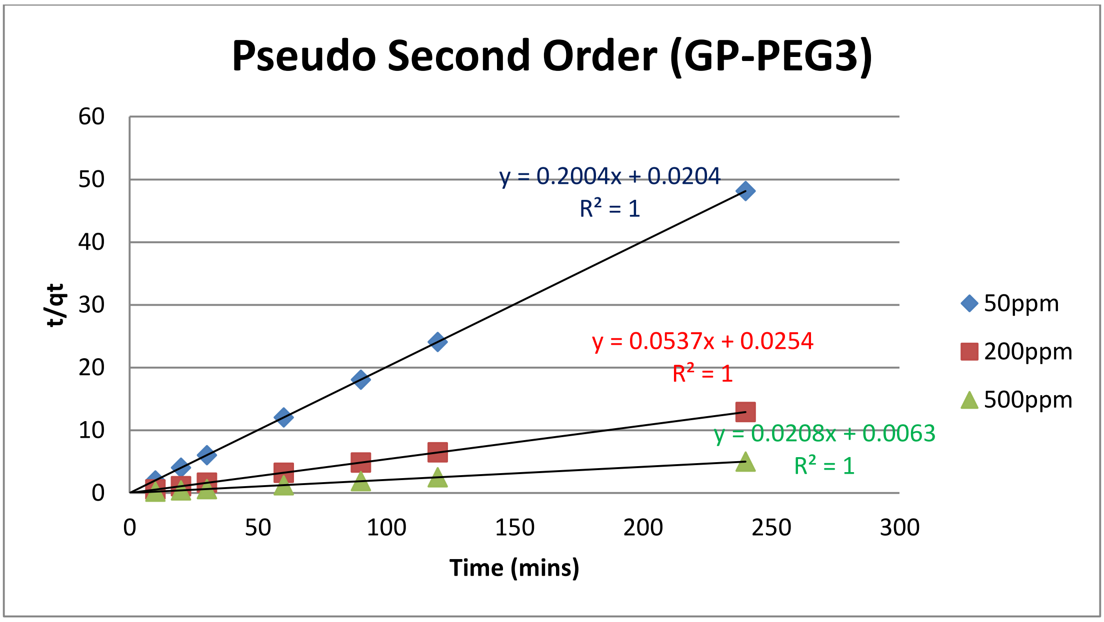

Figure 4.21: Pseudo Second Order of GP-PEG3

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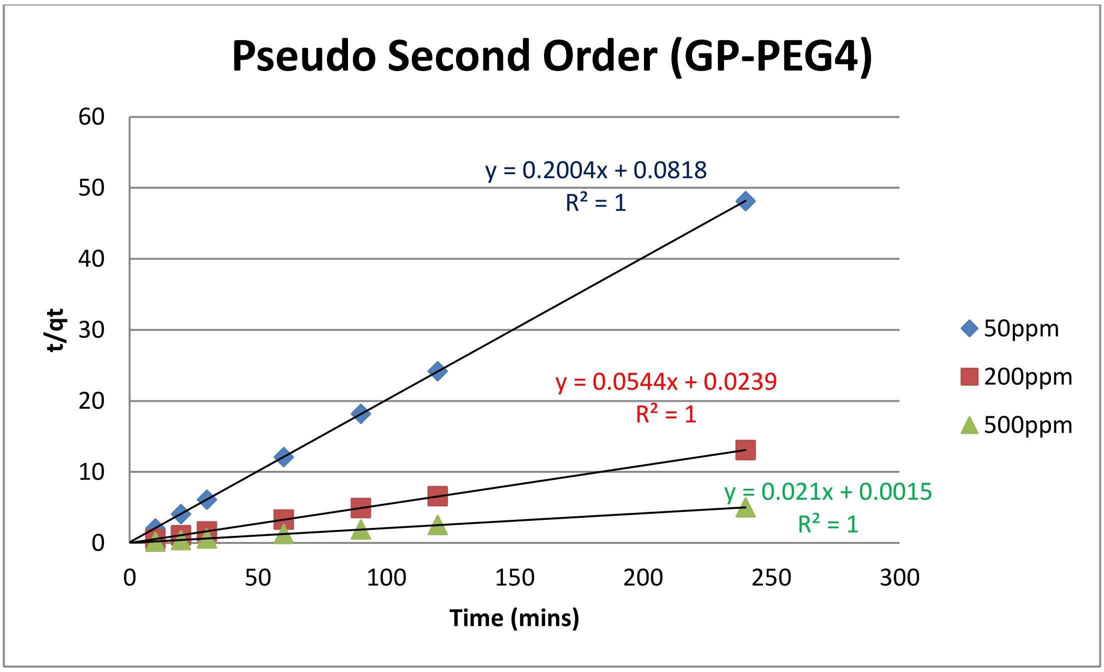

Figure 4.22: Pseudo Second Order of GP-PEG4.

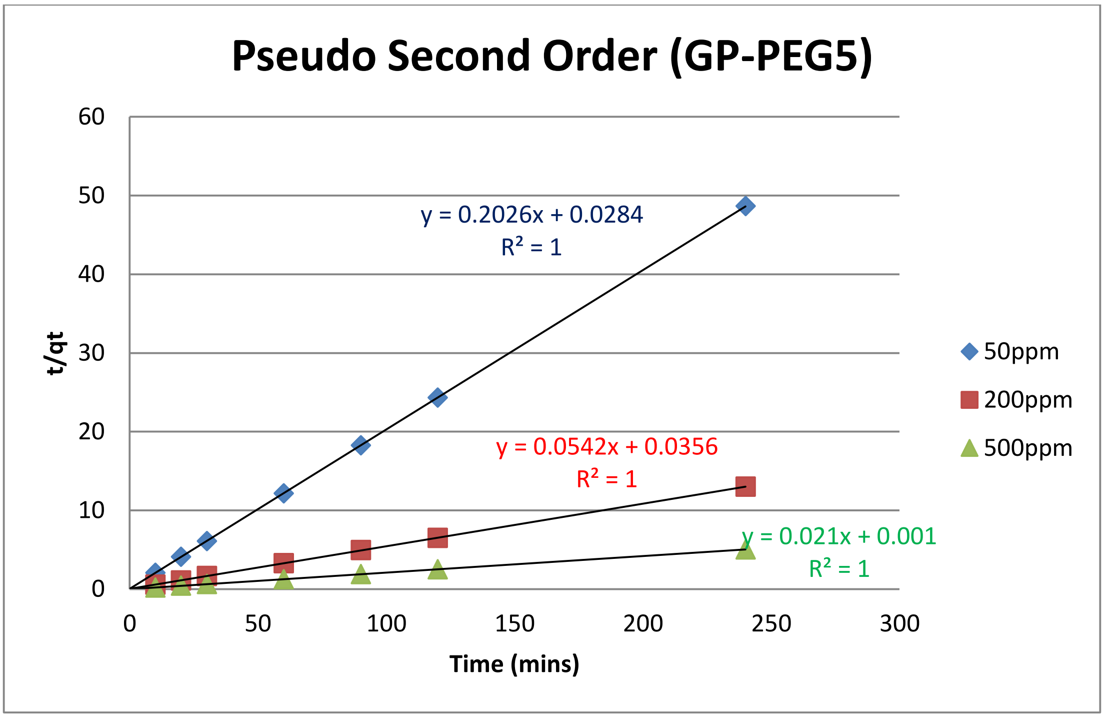

Figure 4.23: Pseudo Second Order of GP-PEG5.

The graph of pseudo first order has been plotted by using Equation 4.2 while graph of pseudo second order was plotted by using Equation 4.3.

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} t \qquad \text{Equation 4.2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^e} + \frac{1}{q_e} t \qquad \text{Equation 4.3}$$

Where q_t is the amount adsorbed (mg/g) at time t and the amount adsorbed at equilibrium, q_e can be determined using Equation 4.4:

$$q_e = \frac{c_i - c_e}{M} V \qquad \text{Equation 4.4}$$

Where,

K_1 = rate constant for pseudo first order rate of reaction model

K_2 = rate constant for pseudo second order rate of reaction model

C_i = initial adsorbate concentration, ppm

C_e = adsorbate concentration at equilibrium

V = volume of solution, L

M = mass of adsorbent used, g

By using correlation of Equation 4.2 and Equation 4.3, the values of k_1, q_e, and k_2 for both pseudo first order and pseuso second order can be determined respected to the graph plotted (Table 4.2 and Table 4.3)

Table 4.2: Comparison of $k_{1,}$ q_e and R^2 values for pseudo first order reaction model for methylene blue adsorption.

1st order	**ppm**	**slope**	**intercept**	**R2**	**k1**	**qe**
GP-PEG2	50	-0.021	-0.334	0.76	0.0484	0.4634
	200	-2.30E-02	0.389	0.823	0.0530	2.4491
	500	-0.025	0.231	0.692	0.0576	1.7022
GP-PEG3	50	-2.30E-02	0.627	0.699	0.0530	4.2364
	200	-1.40E-02	0.24	0.609	0.0322	1.7378
	500	-9.00E-03	0.281	0.278	0.0207	1.9099
GP-PEG4	50	-1.10E-02	-0.514	0.403	0.0253	0.3062
	200	-1.10E-02	0.082	0.412	0.0253	1.2078
	500	-1.50E-02	-0.013	0.386	0.0345	0.9705
GP-PEG5	50	-2.10E-02	-0.595	0.656	0.0484	0.2541
	200	-1.30E-02	0.271	0.566	0.0299	1.8664
	500	-1.70E-02	-0.085	0.435	0.0392	0.8222

Table 4.3: Comparison of k_1, q_e and R^2 values of for pseudo second order reaction model for methylene blue adsorption.

2nd order	ppm	slope	intercept	R2	k2	qe
GP-PEG2	50	2.03E-01	0.057	1.000	0.7230	4.9261
	200	5.40E-02	0.021	1.000	0.1389	18.5185
	500	2.10E-02	0.001	1.000	0.4410	47.6190
GP-PEG3	50	2.00E-01	0.02	1.000	2.0000	5.0000
	200	5.30E-02	0.025	1.000	0.1124	18.8679
	500	2.00E-02	0.006	1.000	0.0667	50.0000
GP-PEG4	50	2.00E-01	0.081	1.000	0.4938	5.0000
	200	5.40E-02	0.023	1.000	0.1268	18.5185
	500	2.10E-02	0.001	1.000	0.4410	47.6190
GP-PEG5	50	2.02E-01	0.028	1.000	1.4573	4.9505
	200	5.40E-02	0.035	1.000	0.0833	18.5185
	500	2.10E-02	0.001	1.000	0.4410	47.6190

Results show that the adsorption activities for all GP-PEG1, GP-PEG2, GP-PEG3 and GP-PEG5 are fitted well in pseudo second order kinetic model.

4.3.4 **Isotherm Study**

Isotherm study was conducted using the same experimental data obtained from kinetic study experiment. Figure 4.18, Figure 4.19 and Figure 4.10 shows the Langmuir, Freundlich and Temkin isotherms respectively for all GP-PEG2, GP-PEG3, GP-PEG4 and GP-PEG5.

The studies of isotherms are based on the correlation from Equation 4.5 to equation 4.7. The graph for Langmuir, Freundlich and Temkin isotherms were plotted in Figure 4.24, Figure 2.45 and Figure 2.46 respectively. Meanwhile, all the constant values of Langmuir, Freundlich and Temkin isotherms were tabulated in Table 4.4, Table 4.5 and Table 4.6.

Equation 4.5 shows the relationship between q_e and C_e for Langmuir Isotherm.

$$\frac{1}{q_e} = \frac{1}{q_m K_L}\frac{1}{C_e} + \frac{1}{q_m}$$ Equation 4.5

Where,

q_m = maximum amount of adsorbates adsorbed into the adsorbent, mg/g

K_L = Langmuir constant of adsorption, L/mg

(Cheng et al., 2012)

For Freundlich isotherm, the relationship between q_e and C_e can be represented using correlation as shown in Equation 4.5.

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e$$ Equation 4.6

Where,

K_F = indicators of adsorption capacity

n = adsorption intensity

For Temkin isotherm, the relationship between q_e and C_e can be represented using correlation as shown in Equation 4.5.

For Temkin isotherm, the relationship between q_e and C_e can be represented using correlation as shown in Equation 4.6.

$$q_e = \frac{RT}{b}\ln K_T + \frac{RT}{b} lnC_e$$ Equation 4.7

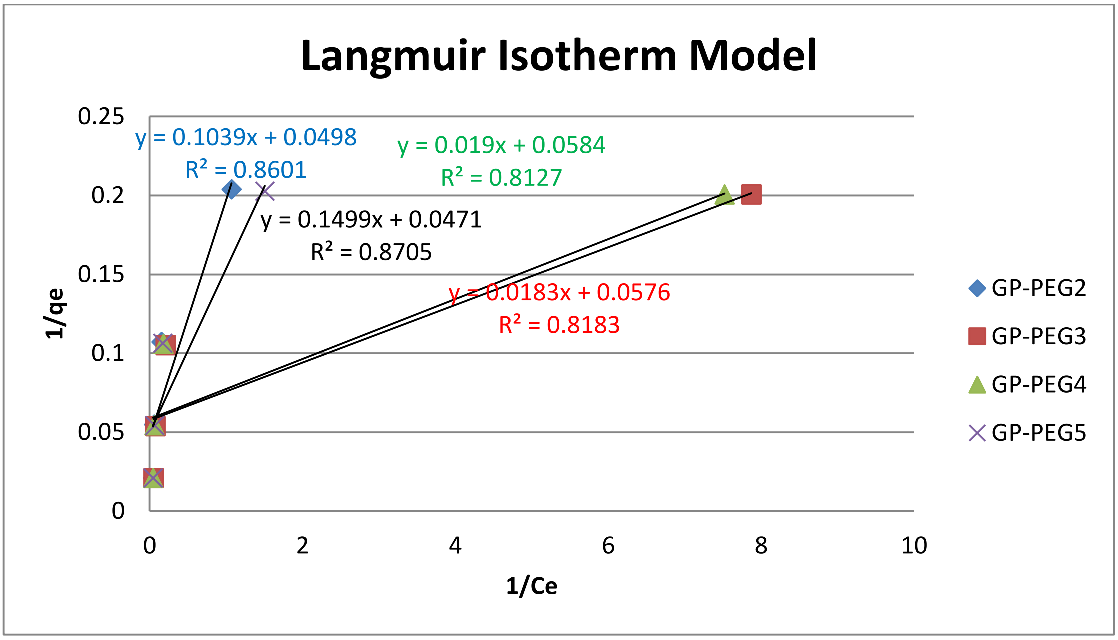

Figure 4.24: Langmuir Isotherm Study for GP-PEG1, GP-PEG2, GP-PEG3 and GP-PEG5.

Table 4.4: Values for Langmuir Isotherm constant for GP-PEG1, GP-PEG2, GP-PEG3 and GP-PEG5 in methylene blue adsorption test.

Langmuir	slope	intercept	qm(mg/g)	k	R2
GP-PEG2	0.149	0.047	21.27659574	0.315436242	0.87
GP-PEG3	0.018	0.057	17.54385965	3.166666667	0.818
GP-PEG4	0.019	0.058	17.24137931	3.052631579	0.812
GP-PEG5	0.103	0.049	20.40816327	0.475728155	0.86

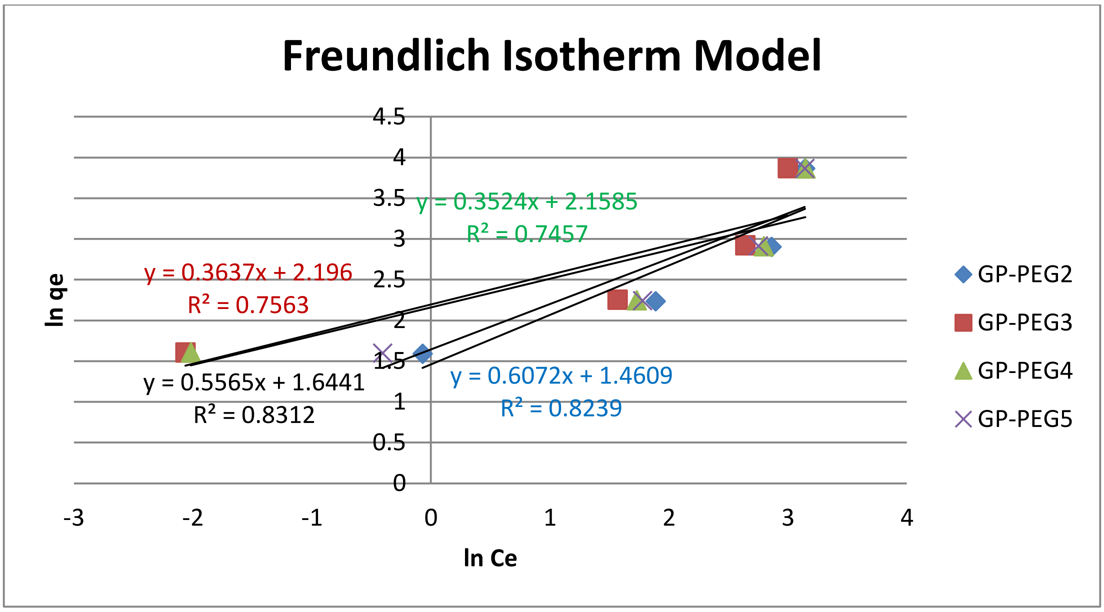

Figure 4.25: Freundlich Isotherm Study for GP-PEG1, GP-PEG2, GP-PEG3 and GP-PEG5.

Table 4.5: Values for Freundlich Isotherm constant for GP-PEG1, GP-PEG2, GP-PEG3 and GP-PEG5 in methylene blue adsorption test.

Freundlich	Slope	n	intercept	Kf	R2
GP-PEG2	0.607	1.647446458	1.46	4.305959528	0.823
GP-PEG3	0.363	2.754820937	2.196	8.988985549	0.756
GP-PEG4	0.352	2.840909091	2.158	8.653812714	0.745
GP-PEG5	0.556	1.798561151	1.644	5.175831487	0.831

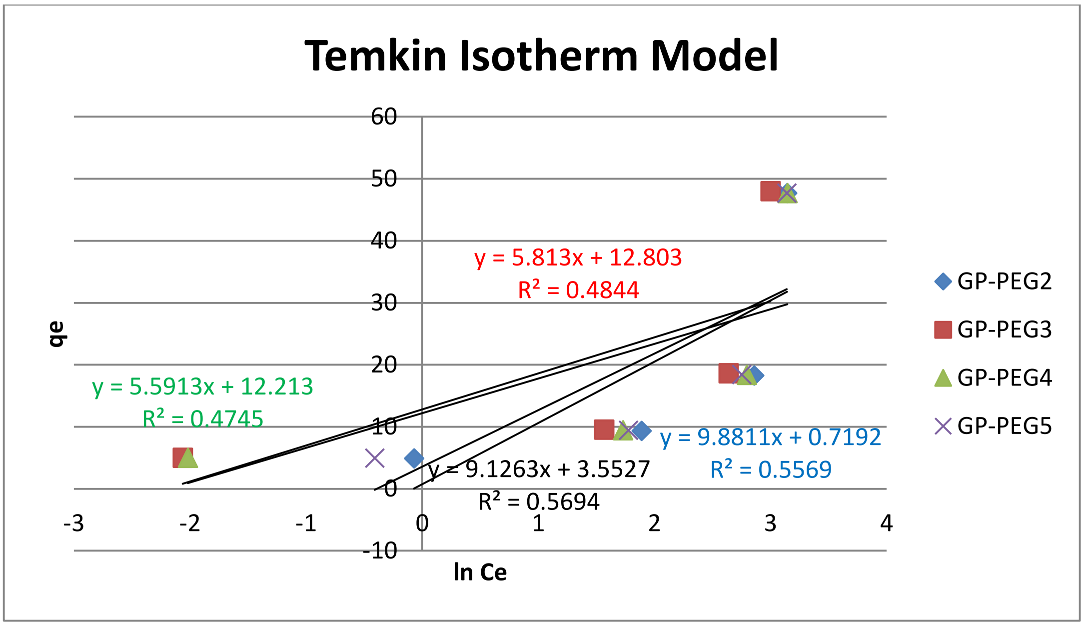

Figure 4.26: Temkin Isotherm Study for GP-PEG1, GP-PEG2, GP-PEG3 and GP-PEG5.

Table 4.6: Values for Temkin Isotherm constant for GP-PEG1, GP-PEG2, GP-PEG3 and GP-PEG5 in methylene blue adsorption test.

Temkin	**slope**	**B**	**intercept**	**A**	**R2**
GP-PEG2	9.881	9.881	0.719	1.075478753	0.556
GP-PEG3	5.81	5.81	12.8	9.053017311	0.484
GP-PEG4	5.591	5.591	12.21	8.880580522	0.474
GP-PEG5	9.126	9.126	3.552	1.475825686	0.569

The best fitted isotherm for the adsorption activities will be determined using the highest R^2 value. Results obtained shows that adsorption activities of GP-PEG1, GP-PEG2, GP-PEG3 and GP-PEG5 fitted well into Langmuir isotherm as compared to Freundlich and Temkin isotherm due to high correlation factor, R^2 observed.

4.3.5 Effect of Calcination

In this study, 0.25g of adsorbents was added into 50mL of adsorbate at different initial concentration. The effect of calcinations in adsorption test is showed in Figure 4.27.

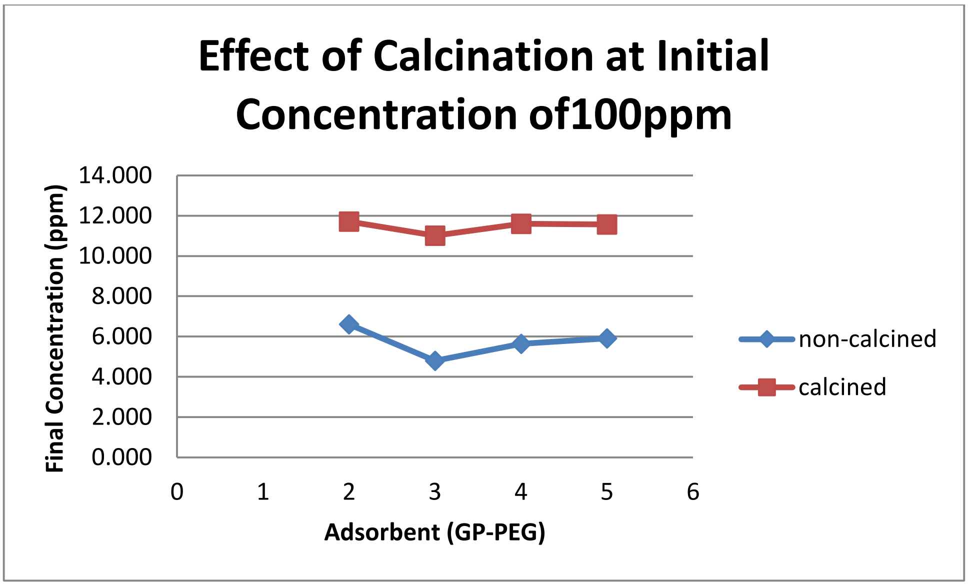

Figure 4.27: Effect of Calcination at Initial Concentration 100ppm.

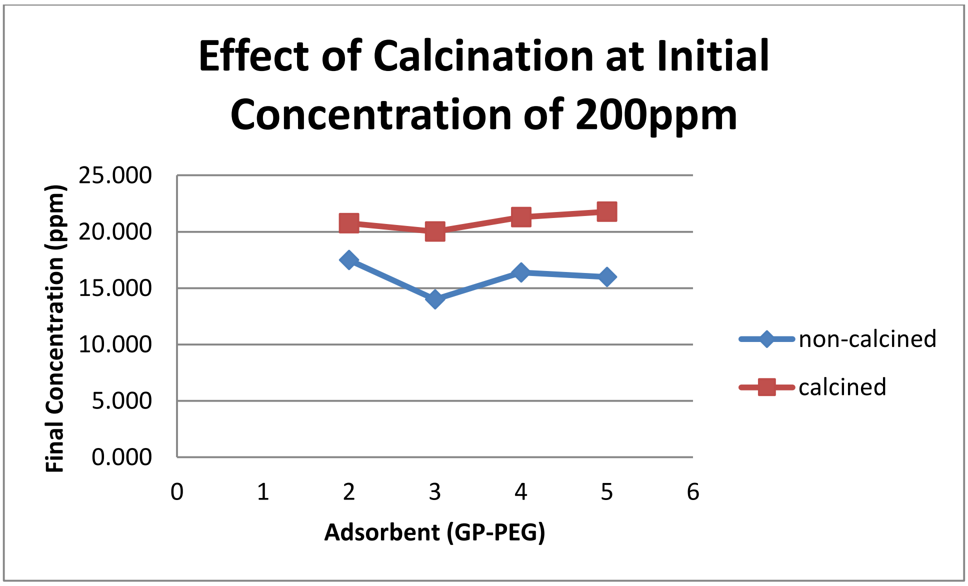

Figure 4.28: Effect of Calcination at Initial Concentration 200ppm.

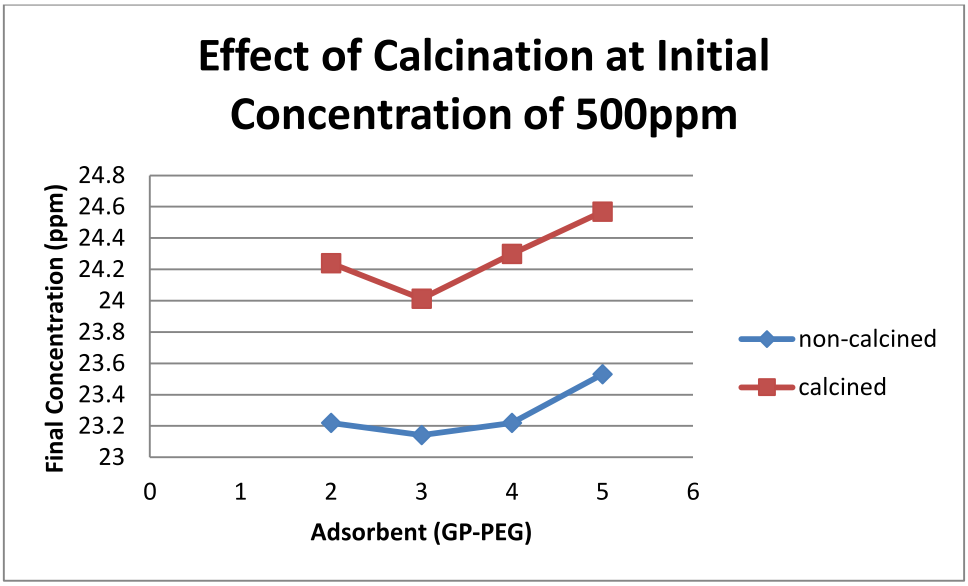

Figure 4.29: Effect of Calcination at Initial Concentration 500ppm.

Based on Figure 4.27 to Figure 4.29, it can be concluded that the adsorbent without calcined had a better adsorption activities compared to the calcined adsorbent. Thus, it is economically feasible as it did not consume much energy..

CHAPTER 5

CONCLUSION & RECOMMENDATIONS

5.1 CONCLUSION

The optimum silica to alumina ratio is 2.4 as it gives up to 90% removal, exhibits a better adsorption capabilities as compared to ratio 1, 2 and 3 which only gave 70%-80% removal. Thus, from these four geopolymers without polyethylene glycol, GP-R2.4 exhibits better adsorption capabilities as compared to GP-R1, GP-R2, and GP-R3.

As for another study which is by adding polyethylene glycol (PEG) into the GP-R2.4 substances during mixing, it can be concluded that GP-PEG3 (contained 3% of PEG) exhibits better adsorbent properties as compared to GP-PEG2, GP-PEG4, and GP-PEG5. The percentage removal of this GP-PEG3 is up to 99.9%.

In the adsorption test, the adsorption activity of geopolymer is favorable at higher alkaline condition in which the optimum pH for the MK phosphoric acid-based geopolymers is 10. Besides, for the PAGP with PEG, it can be reported that the adsorption activities favor at higher adsorbent dosage and high percentage removal can achieve equilibrium at low contact time with the optimum dosage of 0.4g.

Besides, the adsorption activities fitted well in pseudo second order and Langmuir isotherm model as they have the highest value of R^2.

5.2 RECOMMENDATIONS

For the future works, it is suggested that desorption test should be conducted in order to know the possibility of regeneration of the geopolymers. Besides, more properties of phosphoric acid-based geopolymers can be tested and identified. For instance, the effect of solution pH on the compressive strength of geopolymers and the thermal stability of geopolymers can be studied.

Other than that, effect of calcinations also should be further studied. It is also preferable to use glass cuvette instead of plastic cuvette in UV-Vis Spectrometer while measuring the solution concentration as the scratch or mark on plastic cuvette could affect the reading obtained.

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