APPLICATION OF CHITOSAN AS A NATURAL COAGULANT IN GROUNDWATER TREATMENT

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ABSTRAK

Salah satu kebimbangan utama bekalan air di Malaysia adalah keupayaan untuk menyediakan bekalan air minuman yang selamat untuk penggunaan seumur hidup kepada pengguna. Air minuman yang selamat bermakna air yang bebas daripada sebarang risiko kepada kesihatan manusia akibat daripada air minuman yang terdedah kepada pencemaran. Terdapat pelbagai masalah yang menyumbang kepada pencemaran air misalnya perindustrian yang pesat dan peningkatan pertumbuhan penduduk. Kajian ini dijalankan untuk mengenal pasti kualiti air bumi yang diekstrak daripada tiub air bawah tanah USM sebagai alternatif untuk bekalan air minuman. Ujian balang telah digunakan untuk mensimulasikan prestasi (penyingkiran warna, kekeruhan dan pepejal terampai) menggunakan bahan penggumpal semulajadi (kitosan) dan membandingkannya dengan bahan penggumpal sintetik, polyaluminium klorida (PACl). Kekeruhan dan pepejal terampai bahan penggumpal semula jadi (kitosan) dan membandingkannya dengan bahan penggumpal komersial polyaluminium klorida (PACl). Ujian balang telah dijalankan pada pH 3.0 hingga pH 10.0 dan pada dos bahan penggumpal 30mg/L, 60mg/L, 90 mg/L, 120mg/L dan 150mg/L. Keputusan menunjukkan bahawa pH optimum untuk kitosan dan PACl adalah 10.0. Kitosan mencapai peratusan penyingkiran kekeruhan tertinggi pada 89.93% manakala PACl memperolehi penyingkiran peratusan pepejal terampai tertinggi pada 85.63%. Perbandingan antara kitosan dan PACl untuk ujian balang di bawah dos yang berbeza masing-masing menunjukkan dos optimum 30mg/L dan 150mg/L. Penyingkiran warna juga telah dijalankan, tetapi telah mencapai penyingkiran peratusan yang kurang ketara. Ini menunjukkan bahawa kitosan boleh mencapai penyingkiran peratusan yang sama seperti PACl dibawah pH optimum yang sama tetapi dengan dos yang jauh lebih rendah. Walau bagaimanapun, semua keputusan menunjukkan bahawa nilai yang

diperoleh masih melebihi nilai yang dibenarkan untuk piawaian air minuman oleh Piawaian Kualiti Air Kebangsaan Malaysia (NWQSM) dan Pertubuhan Kesihatan Sedunia (WHO). Oleh itu, air ini perlu digunakan untuk tujuan rekreasi atau pengairan yang memerlukan permintaan air tinggi.

ABSTRACT

One major concern of water supply in Malaysia is the ability to provide safe access drinking water over lifetime consumption to the consumer. Safe drinking water means that it is free from potential risks to human health from exposure to contaminants in drinking water. There are various problems contributing to water pollution for instance the rapid industrialization and increasing population growth. This study was conducted to identify the quality of groundwater extracted from USM groundwater tube well as an alternative for drinking water supply. Jar testing was used to simulate the drinking water supply. Jar testing was used to simulate the performance (removal of colour, turbidity and suspended solids) of natural coagulant (Chitosan) compared to commercial polyaluminium chloride (PACl). The jar testing was conducted at different set of pH (pH 3.0 to pH 10.0) and various coagulant dose (30mg/L, 60mg/L, 90 mg/L, 120mg/L and 150mg/L). The results show that the optimum pH for chitosan and PACl are pH 10.0 with high percentage turbidity removal of 89.93% and percentage suspended solids removal of 85.63%, respectively. Comparison between chitosan and PACl for jar test under varied dosage shows optimum dose of 30mg/L and 150mg/L, respectively. Colour removal was also conducted, but with less significant percentage removal. This shows that chitosan can achieve the same percentage removal as PACl under the same optimum pH but with by far lower dosage. However, all the results shows that the value still exceed the permissible value for drinking water standards by National Water Quality Standards for Malaysia (NWQSM) and the World Health Organization (WHO). Hence, this water should be used for other water classes which require high water demand such as irrigation or recreational purposes.

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LIST OF ABBREVIATIONS

ACH	Aluminium Chlorohydrate
Alum	Aluminium Sulphate
APHA	American Public Health Association
BOD_5	Five-day Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EQA	Environmental Quality Act
$FeCl_3$	Ferric/ Iron Chloride
HCl	Hydrochloric Acid
H_2SO_4	Sulfuric Acid
MW	Molecular Weight
NaOH	Sodium Hydroxide
NWQSM	National Water Quality Standards for Malaysia
PACl	Polyaluminium Chloride
PFS	Polyferric Sulphate
PRB	Permeable Reactive Barriers
SS	Suspended Solids
US EPA	United States Environmental Protection Agency
WHO	World Health Organization

NOMENCLATURES

PtCo	Platinum-Cobalt
rpm	Rotation per minute
min	Minutes
^{o}c	Degree Celcius
M	Molarity of concentrated stock solution
V	Volume of concentrated stock solution
L	Litre
g	Gram
NTU	Nephelometric Turbidity Unit
nm	nanometre
ml	Mililitre

CHAPTER 1

INTRODUCTION

1.1 Background

Access to safe drinking water is essential as a health and development issue at a national, regional and local level. It has been showed that investment and effort to treat water for a better water supply can provide a net economic benefit since the reduction in adverse health effects and health care cost less than the interventions (WHO, 2011). Other than surface water, groundwater has also been treated to be used as secondary water supply. In Malaysia, groundwater usage is as low as 1.20 % compared to the surface water usage of 98.80 %.

As defined by the Guidelines, safe drinking water should be free from any significant risk to health over the lifetime consumption and should be able to prevent waterborne disease which can infect infants, young children, elderly and people who lives under unsanitary conditions. Therefore, if groundwater meets these requirements after being treated, it can also be widely used as drinking water. One of well-known water treatment is the jar test which involves several steps such as coagulation and flocculation to ensure the water is safe to be used as drinking water.

Coagulation is a well-known method of water or wastewater treatment where it involves the process through which suspended, colloidal and dissolved matter is destabilized by the addition of chemical (coagulant). Coagulants hydrolyze rapidly when dispersed in water forming insoluble precipitates. The precipitates adsorb to the particles in the water neutralizing their charge, and subsequently allow for interparticle bridging (Yonge, 2011). Flocculation is the process by which the destabilized particles agglomerate and form flocculants particles, or “floc.” Velocity gradients and particles undergoing random Browning motion cause particles to collide and attach to other particles, increasing the effectiveness of removing turbidity and dissolved material (Crittenden et al., 2005).

1.2 Problem Statement

With increasing population growth rate and rapid social-economical development, the demands for water demand and wastewater production are abruptly increasing, and the gap is wider between water supply and demand. In addition, research on surface water found that the samples were polluted by heavy metals such as lead present in the soil ranges from 3.40 – 99.40 mg/kg and pH which deviates significantly from WHO standard for potable water and this implies pollution (Ize-Iyamu, 2007). Therefore, groundwater is a significant source of water as one of the alternatives to cope the rising constraints for water resources development.

However in the first place this task was not easy to deal with since there are still lots of problems related to groundwater which is the reddish colour that caused by the presence of ferrous and manganese. At first, this colour cannot be seen but the oxidation of groundwater will promote the precipitation of ferrous and manganese after it has been exposed to the air (Jusoh et al., 2005) . Eventually, the groundwater turns into reddish in colour and in a few hours after the samples were taken the colour will slowly turns into black.

Colour is one of the parameters that can be considered as a secondary contaminant in potable water, since there is no record stating that it is harmful to health (Bryant et al., 1992). Nevertheless, it is still a problem since it can cause loss of confidence to the consumer in the quality of the potable water. Besides, characteristic test obtained always shows that the values are always beyond the recommended limit of 15 PtCo. Other physical characteristics such as temperature, chemical oxygen demand (COD), turbidity, suspended solids and pH are also observed and therefore water treatment is concluded necessary.

In the treatment, other than chemical coagulant, natural biopolymer can be used as organic coagulant. Chitosan is a more readily available natural coagulant which is derived from arthropods, the carapace of crustaceans as well as certain fungi and yeasts (Fabris et al., 2010). This study evaluates the characteristics of groundwater and the effectiveness of Chitosan in groundwater treatment comparing to one of the typically used conventional coagulant.

1.3 Objectives of the Study

The following objectives are set up to serve as a basis of problem solving and to be a guideline objectives are listed as follows:

1. To identify the characteristics of Universiti Sains Malaysia (USM) Tube Well Groundwater.
2. To determine the efficiency of chitosan and polyaluminium chloride (PACl) as coagulant in removal of colour, turbidity and suspended solids removal under optimum dose and pH.

1.4 Scope of the Research

To achieve the above objectives, the scopes of the study built as follows:

a) The sample was collected at USM Groundwater Tube Well, Penang and the groundwater characteristics will be tested in-situ and analysed in USM School of Civil Engineering Environmental Lab 1. The sample was stored in the refrigerator under 4^{o}c throughout the experimental work.

b) This study was done experimentally to prove and justify the potential of chitosan as natural coagulant to effectively remove colour, turbidity and suspended solids in groundwater treatment using jar test.

c) Using jar test, other than the conventional coagulant, PACl the natural coagulant chitosan is being used as the coagulation agent and their effectiveness was compared.

d) This research can be made as a guideline to improve groundwater quality, solve problems, and more understanding on the application of Chitosan for water treatment. However many unforeseeable parameters were taken into consideration for instance; changes in the groundwater characteristic and temperature of the sample.

1.5 Thesis Structure

The proposal has been categorized into three chapters:

Chapter One stretches on the background of the study, problem statement, objective of the study, the scope of the research, and advantages of the research.

Chapter Two discussed the previous literature and findings related wastewater treatment using Chitosan as coagulant. This chapter also discussed about the usage of groundwater as drinking water and the usage of organic and inorganic coagulants in drinking water treatment. The influence of pH and coagulant dosage and the optimum results obtained were analysed based on previous study.

Chapter Three explain the details of research methodology that will be used. The equipments and materials used in the experiment will also be explained.

This chapter will also describe the flow and testing procedure in the experiment. Other than test on water characteristics; suspended solids, colour and turbidity test procedure were discussed.

Chapter Four present results, analysis and discussion of the experiment. The potential for both coagulants were discussed in this chapter by comparing the effect of pH and dose to the treated water as well as optimum pH and dose.

Chapter Five contains the conclusions, a statement of whether the research accomplished the objectives or not and the recommendations.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter discussed the basic knowledge and literature cited regarding the wastewater treatment using chitosan as coagulant. This involves all types of water and wastewater with different characteristics and the percentage removal of turbidity, colour, suspended solids and chemical oxygen demand. In addition, the comparison of effectiveness between natural coagulant and chemical coagulant had been discussed as well.

2.2 Groundwater treatment for drinking water usage

In the last few decades, progressive population growth and accelerated pace of industrial development has caused tremendous increase in the demand of fresh water in Malaysia (Ramakrishnaiah et al., 2009). Groundwater is one of the sources of clean water, other than fresh river water and rain available; however, usage of groundwater is still very low. For rain, we receive highest mean monthly rainfall of 314mm (Wong, 2009). This is why in rural areas; groundwater has become an important source of water supply due to its relatively low susceptibility to pollution compared to surface water. Other than that, large storage capacity is also one of the main reasons why it is sometimes reliable to be used as drinking water (Moayedi et al., 2011).

One thing that should be taken into serious attention when using groundwater is water pollution especially in big cities where groundwater are often polluted by harmful toxic materials. The quality of surface and groundwater is identified in terms of its physical, chemical, and biological parameters that have a harmful effect on any living thing that drinks, uses or lives in it (Loukas, 2010). Raw groundwater commonly contains high natural organic materials which produce high colour levels. The issue of protection of groundwater against pollution is of crucial significance (Buselli and Lu, 2001). It is necessary to effectively control water pollution by constructing successful measures in order to minimize the contamination resources but it is often hard to identify the groundwater condition and pollution sources (Singh et al., 2005).

The quantity of water delivered and used for households is an important aspect of domestic water supplies, which influences hygiene and therefore public health. When humans drink polluted water, it often has serious effects on their health. Water pollution can also make water unsuitable for the desired use. Groundwater may exchange mass and energy with soil, air and surface water through adsorption, evaporation, ion-exchange, inflow, outflow and infiltration and other exchange structure since it is an “open” system (Sun, 2013).

Untreated groundwater cannot be directly used as drinking water. This can cause thermal impacts, colour problems, slime growth, and loss of aesthetic beauty in the environment. Since the groundwater extracted can be potentially polluting and very dangerous, before releasing them to the environment, they should be treated.

Treatment of groundwater sources is achieved by using physical, chemical or biological process. In most cases these processes can enhance the quality of the water discharge.

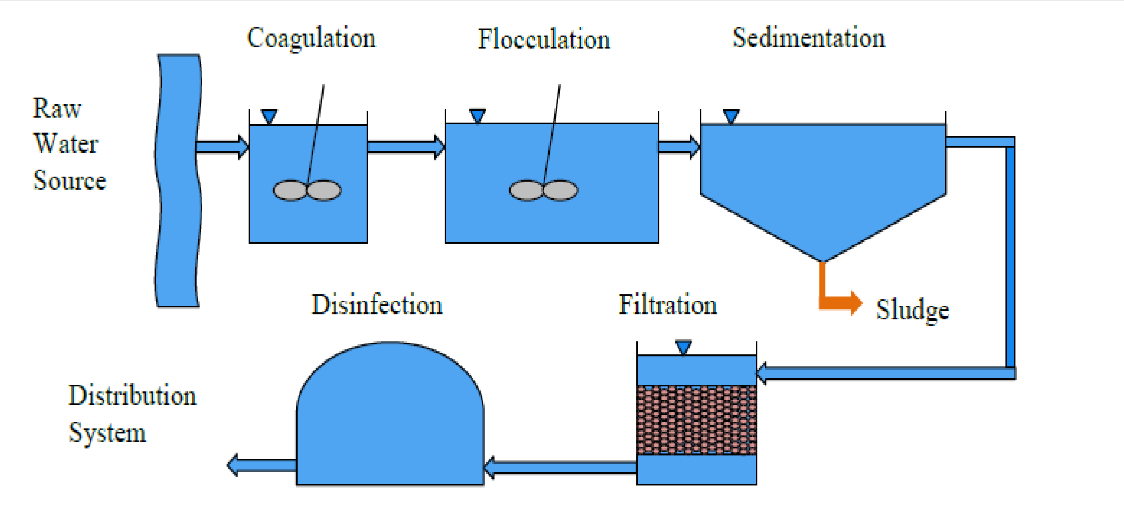

Figure 2.1: Diagram of Conventional Treatment System
(Yonge, 2011)

2.3 Primary treatment: physical treatment

Physical method involves processes where the raw water source undergoes coarse screening to remove larger entrained objects and sedimentation (or clarification). Sedimentation process includes holding the water for a while in a tank and uses a physical phenomenon which is gravity to let the heavier solids in the effluent to settle down. It is a common process in water treatment and usually applied at the beginning and end of the whole treatment.

After sedimentation, the treatment process is followed by grit and grease removal. Grit includes sand, cinder, gravel or other heavy solids materials that have higher specific gravity than organic biodegradable solids in the pulp and paper wastewater. Blockages and unnecessary maintenance schedule can be prevented by removing grit. Besides, primary clarifier is used to slow down the water velocity so that settle able solids can settle to the bottom and readily floatable particles can move to the surface. Permitting them to float then physically removing those materials using scrapers thus will improve the water quality.

2.4 Secondary treatment: biological treatment

Secondary treatment typically utilizes biological treatment processes, in which microorganisms convert non settle able solids to settle able solids. This treatment involves the removal of biodegradable dissolved and colloidal organic matter using aerobic biological treatment processes. Aeration is the first in biological treatment where air is added physically, providing oxygen to the effluent. The oxygen supplied to the microorganisms will metabolize the organic matter.

2.5 Advanced treatment: chemical treatment

In water treatment, coagulation and flocculation are required in chemical treatment process. The production of safe drinking water from most groundwater and raw water sources usually involves the use of a coagulation/flocculation stage to remove turbidity in the form of suspended and colloidal material. This process plays a major role in water treatment by reducing turbidity, bacteria, algae, color, organic compounds and clay particles (Bina et al., 2009).

2.5.1 Mechanism involved in coagulation and flocculation process

Coagulation and flocculation mostly used in most water and wastewater treatment plants which constitute the backbone processes and widely used due to their simplicity and cost-effectiveness. Their purpose is to enhance the separation of particulate species in downstream processes such as sedimentation and filtration (Tzoupanos and Zouboulis, 2008). These processes are usually included, either as pre- or as post-treatment step regardless of the characteristics or sources of the treated sample.

The coagulation and the flocculation of suspended particles and colloids result from different mechanisms including electrostatic attraction, sorption (related to protonated amine groups), bridging (related to polymer high molecular weight). In some cases, the amount of protonated amine groups added to the solution is far below the number of charges necessary for the neutralization of the anionic charges held by the colloids; the removal of particles can be explained in this case by a combination of distinct mechanisms such as electrostatic patch and bridging (Guibal, 2007) . These mechanisms are highly dependent on coagulant dose and pH of the solution. At low dosage of metal salts, presence of charge neutralization can be an effective means of destabilising colloidal particles.

2.5.2 Coagulant reagents: Inorganic coagulants

The commonly used inorganic metal based coagulants fall into two general categories which are coagulants based on aluminium and based on iron. The aluminium coagulants include aluminium sulphate, aluminium chloride and sodium aluminate. The iron coagulants include ferrous sulphate, ferric sulphate, ferric chloride and ferric chloride sulphate. Other chemicals used as coagulants include hydrated lime and magnesium carbonate (Iwapublishing, n.d). PACl is the most common iron salt used to achieve coagulation. Its reactions in the coagulation process are similar to those of alum, but its relative solubility and pH range differ significantly from those of alum. The ability to form multi-charged poly-nuclear and enhanced adsorption characteristics arises the effectiveness of aluminium and iron coagulants. Nonetheless, these few years back, it has been stated out that there may be a possibility for aluminium-based coagulants to link with Alzheimer’s disease (Hassan et al., 2009). Therefore, a special attention has been given to the environmental friendly coagulant or flocculants.

2.5.3 Coagulant reagents: Organic coagulants

For certain water sources, organic coagulants are more appropriate for solids – liquid separation. Natural polymers have long been used as flocculants. Polymers have the ability to enhance flocculation of a water body and are a large range of natural or synthetic. It is a macromolecular compounds and soluble in water. Natural polymers have numerous advantages as they are not only free of toxins, but also biodegradable in the environment and the raw products available locally because they are often derived from food processing waste (Fabris et al., 2010).

2.5.4 Chitosan as natural coagulant

Chitosan, a biopolymer derivative of chitin, is obtained from the waste of shrimp shells (Heidari et al., 2016). It is a natural linear bio-polyaminosaccharide, obtained by alkaline deacetylation of chitin. The degree of deacetylation is one of the important chemical characteristics which influenced the quality of chitosan due to the value of amina chain. The deacetylation degrees are determined by several factors such as temperature, NaOH concentration and time process (Pursetyo et al., 2017). Chitin is converted into chitosan by alkaline hydrolysis using 50 % (w/w) high concentration of alkaline solution of aqueous NaOH solution as shown in Figure 2.2. Chitosan contains 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glucopyranose residues (Bhatnagar and Sillanpaa, 2009). Due to the presence of amino group at position 2 and hydroxyl group at position 3, chitosan forms chelates with almost all metal ions.

Effectiveness of chitosan increase due to the addition of materials extracted from soils at high pH or because of the presence of inorganic solutes (Pan et al., 1999). Chitin and chitosan has various benefits in broad fields of modern industry includes pharmaceutical industry, biochemistry, biotechnology, biomedical, food, nutrition, paper, textile, agriculture, cosmetics, and healthcare membrane. Despite these advantages, the usage of synthetic polymers as coagulant is more widespread since they are more effective as flocculants.

Chitosan is considered an attractive alternative to other biomaterials because of its chemical stability, excellent chelation behaviour, physic-chemical stability and high selectivity towards pollutants (Bhatnagar and Sillanpaa, 2009). Chitin is similar to cellulose in various aspects and available in the largest quantities next to cellulose, but their chemical structures are slightly different (Figure 2.3). Shell of crab and shrimp is the most abundant source of chitin.

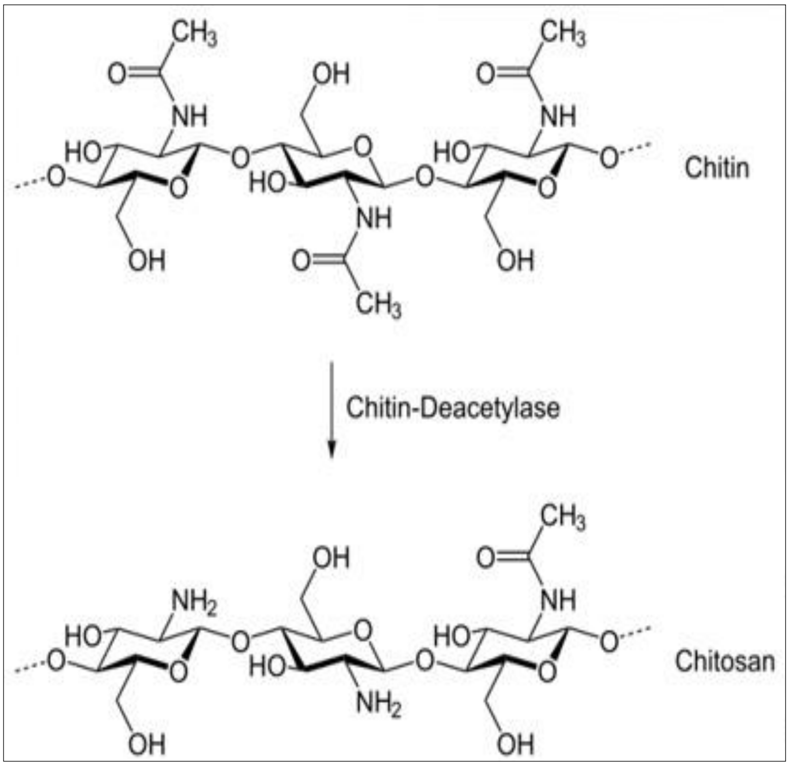

Figure 2.2: Deacetylation of Chitin into Chitosan by Alkali Hydrolysis.
(Ramnani and Sabharwal, 2006)

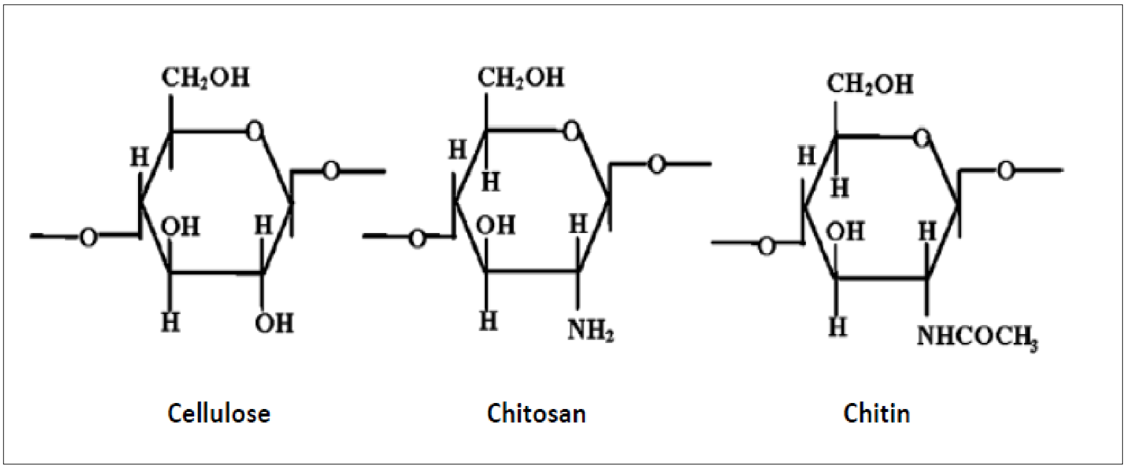

Figure 2.3: Structure of Cellulose, Chitosan and Chitin (Sakkayawong et al., 2005)

When water containing colloidal suspension is dosed with an inorganic coagulant, the negatively charged electric double layer of the colloid is neutralized by the cationic metal ion from the coagulant. Much the same occurs with an organic coagulant, except the positive charge most commonly comes from an amine (NH^{4+}) group attached to the coagulant molecule.

An abundant range of chemicals exist for use in coagulation and flocculation processes to clean raw water. The effectiveness of these coagulants is known to have a complex dependency on the wastewater nature itself. Factors affecting this dependency are pH, temperature, proportions of organic and, inorganic and biological particles that the suspended solids. Likewise, the advantages and disadvantages of some coagulants in wastewater treatment processes have been tabulated in Table 2.1.

Table 2.1: Advantages and Disadvantages of Coagulants
(Source: Comparison of Coagulation/Flocculation, 2010)

Chemical Class	**Chemical**	**Advantages**	**Disadvantages**
Hydrolyzing Metallic Salts	Alum (Aluminium Sulphate)	Attracts suspended solids effectively.	Non-optimal pH Excessive dosage requirements.
	Ferric Chloride	Good at attracting inorganic SS.	Less efficient than alum in SS removal.
	Ferric Sulphate	Low pH sensitivity	pH 5.5 – 8.5. Large dosage required
Pre-Hydrolyzed Metal Salts	PACl / PAC (Polyaluminum Chloride)	pH 4.5 – 9.5. Can reduce dose. Suitable for high colour applications.	Requires an on-site production process from alum.
	Polyaluminum Sulfate		Requires an on-site production process
Natural Polymers	Sodium Alginate	Suited for use with ferric salts. Can be effective when used with alum	Less efficient than synthetic polymers
	Chitosan	Increasing settling velocity Less coagulant dosage.	

2.6 Jar Test

A jar test is essential for most of water treatment plant systems. The results show the treatment efficiency in terms of organic matter and suspended matter removal. However, it is not an easy task to select suitable coagulant to be used in the treatment which can effectively remove one parameter without adding or increasing other parameters (Aragonés-Beltrán, 2009). Therefore, the final coagulant selection is critical since it can determine the treated water quality. Other factors to be taken into consideration to optimally eliminate organic matters presence in the samples are minimal dosage requirement and concentration (Hassan et al., 2009).

The effectiveness of chitosan as a coagulant was evaluated by comparing its performance to PACl in a series of jar tests. PACl is chosen since it shows the highest potential among all conventional coagulant (Yonge, 2011). Chitosan can be modified with various pre-treatments including various deacetylation conditions and dissolution in acid solution conditions to improve its coagulation efficiency (Ruhsing Pan, 1999). But first this coagulant needs to be diluted since it is insoluble in either water or organic solvents. The free amino groups are protonated in diluted organic acids such as acetic acids or hydrochloric acids (HCl) and it becomes fully soluble . Hence, many different approaches have been applied to prepare chitosan stock solutions for jar testing. The approach of Choi (2002) using acetic acid was applied here as the solvent for chitosan solution.

2.7 Previous Study

This section discussed and compares the optimum pH and dose obtained by previous researchers based on their study on a few water and wastewater sample. Optimum dose by means is the maximum of the polymer added into the process under certain condition. The optimum pH varies in different supplies according to the composition of the water system, but is often in the range 6.5–9.5.

2.7.1 Influence of coagulant dose in coagulation process

In Coro (2001) study, their research on groundwater shows that the raw water is rich in natural organic material and produce correspondingly high color levels. Therefore, it is critical to have optimal coagulant dosage for proper floc formation and performance of the filter. The difference between an optimized and poorly run surface plant can be due to the proper control of these chemicals. Inadequate mixing and addition of chemicals at inappropriate points can limit the performance of treatment plant. The application of biopolymer coagulation reagents exhibits some advantages comparing to the pre-polymerized coagulants as such it results in better treatment performance using far lower coagulant dosage (Fabris et al., 2010).

The effectiveness of natural coagulant compared to inorganic coagulant has been proven by Pontius (2016), who conducted his research on chitosan, aluminum sulphate, $Al_2(SO_4)_3$ and $FeCl_3$ in treating algal-ladened waters. The optimum chemical dose for coagulation for efficient algae removal for alum, chitosan and $FeCl_3$ was 30 mg/L, 8 mg/L and 30 mg/L, respectively. Results obtained shows that chitosan used much lower doses than $FeCl_3$ and alum but there are only small differences on the removal percentage with the three coagulants removed more than 95% turbidity.

The same factors were applied separately for the organics, suspended solids (SS), and colour removal to optimise coagulation pre-treatment of the produced water (PW) collected from a natural gas field**.** Optimum PACl dosage of 25 g/L was used to remove COD, suspended solids and colour of 90.1%, 99.0% and 99.9%, respectively which performed better than polyferric sulphate (PFS) as coagulant in the treatment (Zhai, 2016).

2.7.2 Influence of pH value in coagulation process

pH is also the contributors to the effective removal of COD, turbidity and colour after coagulation and flocculation process. The maximum turbidity removal seemed to be more correlated to the pH ranges for minimum solubility for experimental jar test using conventional coagulant for instance $FeCl_3$, alum and PACl. PACl and aluminum chlorohydrate (ACH) had similar percent removals for color and turbidity achieving consistent percent removals of 95% and 45%, respectively, but PACl was less effective than ACH at removing organics. The evaluation indicated that ferric chloride and ACH were the most effective coagulants for colour removal with lower dose concentrations (Yonge, 2011).

One of past study uses modified chitosan mixed with PACl in various mass ratios to prepare the mixed coagulants, and the effectiveness of coagulation on natural water was evaluated. At lower pH, better turbidity removal is observed and the resulting floc diameter is smaller, accompanied by a slower settling velocity. This can happened due to the variation in the configuration of chitosan. In neutral condition, chitosan is able to produce larger and denser flocs while and the opposite situation occur in acidic solutions.

2.7.3 Optimum dose and pH

As in previous research from Bhatnagar and Sillanpaa (2009) in treating effluent from the discharged of an eel culture pond, the highest percentage achieved by chitosan for turbidity and COD was 87.7% and 62.8% respectively. This experiment obtained an optimum dosage of 12 mg/L and pH 6. Besides, this researcher also conducted the experiment with chitin and chitosan-derivatives for the removal of other parameters such as metals cations and anions, radionuclide, phenol and substituted phenol. The results for these experiments also show that these coagulant based coagulants also shows good potential for removal of various aquatic pollutants.

The results obtained from Hassan et al., (2009) research proved that chitosan had successfully reduce the levels of chemical oxygen demand (COD) by flocculate the anionic suspended particles in the textile dye wastewater. The same factors were used but another factor was included which is mixing time. The removal was up to 72.5% of COD reduction and 94.9% of turbidity reduction using optimum concentration of 30 mg/L of chitosan and pH 4. The optimum conditions for mixing time is 20 minutes with 250 rpm of mixing rate for 1 minute, 30rpm of mixing rate for 20 minutes and 30 minutes of settling time.

Next, in order to remove hexavalent chromium in groundwater, a series of experiments have been performed under adsorption by permeable reactive barriers (PRBs) using modified chitosan. First, the adsorption characteristics of the modified chitosan was estimated in a column test and the PRB adsorption parameters then calibrated in a sandbox test. Lastly, the optimal width, depth and length of the PRB were designed. Chitosan is proven to be a potential medium for adsorption since the results conform to the water quality standard of 0.1 mg/L Cr(VI) (Zengguang, 2013).

Treatment of industrial wastewater with PACl proved to be effective in a pH range between 7 and 9. Reduction of COD obtained is 88 % and there were an increased in BOD_5/COD index from 0.71 to 0.41 (Aboulhassan et al., 2006). The results for colour and turbidity from using PACl and ACH achieved consistent percentage removal of 95% and 45% respectively. It was stated in Yonge, (2011) research which compared the effectiveness of alum and iron based coagulant as in Figure 2.4. This graph shows that PACl and ACH are more effective than the other conventional coagulant. However, PACl was less effective than ACH at organics removal.

The optimum pH and coagulant dose obtained for each coagulants involved are shown in Table 2.2. PACl shows the best performance at pH more to neutral condition and recorded the lowest required coagulant dosage of 80 mg/l to 100 mg/l compared to other coagulants. The highest optimum coagulant concentration range is for alum with the lowest value of 180 mg/l followed by ferric sulphate which showed the highest reduction at pH 4.0 to 4.5 and coagulant dose slightly lower than alum. $FeCl_3$ and ACH showed moderate results with the same optimum value for both factors. Reduction for each parameter is the best at coagulant dosage of 100 mg/l to 120 mg/l.

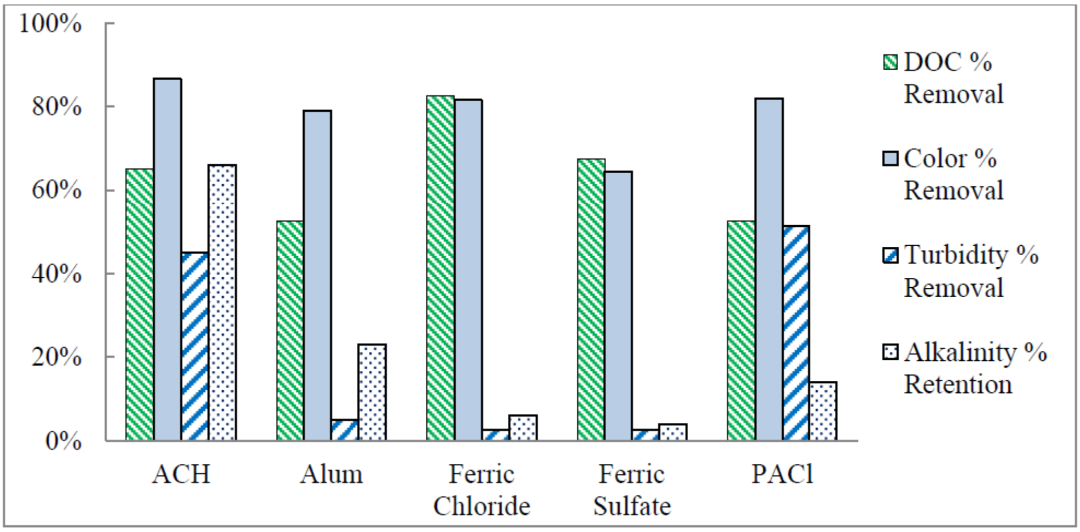

Figure 2.4: Percentage Removal of Conventional Coagulant
(Source: Yonge, 2011)

Table 2.2: Optimum pH and Optimum Coagulant Dose (Source: Yonge, 2011)

Coagulant	Optimum pH range	Optimum concentration range (mg/L)
Ferric Chloride ($FeCl_3$)	4.5 – 5.0	100 – 120
Ferric Sulphate ($Fe_2(SO_4)_3$)	4.0 – 4.5	160 – 180
Alum ($Al_2(SO_4)_3$)	5.0 – 5.5	180 – 200
Aluminium chlorohydrate (ACH)	4.5 – 5.0	100 – 120
Polyaluminium Chloride (PACl)	6.5 – 7.0	80 – 100

2.8 Summary

This chapter presents an overall literature review of past studies for water and wastewater treatment using jar test. From this literature review, most researchers studied about the comparison of the performance of conventional and natural coagulant on wastewater samples. Besides, those who use chitosan as coagulant for their groundwater samples focus on the heavy metals (Cd, Cr, Cu, Pb and Zn) content and removals. Some researchers used other methods such as adsorption, ultra filtration, reverse osmosis and others. From their research, the groundwater quality also differs a lot in characteristics parameters of the tested water. Some are high in heavy metals meanwhile some are high in colour or other parameters.

CHAPTER 3

METHODOLOGY

3.1 General

This chapter discussed on how the laboratory work was conducted and it involves two phases which are preparation of coagulants and comparison study using two different coagulants (chitosan and polyaluminium chloride). Experimental work involving jar test was done to determine the optimum dosage of chitosan and PACl, data collection as well as data analysis.

3.2 Research Flowchart

Flowchart of this research (Figure 3.1) was made according to the two objectives. First, in obtaining the first objective which is water characteristics, literature reviews based on previous research were conducted and survey of the appropriate location to be used as the site for sample extraction was made. Next, after site selection, materials were prepared and the method of samples extraction had been finalized. After the raw samples were extracted, the characteristic tests were done on the same day as the sampling and the samples were then preserved in the cool room.

Next phase involved more detailed procedure in achieving the second objective. Few set of jar test experiment were conducted using different coagulant; organic and inorganic coagulant. These experiments were done considering two main factors which are coagulant dosage and pH under the same mixing speed. After that, the results were compared and analysed in order to obtain the optimum pH and optimum dose and was preceded with the report writing.

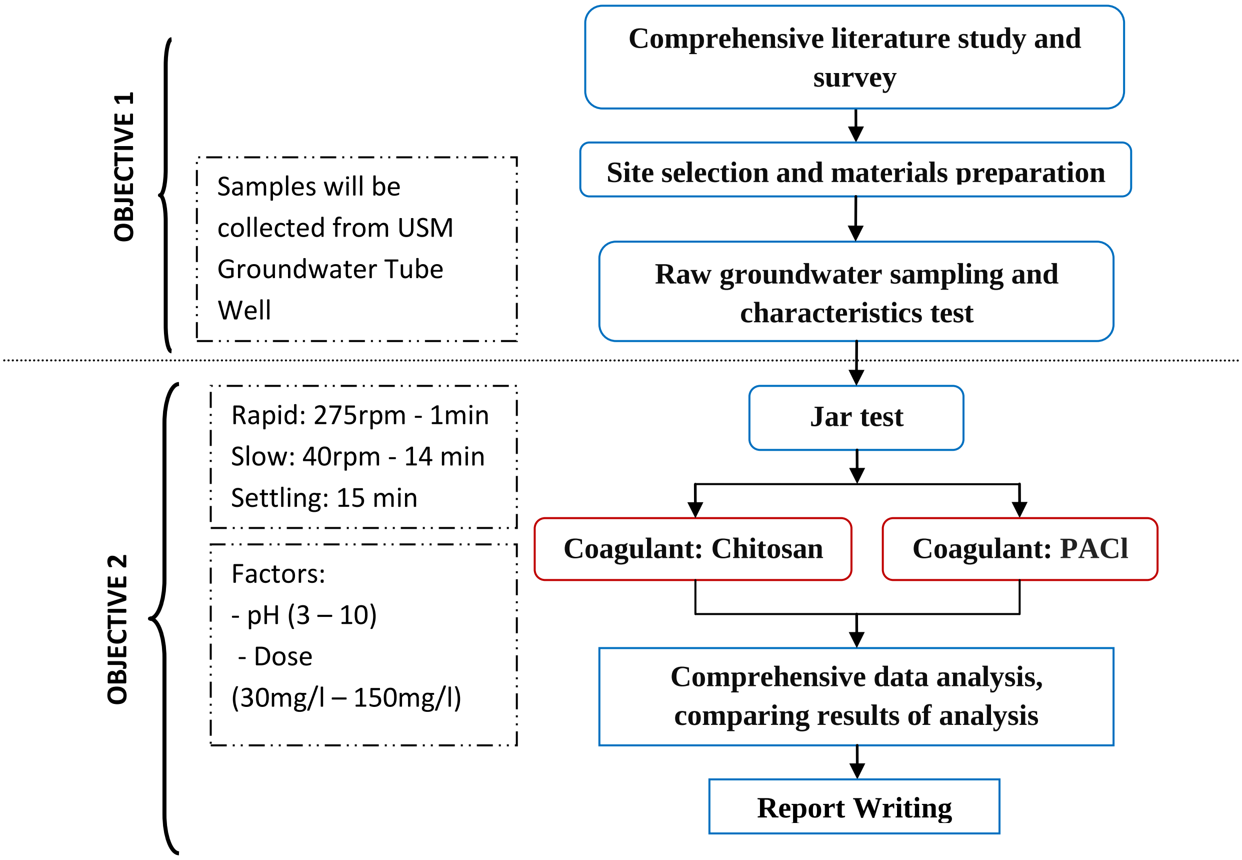

Figure 3.1: Research Flowchart

3.3 Wastewater sample collection

Groundwater sample was obtained from the tube well located at 5° 08’ 50.5”N and 100° 29’ 34.7”E next to School of Civil Enginering of USM Engineering Campus (Figure 3.2). The groundwater samples were taken more than once since the water characteristics can change during storage period and to get average results so that it can be applied to the treatment. In-situ test on the groundwater characteristics was conducted using YSI Multiparameter Probe.

Characteristic test were conducted on the samples each time new fresh sample were taken every two weeks starting early March 2017. Parameters including colour, turbidity, suspended solids, pH, temperature, BOD_5 and COD of the raw water samples were determined immediately upon arrival at the laboratory. Sample is then stored in the refrigerator at 4^{o}c so that the potential for volatilization or degradation of the samples can be kept at minimal condition. Collection and preservation of samples were done according to the Standard Method for the Examination of Water and Wastewater (APHA, 2005). Chitosan and PACl stock solutions were prepared to be used as coagulant during jar test using the readily made powder bought from R&M Chemicals. Chitosan and PACl powder were bought from R&M Chemicals and the composition Analytical grade of NaOH and HCL are used for pH control during coagulation.

Figure 3.2: USM Groundwater Tube Well

3.4 Preparation of Chitosan and PACl stock solution

A solution is a homogeneous mixture created by dissolving one or more solutes in a solvent. The chemical present in a smaller amount, the solute, is soluble in the solvent (the chemical present in a larger amount). Solutions with accurately known concentrations can be referred to as standard (stock) solutions. Chitosan solution should be prepared before conducting the experiment. It was in the form of a white fine powder and soluble in dilute acetic and hydrochloric acids which makes it available for application.

For this jar test, approach using acetic acid to dilute chitosan is used but 0.1 M of acetic acid must be prepared beforehand. First, 5.742 ml of acetic acid is slowly added into 250 ml distilled water and more distilled water are added until the meniscus of the liquid reaches the calibration mark on the neck of the volumetric flask (a process called "diluting to volume"). Then, 100 gram of chitosan is weighed out in a small crucible and then transferred directly to the volumetric flask containing 0.1 M acetic acid. Then, the volumetric flask is capped and inverted several times until the contents are thoroughly mixed. The final working solution of chitosan is a transparent liquid.

Next, different procedure was applied in preparing PACl stock solution. First, 1gram of this solute is weighed out in the crucible and the dilution is done by transferring the white powder into 100 ml distilled water in a beaker and stirred with a glass rod until it is completely dissolve. Before adding additional solvent to the flask, the beaker, stirring rod, and funnel must be rinsed carefully to make sure all remaining traces are washed. The final working solution of PACl is a transparent light yellowish liquid compared to chitosan.

This solution was prepared freshly before the experiments, because it was observed that chitosan solution undergo some changes in their properties after acid addition (Divakaran and Pillai, 2002). Volume of chitosan and PACl solution to be used in the jar test is calculated as follows:

In general molarity is the most commonly used concentration unit:

$$\text{Molarity, M} = \frac{\text{Grams of solute}}{\text{Molar mass solute x Liters of solution}} \qquad (2.7.3.1)$$

$$M_1V_1 = M_2V_2 \qquad (2.7.3.2)$$

Where: