PREPARATION AND APPLICATION OF POLYALUMINIUM SILICATE CHLORIDE IN COAGULATION PROCESS

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PREPARATION AND APPLICATION OF POLYALUMINIUM SILICATE CHLORIDE IN COAGULATION PROCESS

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A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
University Malaysia Pahang

APRIL 2010

I declare that this thesis entitled "Preparation And Application Of Polyaluminium Silicate Chloride In Coagulation Process" is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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Name : Selvan A/L Murugan
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Dedicated To Mother Nature

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I hope this thesis will be of benefit to both present and future students of UMP who study and practice in the area of the water environment. Thank you.

ABSTRACT

Coagulation is one of the most important method in chemical treatment of water and wastewater. There are several types of coagulant used in water and wastewater treatment. Most of the inorganic and some polymer coagulants are still not very effective on removing suspended solid and give side effects. A lot of research were done by scientist around the world in coagulation and flocculation field to improve the properties of prepolymerized coagulants, such as polyaluminium chloride (PAC). Recently, Bao-Yu Gao et al.reported that under certain conditions polyaluminum silicate chloride (PASiC), a new type of inorganic polymer coagulant,having a larger particle size and better turbidity removal efficiency than PAC. Coagulation test were done for both water and wastewater PASiC and the results were compared with conventional coagulants (Alum and PAC). For water treatment, PASiC removed 99.45% of turbidity, 68.75% of COD and 48.31% of BOD at optimum coagulant dosage. And for wastewater, it removed 90.14% of turbidity, 89.72% of COD and 46.7%BOD. From this research we can conclude that polyaluminium silicate chloride is very effective in removing suspended solids in both water and wastewater and very good in every aspect compare to other two conventional coagulant, Alum and PAC.

ABSTRAK

Koagulasi adalah salah satu kaedah yang paling penting dalam rawatan kimia air dan air sisa. Ada beberapa jenis koagulan yang digunakan dalam air dan pemprosesan air sisa. Sebahagian besar anorganik dan beberapa koagulan polimer masih belum sangat berkesan menghilangkan pepejal tersuspensi dan memberikan kesan samping. Banyak kajian dilakukan oleh saintis di seluruh dunia dalam bidang koagulasi dan flocculation untuk meningkatkan sifat koagulan prepolymerized, seperti klorida polyaluminium (PAC). Baru-baru ini, Yu Bao-Gao et al.reported bahawa dalam keadaan tertentu polyaluminum klorida silikat (PASiC), sebuah jenis baru koagulan polimer anorganik, memiliki ukuran zarah yang lebih besar dan lebih baik kecekapan removal kekeruhan dari PAC. Ujian koagulasi dilakukan untuk kedua-dua air dan air sisa PASiC dan hasilnya dibandingkan dengan koagulan konvensional (Alum dan PAC). Untuk rawatan air kekeruhan sebanyak 99.45%, 68.75% COD and 48.31% BOD telah dihilangka. Manakala kekeruhan sebanyak 90.14%, 89.72% COD and 46.7% BOD telah dirawat untuk air sisa. Dari kajian ini kita boleh menyimpulkan bahawa klorida polyaluminium silikat sangat efektif dalam menghilangkan pepejal tersuspensi dalam air dan air sisa baik dan sangat baik dalam setiap aspek berbanding dengan dua yang lain koagulan konvensional, Alum dan PAC.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

All waters, especially surface waters, contain both dissolved and suspended particles. Coagulation and flocculation processes are used to separate the suspended solids portion from the water. The Egyptians practiced a form of coagulation as early as 2000 BC by using sweet almonds as coagulant.(Samuel D.Faust and Osman M.Aly,1998). The most widely used coagulants for water and wastewater treatment are aluminum and iron salts. The common metal is aluminum sulfate (Warren Viessman,Jr and Mark J. Hammer,1998). Nowadays Polymers are becoming more widely used, especially as coagulant aids together with the regular inorganic coagulants. A lot of research were done by scientist around the world in coagulation and flocculation field to improve the properties of prepolymerized coagulants, such as polyaluminium chloride (PACl).Recently, Bao-Yu Gao et al (2003) reported that under certain conditions polyaluminum silicate chloride (PASiC), a new type of inorganic polymer coagulant, having a larger particle size and better turbidity removal efficiency than PAC.

1.1.1 Coagulation

Suspended solids (colloids) in water consist of both organic and inorganic particles. A colloid can be define as a particle held in suspension by its extremely small size (1-200 millimicrons),and surface electrical charge (Nelson Leonard Nemerow,2007). Two approaching colloid particles cannot come close to each other because of the thicker electric double layer, therefore the colloid is stable. The main function of coagulation is to destabilize these suspended particles by neutralizing their charges (normally negative) by adding coagulants with opposite charge (normally positive) and aggregate destabilized particles into flocs, which could be removed by subsequent sedimentation and filtration. Figures below shows the process of coagulation and bridging of colloids.

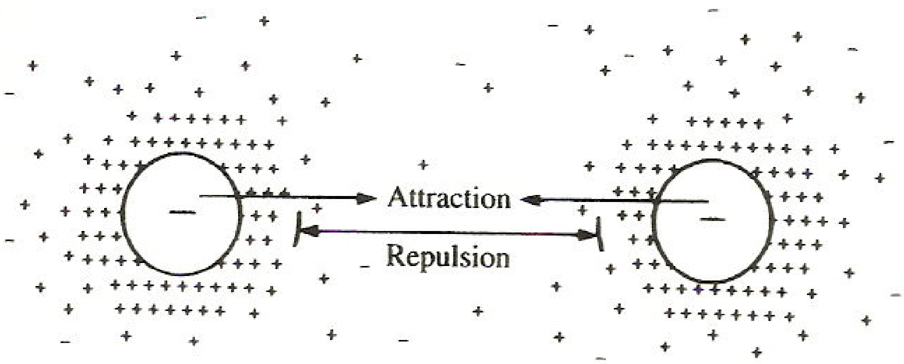

Figure1.1: A stable suspension of particles where forces of repulsion exceed the forces of attraction.

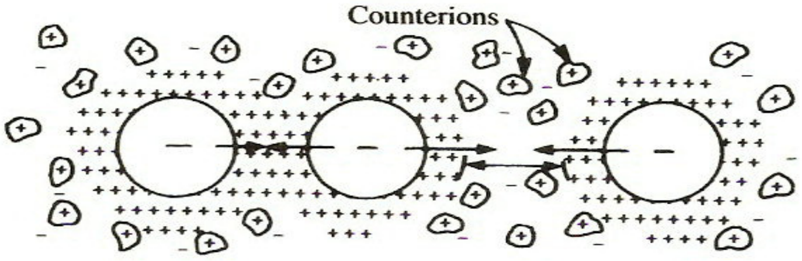

Figure1.2: Destabilization and coagulation caused by counter-ions of a coagulant suppressing the double layer charges.

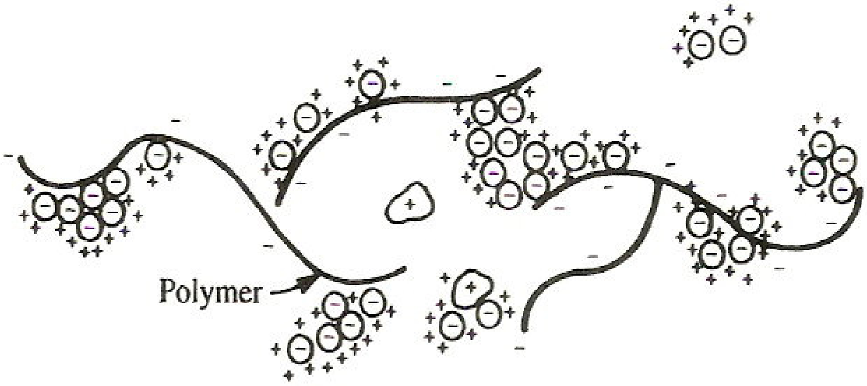

Figure1.3: Agglomeration of destabilized particles by attaching of coagulant ions and bridging of polymers.

1.1.2 Flocculation

Flocculation is agitation of chemically treated water to induce coagulation (Warren Viessman,Jr and Mark J. Hammer,1998) and during this process, a gentle mixing is needed to bring electrically neutralized particles into contact with each other (Yuefeng F.Xie,2004). The agitation provided is mild, just enough for the suspended particles to stick together and not rebound as they hit each other in the course of agitation (Arcadio P.Sincero and Gregoria A.Sincero,2000). These particles will collide and agglomerate into larger and heavier floc that can be settle out by gravity. Figure 1.4 shows simple flocculation force

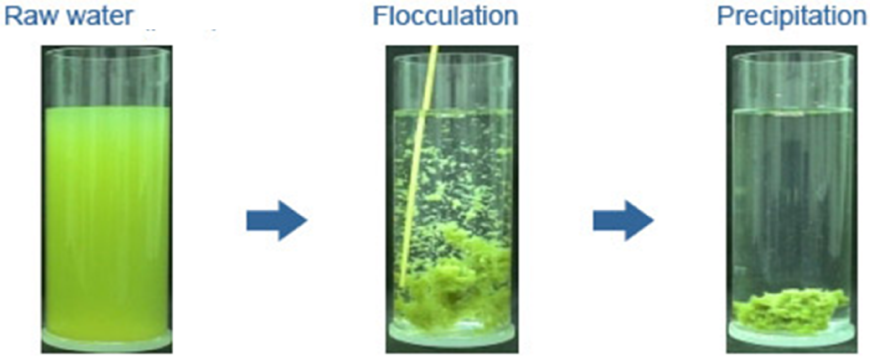

Figure 1.4 : Flocculation Process

1.2 Problems statement.

Most of the inorganic and some polymer coagulants are still not very effective in removing suspended solid and sometimes give side effect. Inorganic coagulant such as aluminum sulfate (a very common coagulant) may alter the pH of the water since its consume alkalinity in coagulation process; if water does not contain sufficient alkalinity, we need to add lime or soda to initiate the coagulation process. So there will be extra cost to treat the water. Meanwhile when use newly developed inorganic polymer like polyaluminum chloride; can avoid this kind of side effects but their molecular weight and size for aggregating action and their stability to resist further hydrolysis are still low. So it is important to develop new inorganic polymer to avoid all these problems.

1.3 Objective

- Prepare polyaluminium Silicate Chloride using method where combining hydroxylated polyaluminium chloride with polysilicic acid aged two hours in optimum ratio of Al/Si which is more than 5.

- Apply and test the prepared coagulant for surface water treatment (Kuantan River).

- Apply and test the prepared coagulant for wastewater treatment using paper pulp water from PASCORP, Bentong.

1.4 Scope of Study

- Conduct jar test experiments for surface water; from Kuantan river and wastewater from paper Industry (PASCORP, Bentong)

- Use newly prepared coagulant (PASiC) and conventional coagulant (Alum and PAC) for coagulation – flocculation experiments.

- Use different pH to study the effect of pH on coagulation and flocculation process for different types of coagulants and the range is from pH 5 to pH 9.

- Ranges of the coagulant dosage are between 1mg/L to 50 mg/L amount needed to get clear water. The maximum amount varies depends on the type of coagulant.

CHAPTER 2

LITERATURE REVIEW

Water and wastewater treatment consist of three methods; physical, chemical and biological method. Coagulation is under the chemical method. This chapter covers the conventional method used to treat water and wastewater and also types of coagulant used in coagulation process.

2.1 Water and wastewater Treatment

Public water systems vary in the treatment of water that is delivered to the consumer, depending on whether the system uses a groundwater source or a surface-water source. Some public water systems, primarily those that utilize groundwater wells, deliver untreated water directly to the customer's tap. Groundwater is usually less susceptible to contamination than surface water, and therefore requires little or no treatment.

Many large public water systems, however, draw their water from surface sources such as lakes, rivers, and streams, which are vulnerable to many types of contamination. Hence, a multiple-barrier approach to water treatment is most effective in producing drinking water that is free of health risks, meets regulatory requirements, and is palatable (acceptable in taste) to the consumer (Scott G.Curry).

2.1.1 Groundwater

Although groundwater generally is less likely to be contaminated than surface water, it nonetheless may require contaminant removal. Possible groundwater contaminants include naturally occurring inorganic chemicals such as arsenic, fluoride, and nitrate, as well as human-made chemicals (from solvents, fuels and pesticides, for example) that have found their way into the aquifer .

Other contaminants that present aesthetic concerns are calcium and magnesium (which produce hardness); iron and manganese (which cause staining of laundry and plumbing fixtures); and hydrogen sulfide gas (which produces the unforgettable "rotten-egg" smell). The word "contaminant" includes any substance in water, including those that are not harmful, even though popular usage often refers only to harmful pollutants.

Hard water is usually treated with the water "softening" method, which utilizes a resin-coated media that exchanges its ion (usually sodium) for the calcium and magnesium ions that are responsible for hardness. The watersoftening media must be regenerated periodically with a brine (very salty) solution.

Even if the water is not hard, inorganic chemicals such as iron and manganese can cause problems that require treatment. Iron and manganese can be oxidized, or brought out of solution, by chemicals such as chlorine

Settling tanks at a water treatment plant allow coagulated particles to settle to the bottom of the tank. The settled material is periodically drained and collected for eventual disposal in a landfill. or potassium permanganate. The oxidized metals can then be filtered out as the water passes through a sand media. A zeolite sand, commonly known as manganese greensand, is usually used for this filtration.

Some groundwaters have taste and odor problems that require treatment in order for the water to be palatable to the user. Chlorine and ozone are effective in reducing hydrogen sulfide odors, and simple aeration can rid the water of some volatile organic compounds , such as solvents or petroleum by products (Scott G.Curry).

2.1.2 Surface Water

Many large cities are served by surface-water sources; most of these surface waters are exposed to a variety of contaminants. Common contaminant sources are untreated sewage and runoff from fertilized fields, parking lots, or unprotected watersheds. The primary contaminants of concern are microbes, including *Giardia* and *Cryptosporidium.* Effective surface water treatment therefore relies on the multiple-barrier approach, involving a sequence of processes from among the following options(Scott G.Curry).

2.1.3 Pre-Treatment.

Simple screens over intake pipes in lakes or rivers can prevent large debris, such as leaves, sticks, or small fish from entering the treatment plant. Waters that exhibit seasonal changes in turbidity or algae growth may require an oxidant such as chlorine, potassium permanganate, or ozone for pre-treatment.

2.1.4 Coagulation, Flocculation, and Sedimentation.

Coagulants such as alum, ferric chloride, or synthetic polymers are added to the raw water and mixed rapidly. Chemicals to adjust the pH may also be added at this point. The effectiveness of further treatment depends partly on raw water chemical characteristics such as pH, temperature, and alkalinity.

The coagulant chemicals, by the process of coagulation, neutralize the electrical charges of the sediment particles, allowing the binding together of small particles into larger particles that can then be settled or filtered. This process is known as flocculation. The sedimentation process then allows the larger "floc" particles to settle in a basin. The cleaner water at the top of the sedimentation basin flows onto the filter (Scott G.Curry).

2.1.4.1 Mechanism of Coagulation

Although chemical coagulation is a widely used process the mechanisms by which it operates are not fully understood in spite of considerable research effort. Basic colloid stability considerations have been applied to coagulation in attempts to offer explanations for the observed results (Tebbutt, 1998).

The stability of colloids depends upon the electrical charge that they posses. In fact, colloids are subject to two major forces.

1. Van der Waals attraction, which relates to the structure and form of colloids as well as to the type of medium (E_A).
2. The electrostatic repulsive force which relates to the surface charges of the colloids (E_B).

The stability of a colloid suspension depends on the balance between the forces of attraction and repulsion , the energy level of which is :

$$E = E_A + E_B$$

In order to destabilize the suspension , it is necessary to overcome the energy barrier E_S. To accomplish this and , there by, promote the agglomeration of the colloids, it is necessary to reduce the electrostatic repulsive forces. This destabilization is brought about by coagulation (Al-Hashimi, 1978).

2.1.5 Filtration.

The filter media is usually a mixture of carefully graded and specified gravels and sands, specifically designed for particle retention. These removed particles include turbidity and biological contaminants such as *Giardia* and *Cryptosporidium.* Inorganic chemicals such as arsenic and mercury are also removed by proper coagulation and filtration. Small filters made of pleated paper, carbon, or synthetic resins often are used by consumers. Pleated paper filters can remove sand, dirt, and some iron. Carbon filters are effective against chlorine and organic chemicals such as herbicides and pesticides, and can also remove objectionable tastes and odors. Some manufacturers of resin-type filters claim a high removal of lead or other inorganic chemicals(Scott G.Curry).

2.1.6 Disinfection.

This process is designed to kill disease-causing microorganisms such as bacteria, viruses, and protozoa. Chlorine is most commonly used for this purpose, although ozone and ultraviolet light are increasingly being used in public water systems. The single-celled protozoa (*Giardia* and *Cryptosporidium*), which can cause severe intestinal illness, are more resistant to traditional disinfectants than bacteria or viruses, and the disinfection process must therefore be closely monitored(Scott G.Curry).

2.1.7 Other Treatment Technologies

A number of other treatment technologies are employed both by the public and private sector, depending on the needs and desires of the water users. Granular-activated carbon is used for the elimination of objectionable tastes and odors, as well as for removal of organic chemicals such as pesticides and herbicides. Sodium carbonate, commonly known as soda ash, can be used to raise the pH of the water to make it less corrosive to pipes and plumbing fixtures. Some public water systems add small amounts of fluoride in order to aid in the prevention of dental cavities in children.

In addition, many small water treatment units, designed to fit under the kitchen sink or in any other convenient location, are used by individual homeowners regardless of the water source. Cartridge filters, membrane filters, and reverse osmosis units are all able to filter out most contaminants that cause health risks and aesthetic concerns. Water softeners are often necessary to treat hard water. Small ozone or ultraviolet-light disinfection units are becoming popular with homeowners who depend on private water supplies of questionable quality(Scott G.Curry).

Many different types of water treatment units are designed for the individual homeowner. When considering the purchase of such a unit, the homeowner should have the water tested to determine exactly what type of contaminants are in the water, and what, if anything, needs to be removed. No one filter works for all contaminants. A filter that removes iron and manganese, for example, will probably not remove herbicides or pesticides. It is also important to remember that all treatment units require regular maintenance to keep them functioning properly and to prevent the buildup and possible breakthrough of the unwanted contaminants.

2.2 Types of Coagulants

Coagulant chemicals come in two main types – primary coagulants and coagulant aids. Primary coagulants neutralize the electrical charges of particles in the water which causes the particles to clump together. Chemically, coagulant chemicals are either metallic salts (such as alum) or polymers. Polymers are man-made organic compounds made up of a long chain of smaller molecules. Polymers can be either cationic (positively charged), anionic (negatively charged), or nonionic (neutrally charged). The common coagulant chemicals used are

- Aluminum Sulphate (ALUM)
- Ferrous Sulfate (copperas)
- Ferric Sulfate
- Ferric Chloride

The choice of the coagulant to be used for any particular water should preferably be based upon experiment on different coagulants (unknown,2009).

2.2.1 Alum

One of the earliest, and still the most extensively used coagulant, is aluminum sulfate (Al/S04)3 ·14 HP), also known as alum. Alum is acidic with light tan to grey in colour and available in blocks, lumps and powder with a density of 1000 -1100 kg/m3 and specific gravity of 1.25 to 1.36. Alum can be bought in liquid form or in dry form. It is readily soluble in water. When alum is added to water, it reacts with the water and results in positively charged ions. The ions can have charges as high as +4, but are typically bivalent (with a charge of +2.) The bivalent ion . resulting from alum makes this a very effective primary coagulant (unknown,2009).

2.2.1.1 Advantages of alum

- It readily dissolves with water.
- It does not cause the unsightly reddish brown staining of floors, walls and equipment like ferric sulphate.

2.2.1.2 Disadvantages of alum

- It is effective only at certain pH range.
- good flocculation may not be possible with alum in some waters.

2.2.2 Ferrous Sulphate or Copperas

Ferrous sulphate, ordinarily known as copperas, is granular acid compound and green to brownish yellow colour available in granules, crystals and lumps. This is fed usually in solution form with strength of 4 to 8 %. The alkalinity and pH value of natural water are too low to react with copperas to form the desired ferric hydroxide floc, because the reaction involves oxidation by the dissolved oxygen in the water, which does not occur when pH value is less than 8.5. It is necessary, therefore, to add lime with copperas to secure coagulation. For this reason, copperas is not used in coagulation of high coloured water, which coagulates best at pH values less than 6.0. The dose of lime required is approximately 0.27 mg/L to react with 1.0 mg/L of copperas. Generally the floc formed by the reaction of copperas and lime is feathery and fragile, but has a high specific gravity.

2.2.3 Ferric sulphate

Ferric sulphate is available as a commercial coagulant in the form of an anhydrous material that may be transported and stored in wooden barrels. The material will dissolve readily in a limited quantity of warm water so a special solution pot must be used with chemical feeders, in which 1 part ferric sulphate by volume is dissolved in 2 parts water to produce a solution of about 40% strength.

2.2.3.1 Advantages of Ferrous sulphate

- Ferric hydroxide is formed at low ph values, so that coagulation is possible with ferric sulphate at pH values as low as 4.0.
- Ferric hydroxide is insoluble over a wide range of pH values than aluminium hydroxide except for the zone of 7.0 to 8.5.
- The floc formed with ferric coagulants is heavier than alum floc.
- The ferric hydroxide floc does not redissolve at high pH values.
- Ferric coagulants may be used in colour removal at the high pH values required for the removal of iron and manganese and in softening of water.

2.3 Coagulant Aids

Coagulant aid is an inorganic or organic material, when used along with main coagulant, improves or accelerates the process of coagulation and flocculation by producing quick forming, dense and rapid-settling flocs. Coagulant aids when added increase the density to slow-settling flocs and toughness to the flocs so that they will not break up during the mixing and settling processes. Primary coagulants are always used in the coagulation/ flocculation process. Coagulant aids, are generally used to reduce flocculation time and when the raw water turbidity is very low.

The particles of coagulant aids may become negatively charged making them subject to attraction by positively charged aluminium ions. It is especially useful for clear water with very low turbidity that does not coagulate well with usual processes.

Nearly all coagulant aids are very expensive, so care must be taken to use the proper amount of these chemicals. In many cases, coagulant aids are not required during the normal operation of the treatment plant, but are used during emergency treatment of water which has not been adequately treated in the flocculation and sedimentation basin.

Common coagulant aids are:

- Bentonite
- Calcium carbonate
- Sodium silicate
- Anionic polymer
- Non ionic polymer

Lime is a coagulant aid used to increase the alkalinity of the water. The increase in alkalinity results in an increase in ions (electrically charged particles) in the water, some of which are positively charged. These positively charged particles attract the colloidal particles in the water, forming floc.

Bentonite is a type of clay used as a weighting agent in water high in color and low in turbidity and mineral content. The bentonite joins with the small floc, making the floc heavier and thus making it settle more quickly.

Polyelectrolytes, which are polymers containing ionisable units have been used successfully as both as coagulant aids and coagulants but care should be taken to guard against their toxicity. Polyelectrolytes create extraordinary slippery surfaces when spilled on floor and are difficult to clean up.

2.3.1 Synthetic organic

Synthetic organic polymers are also the commonly used coagulant aids for coagulation/flocculation of heavy metal precipitates (EPA, 1987). This is because metallic precipitates typically possess a slight electrostatic positive charge resulting from charge density separation. The negatively charged reaction sites on the anionic polyelectrolyte attract and adsorb the slightly positive charged precipitate (EPA, 1987). Syn-thetic organic polyelectrolytes are commercially marketed in the form of dry powder, granules, beads, aqueous solutions, aqueous gels, and oil-in-water emulsions (EPA, 1987). Generally, liquid systems are preferred because they require less floor space, reduce labor requirements, and reduce the potential for side reactions because the concentrate can be diluted in the automatic dispensing systems (EPA, 1987). Typical dosage requirements for metals-containing waters are in the 0.5- to 2.0-mg/L range. Polyelectrolytes work most effectively at alkaline and intermediate pHs but lose effectiveness at pH levels lower than 4.5 (EPA, 1987).

2.3.2 Natural Organic

Coagulant aids derived from natural products include starch, starch derivatives, proteins, and tannins (EPA, 1987). Of these, starch is the most widely used. The price per kilogram for these natural products tends to be low; however, dosage requirements tend to be high (EPA, 1987). In addition, because of the composition of natural products, they are more susceptible to microbiological attack, which can create storage problems.

2.4 Factors Influencing Coagulation

Coagulation will be affected by changes in the water's pH, salt content, alkalinity, turbidity, and temperature. Within the plant, mixing effects and coagulant effects will influence the coagulation/ flocculation process. The levels of pH, salts, and alkalinity in water are all ways of measuring the amounts of positively charged particles (cations) and negatively charged particles (anions) in the water. As a result, all three factors influence the amount of coagulants which must be used to remove the turbidity in the water.

2.4.1 pH

The pH range of the water may be the single most important factor in proper coagulation. The optimum pH range varies depending on the coagulants used, but is usually between 5 and 7. These lower pH values mean that there are more positively charged particles loose in the water to react with the negatively charged colloids.

Coagulation should be carried out within this optimum zone using alkalis and acids for correction of pH where necessary. For many waters, which are low in colours and well buffered and having pH in the optimum zone, no adjustment of pH is necessary when alum is used as coagulant. Failure to operate within the optimum pH zone, may be a waste of coagulants and may be reflected in the lowered quality of the plant effluent.
When ferrous sulphate is used as a coagulant, the pH should be maintained above 9.5 to ensure complete precipitation of the iron. This is done by the addition of hydrated lime. The treated water should be corrected with the addition of carbondioxide (unknown,2009).

2.4.2 Type and Coagulant Dosage

Type and coagulant dosage are also playing very important role in coagulation process. Polymers are effective compare to conventional coagulant because the chains in polymer supply place for colloid particle to stick or attach which can give high dense particle and this will ease the settling process. Besides that the amount of coagulant added must be at the optimum condition so that the coagulation can give optimum result.

2.4.3 Salt

Salts are compounds which contain both a cation and an anion. In water, the cation and the anion come apart and can interact with other charged particles in the water. All natural waters contain some concentration of cations and anions, such as calcium, sodium, magnesium, iron, manganese, sulphate, chloride, phosphate, and others. Some of these ions may affect the efficiency of the coagulation process.

2.4.4 Alkalinity of water

The alkalinity of water is related to both the pH and the salts in the water. Alkalinity is the capacity of the water to neutralize acids, based on the water's content of carbonate, bicarbonate, hydroxide, borate, silicate, and phosphate. Water with a high alkalinity is preferred for coagulation since ittends to have more positively charged ions to interact with the negatively charged colloids. To provide artificial alkalinity to water so as to have effective coagulation quick lime or hydrated lime are added to water.

2.5 Previous Research In The Field Of Coagulation

The chemical coagulation of turbid and or naturally colored surface waters involves the interaction of particulates with a destabilizing agent (coagulant). Researches were done by people all around the world to create the most effective coagulant.

Inorganic coagulants such as aluminum and iron salts are the most commonly used. Common coagulant chemicals used are alum, ferric sulfate, ferric chloride, ferrous sulfate, and sodium aluminate. The first scientific investigation into the use of alum for was conducted and reported by Austen and Wilbur of Rutgers University in 1885 They concluded that, by the addition two grains of alum to the gallon (with 34ppm), or half an ounce to 100 gallons, water can be clarified by standing, and that neither taste nor physiological properties will be impaired to it by this treatment(Samuel D.Faust & Osman M.Aly,1998). Later, a series of experiments was conducted on turbid Ohio River water at Louisville, Kentucky, in the years 1895-1897. Of the several compound tried; alum,potash alum, and lime-alum was found to be the most suitable. These experiments led to widespread use of alum as coagulant in water treatment. Inorganic coagulants usually offer the lowest price per pound, are widely available, and, when properly applied, are quite effective in removing most suspended solids. They are also capable of removing a portion of the organic precursors which may combine with chlorine to form disinfection by-products. They produce large volumes of floc which can entrap bacteria as they settle. However, they may alter the pH of the water since they consume alkalinity. When applied in a lime soda ash softening process, alum and iron salts generate demand for lime and soda ash. They require corrosion-resistant storage and feed equipment. The large volumes of settled floc must be disposed of in an environmentally acceptable manner.

The use of organic polymers, which can act as either negatively or positively charged ions, has made significant impact on the efficiency of removal colloids by chemical coagulation(Arcadio P.Sincero and Gregoria A.Sincero,2000). Shahnawaz Sinha et al.studied the the effectiveness of conventional and alternative coagulants.In his experiment a source water sample was collected from the inlet to the Denver water Foothills Plant (Denver, Colorado USA) during a run-off period (May, 1999). The raw water sample was analyzed for various water quality parameters, including pH, alkalinity, turbidity, conductivity, temperature, and various cations/metals and anions content.Experiments were performed on the Foothills Plant source water by adding various concentrations of coagulant. A streaming current detector, SCD (Chemtrac, GA) was used to quantify the amount of coagulant dose required for colloidal charge reversal due to addition of metal coagulants (i.e., positively charged coagulants). This technique was employed for the conventional as well as alternative coagulants This study demonstrated the importance of characterization of both the coagulant as well as source water properties for selecting an appropriate coagulant. Among alternative coagulants PACl-4 was found to be an effective coagulant based on both characterization and coagulation results.

Wen Po Cheng et al (2007), conducted an experiment on the removal of organic substances from low-turbidity and low-alkalinity water with metal-polysilicate coagulants. The PASiC and PAFSiC coagulants used in this study were prepared in the laboratory using the method developed by Yang et al. and the commercially available humic acid powder with molecular weights ranging from 2000 to 50,000, extracted from brown coal using NaOH (Aldrich Chemical Co., Inc., USA), was used as the stock solution (humic acid). He found that PASiC or PAFSiC, a new type of polymeric coagulant consisting of long-chain polymers of silicate and aluminum or ferric ions, has a larger molecular weight and carries smaller surface charge than PAC. It is capable of removing colloidal particles through adsorption, charge neutralization, and chemical bridging.

Another very important research was done by Bao-Yu Gao et al (2003). on the Coagulation performance of polyaluminum silicate chloride (PASiC) for water and wastewater treatment. Raw water was taken from Shenzhen Lake, Shenzhen city, which is located in south part of China and a laboratory study was conducted to evaluate the coagulation performance of PASiC in the treatment of water and wastewater, whichwas prepared by combining PAC with PSi, and to compare with that of PAC. Experiments were carried out to investigate the effects of [OH]/[Al] ratio (γ), Al/Si molar ratios, dosage, pH and preparation technique on the efficiency of turbidity, algae, COD, oil and TP removal by PASiC coagulation. The results demonstrate that the coagulating performance of PASiC was dependent upon preparation procedure, Al/Si ratio and γ value. In his experiment he concluded that the coagulation efficiency of PASiC increased with increasing γ value, but the products became unstable during aging at very high γ value. PASiC performed more efficiently than PAC for removing algae, turbidity, oil, COD.

Polymers are effective over a wider pH range than inorganic coagulants. They can be applied at lower doses, and they do not consume alkalinity. They produce smaller volumes of more concentrated, rapidly settling floc. The floc formed from use of a properly selected polymer will be more resistant to shear, resulting in less carryover and a cleaner effluent but polymers are generally several times more expensive in their price per pound than inorganic coagulants. Selection of the proper polymer for the application requires considerable jar testing under simulated plant conditions, followed by pilot or plant-scale trials

CHAPTER 3

METHODOLOGY

3.1 Introduction

In this chapter, a detailed experimental procedure which includes the chemicals used, method to run jar test, test chemical oxygen demand, biochemical oxygen demand and turbidity will be discussed. The main purpose of this experiment is to find the effectiveness of proposed new inorganic polymer in removing turbidity of both water and wastewater used.

3.2 water and wastewater

In this research two types of water source are used. First water from Kuantan river which is a main potable water source for people in Pahang State (Malaysia). This water contains domestic discharges and also mud. The turbidity of Kuantan river is around 70 NTU which is quite high and pH range is 6.5 to 7.5. Another type of water used in this research is, wastewater from paper pulp industry which is taken from a paper pulp chemical plant (PASCORP) situated in Bentong, Pahang. The turbidity is around 208 NTU which is very high and pH is around 6.5 to 7.5 too.

3.3 Chemical

There are two main chemicals used to prepare the proposed coagulant, first is sodium silicate which is also known as waterglass and the second aluminium chloride.

3.3.1 Sodium Silicate

Sodium silicate or waterglass is a commercialized product bought from the R&M Marketing, Essex, U.K. The molecular weight for sodium silicate is 142.07g/mol and it is a neutral solution which contain 5% of water, < 0.005% of Copper, < 0.005% of Lead, and <0.005% of Nickel

3.3.2 Aluminium Chloride

Aluminium chloride ($AlCl3$) is a compound of aluminium and chlorine. The anhydrous material has a very interesting structure: despite being the halide of a highly electropositive metal, its bonding is principally covalent. This chemical is bought from R&M Marketing, Essex, U.K. Molecular weight of this substance is 241.43g/mol and it is hexahydrate.

3.4 Experimental Procedures

3.4.1 Preparation of poly-aluminum Silicate Chloride

Preparation of Polysilicic acid ---Water glass solution (sodium silicate,Na_2SiO_3) was diluted to a concentration of 0.5M. Then the diluted water glass solution was neutralized to pH 2.0 with 0.5M HCl. 0.25M $AlCl_3$ was prepared using de-ionized water. The prepared $Alcl_3$ solution was very slowly titrated with 0.5 M NaOH solution. During titration the solution was vigorously stirred to ensure that homogeneous solution was obtained.The solution was mixed with polysilicic acid aged for 2 hours. The prepared coagulant sample was capped, sealed and stored overnight before jar test was conducted.Coagulation tests were performed by using water from Kuantan River and wastewater from paper mill. Turbidity, COD and BOD were measured for each jar test experiment.

3.4.2 Jar Test Experiment

1 L of water from Kuantan River was measured and place in a beaker and repeated for the remaining beakers. pH and turbidity was measured for each sample. The beakers were placed in the stirring machine. With a measuring pipet, different dosage of prepared polyaluminum silicate chloride solution was added to each beaker as rapidly as possible. Rapid mixing was conducted; with the stirring paddles lowered into the beakers, the stirring machine was started and operated for 2 minute at a speed of 200 RPM to ensure coagulant is thoroughly mixed. The stirring speed was reduced to 40 rpm to promote flocculation process and 30 minutes sedimentation followed. After sedimentation supernatant sample was withdrawn from each beaker for pH, turbidity, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) measurement. Optimum dosage of coagulant was determined. These were repeated for different pH (using HCl and NaOH) and coagulant (polyaluminium chloride and aluminum sulphate; using optimum dosage as stated by previous

research). Graph of turbidity, COD, BOD versus coagulant dosage and graph of turbidity, COD, BOD versus pH were plotted for each run. The steps were repeated for wastewater from paper mill. Results were analyzed and comparison test was made.

3.5 Measurement and Analysis

3.5.1 Chemical Oxygen Demand

1 ml of supernatant from jar test was diluted with 100 ml of deionized water. The COD Reactor was turned on and preheated to 150°C. The safety shield was in front of the reactor. The caps were removed from two COD Digestion Reagent Vials. (*Be sure to use vials for the appropriate range). One vial was held at a 45-degree angle. 2 mL of sample was added to the vial using a clean volumetric pipet. This is the prepared sample. Second vial was held at a 45-degree angle. 2 mL of sample was added to the vial using a clean volumetric pipet. This is the blank. The vials was capped tightly and rinsed with de-ionized water and wiped with a clean paper towel. The vials was held by the cap over a sink and inverted gently several times to mix. The vials were placed in the preheated COD Reactor. (*The sample vials will become very hot during mixing.) The vials was heated for two hours. The reactor was turned off and waited about 20 minutes for the vials to cool to room temperature. Each vial was inverted several times while still warm. The vials were placed into a rack and cool to room temperature. Proceeded with Colorimetric Determination Method 8000. Program **435 COD HR** (High Range/High Range Plus) was selected and COD readings were taken.

3.5.2 Biochemical Oxygen Demand

Dilution water was prepared by adding 1mL each of phosphate buffer, magnesium sulfate, calcium chloride, ferric chloride solution into 1L volumetric flask. Distilled water is added to 1L. 1mL of supernatant sample was into a 500mL beaker. Dilution water was added up to 300mL into the same beaker. pH value was adjusted to 6.5 to 7.5 by adding acid/base. 300mL dilution water was prepared as control. All the prepared samples was poured and controlled in 300mL-incubation bottle. DO for each sample was measured by using Dissolved Oxygen Meter. All the bottles is placed in BOD Incubator for 5 days. The temperature was set at 20°C. The final DO value was
measured after 5 days.

BOD_5 was calculated according to the formula below;

BOD_5, mg/L = $(D_1 - D_2) / P$
Where;
D_1 = DO value in initial sample
D_2 = DO value in final sample
P = Decimal volumetric fraction of sample used
Or;
BOD_5, mg/L = $(D_1 - D_2)$ x Dilution factor
Dilution factor = Bottle volume (300mL) / Sample volume

3.5.3 Turbidity

10 ml of supernatant from jar test is taken using pipette and placed into a turbidity vial. The vial is capped and cleaned. Then the vial is placed in a turbidity meter and reading was taken (turbidity unit is in NTU).

3.5.4 Equipment Used

Figure 3.1 : Jar Test

Figure 3.2 : pH Meter

Figure 3.3 : Turbidity Meter

Figure 3.4 : Analytical Balance

Figure 3.5 : COD Reactor

Figure 3.6 : Spectrophotometer

Figure 3.7 : DO Meter

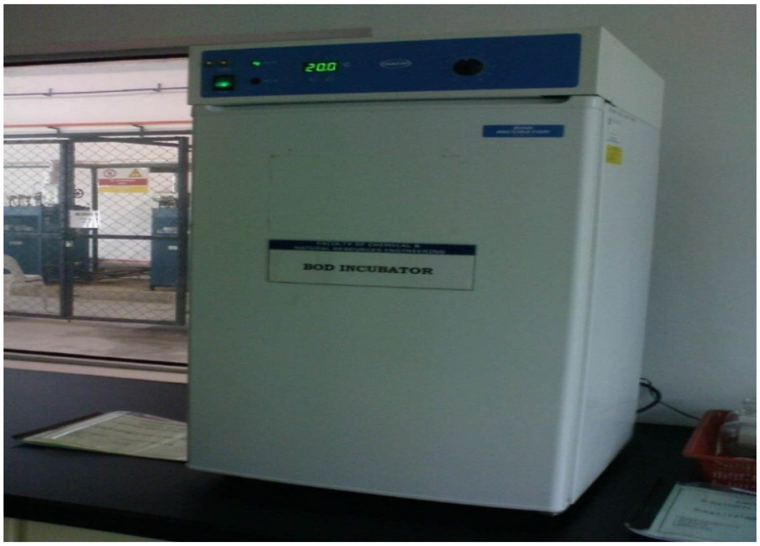

Figure 3.8 : BOD Incubator

CHAPTER 4

RESULTS AND DISCUSSION

Coagulation test was conducted for both water and wastewater. For water treatment the source was from Kuantan river and for wastewater the was from PASCORP,Bentong (paper pulp). Both sample of water and wastewater were treated with polyaluminium silicate chloride, polyaluminum chloride and also aluminium sulphate. Comparisons and the discussions of the result is made for the three of the coagulant mentioned based on three factors; turbidity, chemical oxygen demand and biochemical oxygen demand.

4.1 Kuantan River

Since, the optimum pH and coagulant dosage for polyaluminium chloride and aluminium sulphate is already known; jar test was not conducted to determine optimum pH and dosage for these two coagulant.

But polyaluminium silicate chloride is a very new coagulant and we still don't know the exact value for optimum pH and optimum dosage for this coagulant. So experiment was conducted to find out these values for both water samples.

4.1.1 Coagulation by PASiC

4.1.1.1 Effect of pH

For optimum pH measurement, hydrochloric acid and sodium hydroxide solution was used to alter the pH of wastewater to a certain range including both acidic and basic condition. From the observation, the pH does effect the coagulation properties of PASiC like other conventional coagulant but the effect is not much compare to polyaluminium chloride and aluminium sulphate. From the 4.1 we can see that the range for optimum pH is from 6.5 to 7.5. The optimum pH for both alum and polyaluminium chloride is 6. But for polyaluminium chloride, even though the optimum pH is 6.5 to 7.5 but pH for other pH range the percentage of turbidity was not change significantly. For instance percentage of turbidity removal for pH 5 (acidic condition) was 96.6% while for pH 9 (basic condition) was 95.3%. The difference between these two values and the optimum value which was 99.2% is not much.

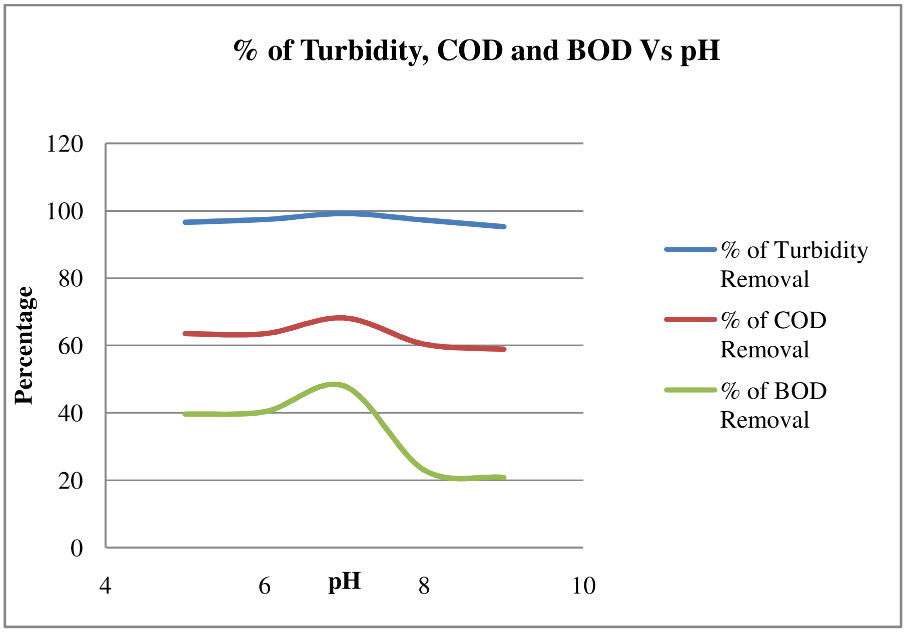

Figure 4.1 : Effect of pH On The Percentage Removal of Turbidity, COD and BOD for Kuantan River (PASiC)

4.1.1.2 Effect of PASiC Dosage

In the experiment to determine the optimum PASiC dosage for Kuantan river. In order to determine the value amount of dosage were manipulated for one liter of water sample starting from 1mg/L and the value 5mg/L was chosen as the optimum dosage because figure 4.2 shows that the percentage removal was almost the same or doesn't change much for 5mg/L and 6mg/L.

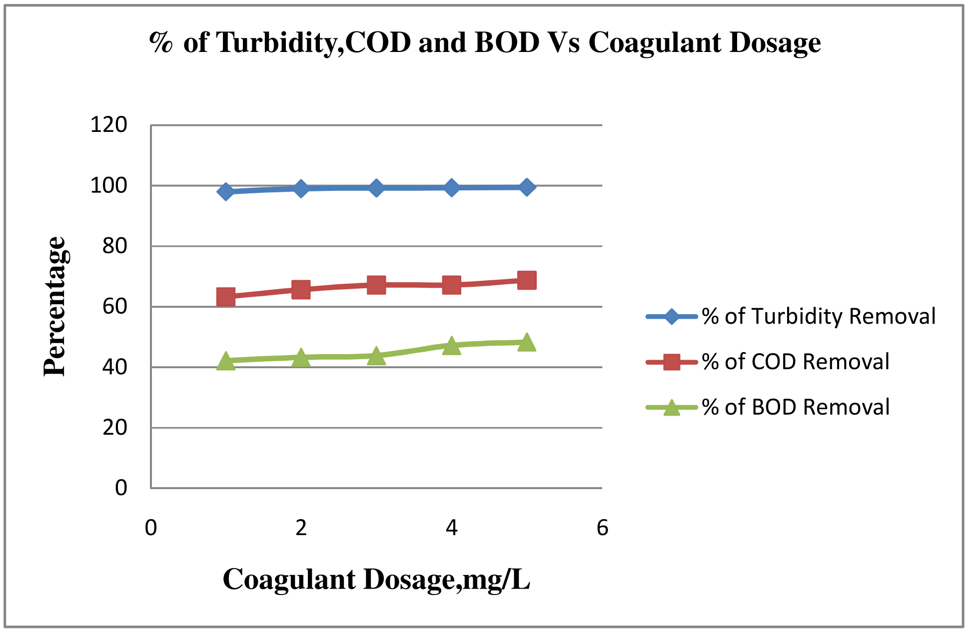

Figure 4.2 : Effect of Dosage of PASiC On The Percentage Removal of Turbidity, COD and BOD for Kuantan River.

4.1.2 Coagulation by Alum

The results from figure 4.3 shows that the optimum dosage of Alum needed to treat Kuantan River is around 23mg/L which is very high compare to the amount needed for PASiC.

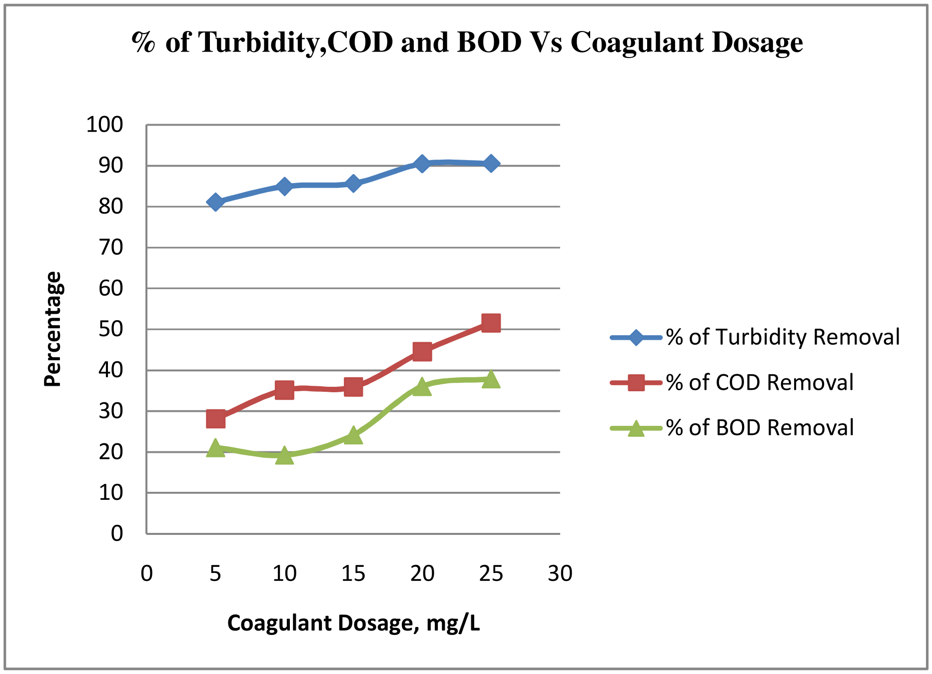

Figure 4.3 : Effect of Dosage of Alum On The Percentage Removal of Turbidity, COD and BOD for Kuantan River.

4.1.3 Coagulation by PAC

The results from figure 4.4 shows that the optimum dosage of PAC needed to treat Kuantan River is around 23mg/L which is almost same with the alum and very high compare to the amount needed for PASiC.

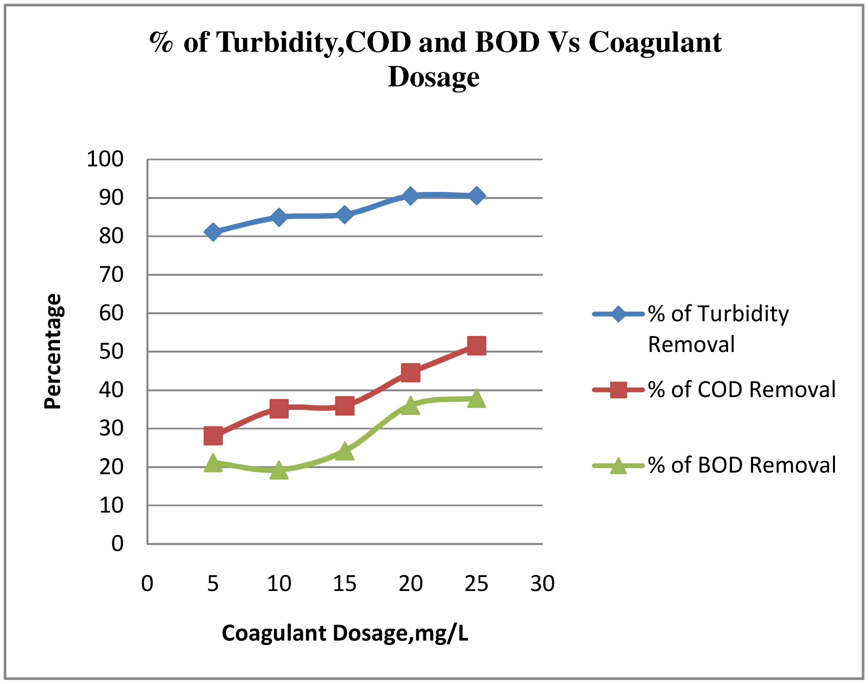

Figure 4.4 : Effect of Dosage of PAC On The Percentage Removal of Turbidity, COD and BOD for Kuantan River.

4.2 Comparison of Efficiency of PASiC, PAC and Alum for water treatment

Figure 4.5 shows the percentage of turbidity removal for PASiC, PAC and Alum for Kuantan river. PASiC removed about 99%, alum is slightly higher than PAC. But only small amount of dosage is required for PASiC and still efficiency is higher compare to PAC and Alum.

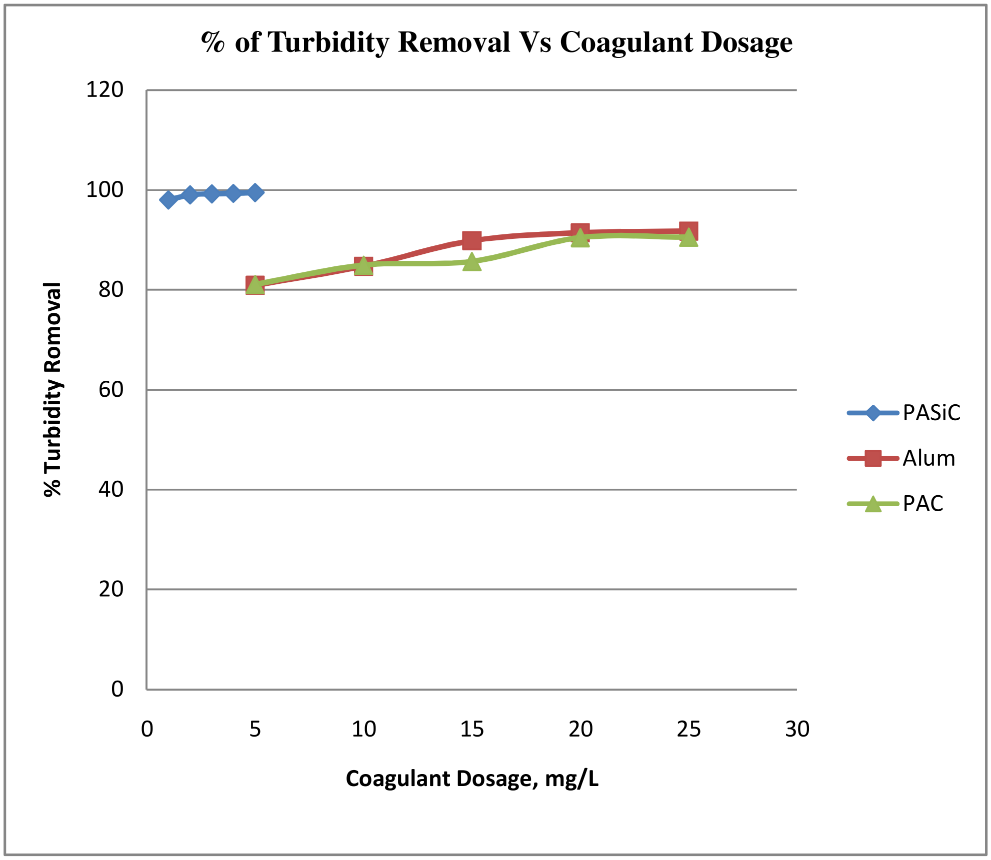

Figure 4.5 : Percentage of Turbidity Removal for PASiC, PAC and Alum for Kuantan River.

Figure 4.7 shows the percentage of COD removal for PASiC, PAC and Alum for Kuantan river. Highest percentage of COD removal was achieved using PASiC and lowest is Alum. Percentage of COD removal for PAC is higher than Alum but still lower than PASiC.

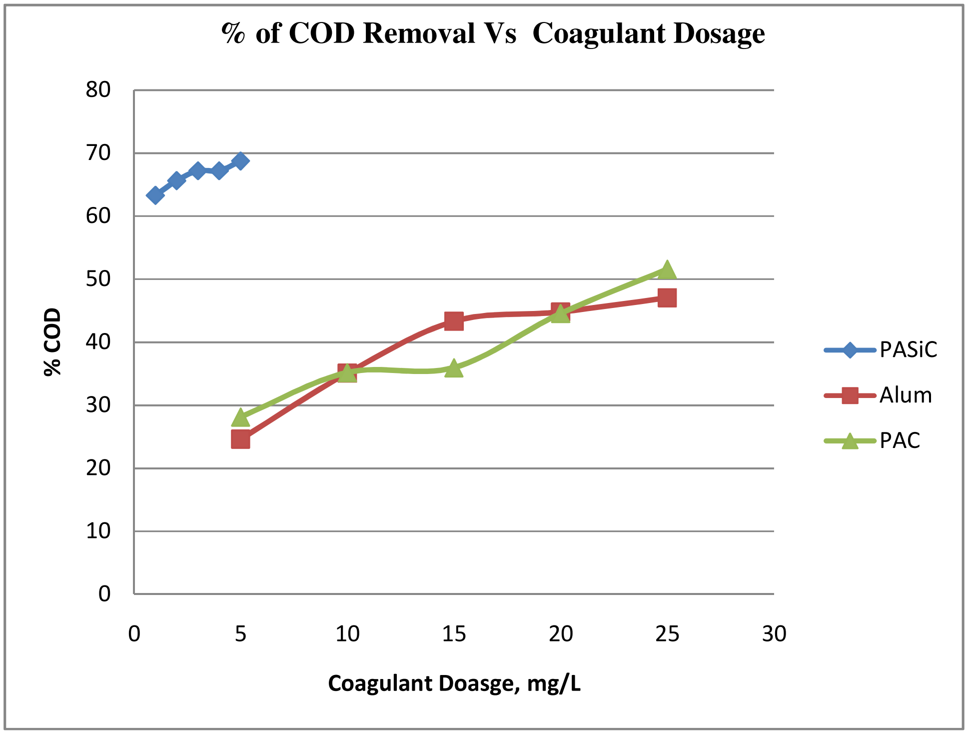

Figure 4.6 : Percentage of COD Removal for PASiC, PAC and Alum for Kuantan River.

The percentage of BOD removal for Kuantan River is not satisfactory for three of the coagulants used because we need biological treatment to remove BOD in higher amount but PASiC shows higher removal compare to other two. Figure 4.7 shows percentage of BOD removal for Kuantan River using these three coagulants.

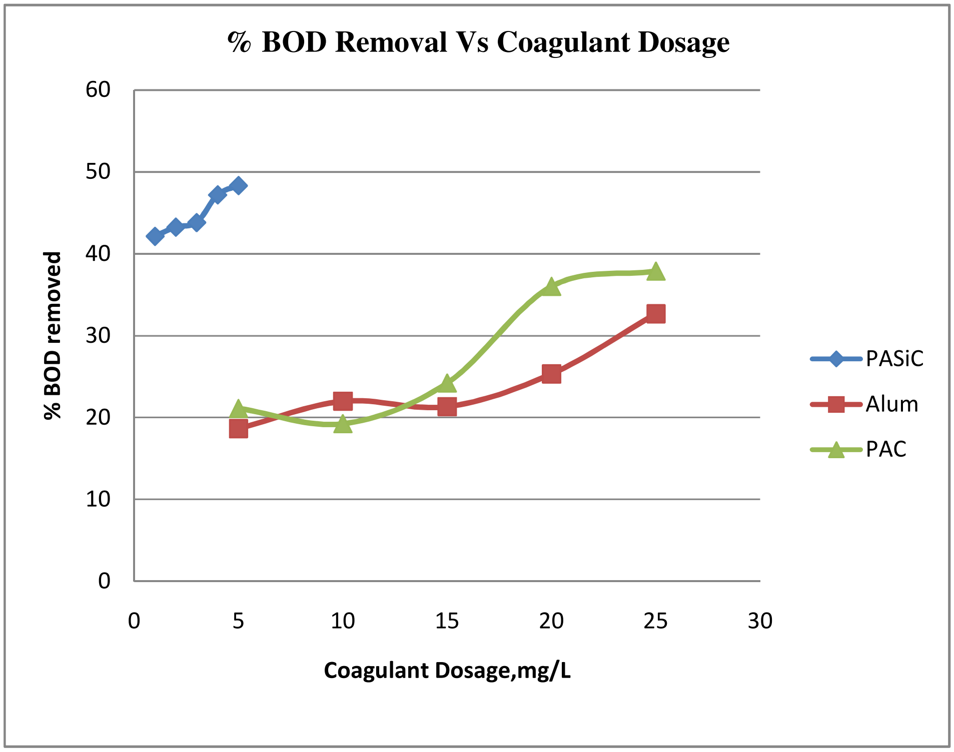

Figure 4.7 : Percentage of BOD Removal for PASiC, PAC and Alum for Kuantan River.

4.3 Wastewater (Paper Pulp)

For wastewater the same method is used and treated with PASiC, PAC and Alum and efficiency of removing turbidity, chemical oxygen demand (COD) and biological oxygen demand (BOD) is compared.

4.3.1 Coagulation by PASiC

4.3.1.1 Effect of PASiC Dosage

In the experiment to determine the optimum PASiC dosage for wastewater. In order to determine the value amount of dosage were manipulated for one liter of water sample starting from 10mg/L and the value 40mg/L was chosen as the optimum dosage because figure 4.8 shows that the percentage removal was almost the same or doesn’t change much for 40mg/L and 50mg/L.

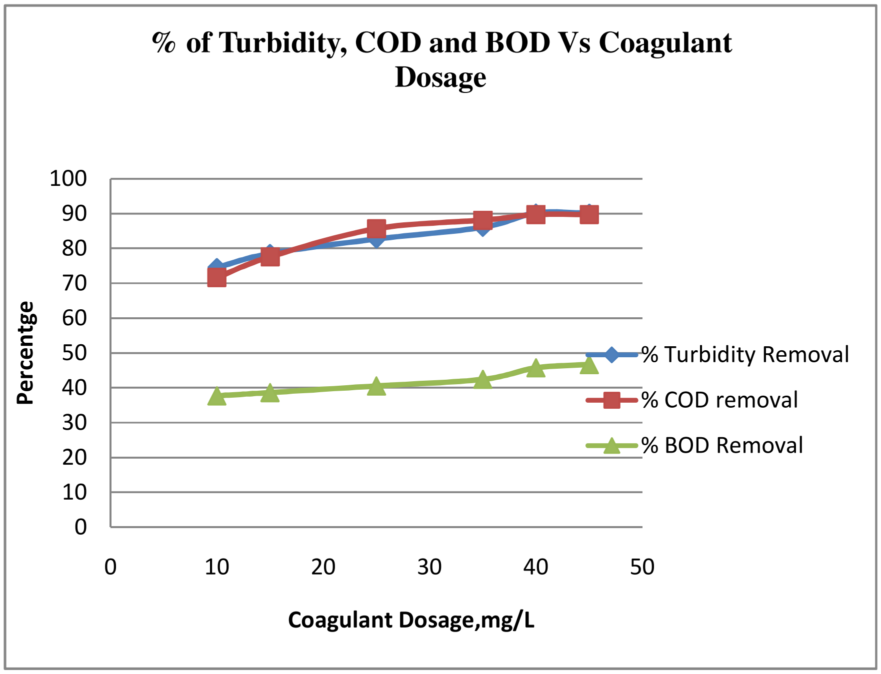

Figure 4.8 : Effect of Dosage of PASiC On The Percentage Removal of Turbidity, COD and BOD for wasterwater

4.3.2 Coagulation by PAC

Figure 4.9 shows the graph actually fluctuating for different dosage and different factors. This is because PAC needs coagulant aid, but considering the all three factors we can choose 150 mg/L as the optimum dosage and when compare this value to PASiC, this value is too high and not economic as PASiC.

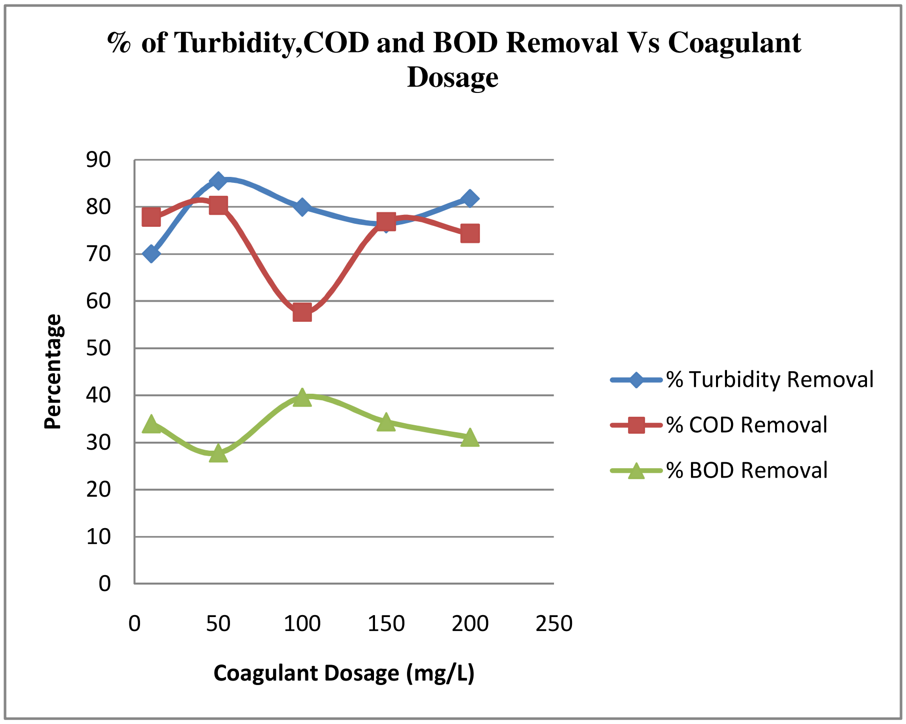

Figure 4.9 : Effect of Dosage of PAC On The Percentage Removal of Turbidity, COD and BOD for wasterwater

4.3.3 Coagulation by Alum

By analyzing figure 4.10, we can say that the optimum dosage of alum required is around 110 mg/L. this value is quite low compare to PAC but still high if compare with PASiC. When we add more alum to the wastewater than the required amount (optimum dosage) we can see that the efficiency Alum decrease, this is because of the shearing effect.

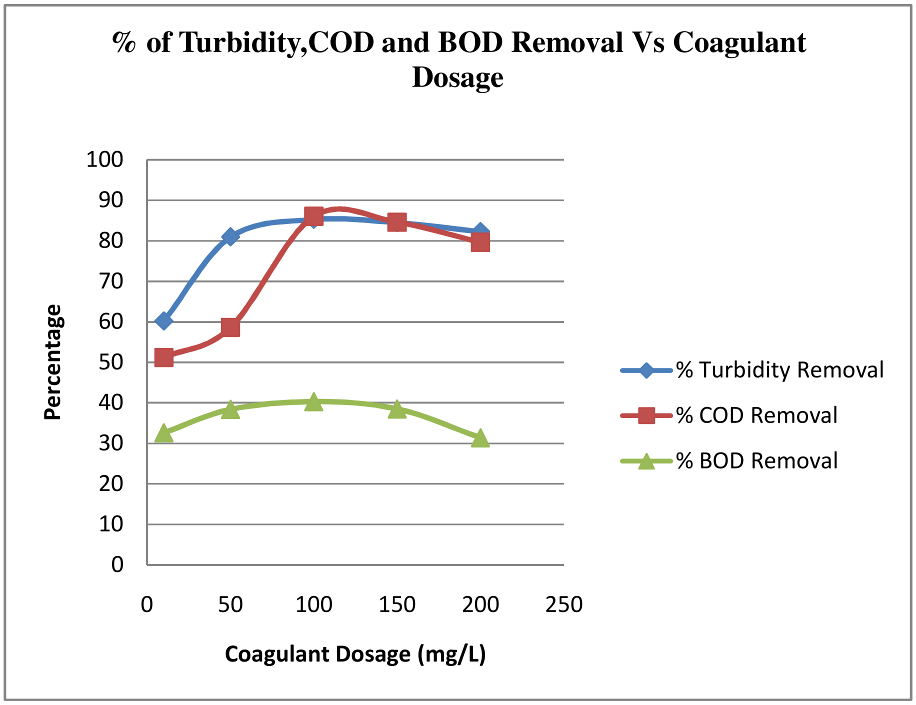

Figure 4.10 : Effect of Dosage of Alum On The Percentage Removal of Turbidity, COD and BOD for wasterwater

4.4 Comparison of Efficiency of PASiC, PAC and Alum for Wastewater Treatment (Paper Pulp, PASCORP, Bentong)

Figure 4.11 shows that the efficiency of turbidity removal for paper pulp wastewater for PASiC, PAC and Alum. From this figure we can see that about 90% of efficiency is achieved with PASiC with only 40-50mg/L of dosage. The amount of dosage needed for PAC is same like PASiC but it only removed 86% which is almost same with PASiC. In this experiment Alum shows least efficiency in removing turbidity and required about 130 mg/L of dosage which is very high and not economic.

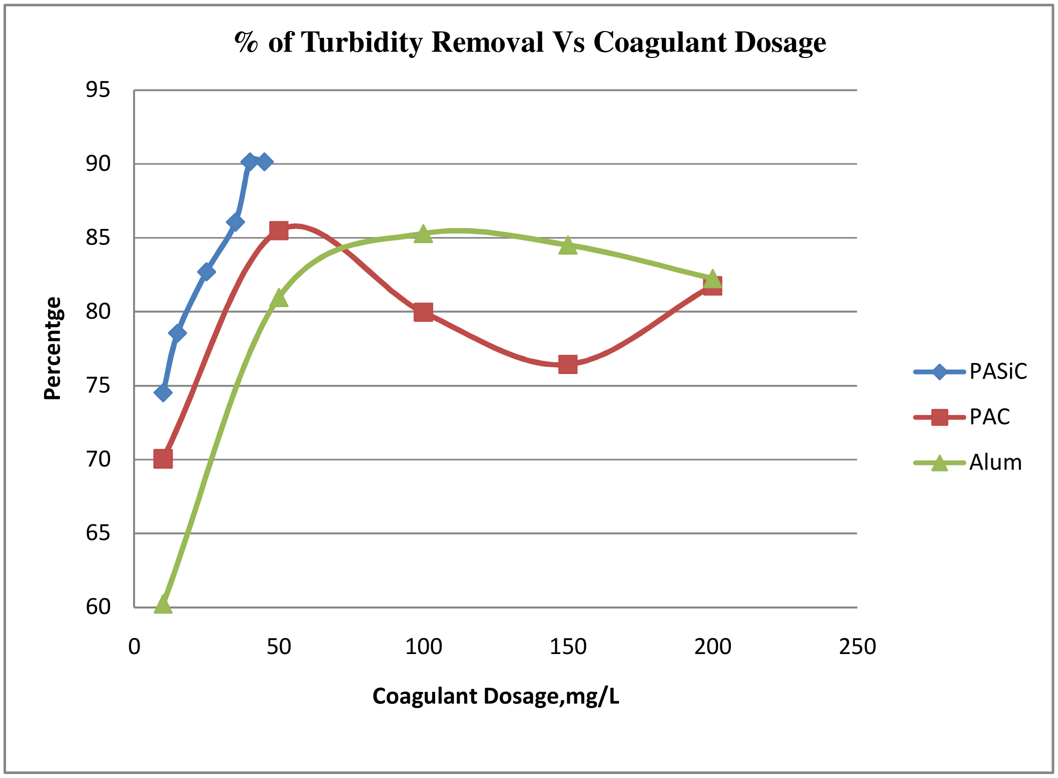

Figure 4.11 : Percentage of Turbidity Removal for PASiC, PAC and Alum for Wastewater (PASCORP,Bentong).

Figure 4.12 shows that the efficiency of COD removal for paper pulp wastewater for PASiC, PAC and Alum. From this figure we can see that about 90% of efficiency is achieved with PASiC with only 40-50mg/L of dosage. The amount of dosage needed for PAC is same like PASiC but the COD removal is very low which is only about 80%, even Alum removed higher amount of COD compare to PAC but the dosage of coagulant needed for alum to remove about 86% of COD is 130mg/L and again not economic.

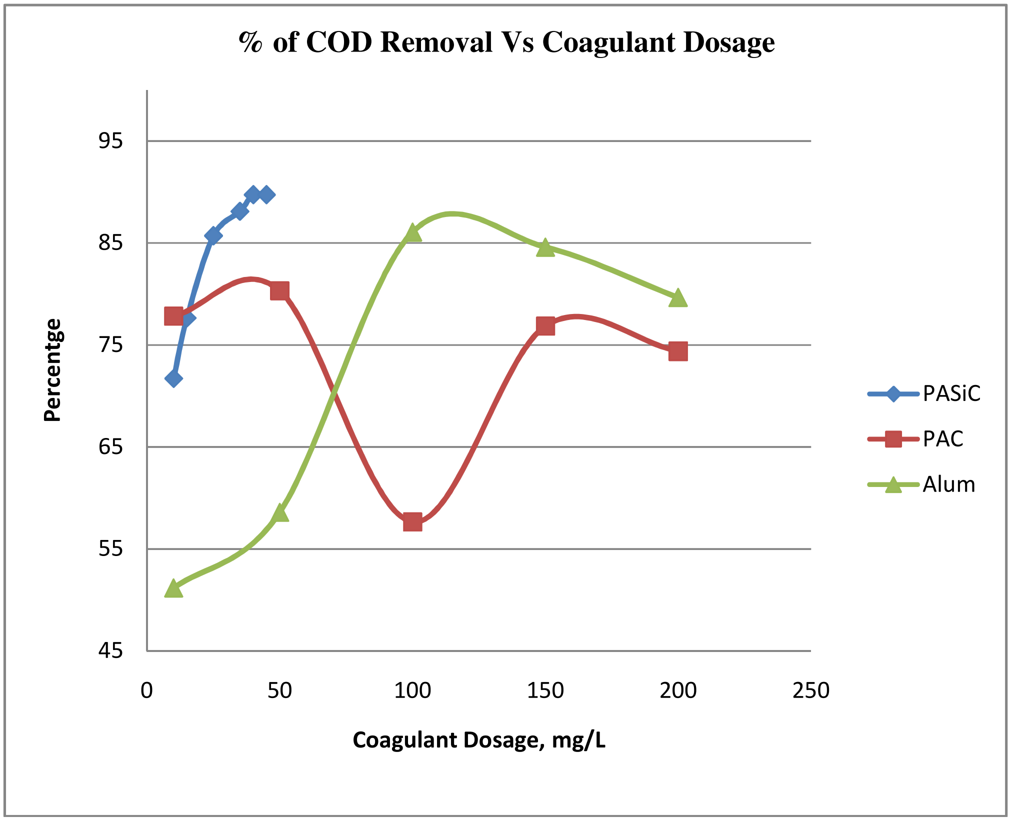

Figure 4.12 : Percentage of COD Removal for PASiC, PAC and Alum for Wastewater (PASCORP,Bentong).

Figure 4.13 shows that the efficiency of BOD removal for paper pulp wastewater for PASiC, PAC and Alum. All the three coagulant doesn't remove BOD much because to remove BOD from wastewater it must undergo biological process so that microorganism consume biodegradable matter in the wastewater and reduce the BOD level. Anyway, again PASiC showed better performance compare to other two coagulants used and the most important thing is the amount of PASiC needed is again lower compare to Alum and PAC.

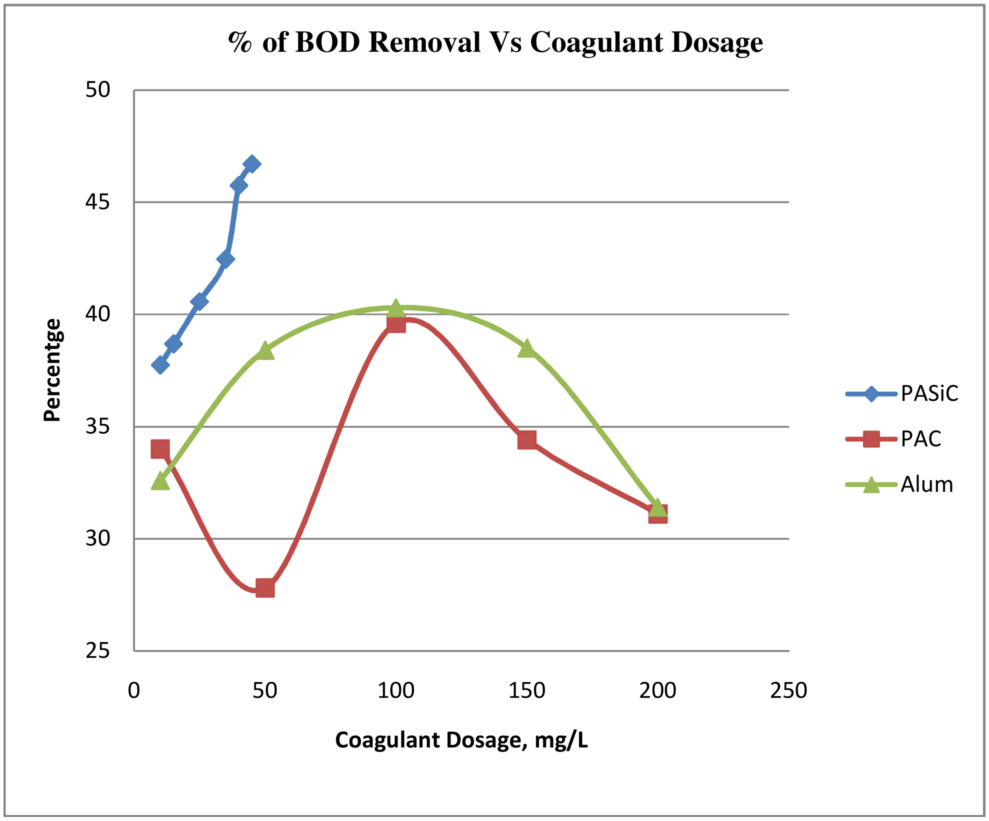

Figure 4.13 : Percentage of BOD Removal for PASiC, PAC and Alum for Wastewater (PASCORP,Bentong).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research consist of many parts. First the preparation of new inorganic polymer called polyaluminium silicate chloride. The preparation method is quite easy but must done carefully and very slowly (titration) to get the coagulant. The second part of this research is jar test and other tests like turbidity, chemical oxygen demand and biochemical oxygen demand. The results from these experiments shows that polyaluminium silicate chloride worked very well for water and wastewater sample (Kuantan river and paper pulp water).

a) Although the turbidity removal is almost same with conventional coagulant, in this case; aluminium sulphate and polyaluminium chloride but the amount of coagulant dosage needed for PASiC is much smaller compare to other two coagulants, about 20% only. This very economic especially when we use in large scale in industry.

b) pH doesn't play important factor so we don't need to monitor and alter the pH of water for treatment and we also never have to add coagulant aid like we did to aluminum sulphate and this will make the procedure to treat water or wastewater much simpler and cheaper.

c) polyaluminium silicate chloride is very effective in removing suspended solids in both water and wastewater and very good in every aspect compare to other two conventional coagulant, Alum and PAC.

5.2 Recommendations

Polyaluminium silicate chloride was created by introducing silica compound to polyaluminium chloride to make the chain longer and more space for colloid particles to attach and grow into bigger particle and eventually have certain density and settle down. So in future, instead of finding new coagulant aids for conventional coagulant like aluminium sulphate chemist all around the world must concentrate on inorganic polymer by trying to introduce new compound to existing inorganic polymer to make their chain more longer in order to get denser particle.

a) Research or experiment must conducted using polyaluminium silicate chloride for various industrial wastewaters like wastewater from food processing plant, clothes and other chemical plant.

b) Chemical industry should try to use inorganic polymer this case polyaluminium silicate chloride in their waste treatment instead of using normal coagulant with their aid; by doing this first they can save cost because for polyaluminium silicate chloride we don’t need any coagulant aid and we also no need to adjust pH and these will make the steps to produce cleaner water, easier and cheaper.

c) Scientist around the world should focus and conduct studies on inorganic polymer and other type of coagulant which will improve the chemical process of water and wastewater treatment and process of coagulation and flocculation will be improved and eventually we can produce cleaner water for lower cost and most importantly we can preserve mother nature.

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APPENDIX

APPENDIX A : Experiment Results For Kuantan River

A.1 Effect Of pH

Table A.1

pH	Percentage Of Removal (%)		
	Turbidity	COD	BOD
5	96.6084	63.5659	39.6985
6	97.409	63.5657	40.4523
7	99.2285	68.2171	47.9899
8	97.2635	60.4652	23.1156
9	95.2984	58.9147	20.8543

Effect Of PASiC Dosage

Table A.2

Dose (ml/L)	Percentage Of Removal (%)		
	Turbidity	COD	BOD
1	97.9712	63.2813	42.1348
2	98.9784	65.625	43.2584
3	99.1942	67.1875	43.8202
4	99.2806	67.1875	47.191
5	99.4532	68.75	48.3146

A.3 Coagulation by Aluminium Sulphate

Table A.3

Dose (ml/L)	Percentage Of Removal (%)		
	Turbidity	COD	BOD
5	80.9244	24.6269	18.6667
10	84.7339	35.0746	22
15	89.8319	43.2836	21.3333
20	91.4286	44.7761	25.3333
25	91.7647	47.0149	32.6667

A.4 Coagulation by Polyaluminium Chloride

Table A.4

Dose (ml/L)	Percentage Of Removal (%)		
	Turbidity	COD	BOD
5	81.068	28.125	21.118
10	84.9191	35.1563	19.2547
15	85.6634	35.9375	24.2236
20	90.4531	44.5313	36.0248
25	90.5502	51.5625	37.8882

APPENDIX B : Experiment Results For Paper Pulp Wastewater from PASCORP,Bentong

B.1 Effect Of PASiC Dosage

Table B.1

	Turbidity (NTU)						
Dose (ml/L)	Before	After	% removal	COD	% COD removal	BOD	% BOD removal
10	208	53	74.51923	57.449	71.7	396	37.7358
15	208	44.6	78.55769	45.3908	77.64	390	38.6792
25	208	36	82.69231	29.029	85.7	378	40.566
35	208	29	86.05769	24.1164	88.12	366	42.4528
40	208	20.5	90.14423	20.8684	89.72	345	45.7547
45	208	20.52	90.13462	19.68	89.72	339	46.6981

B.2 Coagulation by Polyaluminium Chloride

Table B.2

	Turbidity (NTU)						
Dose (ml/L)	Before	After	% removal	COD	% COD removal	BOD	% BOD removal
10	208	53	74.51923	57.449	71.7	396	37.7358
15	208	44.6	78.55769	45.3908	77.64	390	38.6792
25	208	36	82.69231	29.029	85.7	378	40.566
35	208	29	86.05769	24.1164	88.12	366	42.4528
40	208	20.5	90.14423	20.8684	89.72	345	45.7547
45	208	20.52	90.13462	19.68	89.72	339	46.6981

B.3 Coagulation by Aluminium Sulphate

Table B.3

	Turbidity (NTU)						
Dose (ml/L)	Before	After	% removal	COD	% COD removal	BOD	% BOD removal
10	208	53	74.51923	57.449	71.7	396	37.7358
15	208	44.6	78.55769	45.3908	77.64	390	38.6792
25	208	36	82.69231	29.029	85.7	378	40.566
35	208	29	86.05769	24.1164	88.12	366	42.4528
40	208	20.5	90.14423	20.8684	89.72	345	45.7547
45	208	20.52	90.13462	19.68	89.72	339	46.6981