A STUDY OF LANDFILL LEACHATE TREATMENT BY PACl, SAGO STARCH AND TAPIOCA STARCHES, *HYMENOCALLIS LIRIOSME* AND *ALOE VERA* AS COAGULANTS

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by

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LIST OF ABBREVIATION

ANOVA	Analysis of Variance
BOD_5	Biological Oxygen Demand
COD	Chemical Oxygen Demand
GSE	Grape Seed Extract
HA	Humic Acid
MeSP	Methylated Soy Protein
NH_4-N	Ammoniacal Nitrogen
PACl	Poly-aluminium chloride (liquid)
PBLS	Pulau Burung Landfill Site
PDADMAC	Polydiallyldimethylammonium
PFC	Polyferric chloride
SMWW	Standard Method of the Examination of Water and Wastewater
SOP	Standard of Procedure
SS	Suspended Solids
TANFLOC	Tannin-based Flocculant
TKN	Total Kjeldahl Nitrogen

KAJIAN RAWATAN OLAHAN LARUT RESAPAN OLEH PACl, TEPUNG SAGU DAN UBI KAYU, BUNGA BAKUNG DAN LIDAH BUAYA SEBAGAI BAHAN PENGGUMPAL

ABSTRAK

Ciri-ciri dan mekanisme tindak balas keupayaan tepung ubi kayu, tepung sagu, bunga bakung dan bunga lidah buaya dalam rawatan olahan larut resapan masih belum sepenuhnya didalami dan dikaji. Oleh itu, kajian ini bertujuan untuk mencari dos yang optimum bagi PACl, tepung sagu, tepung ubi kayu, bunga bakung dan bunga lidah buaya serta pH dalam penyingkiran COD, NH_4-N, warna dan pepejal terampai. Potensi zeta bagi setiap bahan penggumpal diuji dan keupayaan bagi tepung sagu, tepung ubi kayu, bunga bakung dan lidah buaya sebagai bahan bantu penggumpal dalam mengurangkan penggunaan PACl juga ditentukan. Sampel bagi olahan larut resapan diambil daripada PBLS. Empat parameter utama dikaji iaitu pepejal terampai, warna, NH_4-N dan COD. Penentuan potensi zeta juga dijalankan bagi sampel asal, dan sampel selepas penggumpalan dengan penggunaan PACl bersama dengan empat jenis bahan penggumpal semula jadi. Keputusan menunjukkan dos optimum bagi PACl ialah 7200mg/L pada pH 7.5. Dos PACl dapat dikurangkan sebanyak 62.5% dengan kehadiran tepung sagu sebagai bahan bantu penggumpal. Sementara itu, tepung ubi kayu dapat mengurangkan dos PACl sehingga 40%. Bagi tumbuhan hijau seperti bunga bakung dan lidah buaya, keupayaan dalam mengurangkan dos PACl mampu mencapai 75%. Antara bahan penggumpal semula jadi ini, bunga bakung dan lidah buaya menunjukkan keupayaan yang paling tinggi sebagai bahan bantu penggumpal dalam mengurangkan dos PACl. Komposisi dan struktur bagi bunga bakung dan lidah buaya memerlukan kajian selanjutnya untuk mendapat keupayaan penyingkiran

bahan sisa yang lebih tinggi. Lebih banyak kajian kuantitatif diperlukan untuk mendapat keputusan yang lebih baik. Kajian lanjutan yang memfokuskan pada aspek kuantitatif bahan penggumpal yang dikaji mampu memberikan perbandingan serta keputusan yang lebih jitu.

A STUDY OF LANDFILL LEACHATE TREATMENT BY PACl, SAGO STARCH AND TAPIOCA STARCHES, *HYMENOCALLIS LIRIOSME* AND *ALOE VERA* AS COAGULANTS

ABSTRACT

The properties and mechanism of reaction of tapioca starch, sago starch, *Hymenocallis liriosme* and *Aloe vera* potential in landfill leachate treatment has not yet been fully discovered and examined. Thus this study aims to determine the optimum dosage of PACl, tapioca starch, sago starch, *Hymenocallis liriosme*, *Aloe vera* and pH in the removal of COD, NH_4-N, colour and SS for treating landfill leachate. Zeta potential for each coagulant used is measured and the capability of sago starch, tapioca starch, *Hymenocallis liriosme* and *Aloe vera* act as coagulant aids in reduce the dosage of PACl as coagulant is estimated. The sample of leachate is taken from PBLS. Four main parameters were studied including suspended solid, colour, chemical oxygen demand (COD), and ammoniacal nitrogen (NH_4-N). Determination of zeta potential also was done for raw sample, and after coagulation using PACl and other four types of natural coagulants. Results indicated that the optimum dosage for PACl in landfill leachate treatment is 7200mg/L at pH 7.5. The dosage of PACl successfully reduce up to 62.5% in the assisted of sago starch as coagulant aid. While for tapioca starch, it reduces the PACl dosage up to 40%. For the green plants, *Hymenocallis liriosme* and *Aloe vera*, they show the capability in reduce the PACl usage up to 75% respectively. Among these natural coagulants, *Hymenocallis liriosme* and *Aloe vera* show highest capability as coagulant aids in reduce the dosage for PACl as coagulant. Composition and the structural of *Hymenocallis liriosme* and *Aloe vera* need for further investigation to obtain the higher pollutant removal efficiency. More quantitative research is

necessary to get a better result for this study. Further research focused on the quantitative aspects of the coagulants studied would provide comparative data and more reliable results.

CHAPTER 1

INTRODUCTION

1.1 Background

Landfill is an engineered waste disposal site facility with specific pollution control technologies designed to minimize potential impacts. Landfills are usually either places above ground or contained within quarries and pit. Landfills are sources of groundwater and soil pollution due to the production of leachate and its migration through refuse (Christensen and Stegmann, 1992).

Landfill leachate is the wastewater that moves through or drains from a landfill. Leachate can pose serious environmental problems such as pollution of groundwater and surfacewater if it is not properly managed and collected. Landfill leachate may be virtually harmless or dangerously toxic, depending upon the characteristics of the material in the landfill. Typically, landfill leachate has high concentrations of nitrogen, iron, organic carbon, manganese, chloride and phenols. Other chemicals including pesticides, solvents and heavy metals may also be present.

The leachate produced from the waste reclamation final disposal site has a large quantitative and qualitative fluctuations governed by the weather and the kind or quantity of reclaimed objects. Therefore, it is required to treat the leachate efficiently to the required water quality level. The treatment plant mainly consists of water quantity regulating process, calcium removal process, bio-treatment process, flocculation and sedimentation process, advanced treatment process, disinfecting process. Two or more processes can be combined depending on the kind of reclaimed objects and the effluent discharge standards. Furthermore, for the removal of heavy metals and salinity, demineralizer are added to the existing treatment plan. Recently, more dioxin degradation systems are getting installed in landfill leachate treatment.

Coagulation is a process for combining small particles into larger aggregates to remove colour, organic and inorganic substances (Renou *et al*., 2007). Coagulation-flocculation is one of the important processes in conventional wastewater treatment; for the removal of suspended solids (SS). Coagulation is a processes to add substances capable to remove colloidal impurities from wastewater. The purpose of coagulation is to turn the small particles of colour, turbidity and bacteria into large flocs, either as precipitate or suspended particles (Davis and Cornwell, 1998).

Poly-aluminium chloride (PACl) is effective at low temperature, faster floc formation, lower dosage rates, savings in pH adjustment chemicals and possibly the removal of algae (Binnie *et al*., 2002). It is increasingly used for water treatment. It shows distinct advantages against the conventional use of aluminium sulphate (alum). Poly-aluminium chloride is synthetic polymers dissolved in water. They react to form insoluble aluminium poly-hydroxides which precipitate in big volumetric flocs. The flocs absorb suspended pollutants in the water which are precipitated with the PACl and can together be easily removed.

Zeta Potential is the electrical potential that exists at the "shear plane" of a particle, which is some small distance from its surface. As this electric potential approaches zero or neutral, particles tend to aggregate. Zeta Potential is derived from measuring the mobility distribution of a dispersion of charged particles as they are subjected to an electric field. Mobility is defined as the velocity of a particle per electric field unit and is measured by applying an electric field to the dispersion of particles and their average velocity.

1.2 Problem Statement

Aluminium salts are widely used as chemical coagulants in the water purification process all over the world. However, recent studies have raised doubts about the advisability of introducing aluminium into the environment, especially concerning about residuals in the treated water, large production of sludge volume and Alzheimei's desease (Diaz *et al.*, 1999). Poly-aluminium chloride (PACl) as polymerized forms of metal coagulants has been widely used for water treatment in Europe, Japan and North America due to its reduced cost and wider availability. PACl is claimed to be more advantageous over conventional coagulants because of its higher removal of particulate and organic matters and intrinsic benefits of lower alkalinity consumption and lesser sludge production (Sinha *et al.*, 2004).

Natural coagulants of vegetable and mineral origin were widely used in water and wastewater treatment before the advent of synthetic chemicals like aluminium and ferric salts (Ndabigengesere *et al*., 1998). Previous studies however, have not determined whether such natural coagulants are economically and environmentally more acceptable than chemical coagulants. Recently there has been more interest in the subject of natural coagulants, especially to resolve the problems of water and wastewater treatment. Natural macromolecular coagulants show bright future and are considered by many researchers because of their abundant source, low price, innocuity, multifunction and biodegradation (Zhang *et al.*, 2006). The material that has recently received a great degree of attention is the seed of *Moringa oleifera* and it has been reported by various authors (e.g, Ndabigengesere *et al*., 1998; Okuda *et al*., 2001; Heredia and Martin, 2009). Recently, natural coagulants based on mucilags like cactus and Opuntia ficus indica have been explored by many researchers (e.g. Young *et al*., 2005; Sepulveda *et al*., 2007; Heredia and Martin, 2009).

Spider lilies, also known as *Hymenocallis liriosme* are bulbous perennial herbs. Hymenocallis is a genus of plants in the family Amaryllidaceae. The flowers have their stamens united to a characteristic corona. *Aloe vera* also known as the medicinal aloe belongs to the Asphodelaceae family is a species of succulent plant. *Aloe vera* extracts are useful in the treatment of wound and burn healing, diabetes and elevated blood lipids in humans. These positive effects are thought to be due to the presence of compounds such as polysaccharides, mannans, anthraquinones and lectins. The potential transformation of *Hymenocallis liriosme* and *Aloe vera* from flora to natural coagulants should be explored to assess their removal performance. No reference to work involving the use of *Hymenocallis liriosme* and *Aloe vera* as coagulants for water, wastewater and leachate treatment has been found in the literature to date.

Previous researches have proven natural polymers can be used as coagulants and coagulant aids during the coagulation process (Aziz *et al*., 2000; Omar *et al*., 2008). Malaysia is rich with many kinds of natural polymers such as tapioca, sago and corn. These polymers can potentially be used as alternative coagulants and coagulant aids to replace synthetic polymers in water or wastewater treatment. These natural polymers are widespread in nature and are efficient in terms of cost. The latest market price for tapioca starch and sago starch was RM 1.20 and RM 1.30 per kilogram, respectively.

Further research is required to establish optimum coagulant dosages, pH, and temperature to increase the efficiency of coagulation process. The study on the efficiency of coagulation should be improved in order to achieve better results for future use. More advanced parameters/indicators such as zeta potential should be developed. Increased analytical sophistication also allows the scientists and engineers to gain grater knowledge of the behavior of wastewater constituents and how they affect process performance and effluent quality (Tchobanoglous *et al*., 2004).

The properties and mechanism of reaction of tapioca starch, sago starch, *Hymenocallis liriosme* and *Aloe vera* potential in landfill leachate treatment has not yet been fully discovered and examined.

1.3 Objectives of the Study

Thus this study will include the objectives as follows:

(i) To determine the optimum dosage of PACl, tapioca starch, sago starch, spider lily, *Aloe vera* and pH in the removal of COD, ammoniacal nitrogen, colour and SS for treating landfill leachate.

(ii) To estimate the capability of sago starch, tapioca starch, spider lily and *Aloe vera* as coagulant aids in reducing the dosage of PACl as coagulant.

(iii) To measure the zeta potential for each coagulant used and its influence on the removal performance.

1.4 Scope of the Study

This study was focused on the process of coagulation-flocculation of landfill leachate from Pulau Burung Landfill Site (PBLS) only. This study involved using of PACl and four types of natural coagulants which were tapioca starch, sago starch, *Hymenocallis liriosme* and *Aloe vera*. The removal efficiency of COD, ammoniacal nitrogen, suspended solids (SS) and colour was determined.

The experiments involved were determination of optimum coagulant dosages and pH on the removal capacity of each parameter. The behaviour of sago starch, tapioca starch, *Hymenocallis liriosme* and *Aloe vera* as coagulant aids to PACl was also examined.

CHAPTER 2

LITERATURE REVIEW

2.1 Landfill Leachate

Landfill leachate is a complex wastewater that forms when rain water percolates through the waste deposited in a landfill. As the water passes through the landfill deposits, landfill waste contaminates the water, thus producing highly polluted wastewater termed as landfill leachate.

According to Renou *et al.* (2007), leachates are defined as the aqueous effluent generated as a consequence of rainwater percolation through wastes, biochemical processes in waste cells and the inherent water content of the wastes themselves. Leachates may contain large amounts of organic matter, where humic-type constituents consist an important group, as well as ammonia-nitrogen, heavy metals, chlorinated organic and inorganic salts. The removal of organic material based on chemical oxygen demand (COD), biological oxygen demand (BOD_5) and ammonium from leachate is the usual prerequisite before discharging the leachates into natural waters.

Most landfills containing organic materials will produce methane, some of which dissolves in the leachate. This could in theory be released in weakly ventilated areas in the treatment plant. The most important requirement is the prevention of discharge of dissolved methane from untreated leachate when it is discharged into public sewers.

2.1.1 Risks of Landfill Leachate Pollution

The greatest environmental risks occur in the discharges from older sites constructed before modern engineering standards became mandatory and also from sites in the developing world where modern standards have not been applied. There are also substantial risks from illegal sites and ad-hoc sites used by criminal gangs to dispose of waste materials. Leachate streams running directly into the aquatic environment have both an acute and chronic impact on the environment which may be very severe and can severely diminish bio-diversity and greatly reduce populations of sensitive species. The presence of toxic metals and organics can lead to chronic toxin accumulation in both local and far distant populations. Rivers impacted by leachate are often yellow in appearance and often support severe overgrowths of sewage fungus.

The risks from waste leachate are due to its high organic contaminant concentrations and high concentration of ammonia. Pathogenic microorganisms that might be present are often cited as the most important, but pathogenic organism counts reduce rapidly with time in the landfill, so this only applies to the fresh leachate. Toxic substances may however be present in variable concentrations and their presence is related to the nature of waste deposited.

The health risks, if leachate is left untreated and allowed to contaminate groundwater supplies, include: skin irritation, nausea, vomiting, and headache. While chronic exposure can lead to anemia, kidney damage, prostate cancer, lung cancer, memory loss, coma, headaches, and depression.

Leachate pollution is the result of a mass transfer process. Waste entering landfill undergoes biological, chemical and physical transformations which are controlled, among other influencing factors, by water input fluxes. In the landfill three physical phases are present: the solid phase (waste), the liquid phase (leachate), and the gas phase. The liquid phase is enriched by solubilized or suspended organic matter and inorganic ions from the solid phase. In the gas phase mainly carbon (prevalently in the form of CO_2 and CH_4) is present. The main environmental aspects of landfill leachate are the impacts on surface water and groundwater quality if leachate is discharged into these water bodies (Christensen and Stegmann, 1992). Groundwater is an important source of drinking water for human. It contains over 90% of the fresh water resources and is an important reserve of good quality water (Armon and Kott, 1994).

Landfilling is currently upgraded in order to reduce environmental impacts to the minimum. Indeed, while sanitary landfills are common economically and environmentally acceptable methods to dispose solid wastes, the leachates generated during their operation represent a threat to the environment as they may carry toxic contaminants to groundwater supplies (Christensen *et al*., 1994) and to the surrounding soil. Their composition must thus be controlled and adequate treatment shall be provided to avoid potential threats/ impacts on the environment.

The natural waste biodegradation is very slow, so landfills present a potential environmental threat for many years. Treatment of leachate is thus required for a long time, even after the closure of the sites, involving high costs. For these environmental and economical reasons, studies are now being conducted to enhance leachate treatment processes to minimise potential long-term environmental impacts (Labanowski *et al*., 2010).

2.1.2 Landfill Leachate Characteristics

The characteristics of the landfill leachate can usually be represented by the basic parameters COD, BOD_5, the ratio BOD_5/COD, pH, suspended solids (SS), ammonium nitrogen (NH_3-N), total Kjeldahl nitrogen (TKN) and heavy metals. Table 2.1 illustrates the characteristics of the leachate in the three phases which are young, medium and old.

Table 2.1: Characterisic of the leachate in the three phases (Amokrane *et al*., 1997).

Landfill Age (years) Type of leachate	<5 (young) young	5-10 (medium) intermediate	>10 (old) stabilized
pH	<6.5	6.5-7.5	>7.5
COD (g/L)	>10	<10	<5
COD/TOC	<2.7	2.0-2.7	>2.0
BOD_5/COD	<0.5	0.1-0.5	<0.1
Volatile fatty Acid (% TOC)	>70	5-30	<5

The characteristics of landfill leachate varies greatly both in terms of quality and quantity. Flows change literally with the weather such as increasing during rainy periods and decreasing during dry. The waste concentrations can change dramatically over the life of the landfill. Leachate from young landfills is high in biodegradable organics. But later on, as the landfill ages, contents degrade and produce concentrations of complex organics, which are not readily biodegradable. In addition, the characteristics of leachates from new landfills cannot be predicted. As a result, no landfill leachate is constant over time, and no two leachates are the same. The variables affecting the leachate quality are landfill age, ambient air temperature, rainfall, refuse permeability, refuse depth, refuse temperature and refuse composition, precipitation, seasonal and weather variations, waste type and composition (depending on the standard of living of the surrounding population, structure of the tip). In particular, the composition of landfill leachates varies greatly depending on the age of the landfill (Baig *et al.*, 1999). Thus, age of landfill is a major criterion for the selection of an appropriate leachate treatment method (Ghafari *et al*., 2010).

2.1.3 Landfill Leachate Treatment

Sanitary landfill leachate, a highly polluted industrial wastewater, has been a cause for significant concern with landfilling being the most common technique in solid waste disposal (Ghafari *et al.*, 2005). Selection of a leachate treatment process is highly site specific. It depends on many factors such as effluent discharge alternatives and limitations, treatment process residuals, permit requirements, and cost-effectiveness of treatment. Generally, inorganic constituents are removed first, before the organic constituents. This protects the biological, absorption, and stripping processes from problems caused by the metal's toxicity, corrosivity, and scaling.

Because of the large fluctuations in leachate composition, the treatment process always begins with equalization. Equalization involves mixing incoming leachate in a large tank to create a uniform product which is then discharged at a constant rate into the leachate treatment plant. After the leachate has been equalized, many methods can be employed to treat the inorganic portion. These methods include neutralization, precipitation/flocculation/sedimentation, oxidation/reduction, reverse osmosis and ion exchange.

Precipitation is the most common method of removing soluble metals. In precipitation reactions chemicals are added to transform dissolved constituents to form insoluble precipitates. Metals are precipitated as hydroxides, sulfides, and carbonates by adding appropriate precipitant and adjusting the pH to favor insolubility. Precipitation can be used to remove most metals (arsenic, cadmium, chromium III, copper, iron, lead, mercury, nickel, zinc) and many anionic species (phosphates, sulfates, fluorides). Better removal efficiencies can be achieved with sulfite precipitation, but hydroxide precipitation, using lime or caustic, is more practiced. This is due to the fact that sulfide precipitation is more expensive and may produce H_2S gas, and hydroxide precipitation is cheaper and less dangerous. The selection of the best precipitant, flocculant, pH, rapid mix requirements, and dosages is determined by laboratory test jar studies.

Precipitation reactions occur in separate basins from flocculation reactions. Precipitation reactions require rapid mixing, while flocculation reactions require slow, gentle mixing to encourage particle contact.

After the contaminated product has reacted in the precipitation tank, it flows into the flocculation tank. In a flocculation reaction, alum, lime, ferric chloride, or polyelectrolytes are added to the inflow to reduce the repulsive forces between the precipitated particles. These particles aggregate, forming large flocs of material which can be settled out in a sedimentation tank.

Precipitation and flocculation reactions also have few disadvantages. These reactions produce a large quantity of sludge which must be treated as hazardous waste due to its heavy metal content. All these reactions occur under elevated pH, and metal concentrations in the treated effluent can theoretically reach concentrations of less than 1 mg/L. However, before undergoing this treatment process, non-aqueous liquids should be removed during pre-treatment.

Several factors are required to be considered in order to make the treatment method successful and cost effective. Recycling and collection are the most common ways of dealing with landfill leachate, but these methods of eliminating contaminants are neither effective nor economically attractive. The ideal solution shall have the following attributes: (i) would not require any manpower, (ii) would not generate any waste, odour, or off-site disposal, (iii) would automatically collect and process the leachate, (iv) would be low cost, (v) would be simple to implement and maintain and (vi) would be remotely operated and controlled operator involvement.

2.2 Coagulation-flocculation

Coagulation–flocculation is a relatively simple physical-chemical technique commonly used for water and wastewater treatment. The removal mechanism of this process mainly consists of charge neutralization of negatively charged colloids by cationic hydrolysis products, followed by incorporation of impurities in an amorphous hydroxide precipitate through flocculation (Duan and Gregory, 2003). This technique may be employed successfully for the treatment of older landfill leachates (Amokrane *et al.*, 1997). 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.

Coagulation using chemical coagulants consists of combining insoluble particles and dissolved organic matter into larger aggregates, thereby facilitating their removal in subsequent sedimentation, floatation and filtration stages. It usually involves the dispersal of one or several chemical reagents which destabilizes the colloidal particles, leading to the formation of micro-floc. Bonding the micro-floc particles together by the addition of a flocculation additive forms larger, denser flakes that are easier to separate. A simple separation step then eliminates the flocs (Renault *et al*., 2009).

The coagulation-flocculation process is a widely applied physicochemical technology to treat wastewater. For example, it has been used in the pre- or post-treatment of landfill leachate to enhance the biodegradability of leachate or to remove recalcitrant organic matter (Tatsi *et al.*, 2003; Aziz *et al.*, 2007).

Coagulation is a process by which small particles are separated from solution in a reasonable amount of time using simple or prehydrolyzed metal salts, polyelectrolytes, or long chain polymers as the primary coagulants (Chatterjee *et al*., 2009). Generally, colloidal particles are thought to be coagulated and aggregated through the actions of charge neutralization, patch aggregation, bridge connection and sweep flocculation in series or synchronously (Wu *et al*., 2009).

According to DLVO theory (Olphen, 1977), at the critical polyelectrolyte concentration, the van der Waals forces overcome electrical repulsion and the particles coagulate. The DLVO theory primarily addresses electrical double layer and physical interactions (Wu *et al*., 2009).

Particles suspended in an aqueous medium have usually a net surface charge. The repulsive interactions, in spite of the Van der Waals forces trying to bring the particles together, stabilize the suspension. Aggregation of particles is fundamental for improving the performance of many solid–liquid separation processes (Rojas-reyna *et al.*, 2010). The postulated mechanisms by which polyelectrolytes can bring about flocculation are charge neutralization, bridging and/or electrostatic patch (Bratby, 2006). Figure 2.1 below shows the bridging mechanism with/where each polymer chain attaches to many colloids.

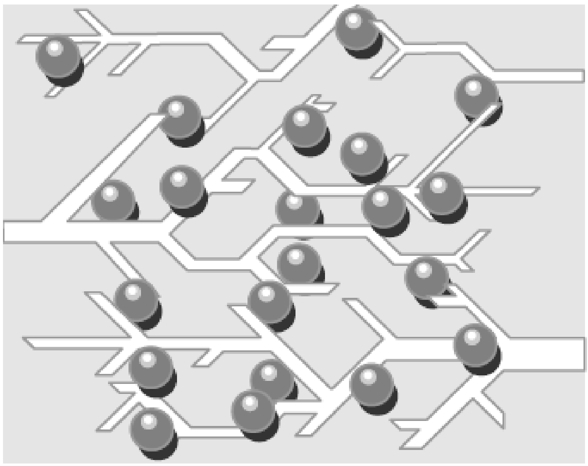

Figure 2.1: Each polymer chain attaches to many colloids.

(Source: Ravina, 1993)

Charge neutralization leads to the reduction of the electric double layer between particles due to the adsorption of charged polyelectrolytes on oppositely charged particles. It is generally believed that polymers with low molecular weight tend to adsorb on and neutralize the opposite charges of the particles, while long-chain high molecular weight polymers can lead to bridging flocculation. In such cases, segments of a single polymeric chain are attached to more than one particle, thereby linking the particles together. The electrostatic patch flocculation resembles the concept of bridging; the main difference being the charge densities of the polymer and the particle. Low molecular weight polymers with high charge density, when interact with oppositely charged particles of low charge density, lead to the formation of dense particle aggregations sharing the same polymeric chain, which can be visualized as a “polymeric patch” (Rojas-reyna *et al.*, 2010).

According to Wu *et al*. (2009), as charge-neutralization dominates the particle destabilization and aggregation for both alum and PACl, electrostatic force outweighs other forces in coagulation with inorganic coagulants.

The formation, breakage, and re-growth of flocs were realized to investigate the efficiency of particles removal (Yu *et al*., 2009). During the break-up process, the newly exposed surfaces of aggregates may have a net negative, positive or neutral charge and this may depend on the nature of the original coagulation process (McCurdy *et al*., 2004).

According to Tan *et al*. (2007), when charge neutrality dominates the coagulant mechanism, some of the particles in water, adsorb Al^{3+} or its variation unevenly, contain positive charge and flocculate with negative particles. There also exist many particles that cannot congregate with other particles, and they can be therefore considered as residual turbidity. Normally, the flocs formed by charge neutralization could be more compact in structure and surface-erosion breakage model would happen. Also the broken flocs will coagulate with the residual particles. Therefore, lower residual turbidity would be attained. When sweep flocculation dominates the coagulate mechanism, almost all the particles will trap positive charge, while only a small portion of particles trap few positive charges and remain negative charged. Colloid entrapment involves adding relatively large doses of coagulants, usually aluminum or iron salts which precipitate as hydrous metal oxides.

These two species of particles can coagulate sufficiently with each other. The flocs, with loose and branchy structures which were formed by sweeping mechanism, shows large fragment breakage model. The broken flocs which contain positive charge will yield repulsive force between particles and reduce the efficiency of collision.

Ghafari *et al.* (2008) monitored the removal of COD, turbidity, colour and TSS using PACl and alum in leachate treatment. From the research, the operating parameters were adopted as rapid mixing speed 80rpm, slow mixing speed 30rpm, rapid mixing time 1min, slow mixing time 15min, and settling time 30min.

2.3 Coagulants and Its Classification

The choice of a coagulant chemical depends upon the nature of the SS to be removed, the raw water conditions, the facility design, and the cost of the amount of chemical necessary to produce the desired result.

Final selection of the coagulant (or coagulants) should be made following thorough jar testing and plant scale evaluation. Considerations must be given to required effluent quality, effect upon down stream treatment process performance, cost, method and cost of sludge handling and disposal, and net overall cost at the dose required for effective treatment.

The coagulants and flocculants frequently used are mineral additives including metal salts such as poly-aluminium chloride and synthetic polymers such as poly-acrylamide (Renault *et al*., 2009). Using these chemical substances may have several environmental consequences (i) an increase in metal concentration in water (which may have human health implications); (ii) production of large volumes of (toxic) sludge; (iii) dispersion of acrylamide oligomers which may also be a health hazard. For these reasons, alternative coagulants and flocculants have been considered for environmental applications (Bratby, 2006). Biopolymers may be of great interest since they are natural low-cost products, characterized by their environmentally friendly behaviour.

According to Bratby (2006), there are two major classes of materials used in coagulation/ flocculation processes:

(1) inorganic and organic coagulants including mineral additives (lime, calcium salts, etc.), hydrolyzing metal salts (aluminium sulphate, ferric chloride, ferric sulphate, etc.), pre-hydrolysed metals (poly-aluminium chloride, poly-aluminosilicate sulphate, etc.) and polyelectrolytes (coagulant aids);

(2) and organic flocculants including cationic and anionic polyelectrolytes, non-ionic polymers, amphoteric and hydrophobically modified polymers, and naturally occurring flocculants (starch derivatives, guar gums, tannins, alginates, etc.).

2.3.1 Polymerized Forms of Metal Coagulants

Polymers of long-chained, high molecular weight, organic chemicals are becoming more widely used, especially as coagulant aids together with the regular inorganic coagulants. Anionic (negatively charged) polymers are often used with metal coagulants. Low-to-medium weight positively charged (cationic) polymers may be used alone or in combination with the aluminum and iron type coagulants to attract the SS and neutralize their surface charge.

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 flocs. The flocs formed by using a properly selected polymer will be more resistant to shear, resulting in less carryover and a cleaner effluent.

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. On a price-per-pound basis they are much more expensive than inorganic coagulants, such as alum, but overall operating costs can be lower because of the reduced need for pH adjusting chemicals and lower sludge volumes and disposal costs.

The possible slightly higher unit price of PACl is compensated by a lower dosage requirement, no requirement for any neutralising agent (soda, lime), shorter flocculation time, smaller amount of sludge, reduced number of back washing steps and higher quality of the treated water. PACl can be used as a flocculant for all types of water and wastewater treatment, drinking water, industrial wastewater, and urban wastewater. Recently, PACl has been widely used in water and wastewater treatment to remove contaminants (Zhao *et al*., 2010). Positively charged keggin-Al_{13} of PACl causes efficient charge compensation and results in effective particle aggregation at the lower dosage (Duan and Gregory, 2003). Hence, strong charge-neutralization and electro-patch coagulation are thought to be the dominant mechanisms for PACl (Wu *et al*., 2009).

This kind of electro-patch coagulation differs from that of alum, with polycations adsorbing and complexing on the particle's surface rather than precipitates (Ye *et al*., 2007). On the other hand, bridge-connection can also be included since aggregated Al_{13} and other polymeric species are formed during pre-hydrolyzation (Wu *et al*., 2007). With stable and high positively charged keggin-Al_{13}, PACl can easily adsorb and neutralize more than one of the negatively charged silica particles. Due to the strong electrostatic attraction and inorganic polymer bridging, they may bind together to form the primary aggregates. In virtue of the open surface structure and residual positive charge, these primary aggregate can continue to agglomerate each other so as to form micro-flocs through self-assembling. Accordingly, particle aggregation mechanisms as polycation-patch coagulation and bridge connection are thought to be operative besides charge neutralization for PACl (Wu *et al*., 2009). For PACl containing keggin-Al_{13} with high positive charge, electrostatic force is the driving force to create effective particle collisions and later particle aggregation.

Alternative coagulants based on pre-hydrolysed forms of aluminium (such as poly-aluminium chloride) and iron (polyferric sulfate) are more effective than the traditional additives. Their significant advantage is that their hydrolysis occurs under specific experimental conditions during the preparation stage of the coagulants, and not after their addition to the raw solution. This results in a much tighter control of the procedure. It is known that Poly-aluminium chloride based products provide better coagulation than alum at low temperatures and also produce lower volumes of sludge. Because they are already partially neutralised, they have less effect on the pH of the water and thus reduce the need for pH correction (Renault *et al.*, 2009). Table 2.2 shows the composition and physical properties of Poly-aluminium chloride 18% Al_2O_3. PACl 18% can be used for most applications including in laboratory test.

Table 2.2: Characteristics of Poly-aluminium chloride 18% Al_2O_3

Appearance	Liquid With Yellow Colour
Al_2O_3 content	17-19 %
Cl	21-22 %
Basicity	36-42 %
Specific Weight at 20 ℃	1.36-1.38 g/mL
pH	0.4 - 1.2
Solidification Point	-10 ºC

2.4 Coagulant Aids

Polyelectrolytes which enhance the flocculating action of metal coagulants (such as alum), are called coagulant aids or flocculant aids. They provide a means of tailoring floc size, settling characteristics and shear strength. Coagulant aids are excellent tools for dealing with seasonal problem periods when alum alone is ineffective. They can also be used to increase plant capacity without increasing physical plant size. Coagulant aids may also be used to reduce coagulant consumption, shorter sedimentation periods and higher rates of filtration, (Schulz and Okun, 1985).

The coagulation process is not always perfect as it may result in small flocs when coagulation takes place at low temperatures or produce fragile flocs which break up when subjected to physical forces. It is not only necessary to overcome these problems but also to improve the process to obtain good quality effluent and rapid sedimentation of the flocs formed. To do so, several products known as coagulant aids or polymeric additives can be used to bring together and agglomerate the flocs formed by the coagulant (Bratby, 2006). These water-soluble polymers, regularly used in water treatment, are mainly synthetic, although a few natural products may be of interest. The polymeric additives are broadly characterized by their ionic structure: cationic, anionic and non-ionic (Bolto, 1995). Ionic polymers or ‘‘polyelectrolytes” of various structures are usually used as coagulant aids to enhance the formation of larger floc in order to improve the rate of sedimentation. Coagulant aids can act either by polymer bridging or by charge neutralization (Bratby, 2006; Bolto, 1995).

2.5 Natural Coagulant

Because of the limitations of these flocculants, substitute natural polymers such as starch, chitosan, cellulose, konjac glucomannan, etc., are being investigated as attractive alternatives because natural polymers and their derivatives are biodegradable as well as their degradation intermediates are harmless to human beings and the environment (You *et al*., 2009). In recent years, the use of bioflocculants has been considered as a solution to the secondary environment pollution caused by the traditional flocculants (Joung *et al*., 2007).

Some of the reported products named ‘‘bioflocculants” include biopolymers (starches, chitosan, alginates) and microbial materials produced by micro-organisms including bacteria, fungi and yeast (Wang *et al.*, 2007). Compared with conventional chemical flocculants, bioflocculants are safe and biodegradable polymers, and produce no secondary pollution (Sharma *et al*., 2006). They may potentially be applied not only in food and fermentation processes, and downstream processing but also in water and wastewater treatment. Because of the above concerns on polyelectrolyte toxicity, it is believed that the use of bioflocculants will increase (Bratby, 2006).

Over the usual range of water pH 5-9, particles nearly always carry a negative surface charge and are often colloidally stable and resistant to aggregation. Coagulants are then needed to destabilise the particles. Destabilisation can be brought about by either increasing the ionic strength giving some reduction in the zeta potential and a decreased thickness of the diffuse part of the electrical double layer or by specifically adsorbing counterions to neutralize the particle charge. It is well known that bioflocculants can play these roles because they have particular macromolecular structures with a variety of functional groups which can interact with contaminants (Sharma *et al*., 2006). Bioflocculation is a novel approach that is effective and competitive.

In recent years there has been considerable interest in the development of natural coagulants which can be produced or extracted from microorganisms, animal or plant tissues. These coagulants should be biodegradable and are presumed to be safe for human health. In addition, natural coagulants produce readily biodegradable and less voluminous sludge that amounts only 20–30% that of alum treated counterpart (Narasiah *et al.*, 2002).

2.5.1 Coagulants of Plant Origin

The use of natural materials of plant origin to clarify turbid raw waters is not a new idea. Natural coagulants have been used for domestic household for centuries in traditional water treatment in tropical rural areas (Fuglie, 2001). Nowadays, some reports describe the use of natural coagulants from Nirmali seed and maize (Raghuwanshi *et al*., 2002), mesquite bean and Cactus latifaria (Diaz *et al*., 1999), Cassia angustifolia seed (Sanghi *et al*., 2002) and different leguminose species (Šc´iban *et al*., 2005). Nevertheless, the material which has recently received the greatest degree of attention is the seed of *Moringa oleifera* indigenous to Sudan. The water extract of *Moringa oleifera* seeds compares quite favourably with aluminium salt (Ghebremichael *et al*., 2006).

Of all plant materials investigated, seeds of *Moringa oleifera* are one of the most effective sources of primary coagulant for water treatment. The *Moringa oleifera* tree, commonly known as drumstick and horseradish, is a native of Northern India. It is widely grown throughout the tropics. The tree is drought resistant, fast growing and even grows in poor soils.