

**CHARACTERIZATION OF PECTIN AS BIOPOLYMERIC FLOCCULANT
AND ITS EFFECTIVENESS IN THE TREATMENT OF
TURBID WASTE WATER**

by

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
BBD	Box-Benkhen Design
CCD	Central Composite Design
COD	Chemical Oxygen Demand
DE	Degree of Esterification
DoE	Design of Experiments
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infra Red
HMP	High Methoxyl Pectin
LMP	Low Methoxyl Pectin
NTU	Nephelometric Turbidity Unit
OD	Optical Density
PAC	Polyaluminium Chloride
PAM	Polyarylamide
RSM	Response Surface Methodology
SEM	Scanning Electron Micrograph
SS	Suspended Solids
TGA	Thermogravimetric Analysis
TSS	Total Suspended Solids
UV	Ultraviolet

LIST OF SYMBOLS

dT	energy released or absorbed
°C	Degree Celsius
α	alpha
%	percent
	micron
>	More than
>>	much more than
[]	concentration
=	equal to

PENCIRIAN PEKTIN SEBAGAI PEMBUKU BIOPOLIMER DAN KEBERKESANANNYA DALAM PERAWATAN AIR SISA KERUH

ABSTRAK

Proses penggumpalan dan pembukuan digunakan dalam rawatan air sisa keruh. Dua jenis penggumpal, Al^{3+} dan Fe^{3+} dan tiga jenis pembuku, seperti pektin komersial, pembuku industri dan ekstrak pektin dari kulit oren dengan sendirinya digunakan untuk membandingkan keberkesanan rawatan. Kaedah respon permukaan untuk dua respon, aktiviti pembukuan dan pengurangan keruhan untuk mengoptimumkan respon. Sifat fizikal kimia untuk ketiga-tiga pembuku dianalisiskan. Keputusan ujikaji menunjukkan pembuku industri mempunyai purata berat molekul yang tertinggi, rantai molekul yang terpanjang dan stabil terhadap haba berbanding dengan pektin komersial dan pektin ekstrak sendiri. Kumpulan reaktif utama bagi pektin adalah kumpulan karboksil dan hidroksil. Manakala, untuk pembuku industri, kumpulan reaktif utama ialah kumpulan primer Amide. “Box-Behnken Design” digunakan untuk mengoptimumkan semua set eksperimen. Kawasan optimum untuk pembuku industri adalah di antara pH 7.5 dan 8.2, kepekatan Al^{3+} adalah di antara 0.02 mM dan 0.05 mM dan kepekatan pembuku industri di antara 6.5 mg/L dan 8.0 mg/L. Untuk pektin komersial, kawasan optimum bagi pH adalah di antara 3 dan 9, kepekatan Fe^{3+} di antara 0.5mM dan 1.0 mM dan kepekatan pektin komersial 3 mg/L. Manakala, untuk pektin ekstrak sendiri, kawasan optimum pH adalah di antara 4.6 dan 7.5, kepekatan Al^{3+} adalah di antara 0.60 mM dan 0.95 mM dan kepekatan pektin ekstrak sendiri ialah 4 mg/L dan 6 mg/L. Jumlah sisa pepejal yang terhasil di penghujung rawatan mencatatkan keputusan ujikaji yang sama bagi ketiga-

tiga pembuku bila Al^{3+} digunakan sebagai penggumpal. Akan tetapi, semasa menggunakan Fe^{3+} sebagai penggumpal, jumlah sisa terhasil adalah paling tinggi untuk pektin ekstrak sendiri dan diikuti dengan pembuku industri dan pektin komersial. COD dianalisiskan pada air selepas rawatan. COD adalah terendah bagi pektin ekstrak sendiri dan mencatatkan 18.3 mg/L semasa Al^{3+} digunakan sebagai penggumpal. Sebaliknya, keputusan COD adalah paling tinggi, 59.0 mg/L untuk pembuku industri semasa menggunakan Fe^{3+} sebagai penggumpal.

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ABSTRACT

Coagulation and flocculation processes were applied in the treatment of turbid wastewater. Two coagulants, namely, Al^{3+} and Fe^{3+} and three flocculants, namely, commercial pectin, industrial flocculant and self-extract pectin from orange peel were used to compare the effectiveness of the treatments. Response Surface Methodology for two responses, namely, flocculating activity and turbidity reduction was applied for the optimization of the treatment conditions. The physicochemical characteristics of the three flocculants were analyzed. The results showed that the industrial flocculant had the highest average molecular weight, the longest chain, and were thermally stable when compared to the commercial and the extracted pectin. The main reactive groups for pectin were carboxyl and hydroxyl groups while it was the primary amide group for the industrial flocculant. Response Surface Methodology was used to optimize all sets of experiments. The optimum treatment conditions for the industrial flocculant was pH between 7.5 and 8.2, Al^{3+} concentration between 0.02 mM and 0.05 mM, and industrial flocculant concentration between 6.5 mg/L and 8.0 mg/L. For the commercial pectin, the optimum treatment conditions were at pH between 3 and 9, Fe^{3+} concentration between 0.5 mM and 1.0 mM, and commercial pectin concentration around 3 mg/L. Optimum treatment conditions for the extracted pectin were pH between 4.6 and 7.5, Al^{3+} concentration between 0.60 mM and 0.95 mM and extracted pectin concentration

between 4 mg/L and 6 mg/L. When Al^{3+} was used as a coagulant, the amount of sludge produced were similar for all of the three flocculants, while the extracted pectin showed the highest sludge production value followed by the industrial flocculant and the commercial pectin respectively when Fe^{3+} was used as a coagulant. The Chemical Oxygen Demand (COD) of the clarified supernatant was the lowest using the extracted pectin as a flocculant and Al^{3+} as a coagulant (COD = 18.3 mg/L), while it was the highest when the industrial flocculant was applied using Fe^{3+} as coagulant (COD = 59.0 mg/L).

CHAPTER ONE

INTRODUCTION

1.1 Research background

The increasing demand for a proper solid waste disposal sites and the closure of the sanitary landfills posed a problem in the management of solid wastes. Reusing waste is considered to be a good alternative in order to reduce sanitary landfills load. Reusing organic waste, like fruit waste, and turning it into flocculant for wastewater treatment application is the main idea behind this research.

1.2 Turbidity

In general, turbidity can be defined as any cloudy appearance of water caused by the presence of suspended and colloidal matter. The common natural source of turbidity in drinking water is storm water run-off, humic acid or other organic compound resulting from the decay of plants or leaves. Moreover, algae and products of their breakdown in water reservoirs, rivers or lakes, and high iron concentrations could also contribute to the high turbidity in surface water. The man-made turbidity to surface water includes mining, waste discharge, particles from treatment process and debris from construction site (www.epa.gov, 2010).

1.2.1 Natural Occurrence Turbidity

Natural turbidity in surface and underground water is mainly due to the storm water and agricultural runoff. The storm water and agricultural run-off carry excessive sediments, nutrients and pesticides to surface water or some percolated in to underground water. These two factors are not only increasing the turbidity in water,

but also are giving a negative impact on the aquatic lives. This type of pollution is known as Nonpoint Source (NPS) pollution (Brian et al., 2008). NPS could cause deterioration in water quality and turn it into a hazardous material which makes it unsuitable for drinking purposes.

In Malaysia, there is no regulation to monitor the water quality from storm water discharges and agricultural run-off. However, according to the World Health Organization (WHO), the level of turbidity in drinking water should not exceed five Nephelometric Turbidity Units (NTU), and ideally should be less than one NTU. (<http://www.who.int>, 2009)

Environmental Protection Agency (EPA) gave some guidelines on the limits of drinking water. Table 1.1 illustrated the limits in drinking water and the potential health risk.

Table 1.1 Drinking water limits and potential health effects

Type	MCLG, mg/L	MRDLG, mg/L	Potential health Effects
Cryptosporidium	zero	-	Gastrointestinal illness
Giardia lamblia	zero	-	Gastrointestinal illness
Legionella	zero	-	Legionnaire's Disease, a type of pneumonia
Total Coliforms (including fecal coliform and <i>E. Coli</i>)	zero	-	Gastrointestinal illness
Viruses (enteric)	zero	-	Gastrointestinal illness
Bromate	zero	-	Increased risk of cancer
Chlorite	0.8	-	Anemia; infants & young children: nervous system effects
Chlorine (as Cl ₂)	-	4	Eye/nose irritation; stomach discomfort
Cadmium	0.05	-	Kidney damage

Table 1.1 continued

Lead	zero	-	<p>Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities</p> <p>Adults: Kidney problems; high blood pressure</p>
Chlorobenzene	0.1	-	Liver or kidney problems
Copper	1.3	-	<p>Short term exposure: Gastrointestinal distress</p> <p>Long term exposure: Liver or kidney damage</p> <p>People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level</p>
Mercury (inorganic)	0.02	-	Kidney damage

MLCG = Maximum Contaminant Level Goal

MRDLG =Maximum Residual Disinfectant Level Goal

Source: <http://www.epa.gov> , 2010)

1.2.2 Man-made Occurrence Turbidity

The high intensity of rainfall like storm water could carry sediment and soil to surface water sources such as reservoir, lakes, river and even ocean. However, the discharge from industries, such as semiconductor industry and construction field, could also increase the concentration of colloidal silica and soil in surface water which, in turn, will increase the turbidity of surface water (Chuang et al., 2006). The discharge from industry is known as point source pollution. Recently, Environmental Protection Agency (EPA) in the United States of America has proposed a guideline to control the pollution from construction sites. This guideline was released in November, 19th, 2008 and it limited the allowable turbidity levels to be up to 13 NTU

at construction sites of 30 acres and above (<http://www.epa.gov>, 2010). This showed that the country realized the importance of controlling and monitoring the turbidity levels in surface water.

1.3 Types of water and wastewater treatment methods

There are three main types of water and wastewater treatments. They are physical, chemical and biological treatments. Physical treatment involves few basic processes like screening, sedimentation, filtration, flotation and skimming in order to separate particles and microbes from water. All particle separation processes depend on the particle size (Fitzpatrick and Gregory, 2003).

Coagulation, adsorption, ozonation, chlorination are examples for chemical treatment. It uses chemical reaction to improve the water quality. For example, activated carbon is used in water treatment in order to remove particles from water through adsorption (Tan et al., 2009).

Biological treatment uses microorganism to breakdown the organic composition in water. Biological treatment can be carried out either under aerobic or anaerobic conditions. The aerobic biological treatment includes aerobic digestion, oxidation ponds, and activated sludge treatment methods where oxygen is required during the processing. Anaerobic biological treatment must be carried out in the absence of oxygen. Anaerobic process is commonly used in Palm Oil Mill Effluent (POME) treatment for it is high in Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD₅), Total Kjeldahl Nitrogen (TKN), oil and grease and Total Suspended Solids (TSS) (Ahmad et al., 2003).

1.3.1 Water Treatment for Drinking Water Supply

Drinking water treatment includes a series of processes such as coagulation, flocculation, and clarification through sedimentation, filtration and disinfection (Betancourt and Rose, 2004).

Treatment of drinking water starts with coagulation to agglomerate fine particles in turbid water. Coagulation is usually followed by flocculation. These two processes work hand in hand to destabilize the colloidal impurities and to aggregate flocs that will be removed during the clarification stage (Betancourt and Rose, 2004). Aluminium salts and ferric salts both are the most commonly used coagulants in water treatment. Furthermore, organic polymers are widely used as flocculants. Polyacrylamide (PAM) is the most commonly used synthetic organic flocculant.

After coagulation and flocculation, aggregates (commonly known as flocs) will be removed during clarification process. This process involves two stages: sedimentation and filtration. Clarification is the primary barrier against microbe's passage. An alternative for sedimentation is Dissolved Air Flotation (DAF). DAF removes light flocs through air bubbles.

By filtration, the turbidity and microbe can be filtered out. There is a various type of filtration, from the conventional, sand-bed filtration to the latest membrane filtration. There are four mechanisms for sand-bed filtration. The removal of particles occurs by adsorption of the particles to the filter grains, sedimentation of the particles while in the media pores, by coagulation while travelling through the pores or by biological mechanism

Another type of filtration is through membrane. Recently, membrane filtration becomes very popular. Membrane filtration is not only removing fine particles in water but microbe removal. Pressure driven membrane filtration includes

microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) depending on the size particles that pass through and the chemistry of solution. Low-pressure filtration such as MF and UF has high turbidity removal. The potential mechanism for MF and UF includes sieving or size exclusion, adsorption to the membrane surface or internal structure, attachment to particles in the feedwater and subsequent removal by the membrane, removal by the cake layer formed at the membrane surface, removal by non-hydraulically reversible membrane foulants and the characteristics of the membrane (Jacangelo et al., 1995).

The last stage of drinking water treatment is disinfection. This can be achieved using chlorination, ultra violet (UV) radiation, and ozone (Betancourt and Rose, 2004).

For wastewater treatment, such as colloidal silica wastewater, coagulation and flocculation could bring benefit to the industry. The process could help the industry to collect the silica from wastewater and reuse it. Furthermore, this process reduces the amount of silica colloidal to RO membrane. This can reduce the silica fouling at the membrane (Chuang et al., 2006). This treatment usually becomes a pretreatment for the wastewater rich in colloids.

1.4 Coagulation and Flocculation Process in Water and Wastewater Treatment

Various existing primary conventional wastewater plants are shifting towards chemically enhanced treatment to improve the quality of the treated effluent. Coagulation–flocculation has always attracted considerable attention for yielding high removal efficiency in wastewater treatment. The increasing popularity of chemical treatment can be rationalized according to the fact that the chemical treatment is fast (due to the chemical reaction involved), predictable, and controllable

when compared to the conventional methods. Moreover, it consumes lower operating area and adapts to input load changes on the contrary of the biological treatment (Semerjian and Ayoub, 2003).

In a general case, wastewater colloidal is negatively charged particles. When particles have similar charge, they tend to prevent agglomeration by repulsive force separated (Brostow et al., 2007). Coagulation is basically a chemical addition and mixing process. Coagulation achieves charge neutralization or particles destabilization through addition of different charge of ion which allow the particles to agglomerate and subsequently to be removed (Fitzpatrick and Gregory, 2003).

Flocculation is always used in conjunction with and preceded by coagulation. It bridges the stabilized particle together and form bigger aggregates in size. The bigger aggregates are usually known as flocs. This process is usually accomplished by slow mixing. Slow mixing allows particles to collide with each other and adhere on to one another until it is heavy enough to settle. In short, this mechanism is known as particles linking and binding or bridging. Sedimentation usually followed by flocculation as a clarification process for the wastewater (Semerjian and Ayoub, 2003). The clarified wastewater will undergo another treatment to remove the remaining impurities in water.

The most commonly used coagulant in wastewater treatment is Ferric Chloride (FeCl_3), Ferric Sulphate ($\text{Fe}_2(\text{SO}_4)_3$), Alumimium Sulphate ($\text{Al}(\text{SO}_4)_3$), Ferrous Sulphate (FeSO_4) and Calcium hydroxide ($\text{Ca}(\text{OH})_2$), polyaluminum chloride (PACl), lime and alum (Semerjian and Ayoub, 2003; Annadurai et al., 2004). Flocculants that are used for wastewater treatment can be classified into three categories:

- i. inorganic flocculants

- ii. organic synthetic flocculants
- iii. natural flocculants (Xia et al., 2007)

Synthetic polyelectrolytes (anionic, cationic or nonionic polymers) are more commonly used. Polyacrylamide is a synthetic organic polymer that widely used as flocculant in industry.

The effectiveness is the most important attribute a specific coagulant or flocculant should have in order to be used in water treatment and then cost (Semerjian and Ayoub, 2003).

1.5 Rationale of the proposed project

Organic synthetic polymer flocculants, such as polyacrylamide and its derivatives, posed environmental problems as some of the derivatives are non-biodegradable and the intermediate products of their degradation are hazardous to human health because the monomer is neurotoxic and carcinogenic (Rudén, 2004). Hence, a potentially safe flocculant should be introduced to replace the existing harmful flocculant. Therefore, bio-based flocculants are attracting great research interest due to their safety and biodegradable properties (Salehizadeh and Shojaosadati, 2001).

The characteristic of the biopolymeric flocculant can be determined by its thermal degradability, functional group, average molecular weight and surface morphology. Most importantly, the effectiveness of the biopolymeric flocculant in wastewater treatment will be compared with common industrial flocculant. Optimum application conditions will be investigated by using Response Surface Methodology. Operating cost will be taken into consideration.

1.6 Objective

The objectives of this research are:-

- 1) To characterize the commercial pectin, industrial flocculant and extracted pectin in terms of thermal degradation, molecular weight-viscosity, surface morphology, functional group, and the amount of the sludge produced.
- 2) To determine the factor(s) that affect(s) the effectiveness of both flocculants.
- 3) To compare the performance of both flocculants on two responses: flocculating activity and turbidity reduction.
- 4) To optimize the responses using Response Surface Methodology (RSM).

1.7 Outline

This thesis consists of five chapters. It describes the literature studies, empirical work done, and scientific discussion on the results and finally conclusion. This thesis is mainly designed to produce a biopolymeric flocculant and to compare it with the other industrial flocculants through the characterization and the optimization of the effectiveness in turbidity reduction by using synthetic wastewater and studying the flocculating activity of the flocculant:-

Chapter two discusses literature studies on the biopolymeric flocculant and industrial flocculant. The coagulation and flocculation processes are explained in depth. Acid-extraction process for the biopolymeric flocculant and a straight forward characteristic study on thermal degradation, average molecular weight, intrinsic viscosity, surface morphology, and functional group are explained. Furthermore, the statistical analysis such as Factorial Design and Box Behnken design are further described in details.

Chapter three illustrates the procedures and specific conditions to perform laboratory analyses, while, chapter four presents the research findings from characterization analyses, optimization of the effectiveness of the two responses, namely, turbidity reduction and flocculating activity of the flocculant. The results are further explained and discussed in chapter four.

Finally, based on the results and discussion, conclusions have been made in chapter five. Moreover, some recommendations for future research to wrap up chapter five.

CHAPTER TWO

LITERATURE REVIEW

2.1. Wastewater treatment

One of the major wastewater treatment processes which are used to remove fine particles or colloids from wastewater is coagulation and flocculation. These two processes are considered to include all reaction, mechanism and result in overall process of particles aggregation. Chemical coagulation involving the use of inorganic coagulant such as aluminium salts, and ferric salts, have been successfully applied. Easily degradable coagulants raised the attention of researchers. In recent years, Chitosan, Moringa Oleifera which is known as biocoagulant became the interest of researchers (Ndabigengesere et al., 1995; Ravi and Sivasankara, 2001)

2.1.1 Aluminium salts

In coagulation process, metal salts are an important and widely used coagulant in wastewater treatment plant. This is because of their high effectiveness in treating a wide range of waste water and their low cost. The mostly used aluminium based coagulant is Alum, Aluminium Chloride and Polyaluminium Chloride (PACl). PACl is a prehydrolyzed aluminium based coagulant (Wu et al., 2007).

When the coagulant is added into water, Aluminium salts dissociate and react to yield hydrolysis products. These hydrolysis products form the coagulant species that remove fine particles in waste water (Mattson, 1928). For example, PACl contains many pre-formed Al^{3+} hydrolysis species that are stable for further hydrolysis, resulting in higher coagulation efficiency (Wu et al., 2007). The species proposed to form during hydrolysis include the monomers Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$,

Al(OH)_3 and Al(OH)_4^- and $\text{Al}_2(\text{OH})_2^{4+}$ and trimer $\text{Al}_3(\text{OH})_4^{5+}$ and tridecamer $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ (Wang et al., 2009).

2.1.2 Ferric salts

Trivalent cation such as Fe^{3+} is one of the most effective cation used for coagulation. Fe^{3+} is found to be effective in wide ranges of pH and temperature for removing fine particles from wastewater. Like Aluminium salts, when added into water, ferric ions will associate with water and resulting in the formation of various iron species. For polyferric salts, it is partially hydrolyzed before they are added into water. When it associate with water, it will produce hydrolysis products such as $[\text{Fe(OH)}_x]^{(3-x)+}$, and polynuclear complexes of Fe(III) and $[\text{Fe}_m(\text{OH})_x]^{(3m-x)n+}$ (Shi et al., 2004). However, the range of species forming is affected by some factors such as the nature and the temperature of wastewater, the pH during coagulation, the concentration of coagulant which directly affects the treatment efficiency (Zouboulis et al., 2008).

2.1.3 Biopolymeric coagulant –Moringa Oleifera

According to Bhuptawat et al. (2007), Moringa Oleifera Lam (Moringa Oleifera) is a multipurpose tree originating from northern India. It is also used in traditional medicines. The seed of Moringa Oleifera contains around 40% by weight of quality edible oil and more than 80% of unsaturated fatty acids. The active components of Moringa Oleifera seeds have been determined by researchers to have low molecular weight, a cationic peptides with pH value of 10. In wastewater treatment application, Moringa Oleifera seeds are extracted and purified. They are proved to be effective in removing fine particles from wastewater and produce low sludge amount compared to alum.

2.1.4 Biopolymeric coagulant – Chitosan

Chitosan is a linear copolymer of glucosamine and N-acetyl glucosamine that is a natural deacetylated marine polymer. It has been used in a variety of practical fields including wastewater management, pharmacology, biochemistry, and biomedicine. Chitosan has excellent properties such as biodegradability, hydrophilicity, biocompatibility, adsorption property, flocculating ability, polyelectrolyticity, antibacterial property, nontoxic, soluble, and positively charged in acidic media (Majeti, 2000; Feng et al., 2000; Chatterjee et al., 2009). Chitosan can be used as an eco-friendly coagulant.

2.1.5 Synthetic flocculants

Synthetic flocculant has been used widely in removing fine particles in wastewater because it is economical and has a high efficiency. Organic synthetic flocculant such as Polyacrylamide (PAM) is commonly used in waste water treatment plants. PAM is an amorphous and a water soluble polymer ($-\text{CH}_2\text{CHCONH}_2-$) formed from acrylamide monomer. However, some of PAM derivatives are non-biodegradable and its by-product during degradation is hazardous to human health (Rudén, 2004).

2.1.6 Biopolymeric flocculant – microbial

Chemically synthesized flocculants are playing dominant roles in wastewater treatment due to their low cost. However, they posed severe problems to human health and they are difficult to degrade. Thus, bio-based flocculants are attracting great research interest due to their safety and biodegradable properties. In recent 25 years, more than 50 microorganisms, ranging from prokaryotic to eukaryotic cells,

have been found to produce extracellular biopolymeric flocculants (Salehizadeh and Shojaosadati, 2001). However, none of the biopolymeric flocculants has been commercially produced or applied in wastewater treatment plants so far. It is due to the low yield and the high cost in bioflocculants production (He et al., 2004). Biopolymeric flocculants usually secreted by algae, bacteria, fungi and yeast. They are extracellular biopolymers, which includes proteins, glycoproteins, polysaccharides, lipids and glycolipids (Salehizadeh and Shojaosadati, 2003).

According to Salehizadeh and Shojaosadati (2001), there are several factors that affect the production of biopolymeric flocculant such as carbon and nitrogen sources, pH, temperature, and presence of cations. The carbon and nitrogen source are important for bacteria growth. The amount of carbon, nitrogen, pH value, temperature, type and concentration of cation depend on the type of bacteria. Nevertheless, the factors that affect the performance of biopolymeric flocculant include molecular weight, temperature, pH and addition of cations. The biopolymeric flocculant not only can remove the fine particles from wastewater, but also can remove heavy metals such as Mn^{2+} , Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Cr^{3+} and Fe^{3+} from wastewater. It is reported by Takeda et al. (1991), a crude biopolymeric flocculant, *Alc. Latus* was able to separate oil from water in oil-in-water emulsion. This biopolymeric flocculant can reduce the Chemical Oxygen Demand (COD) in wastewater.

2.1.7 Biopolymeric flocculant – Polysaccharide

Polysaccharide is one of the extracellular biopolymeric flocculant. Natural polysaccharides can be found in various sources such as cellulose, guar gum and starch. Cellulose is the most abundant, inexpensive, renewable, fully degradable

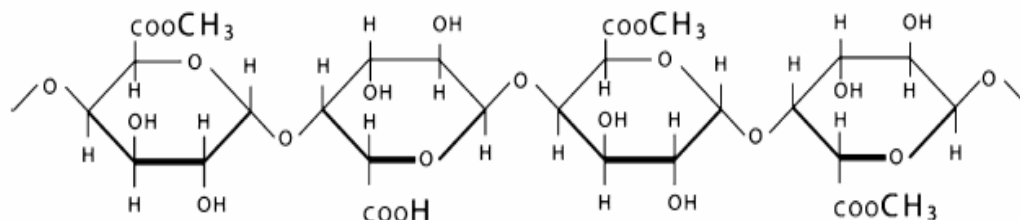
natural resource in the world (Sang and Xiao, 2009). Guar gum is derived from the seeds of guar plant *Cyanaposis tetragonolobus* (Leguminosae). It is a natural nonionic branched polymer with β -D-mannopyranosyl units linked (1-4) with single membered α -D-galactopyranosyl units that occur as side branches. Guar gum and their derivatives have been used in many areas such as thickener, ion exchange resin and flocculating agent (Wang and Wang, 2009).

Starch has a large number of hydroxyl groups, which give the polymer a strong hydrophilic character. In the starch polymer, only three hydroxyl groups of the cyclic glucose units are free and may rotate to one side of the molecule ring, making that side more hydrophilic. They are also used as flocculants because of their large molecular size. Starch has been used in mineral industry for almost 80 years. The application of natural polysaccharides becomes popular due to their bio-degradable and non-toxic characters. Furthermore, natural polysaccharides are abundant, low utilization cost, and renewable (Xia et al., 2009). Also, biodegradable polymers derived from renewable sources (plants and microorganisms) are adequate for land disposal (Telmo et al., 2009).

There is one study conducted by Yokoi et al. (2002), which investigated one new polysaccharide that is able to become biopolymeric flocculant. This new polysaccharide is pectin. Pectin is a heterogeneous polysaccharide occurring in the cell walls and intracellular layers of land plants. It is a complex structure from plant cell wall. Plant cell wall forms a single continuous extracellular matrix through the body of the plant. The cell matrix consists of various types of polysaccharides, protein and lignin (Schols and Voragen, 1996).

Pectin includes a family of acidic polymers like homogalacturonans, and rhamnogalacturonans that may have neutral polymers such as arabinans, galactans

and arabinogalactans attached to them (Schols and Voragen, 1996). The anionic polysaccharide in the cell walls consists of linear α -D-galacturonic acid (“smooth” region) with 1-4 linkages (Aspinall, 1980). The major component in pectin is the carboxyl groups of the α -D-galacturonic acid with either free or esterified with methyl groups (Yokoi et al., 2002). The degree of esterification (DE) of pectin is divided into two category: high methoxyl pectin (HMP) with a DE higher than 50% and low methoxyl pectin (LMP) with a DE lower than 50% (Thakur, 1997; Thibault, 1991). Extraction of pectin may be by aqueous acid or alkaline. The alkaline extraction process yields pectin of low DE as a result of saponification of the ester groups, whereas the acid extraction process generally yields pectin with high DE (Joye and Luzio, 2000). The molecular structure of highly esterified pectin is shown in Figure 2.1.



Source: Khotimchenko et al., (2007)

Figure 2. 1 Molecular structure of highly esterified pectin.

Pectin could be extracted at industrial scale from plant (waste) materials such as citrus peel (lemon, lime, orange and grapefruit) and apple pomace (Stephen, 1995). Although pectin can be found in many plants, but the main commercial sources are citrus peels and beet pulp where it forms around 25% of the dry matter. Dried apple

pomace are considered another pectin source where it forms around 15–18% of the dry matter (Mesbahi et al., 2005).

The other application of pectin is in the food industry due to their ability to form gels under certain circumstances and to increase the viscosity of drinks. They also are widely applied as stabilizers in acid milk products, and some may have other pharmaceutical uses (Stephen, 1995).

This research is to apply this biopolymeric flocculant in turbid waste water treatment. The polysaccharide in this biopolymeric flocculant is responsible to link and bind the particles in waste water. When the particles become larger in size, it will become floc and settle. Subsequently, it will clarify the waste water.

2.2 Coagulation and flocculation mechanisms

Coagulation and flocculation are common processes in the primary purification of industrial wastewater. Coagulation and flocculation removes fine or suspended particles by aggregating particles into larger ones. Coagulation involves the destabilization of particles and the formation of larger particles through flocculation which result in floc formation. The term “flocculation” is used to describe the process whereby the size of particles increases as a results of collisions. Colloidal particles found in wastewater typically have a net negative surface charge. The size of colloids is usually ranging from 0.01 to 1 μ m. At this range of size, the attractive body forced between particles is less than the repelling forces of the electrical charge. Under this condition, Brownian motion keeps the particles in the suspension. Brownian motion or movement is the random motion of fluid molecules. Without Brownian motion during coagulation, it is difficult to remove these fine and suspended particles from the wastewater. The purpose of flocculation is to produce

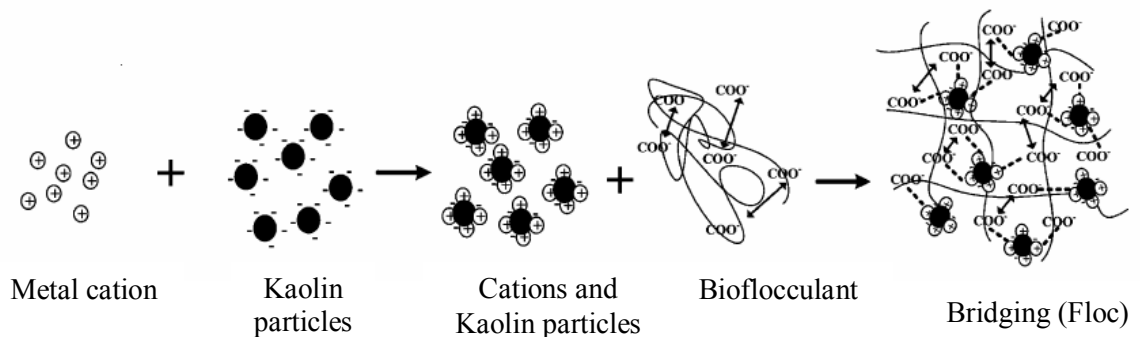
flocs that can be removed by inexpensive particle-separation process such as gravity sedimentation and filtration (Tchnobanoglous et al., 2004).

Coagulants based on metal salts are widely used. The metal salts can hydrolyze rapidly when added into water and form various cationic species, which are adsorbed by negatively charged particles where charge neutralization occurs. This is more commonly known as destabilization of particles. Destabilization of particles can occur even at low coagulant concentrations (Snodgrass et al., 1984). Coagulation is to destabilize the suspended particles by neutralizing the forces that keep the suspended particles separated (Brostow et al., 2007). The aggregates formed during coagulation are small and loosely bound together at low sedimentation velocities.

Flocculation enhances the aggregation of suspended fine particles. It binds and links particles during collision. Flocculation in liquid suspensions may occur without significant changes in the particle surface charges. Flocculation is more effective than coagulation since the so-called flocs are larger and more strongly bound than the aggregates obtained by coagulation (Brostow et al., 2007). The mechanism of binding and linking occurs when a polymer chain is absorbed on more than one particle, thereby bridging the particles together. Specifically, bridging flocculation occurs when many reactive or functional groups of the polymer are absorbed onto the particles, and a particle-polymer-polymer-particle aggregate is found in which the polymer serves as a bridge (Li et al., 2006). Bridging flocculation that leads to flocs formation is much stronger than those formed when particles are destabilized by simple salts (Bolto, 1995; Yukselen and Gregory, 2004). Aggregates formed by polymeric flocculants appear to be significantly more resistant to breakage (Ray and Hogg, 1987). A study performed by Li et al. (2006), showed that floc strength is the weakest during coagulation and it was not enough for physical

bonding between flocs. However, floc strength formed under flocculation is the strongest. At the same time, floc size is larger in flocculation process; thus, the separation will be improved due to the flocculation.

The mechanism for flocculation is illustrated in Figure 2.2 that was proposed by Wu and Ye, (2007). They suggested that the flocculation may be attributed to the decrease in the number of negative charges on the surface of particles when cations are present, which will increase the number of positive charges instead. Thus, the negatively charged reactive group, which is carboxyl group (COO^-), of the flocculant will react with the positively charged site of the suspended fine kaolin particles (Wu and Ye, 2007). Flocculant that has long chain (tails and loops) can extend far beyond the surface and interact with the kaolin particles. Subsequently, floc formed (Sheng et al., 2006).



Source: Wu and Ye, (2007)

Figure 2. 2 Proposed flocculation mechanism of biopolymeric flocculant.

2.3 Factors affecting coagulation and flocculation process

2.3.1 Effect of pH

The pH value is a very important factor in most cases of polymeric binding. It is either the protons or the hydroxyl anions that make the process of binding work

(Aroua et al., 2007). The study conducted by Yokoi et al. (2002), stated that the coagulation and flocculation processes were influenced by pH. The initial pH will be decisive for the efficiency of both of the coagulation and the flocculation process (Canizares et al., 2009). It is due to the pH influences the hydrolysis equilibrium of the coagulant species and addition of metallic cation will automatically decreases the pH, maybe it will need high dose of coagulant and at the same time lower the alkalinity of the water (Dominguez et al., 2007). Also, the pH and concentration of reagent determine the suitable coagulant species used and the characteristic of wastewater (Canizares et al., 2009).

2.3.2 Charges and concentration of cation

The role of cation is to enhance the adsorption of biopolymeric flocculants on the surface of suspended particles by decreasing the negative charge on the particles, which is known as particle charge destabilization. Flocculation occurs due to the decrease in charge density by the added cations. This leads to inter-particle bridging between kaolin particles. In accordance with Schulze Hardy's law, it is suggested that flocculation is a result of changes in the charge density, indicating that addition of cation will result in neutralization of surface on particles. Moreover, charge bridging between flocculants increases floc density, floc size and floc resistance to shear (Wu and Ye, 2007).

Cation stimulates flocculation process by neutralizing or stabilizing the negative charge on the surface of particles, which enables the adsorption of particles to become more effective. It will flocculate the fine and suspended particles easily. Changes resulting from the addition of cations as flocculation enhancers are highly dependent on both of the concentration and valence of the ions (Watanabe et al.,

1999). The coagulation effects usually decreased in the order of trivalent (Al^{3+} , Fe^{3+}) > bivalent (Ca^{2+} , Mg^{2+}) >> monovalent (Na^+). Monovalent cation reduces bonds strength and causes a loose flocs structure. This will result in a decrease in floc density, size and resistance to shear. All this explains the reason of why trivalent and bivalent cations have stronger synergistic effect for flocculation (Wu and Ye, 2007).

2.3.3 Flocculant and concentration of the flocculant

The flocculation of fine particle suspensions is critically dependent on many physicochemical factors including size and distribution of particle, concentration of particles, pH and ionic strength of the suspension medium, molecular weight and charge density of the flocculants, adsorption density and conformation of the adsorbed flocculants. However, the most important factors influence the extent and mechanisms of flocculation are dependent primarily on the nature of polymer adsorption on the surface of particle as well as the conformation of the adsorbed polymer (Chen et al., 2007).

The concentration of flocculant is also a key parameter since the adsorption rate depends on the amount of polymer adsorbed per unit area of the surface of particle (Rasteiro et al., 2008). Hence, the more the particle surface exposure to the polymer, the more the surface area of particles to be adsorbed. High concentration of flocculant in kaolin suspension could lead to competition among the flocculant. This is because the flocculant adsorb relatively fast at low surface concentration and rather slow on crowded surfaces (neighbouring molecules interfere with the re-arrangement) (Rasteiro et al., 2008). When there is low competition on the surface of particles, there will be more surface area for the electrolyte group to extend the tail and get

attached. This situation will induce higher flocculating activity and thus turbidity in the kaolin suspension is reduced.

Moreover, the flocculant concentration influences the conformation rate. Flocculant rearrange relatively fast at low surface concentration. In contrary, the flocculant adsorb slowly in crowded surface because the surrounding particles will interfere with the rearrangement (Rasteiro et al., 2008). Bridging during flocculation will increase with the increase in flocculant concentration, which enables the flocculant to bind more particles (Dihang et al., 2008).

2.3.3.1 Reactive/functional group

At low pH, the concentration of H^+ enhances the bridging mechanism during flocculation. This can be explained due to the presence of acids which form hydrogen-bonding and hydrophobic interactions. The hydrophobic interactions will increase the electrostatic attraction leading to linking and binding during flocculation (Tsoga et al., 2004). For coagulation and flocculation process, the presence of this hydrophobic interaction may reduce the electrostatic repulsion. Hence, the concentration of hydrogen and hydroxyl ions play an important role in flocculation process.

Long-chain biopolymeric flocculants allow the electrolyte groups to be exposed. The negatively charged carboxyl group (COO^-) and hydroxyl group (OH^-) on the molecular chain of biopolymeric flocculant make the chain stretch out because of electrostatic repulsion. Bridging between fine particles and linearly extended biopolymer chains, leads to the formation of a three-dimensional matrix. It is capable to bridge the particles together and settle (Salehizadeh and Shojaosadati, 2001).

On the other hand, the industrial flocculant such as Polyacrylamide (PAM) is adsorbed on the surface of kaolin particles via hydrogen bonding interactions between the silanol and aluminol OH groups on the surface of particle and their primary amide functional groups (Dihang et al., 2008). The interactions between ions and the carbonyl groups of PAM are responsible for the interaction between polymer and particles in water.

Hence, the reactive groups that affect flocculating activity of pectin are mainly carboxyl group (COO⁻) and hydroxyl group (OH). While the reactive group for PAM is their primary amide functional groups. FTIR is used to evaluate the presence of these reactive groups in the biopolymeric flocculant and industrial flocculant.

2.4 Characterization of polymer

2.4.1 Biodegradation

One of the natural-based water soluble polymers is pectin. Pectin has hydrophilic functional group which is carboxyl group. The degradation of polymers in the environment may have several pathways, all of which are sometimes known as biodegradation – the one that's environmental friendly and so call a 'complete degradation'.

There are five different pathways or mechanisms that have been defined and used for water-soluble polymers like pectin. These mechanisms are based on the ASTM definitions which are generally applied by researchers (Swift, 1998):-

- 1) A degradable polymer is designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in the loss of its properties that may vary as measured by standard testing methods

that are appropriate to the polymer and the application in a period of time that determines its classification.

- 2) A biodegradable polymer is one in which its degradation results from the action of naturally occurring micro-organisms such as bacteria, fungi, and algae.
- 3) A hydrolytically degradable polymer is the polymer that degrades by hydrolysis.
- 4) An oxidatively degradable polymer is the polymer that degrades by oxidation.
- 5) A photodegradable polymer is the polymer that degrades by the action of natural daylight.

The degradation pathways or mechanisms that involved are shown in Figure 2.3.

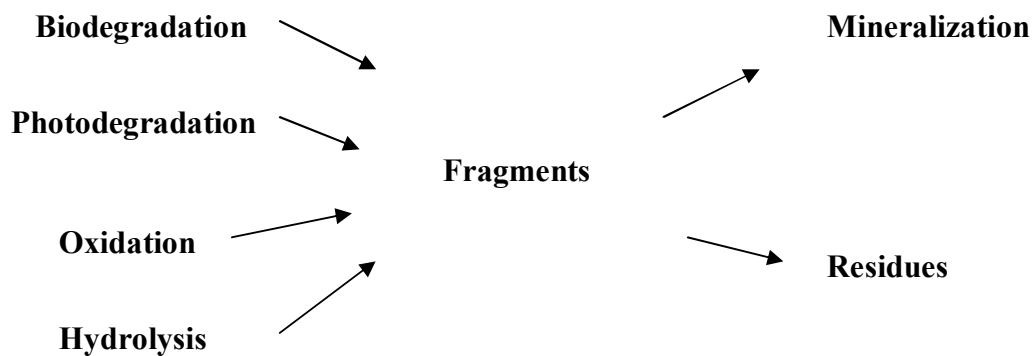


Figure 2. 3 Biodegradation pathways or mechanisms.

The term “complete biodegradation” occurred when the original organic material, water soluble polymer in this case, is converted into carbon dioxide, water, and biomass. Any or all of the degradation pathways are acceptable in the initial stages of environmental degradation. However, for environmental acceptance, the biodegradation of a polymer must be completed with no residues left in the environment, unless they are established as non-harmful.

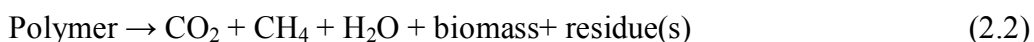
The rate of biodegradation is dependent on many factors, including the environment (Swift, 1998) which is the surrounding temperature, population of microorganism in the soil, microbial cellular transport properties (Raymond et al., 2001), moisture, light, nutrients, pH, metals, salts, metabolites, and cofactors greatly affect the onset and rate of degradation (Mayer and Kaplan, 1993). Therefore, in defining biodegradable polymers, it is crucial to decide on the disposal environment. Residues may be ultimately biodegrade and have no environmental threat. However, this must be established for acceptability of the original polymer.

The analytical requirements for establishing the degree of biodegradation are based on the chemistry of biodegradation in either an aerobic or anaerobic conditions. The biodegradation mechanisms for both environments are represented in Eq. 2.1 and Eq. 2.2, respectively. These equations are related to carbon, hydrogen and oxygen-containing polymers but are readily adaptable to polymers containing other elements where the additional elements appear in oxidized or reduced form depending on the environment, whether it is occurring in aerobic or anaerobic condition.

Aerobic biodegradation.



Anaerobic biodegradation.



There are several pathways or mechanisms for the disposal of water-soluble polymers. Figure 2.4 illustrates these mechanisms. Water-soluble polymers tend to be discarded either into a public or sewage or wastewater treatment system or directly into the aqueous environment. Water-soluble polymers that enter sewage treatment facilities and waterways may remain in solution or can be partially or completely adsorbed onto the sludge/biomass solid component. Those that remain in solution