A STUDY OF POLYDADMAC INDUCED FLOCCULATION IN TREATMENT OF PULP AND PAPER MILLS WASTEWATER

by

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DECLARATION

I declare that this thesis is the result of my own research, that is does not incorporate without acknowledgement any material submitted for a degree or diploma in any university and does not contain any materials previously published, written or produced by another person except where due reference is made in the text.

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LIST OF ABBREVIATION

AOX	Organic Halogens
APS	Ammonium Persulfate
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
EM	Electrophoretic Mobility
FTIR	Fourier Transform Infra-Red
MBS	Sodium metabisulfite
NTPM	Nibong Tebal Paper Mills
Na_4EDTA	Tetrasodiumethylenediaminetetraacetate
PolyDADMAC	Polydiallyldimethylammonium Chloride
PAC	Polyaluminum Chloride
PAM	Polyacrylamide
TSS	Total Suspended Solids
NTU	Nephelometric Turbidity Units

LIST OF SYMBOLS

%	Percentage
^0C	Degree Celcius
ε	Dielectric constant
Δ	Entalphy
ζ	Zeta
η	Viscosity
c	Concentration
cm	Centimeter
cm^3g^{-1}	Cubic centimeter per gram
L	Litre
$Mg\ L^{-1}$	Milligram per litre
mm	Millimetre
µm	Micrometer
r	Radius
m^3	Cubic metre
F	Faraday
Mw	Molecular weights
M	Molar

KAJIAN MENGENAI PENGUMPALAN DIARUHKAN OLEH POLIDADMAC DI DALAM RAWATAN SISA AIR KILANG PULPA DAN KERTAS

ABSTRAK

Kajian dijalankan untuk mengkaji kesan poliDADMAC ke atas rawatan sisa air kilang pulpa dan kertas. PoliDADMAC telah disintesis daripada kepekatan monomer yang berbeza-beza. Inframerah Transformasi Fourier (FTIR) telah dijalankan untuk mengesahkan struktur poliDADMAC yang dihasilkan. Viskometer Ubbelohde digunakan untuk mengukur kelikatan intrinsik dan nilai- nilai ini digunakan untuk penentuan berat molekul dengan menggunakan persamaan Mark Houwink. Didapati, peningkatan berat molekul dan kelikatan intrinksik meningkat dengan kepekatan monomer (1.37 kepada 1.87 M). Walau bagaimanapun, berat molekul yang dihasilkan adalah berkurang selepas kepekatan 1.87 M. Kemudiannya, ujian "jar" dilakukan menggunakan sampel-sampel poliDADMAC yang dihasilkan keatas ampaian kaolin dan air sisa kilang. Keberkesanan poliDADMAC merawat ampaian kaolin iaitu simulasi air sisa dijalankan sebelum menggunakan air sisa yang sebenar. Ujian penggumpalan untuk ampaian kaolin dilakukan pada dos Poliakrilamida yang tetap iaitu 0.2 mg L^{-1} manakala dos poliDADMAC adalah dalam julat 0.2 – 50 mg L^{-1}. Bagi ujian penggumpalan untuk air sisa kilang pulpa dan kertas, ianya dibahagi kepada tiga kajian. Pertama adalah kesan berat molekul poliDADMAC secara bersendirian, kedua kesan dos poliDADMAC secara hibrid dengan PAM manakala yang terakhir adalah kesan berat molekul poliDADMAC yang berbeza dalam sistem hibrid dengan PAM. Julat dos adalah dari 0.4 - 2.0 mg L^{-1} bagi ujian penggumpalan menggunakan polyDADMAC bersendirian manakala bagi sistem hibrid, dos PAM

adalah dalam julat dos 0.4 - 8.0 mg L^{-1}. Kekeruhan, jumlah pepejal terampai (TSS), keperluan oksigen kimia (COD) dan keupayaan ζ digunakan sebagai ukuran dasar pada parameter. Didapati prestasi penggumpalan oleh sampel yang mempunyai berat molekul tinggi adalah lebih efektif berbanding dengan berat molekul rendah bagi sistem secara bersendirian oleh poliDADMAC. Ini adalah disebabkan oleh mekanisma jambatan yang berlaku secara serentak dengan peneutralan semasa proses penggumpalan. Bagi sistem hibrid, peningkatan dos oleh poliDADMAC akan meningkatkan penyahstabilan partikel dan menghasilkan gumpalan- gumpalan kecil manakala penambahan dan peningkatan PAM akan meningkatkan saiz gumpalan untuk partikel.

A STUDY OF POLYDADMAC INDUCED FLOCCULATION IN TREATMENT OF PULP AND PAPER MILLS WASTEWATER

ABSTRACT

This study investigates the effect of polyDADMAC on treating pulp and paper mills wastewater. PolyDADMAC was synthesized with different monomer concentration. Fourier Transform Infrared Spectroscopy (FTIR) was conducted to confirm the structure of polyDADMAC. Ubbelohde Viscometer was used to determine intrinsic viscosity and these values were used to determine molecular weight by employing the Mark Houwink equations. Molecular weight and intrinsic viscosity increased with increasing of monomer concentration (1.37 to 1.87 M). Beyond the monomer concentration 1.87M the molecular weight began to decrease. Subsequently, the jar test was conducted using polyDADMAC produced on kaolin suspensions and factory wastewater. The effectiveness of polyDADMAC on treating kaolin suspensions as simulated wastewater was conducted before tested in actual wastewater. Flocculation tests for kaolin suspension were carried out at constant polyacrylamide (PAM) dosage of 0.2 mg L^{-1} while the dosage of polyDADMAC was varied from 0.2 - 50 mg L^{-1}. Flocculation tests for pulp and paper mills were divided in three studies. Initially, the effect of molecular weight of polyDADMAC alone then the effect of polyDADMAC dosages in hybrid system with PAM and finally the effect of different molecular weight of polyDADMAC in hybrid systems with PAM. Dosage range was from 0.4 - 2.0 mg L^{-1} for flocculation tests using polyDADMAC alone, while in the hybrid system, PAM dosages in the range of 0.4 - 8.0 mg L^{-1}. The effectiveness of the flocculation was measured based on the reduction of the turbidity, the total suspended solids (TSSs), chemical on

demand (COD) reduction and zeta potential measurements. It was found that the flocculation performance of higher molecular weight samples was more efficient compared with that of lower molecular weights. This might be due to the bridging mechanism, which occurred concurrently with the charge neutralization effect during flocculation. Increasing dosages of polyDADMAC increased the destabilization of particles and produce small flocs while adding and increasing PAM was increased the size of flocs for a better synergistic flocculation process.

CHAPTER 1

INTRODUCTION

1.1 Pulp and Paper Mills Industry

The pulp and paper industry is an almost global, being present in most developed and developing countries (Khansorthong and Hunsom, 2009). With rise in literacy, education and income level, and overall economic growth, it is estimated that demand from this industry will become higher (Tewari *et al.*, 2009). There are two main processes involved in the manufacturing of paper which are pulping and bleaching. In pulping process, wood pieces are cooked at very high pressure and temperature in presence of chemicals to separate lignin and hemicelluloses (Singhal and Thakur, 2009) while bleaching is a process use to whiten products by using chlorine or hydrogen peroxide. This industry utilize huge amount of water in different stages of paper manufacturing. On average, each pulp and paper mill factory consumes a large amount of water ranging from 75 to 225 m^3 per tonne of pulp products, while the mill generates bleaching effluents of about 2000 m^3 per day (Khansorthong and Hunsom, 2009).

1.2 Pulp and Paper Mills Wastewater

Pulping and bleaching processes utilize large amounts of water which reappear in form of an effluent. The effluent generated at the pulping process is dark brown in colour due to dissolved lignin, its degradation products, hemicelluloses, resin acids and phenols (Pokhrel and Viraraghavan, 2004). There are residual of lignin and hemicelluloses in the pulp generated after pulping process. The pulp goes

to bleaching process to remove all these residuals. It is bleached using chemicals like chlorine, hydrogen peroxide and ozone. The effluent generated at bleaching stage has absorbable organic halogens (AOX), peroxides and other such derivatives of lignin and hemicellulose (Chuphal *et al.*, 2005). The mills also generate contaminated water, which contains toxic substances such as (AOX) (Pizzichini *et al.*, 2005), inorganic chlorine like chlorate (Yeber *et al.*, 1999), and also organochlorine such as dioxins and furan. It is estimated that 150 m^3 of effluent which is extremely toxic in nature will be generated from 1 tonne of paper (Pokhrel and Viraraghavan, 2004). Table 1.1 reveals the water quality of the pulp and paper mill wastewater.

Table 1.1 Water Quality of the Pulp and Paper Mills Wastewater (Wong *et al.*, 2006)

Parameters	**Value**
Total chemical oxygen demand (mg L^{-1})	3087
Soluble chemical oxygen demand (mg L^{-l})	318
Suspended solids (mg L^{-l})	5240
Turbidity (NTU)	4770
pH	7.3- 8.3

Release of pulp and paper mill wastewater into natural waterways like river and sea causes a variety of clastogenic, carcinogenic, endocrinic and mutagenic effects on aquatic organisms (Ali and Sreekrishnan, 2001). Many studies have been reported about detrimental effects of pulp and paper mill effluent on animals living in water. The studies reported in the form of respiratory stress, oxidative stress, liver damage and geno-toxicity (Vass *et al.*, 1996, Johnsen *et al.*, 1998, Schnell *et al.*, 2000). Exposure to the pulp and paper mill effluent adversely affects diversity and

abundance of phytoplankton, zooplankton and zoobenthos, disrupting benthic algal and invertebrate communities (Karrasch *et al.*, 2006). Therefore, the effluent from the pulp and paper mills wastewater is obligatory to be treated before disposal.

1.3 Treatment of Pulp and Paper Mills Wastewater

To solve the problems with effluent from pulp and paper mills, many studies have been conducted involving biological methods and inorganic chemical coagulation. For the biological approach, conventional aerobic, anaerobic and fungal treatment has been used (Yeber *et al.*, 1999, Pizzichini *et al.*, 2005, Rajeshwari *et al.*, 2000, Van Ginkel *et al.*, 1999). Most biological method takes time to treat the wastewater. The disadvantage of aerobic treatment method is that it takes too many hours to treat the effluent. Treatment by aerobic stabilization basin need about 5 - 10 hours or aeration time to achieve 80 - 90 % removal of Biochemical Oxygen Demand (BOD) while for activated sludge method, it needs 3-8 hours of aeration time to achieve 80-85 % removal of BOD (Springer, 2000). Rajeshwari *et. al* (2000) reported that anaerobic treatment is not suitable to treat chlorine bleaching effluents due to their low biodegradable and presence of toxic substance that affects methanogens (Rajeshwari *et al.*, 2000).

Inorganic chemical coagulation approach like alum, ferric chloride and ferrous sulphate has been studied extensively (Stephenson and Duff, 1996, Nassar, 2003, Beulker and Jekel, 1993). These metal salts enhanced good result in treating pulp and paper mills wastewater. Alum achieved 99% of turbidity reduction, 91 % of COD reduction and 99% of TSS removal at dosage of 1000 mg L^{-1} and at pH 6

(Ahmad *et al.*, 2008). Ferric chloride coagulates effectively over a broader pH range, forms a stronger and heavier flocs (Stephenson and Duff, 1996). Disadvantage of these metal coagulants is it depresses the pH from a slightly alkaline pH of the untreated effluent to very acidic levels and this contributes to necessitate special materials of construction. In addition ferric chloride which is dark brown solution will causes staining (Katja and Mika, 2007).

Recently, the use of flocculants, such as synthetic polyelectrolytes, for the removal of suspended solids in wastewater treatment which include pulp and paper mills has grown rapidly (Sarika *et al.*, 2005, Ebeling *et al.*, 2005). This increase in use is due to their ability to produce a higher sedimentation rate, better final water quality, a lower sludge volume, and better sludge quality compared with those values obtained by mineral coagulation (Mahvi and Razavi, 2005).

Polyacrylamide (PAM) and polyaluminium chloride (PAC) are synthetic polyelectrolyte which has been extensively used in treating pulp and paper mills wastewater. PAC required high dosage as approved by Ahmad *et al*, ((2008) which was 600 mg L^{-1} dosage of PAC needed to achieve 99 % of turbidity removal. Other polyelectrolytes which can be utilized in pulp and paper mills industry is polydiallyldimethylammonium chloride (polyDADMAC). PolyDADMAC belongs to an ionic group because of the positive charge (cation) in its structure. PolyDADMAC molecules have a backbone of cyclic units and a charged quaternary ammonium group found in each chain unit, as shown in Figure 1.1. It is also a high-charge-density cationic polymer, which makes it well-suited for the flocculation process.

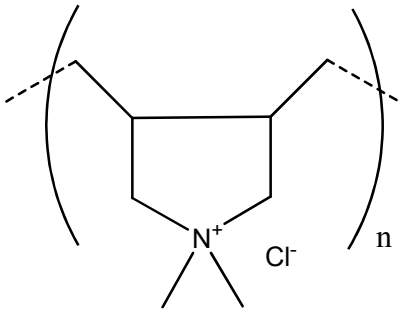


Figure 1.1 Structure of PolyDADMAC

Mostly, polyDADMAC is used in pulp and paper mills processing as wet strength additives and retention agents (Wandrey *et al.*, 1999). Many publications have addressed the flocculation behavior of polyDADMAC in simulated waste (Chen *et al.*, 2007, Zhou *et al.*, 2008, Greenwood and Kendall, 2000) but few have discussed its application in actual industrial waste. A study was conducted using polyDADMAC in coagulation of wood extractive in chemical pulp bleaching filtrate but only compare with other coagulants and no specific explanation on polyDADMAC behavior (Leiviska and Ramo, 2008).

1.4 Problems Statement

The knowledge on the characteristic of the polyDADMAC remains at minimum level although this cationic polymer was a product of commerce and being market for numerous industrial applications. This is due to the literature and patent publications available for polyDADMAC are very scarce. Thus, an experimental study was carried out to obtain a comprehensive understanding of the polymerization and properties of polyDADMAC. It is believed that a successful commercial process will be developed by utilizing and understanding the fundamental behavior of the polymer.

A research work had been conducted on solution properties of polyDADMAC had been conducted, but the influence of molecular weight of the polyDADMAC on its solution properties was not discussed in greater details (Marcelo *et al.*, 2005). Hence, a series of polyDADMAC sample with different molar masses will be synthesized to study the solution properties in order to give a general insight.

1.5 Research Objectives

The main objectives of this work are as follows:

1. To study the effect of monomer concentration on the molecular weight and solution properties of polyDADMAC synthesized by radical polymerization
2. To investigate the flocculation efficiencies of different molecular weights of polyDADMAC in the wastewater treatment plant of pulp and paper mills
3. To investigate synergistic effect of polyDADMAC and polyacrylamide (PAM) on the flocculation enhancement of pulp and paper mill wastewater.

CHAPTER 2
LITERATURE REVIEW

2.1 Colloids Stability of Wastewater

Understanding of colloid stability allowing for characterization and the quantification of solids in wastewater. This characterization and quantification are necessary for the optimisation of treatment processes and for the evaluation of flocculant performances (Azema *et al.*, 2002). According to Lead and Wilkinson, colloids are macromolecules or assemblages, with sizes operationally defined as ranging from 1 nm to 1 mm (Lead and Wilkinson, 2006). Gravity has no effect on settling these macromolecules but instead, they stay in suspension. They are said to be stable due to this suspension condition. These suspension conditions are stable due to the mutual repulsion between colloid particles.

Urban wastewater consist a mixture of organic and mineral pollutants. Their size of distribution is very wide. There are four families of compounds which are usually defined to describe the pollution fractions contained in urban wastewater as shown in Table 2.1

Table 2.1 Families Of Compounds With Their Size (Balmat, 1957)

Name	Size (μm)
Soluble	<0.001
colloidal	0.001–1
supracolloidal	1–100
settleable fractions	>100

In sizes of 0.1 to 2 mm, they can settle rapidly however in the range of the order as in Table 2.1, it takes them a year in the overall to settle a distance of only 1 mm. Basically, colloid system compose of two systems; the dispersion medium and the dispersed phase. Both medium can exhibit all three states which are solid, liquid and gas. For example, the dispersion medium may be liquid and the dispersed phase may be solid.

2.1.1 Colloids Surface

The surfaces of colloids are very important to understand the colloid system since the primary concern is the interaction between particles. The surface to volume ratio of a given particle is inversely proportional to the length of principal axis. Like example, in sphere, the volume increases in proportion to (radius) r^3 but the surface area only increases to r^2. Surface area required energy to appear and this energy required is related to surface tension of a material (Biermann, 1996). The required energy can be calculated as in Equation 2.1:

$$\Delta G = 2\gamma A \qquad \text{(Equation 2.1)}$$

Where G is energy , γ is surface tension and A is new surface area

Colloidal particles behave much differently than larger materials due to high proportion of molecules on the surfaces of small particles. For examples, kaolinite clay tend to be negatively charged while at pH below 7, the kaolinite tend to be positive charge at higher pH and this is reason why kaolin tend to coagulate at lower pH (Silberberg, 1989).

2.1.2 Solution Properties of Colloids

Colloids can be classified into two types which are *lyophilic* (loving solvent) and *lyophobic* (hating solvent). *Lyophilic* colloids occur when the dispersed phase is dissolved in continuous phase while for *lyophobic* colloids, it occur when dispersed phase is suspended in the continuous phase and it thermodynamically unstable.

Coagulation requires very high level of electrolytes for high concentrations of *lyophilic*. High concentration of *lyophilic* usually stable and often increase the viscosity of the continuous phase substantially and leads to dispersion. Meanwhile for *lyophobic* dispersed phase, they are easily precipitated by low level of polyelectrolytes, irreversibly coagulated on drying and tend to give granular precipitates. This *lyophobic* dispersed phase also have levels of light scattering. Examples of this phase are clay particles, metal oxides or silver halides in water.

Based on functional groups, mostly colloids have charged surfaces either cationic or anionic. For example phosphate group will make potato starch negatively

charged. This shows that functional group play central role in colloids behaviours. The amount and type of surface charges are critical to the stability and solubility of colloids. Other factors that play critical roles for the stability and solubility of colloids are the type and amount of polyelectrolytes, pH and temperature.

2.1.3 **Electrical Double Layer**

Most solid surface carries electrostatic charge when contact with aqueous solution. Basically aqueous solution is electrically neutral mean positive charged and negative charged have an equal number of amounts. Electrostatic on solid surface will attract counterions on the solution thus the counterions concentration near the solid surface is higher than that in the bulk liquid far away from the solid surface. However the ion concentration near the surface is lower than in the bulk liquid far away from solid surface due to electrical repulsion. This will create a net charge (excess counterions) in the region close to the surface and they net to balance charged at the solid surface. Electrical double layer is the charged surface and the layer of liquid containing the balancing charges (Vold, 1982), as illustrated in Figure 2.1.

This electrical double layer was firstly studied by Helmholtz in 1879. Helmholtz hypothesized that counter ion would be firmly to charged surfaces. These firmly are depending on the type and concentration of the counter ion in the surrounding solution. In 1910, Gouy and Chapman independently conclude that thermal motion play role on spreading diffusely counter ion from the surface. In

1924, Stern proposed a model that modified some tightly bound ion of Helmholtz and some loosely bound ions of Gouy – Chapman model (Biermann, 1996).

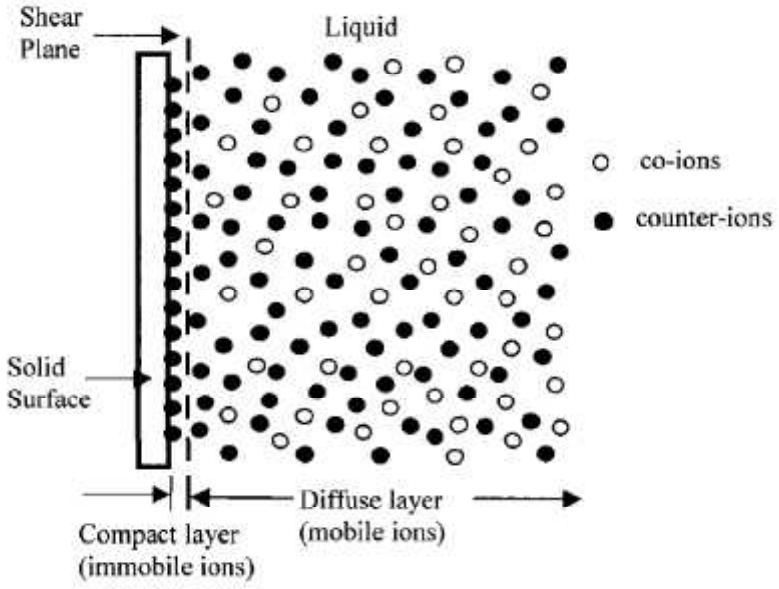


Figure 2.1 The Illustration of The Ionic Concentration Field In An Electrical Double Layer (Dongqing, 2004)

The model conclude that the distribution of counter ions is more highly concentrated at the surface and less concentrated with increasing distance from the surface to yield a Boltzman distribution as shown in Figure 2.2.

The "thickness" ($\frac{1}{x}$) of the double layer can be calculated as Equation 2.2:

$$\frac{1}{x} = \sqrt{\left(\frac{\varepsilon RT}{F^2 \sum CiZi}\right)} \qquad \text{(Equation 2.2)}$$

Where, ε is dielectric constant, R is the gas constant, T is the temperature, F is Faraday's constant, c is the concentration of each inonic species of valance (z).

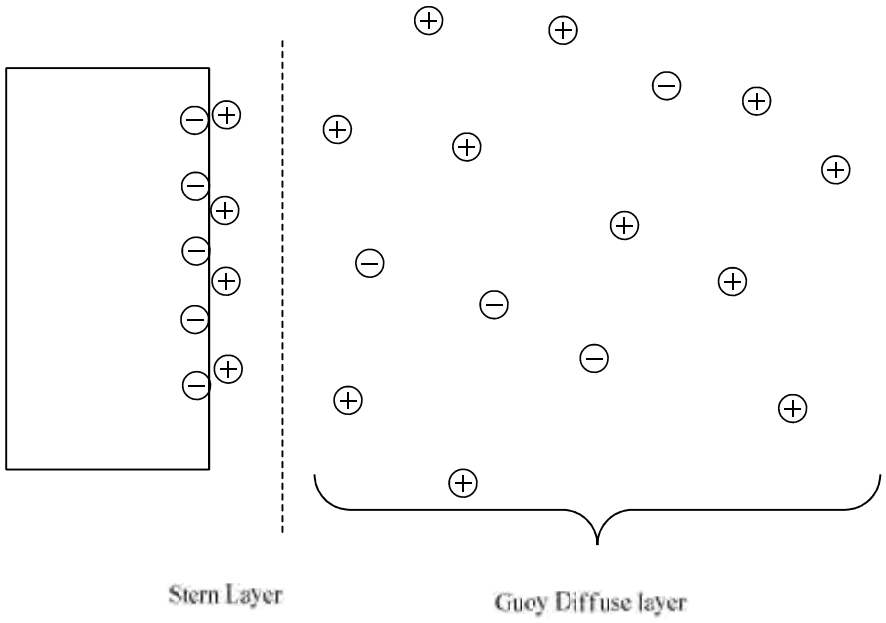


Figure 2.2 Illustration Model Of Stern And Guoy For Electrical Double Layer

2.1.4 Zeta (ζ) Potential

Zeta potential is defined as an average potential in electrical double layer at the zone of shear between a mobile charged particle and the immobile liquid phase as illustrated in Figure 2.3. In other word, zeta potential is the electrical potential at the shear plane of colloid particles (Li and Xu, 2008). Electrophoretic mobility and zeta potential has been an important theoretical and applied tool in flocculation and dispersion of colloid. When an electrical potential is applied, charged particles migrate in the electrical field. Those in the diffuse layer are thought to move with the liquid phase while ion and water in Stern Layer or Helmholtz layers are thought to move with the liquid phase. Therefore, zeta potential is assumed to be in the adjacent to the stern layer or outer Helmholtz plane (Chesworth, 2008).

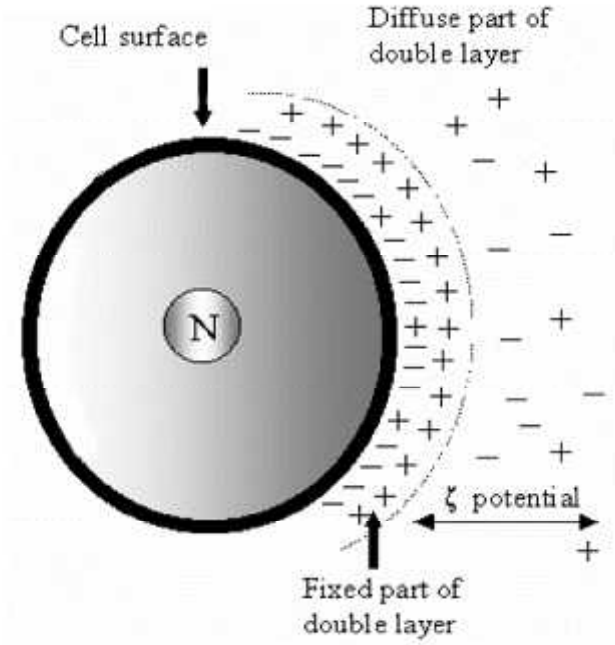


Figure 2.3 The Illustration of Zeta Potential (Li and Tian, 2006)

There are certain techniques to collect data for the calculation of zeta potential. The most common electrokinetic technique used to collect this zeta potential is electrophoretic mobility (EM). Less commonly, techniques such as streaming potential and moving boundary methods have been used to estimate particle charge and potential. Another technique is by electroacoustic and plane face techniques. In electrophoretic technique, measurement is based on the velocity of particles in relation to an applied electrical gradient. Electrophoretic mobility increase with increasing of the electrical potential of the particles in a uniform field thus ions located between the particle surface and the "slipping plane" within the zone of immobile water migrate with the particle. The potential at this slipping plane is the appropriate average potential which determines the particle mobility. The potential which is zeta potential at this slipping plane can be calculated using Helmholtz – Smoluchowski as shown in Equation 2.3 :

$$\xi = \frac{KU\eta}{\varepsilon} \qquad \text{(Equation 2.3)}$$

Where ξ is zeta potential, K is liquid conductivity, U is electrophoretic mobility of a particle, η is the liquid viscosity and ε is permittivity.

Currently, many works and researches used zeta potential measurement to understand flocculation and coagulation done by polyelectrolytes. Schwarz *et al.* (1999) in their work have studied polyelectrolyte adsorption on particles by relating zeta potential They found that maximum charge density increased with increasing of polymer absorption. In other work done by Nasser *et al.,* (2007), they were found anionic polymers have a lower adsorption density than cationic polymers They concluded that the zeta potentials of the kaolinite suspensions, flocculated using anionic flocculant, remain negative and this prevents strong adsorption of the polymer.

2.2 Water Quality Assessment

Water quality is used as indicator and describes water of a good quality. Basically, this water quality depends on the application of the water. For example, the most polluted water can fulfill all criteria for a hydropower system but it will completely fail to be used for drinking purpose. In Malaysia, there are two criterias to be met and followed by any treatment process discharging effluent to an inland waterway. These two criteria are:

- Receiving Water Quality Standard
- Discharge Quality Standard

Malaysian rivers are classified according to the six classes as described in Table 2.2. This classification is under the Under the Interim Water Quality Standard (INWQS). The development of this Receiving Water Quality Standard was initiated by The Department of Environment (DOE) in 1985 which aimed at developing a water quality management approach for the long term water quality of the nation's water resources. Phase 1 study for the development was commissioned by The Water Quality Consultancy Group of the Institute of Advanced Studies, University of Malaya and their study recommended that Malaysia rivers be classified and described in Table 2.2.

Table 2.2 Receiving Water Quality Standard (DOE, 2010)

Parameters	**Units**	**Classes**					
		I	**IIA**	**IIB**	**III**	**IV**	**V**
DO (Dissolved Oxygen)	mg L^{-1}	7	5-7	5-7	3-5	< 3	< 1
COD	mg L^{-1}	10	25	25	50	100	> 100
BOD	mg L^{-1}	1	3	3	6	2	>12
Total Dissolved Solids	mg L^{-1}	1	1000	-	-	4000	-
Total Suspended Solid	mg L^{-1}	500	50	50	150	150	> 300
Faecal Caliform	Counts/100 ml	25	100	400	5000	5000	-
Total Caliform	Counts/100 ml	10	5000	5000	5000	5000	> 5000

The Discharge Quality Standard is forced or authorized under Environmental Quality Act 1974. In this standard, the effluent quality of any discharge from a sewage treatment process to inland water shall meet the minimum requirements as presented in Table 2.3. The limits of this requirement are set down by the Environmental Quality (Sewage Industrial Effluent Regulations, 1979). There are

standard A and standard B in this Discharge Quality Standard. Standard A is for the discharges upstream of drinking water take off while inland water is for Standard B.

There are many characteristics of which water can be explained in details. However, for this study, only a few important water parameters are discussed briefly. These parameters are:

- Turbidity
- Colour
- Total Suspended Solids
- Chemical Oxygen Demand

Table 2.3 - Environmental Quality (Sewage and Industrial Effluents) Regulations, 1979 Maximum Effluent Parameter Limits Standards A and B (DOE, 2010)

Parameters	Units	Standard	
		A	B
Temperature	^0C	40	40
Ph	-	6 - 9	5.5 – 9
BOD @ 25^0C	mg L^{-1}	20	50
COD	mg L^{-1}	50	100
Suspended solids	mg L^{-1}	50	100
Mercury	mg L^{-1}	0.005	0.005
Cadmium	mg L^{-1}	0.01	0.02
Chromium, hexalent	mg L^{-1}	0.05	0.05
Arsenic	mg L^{-1}	0.05	0.10
Cyanide	mg L^{-1}	0.05	0.10
Lead	mg L^{-1}	0.10	0.50
Chromium, trivalent	mg L^{-1}	0.20	1.00
Copper	mg L^{-1}	0.20	1.00
Manganese	mg L^{-1}	0.20	1.00
Nickel	mg L^{-1}	0.20	1.00
Tin	mg L^{-1}	0.20	1.00
Zinc	mg L^{-1}	1.00	1.00
Boron	mg L^{-1}	1.00	4.00
Iron (fe)	mg L^{-1}	1.00	5.00
Phenol	mg L^{-1}	0.001	1.00
Free Chlorine	mg L^{-1}	1.00	2.00
Sulphide	mg L^{-1}	0.50	0.50
Oil and Grease	mg L^{-1}	Not detectable	10.0

2.2.1 Turbidity

Turbidity is an optical property of water sample or in other words is cloudiness of the water. The higher turbidity of the sample, the harder is it to see through the water. In turbidity meter machine, when a light beam passes through the water sample, the light will be subjected to scatter and absorption rather than transmitted in a straight line through the sample as shown in Figure 2.4.

Amount of light transmitted and scattered will be measured by electronic photodetectors which set around the water sample (Pavanelli and Bigi, 2005). Shape, colour and mostly particles size are parameters that affect the scatterance of the sample (Gray *et al.*, 2002). Generally, turbidity measurements are reported either in nephelometric turbidity units (NTU) or Jackson turbidity units (JTU). These different units are depending on which method is chosen to measure the turbidity.

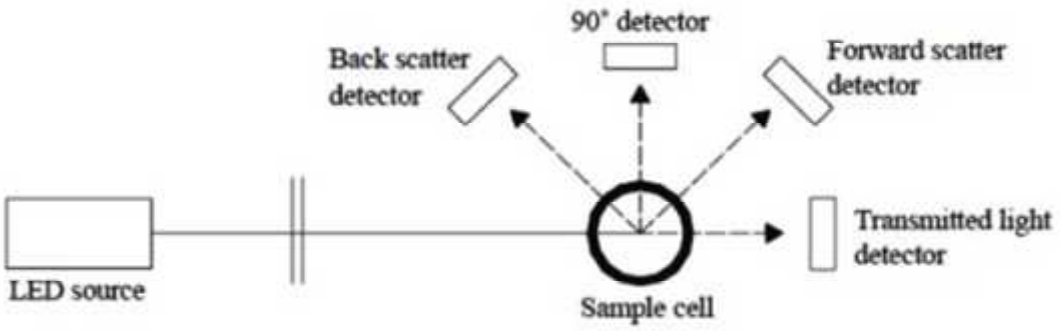


Figure 2.4 Schematic cross-section of a turbidity meter; LED, light-emitting diode (Pavanelli and Bigi, 2005)

2.2.2 Total Suspended Solids

Total suspended solid (TSS) is referring to all particles suspended in water which will not pass through a filter. TSS includes a wide variety of materials such as silt, decaying plant and animal matter, industrial wastes, and sewage (Robenson, 2008). Basically, TSS in mg L^{-1} and can be calculated as Equation 2.4 below:

$$(Z - G)/ \text{ml of sample} * 1000000 \qquad \text{(Equation 2.4)}$$

Where Z is dirty pad weight in grams and G is clean pad weight in grams

TSS needs to be removed or discharge from the water because they may harm the ecosystem like fish habitat and plankton. A water body begins to lose its ability to support a diversity of aquatic life as levels of TSS increase. As level of TSS increase, the water temperature will increase thus decreases levels of dissolved oxygen. Dissolved oxygen will be decreasing due to warmer water hold less oxygen than cooler water. Dissolved oxygen also decreases due to less oxygen produced by plants and algae since less light penetrates the water.

2.2.3 Chemical Oxygen Demand

Chemical Oxygen Demand (COD) can be defined as a measurement of the capacity of water to consume oxygen (O_2) during the decomposition of organic matter and the oxidation of inorganic chemicals, such as ammonia and nitrites

(Fediuc and Erdei, 2002). COD can be measured in two ways which are closed reflux titrimetric and closed reflux colorimetric.

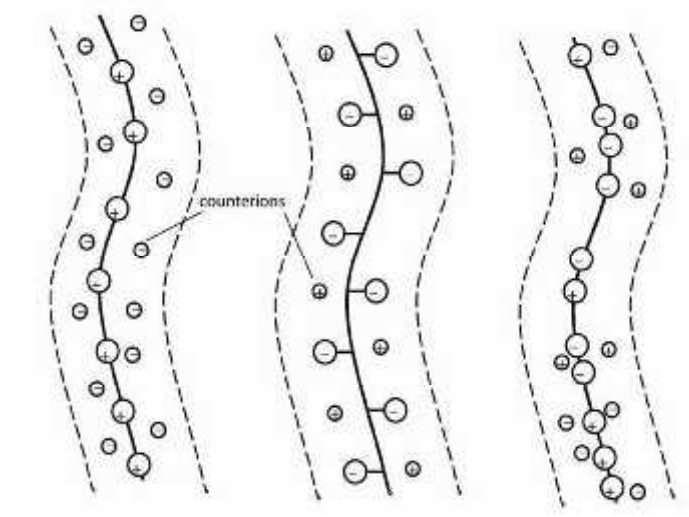
In closed reflux titrimetric, sample will be refluxed in strongly acidic solution. Usually potassium dichromate will be selected as the acidic solution. The remaining unreduced potassium dichromate after digestion is titrated with ferrous ammonium sulphate to determine the amount of potassium dichromate consumed. This procedure only applicable to COD values between 40 and 400 mg L^{-1}. However, higher COD values can be obtained by using higher concentrations of dichromate digestion solution or by careful dilution the solution.

The COD values between 0 to 1500 mg L^{-1} is suitable for calorimetric method. In this method, dichromate ion is oxidizing organic matter when the sample digested. This will change chromium from the hexavalent to the trivalent state. Both chromium species have different color and absorb light in the visible region of the spectrum. The chromic ion absorbs strongly at 600 nm region but absorb less in the 400 nm region while dichromate ion absorb strongly at 400 nm while at 600 nm, it has nearly zero absorption (Sincero and Sincero, 2002).

2.3 Classification of Polyelectrolytes Flocculants

Polyelectrolytes are polymers that disassemble into negative and positive ions when dissolve into polar solvent like water. Polyelectrolytes can be divided into three groups which are natural, modified natural and synthetic polymers. In terms of their charge, polyelectrolyte can be classified into polyanion, polycationic and polyampholytes as shown in Figure 2.5

Compared with uncharged polymers, polyelectrolytes have special properties such as excellent water solubility, propensity to swell and bind large amount of water and ability to interact strongly with opposite charged surfaces and macromolecules (Stuart *et al.*, 2005). Because of these features, they are widely used as flocculants, dispersants, thickeners, flotation depressants, filtration and settling aids throughout a wide range of industries (i.e. mineral, paper, effluent, textile, food) for several decades (Shouci Lu and Eric, 2005)



(a) (b) (c)

Figure 2.5 Classifications of polyelectrolytes into (a) Polycations, (b) polyanions and (c) polyampholytes. (Koetz and Kosmella, 2007)

2.3.1 Polycationic

Polycationic is polyelectrolytes with positive sides on the monomer units. Others name for this polycationic is cationic polyelectrolytes. Recently, these polyelectrolytes are extensively used in many industrial applications due to their ability to interact with negative charged surfaces. Polycationic have a greater variety of molecular structure than in any of the others. Generally, they are containing

quaternary ammonium groups so that the formal positive charge is present irrespective of the pH level. Examples of polycationic are polyDADMAC and epichlorohydrindimethylamine (epiDMA).

According to Fettig *et. al* (1990), the most effective cationic polymer in the physical-chemical treatment of domestic wastewater was highly charged cationic polyelectrolytes. These highly charged polyelectrolytes tend to adsorb in a flat configuration which leads to formation of patches of unevenly charge distribution. Such behavior reduces the likelihood of bridging interactions. Hence, the absorption of charges causes the charge neutralization will be predominant mechanism of destabilization (Gregory, 2006).

These types of polyelectrolyte are normally used as flocculants in the clarification of drinking water, in the cleanup of industrial wastes, sewage and sludge, as well as retention aids in the papermaking industry. This polyelectrolyte generally used in combination with coagulant for effective turbidity removal. Advantages of this polymer is less sensitivity to pH, flocs settling better and flocculation of living organism such as bacteria and algae is improved (Bratby, 2003).

2.3.2 Polyanionic

Polyanionic is polyelectrolyte's that containing anionic groups such as those of a carboxylic acid group. This anionic groups will form negative charged when dissolve. In practice, polyaninonic are usually utilized primarily with aluminum and

iron. They also usually utilized after the flocculation process to increase the size and strength of particle aggregates. These polymers are able to bridge or interconnect particle in the agglomerates due to their high molecular weight to cause polymer bridging becomes predominant mechanism of destabilization (Gregory, 2006). This anionic polyelectrolyte also not materially affected by pH and good settling of flocs.

2.3.3 Polyampholytes

Polyampholytes are polyelectrolyte having balanced or neutral charged. This polyelectrolyte release both positively and negative charged when dissolving. These polyelectrolytes undergo aqueous dissolution only in the presence of salt and coil dimensions increase as the ionic strength of the solution increase. The ratio for these charges can be varied and it could be of a strong or weak electrolyte type. A unique feature of this amphoteric polyelectolytes is their anti-polyelectrolyte behavior when the ratio of charged is 1:1, in the sense that an increase in ionic strength causes an increase rather than a decrease in the viscosity of the solution. This property has been utilized and has significance in applications like enhanced oil recovery. This type of polyelectrolytes normally used in water clarification, sludge conditioning and the adsorption of metal ions and dyes (Bolto, 1995).

2.4 Polyelectrolyte Flocculation Mechanisms

Generally polyelectrolytes play dual role in colloidal system. They can act as stabilizers or flocculants. This subchapter will focuses and explain more on flocculation process. Flocculation is defined as gathering process or aggregation of

small entities usually in liquid media into larger mass called flocs. Practically in industry, jar test is intended to simulate the flocculation process in a water treatment plant. The results from this jar test are used to help optimize the flocculation performance in plant. In order to optimize the flocculation process, it is important to know the predominant interaction and mechanism between particles or suspended solids. There are three possible mechanism of flocculation process. These mechanisms are:

1. Charge Patch Neutralization
2. Chain Bridging
3. Depletion

2.4.1 Charge Patch Neutralization

Charge Patch neutralization is defined as adsorption process by equal number of opposite charges into particles, fibers and colloidal material in aqueous solution and make their net electrical charge become neutral. The early electrostatic patch was proposed by Gregory (1973) in their study on the rates of flocculation of latex particles by cationic polymers. The electrical double layer that preventing these particles, fibers and colloidal material from approaching each other is greatly compressed by counterions. Cationic polyelectrolytes with high charge density, with low and to moderate molecular weight are often effective flocculants for dispersion of negatively charged particles through this mechanism. The charged polymer which usually cationic visualized to be much smaller than the surface area of the particles. This will create a patch on the surface and resulting in heterogeneous distribution surface charges. The surface charges will neutralize and induces an opposite charge